Compositional variation of cooperite, braggite, and vysotskite from the Bushveld Complex

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Abstract

The compositions of coexisting and individual cooperite (ideally PtS) and braggite (ideally (Pt,Pd)S) grains from the Merensky Reef of the Bushveld Complex, as well as cooperite, braggite and vysotskite (ideally PdS) grains from the UG-2 of the Bushveld Complex were investigated. There is a clearly defined miscibility gap between cooperite and braggite, but no evident gap between braggite and vysotskite. Partition coefficients between cooperite and braggite are determined on coexisting phases. The $K_D^{\text{braggite/cooperite}}$ in atomic ratios are estimated to be 0.54 for Pt, 15.81 for Pd and 5.93 for Ni. For Rh and Co the $K_D^{\text{cooperite/braggite}}$ are estimated to be > 1.40 and > 1.46 respectively. No systematic behaviour is detected for Fe and Cu. Coupled substitutions of Pd + Ni for Pt in cooperite and braggite/vysotskite are indicated. Within the cooperite of the Merensky Reef, the Pd:Ni ratio is approximately 9:11. The substitution trend in braggite, which extends to vysotskite in the UG-2, is dependent on the base-metal sulphide (BMS) association. If pentlandite is the dominant Ni-bearing BMS, the Pd:Ni ratio is about 7:3 in the Merensky Reef and in the UG-2. Millerite as the dominant Ni-bearing BMS in the UG-2 changes this ratio to 3:1. It is concluded that the Ni-content in braggite/vysotskite from BMS assemblages does not depend on the NiS activity, but rather on temperature of formation.

KEYWORDS: cooperite, braggite, vysotskite, Merensky Reef, Bushveld Complex, UG-2.

Introduction

COOPERITE, braggite and vysotskite have been described from many localities throughout the world — amongst others, from the Merensky Reef of the Bushveld Complex (e.g. Brynard *et al.*, 1976; Schwellnus *et al.*, 1976; Kingston and El-Dosuky, 1982,; Mostert *et al.*, 1982), from the UG-2 (e.g. Kinloch, 1982; McLaren and De Villiers, 1982; Peyerl, 1982), from the Stillwater Complex (e.g. Todd *et al.*, 1982; Volborth *et al.*, 1986), and from Noril'sk (e.g. Genkin and Evstigneeva, 1986).

Amongst the platinum-group minerals (PGM) in the UG-2 and the Merensky Reef, these three minerals are the dominant ore minerals (Kinloch, 1982). From an economic point of view, cooperite, braggite and vysotskite are therefore probably the most important minerals in ores of the platinum-group elements (PGE). They are also the most common minerals in the system Pt–Pd–S.

Although cooperite (ideally PtS) and braggite (ideally (Pt,Pd)S) have been synthesized by Skinner *et al.* (1976) at 1000°C, and cooperite, braggite, and vysotskite (ideally PdS) by Cabri *et al.* (1978) at 800°C in the Ni-free system, analyses of natural cooperite, braggite, and vysotskite typically contain significant amounts of Ni.

The description of the optical properties of the minerals, particularly those of cooperite and braggite, has caused a considerable amount of confusion in the past. Quantitative and descriptive data given for braggite often correspond to the properties of cooperite, whereas several descriptions of cooperite do not correspond to either of the two minerals. Therefore Criddle and Stanley (1985) reinvestigated the three minerals with the
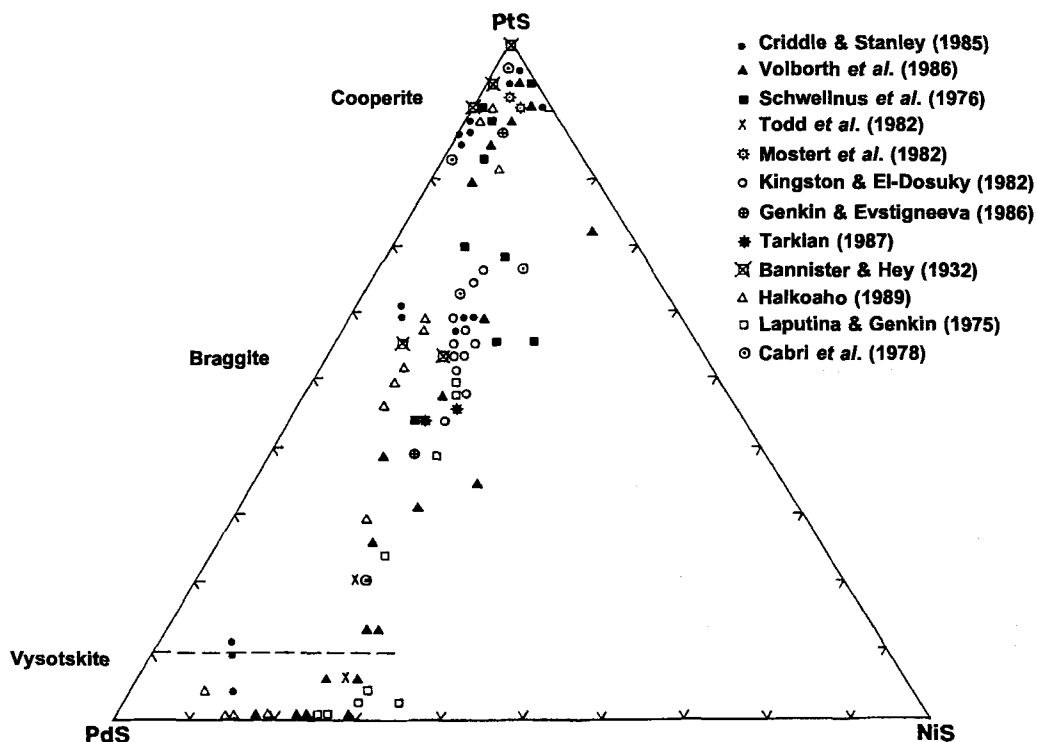
FIG. 1. Compositional variation of 133 braggite, cooperite and vysotskite analyses from various localities (in mol. %; owing to overlap, 36 projection points hidden; the stippled line indicates the arbitrary border between braggite and vysotskite).

aid of reflectivity measurements of analysed grains. Cabri *et al.* (1978) summarized existing compositional data, and Tarkian (1987) also presented compositional data as well as reflectance data. In our investigation it was observed that the frequency of twinning in large grains may aid distinction of braggite and cooperite minerals. Only 3 out of 185 cooperite grains, but 40 out of 161 braggite grains were found to be twinned.

Figure 1 summarizes the compositional variations of cooperite, braggite and vysotskite in the system PtS–PdS–NiS taken from the literature. Cooperite and braggite seem to be separated by a miscibility gap, and there seems to be a continuous solid solution between braggite and vysotskite. An arbitrary content of 10 mol. % PtS is taken as the upper limit for vysotskite compositions (Cabri *et al.*, 1978).

Despite their wide distribution, cooperite and braggite are rarely observed in physical contact with each other. Until the investigation of Merkle and Verryn (1991), which concentrated on

material from the Merensky Reef of the Bushveld Complex, the compositions of coexisting braggite and cooperite had not been addressed.

This investigation forms part of a larger programme to investigate the compositions of cooperite, braggite, and vysotskite from different mineralizations and mineral assemblages. Here we report on the compositions of coexisting braggite and cooperite; and those of individual cooperite, braggite and vysotskite grains; inter-element relationships; the verification of the miscibility gap between cooperite and braggite; and provide partition coefficients between the two minerals where possible.

Samples

The samples used in this investigation originate from various localities of the Merensky Reef and the UG-2 of the Bushveld Complex. Within the samples of the UG-2 chromitite, braggite and

TABLE 1. Analytical conditions, detection limits (3 sigma level in wt.%) and reproducibilities (1 sigma, determined according to Kaiser and Specker (1956) in wt.%; N = 60 (n.d. = not determined).

Element	Standard	Analysing Crystal	X-Ray Line	Detection Limit	Reproducibility	
					Braggite	Cooperite
Pt	$Pt_{0.7}Pd_{0.3}S$	LIF	$L\alpha$	n.d.	0.2564	0.2840
Pd	$Pt_{0.7}Pd_{0.3}S$	PET	$L\alpha$	0.150	0.1952	0.1141
Ni	Ni	LIF	$K\alpha$	0.022	0.0656	0.0102
S	$Pt_{0.7}Pd_{0.3}S$	PET	$K\alpha$	n.d.	0.1183	0.1177
Cu	$CuFeS_2$	LIF	$K\alpha$	0.030	0.0634	0.0076
Fe	FeS	LIF	$K\alpha$	0.022	0.0158	0.0050
Co	CoS_2	LIF	$K\alpha$	0.023	n.d.	0.0086
Rh	Rh	PET	$L\alpha$	0.112	n.d.	0.0430 (N=16)
As	$PtAs_2$	TAP	$L\alpha$	0.055	n.d.	n.d.

vysotskite are the most common phases in the system PtS–PdS–NiS (Kinloch, 1982). Here the PGM are associated with the base-metal sulphides (BMS) pentlandite, pyrrhotite, chalcopyrite, millerite, and pyrite (McLaren and De Villiers, 1982). In contrast, cooperite and braggite are frequently encountered in the silicate dominated Merensky Reef samples (Kinloch, 1982); occasionally, these two phases coexist. The PGM in the Merensky Reef are associated with chalcopyrite, pentlandite, pyrrhotite and minor pyrite (Brynard et al., 1976; Schwellnus et al., 1976; Vermaak and Hendriks, 1976; Mostert et al., 1982).

Analytical methods

The compositional variation of 36 grains of coexisting braggite and cooperite from the Merensky Reef were determined along traverses across their mineral boundaries with a JEOL 733 microprobe at the University of Pretoria. In addition, five and six individual grains respectively of cooperite and braggite from the Merensky Reef were analysed and 49 grains of cooperite, braggite and vysotskite from the UG-2. The accelerating potential was 20 kV and the beam current 5×10^{-8} A. Counting times were 20 s at the peak positions and 10 s for symmetrical backgrounds. The elements analysed were Pt, Pd, Ni, S, Cu, Fe, Co, Rh, and As. Arsenic is hardly ever present in quantities above the detection limit (0.055 wt.%) and therefore omitted in the tables and calculations. Technical data of the analyses are given in Table 1 and a selection of representative analyses is given in Table 2.

A non-linearity in the determination of Pd, similar to the problem for Au–Ag alloys encountered by Reid et al. (1988), was observed and corrected as discussed in Merkle and Verryn

(1991). After correction for Pd, analyses with totals between 98.5 and 101.5 wt.% were used for further calculations. Traverse analyses close to the grain boundary of coexisting braggite and cooperite were discarded for calculation of the means, if cooperite showed abnormally high Pd contents or if the Pd concentrations in braggite were abnormally low compared with the rest of that particular grain. In such cases interference from the neighbouring grain was assumed, because of the large excitation area of about 2.5μm (primary and fluorescent radiation) at 20 kV.

Compositions of coexisting braggite and cooperite (Merensky Reef)

Profiles across the mineral boundaries of composite cooperite-braggite grains indicate that there is occasionally a change in composition of the minerals close to the mineral boundary. Abrupt and continuous changes over the whole mineral grain towards higher and lower Pd contents were observed in both minerals, but no systematic pattern of chemical variability in coexisting braggite and cooperite was detected. Compositional variation in braggite was usually found to be greater than in cooperite. Compositional variations were also observed by Cabri et al. (1978) in individual grains of braggite. The compositional variation is interpreted to reflect incomplete equilibration between, and within, the two phases in response to the reduced stability fields of braggite and cooperite on cooling (see below). Different degrees of homogenization are attributed to differences in the cooling history (i.e. the effects of various postcumulus processes) of individual grains.

Figure 2 shows the compositional variation of coexisting and discrete braggite and cooperite

TABLE 2. Selected cooperite (co), braggite (br), and vysotskite (vy) analysis from the Merensky Reef (MR) and the UG-2 chromitite in assemblages containing pentlandite (pent) or millerite (mill).

|	Mineral Origin Association	co MR pent	co MR pent	br MR pent	br MR pent	co UG-2 pent	br UG-2 pent	vy UG-2 pent	br UG-2 mill	vy UG-2 mill
W	S	14.41	14.56	18.12	18.96	14.83	20.26	22.09	19.02	25.60
e	Rh	<0.11	<0.11	<0.11	<0.11	0.40	<0.11	<0.11	<0.11	0.16
i	Pd	0.80	1.31	19.92	21.45	2.57	23.29	43.55	25.69	60.46
g	Pt	83.81	83.92	57.15	53.38	80.43	47.55	25.43	52.20	1.25
h	Ni	0.58	0.53	4.24	5.67	0.53	7.63	8.85	3.90	12.28
t	Co	<0.02	<0.02	<0.02	<0.02	0.03	<0.02	<0.02	<0.02	0.04
	Cu	0.04	<0.03	<0.03	<0.03	<0.03	0.32	0.06	0.03	0.30
%	Fe	<0.02	<0.02	0.14	0.05	0.47	1.37	0.52	0.12	0.57
	Total	99.64	100.32	99.57	99.51	99.26	100.42	100.50	100.96	100.66
A	S	50.099	50.148	50.445	50.797	50.238	50.394	49.582	50.646	49.921
t	Rh	-	-	-	-	0.423	-	-	-	0.098
o	Pd	0.842	1.355	16.716	17.319	2.625	17.458	29.454	20.607	35.529
m	Pt	47.894	47.496	26.157	23.513	44.773	19.436	9.380	22.842	0.401
i	Ni	1.092	1.001	6.453	8.299	0.973	10.363	10.845	5.675	13.079
c	Co	-	-	-	-	0.052	-	-	-	0.043
	Cu	0.072	-	-	-	-	0.395	0.068	0.043	0.296
%	Fe	-	-	0.230	0.072	0.916	1.954	0.670	0.186	0.633
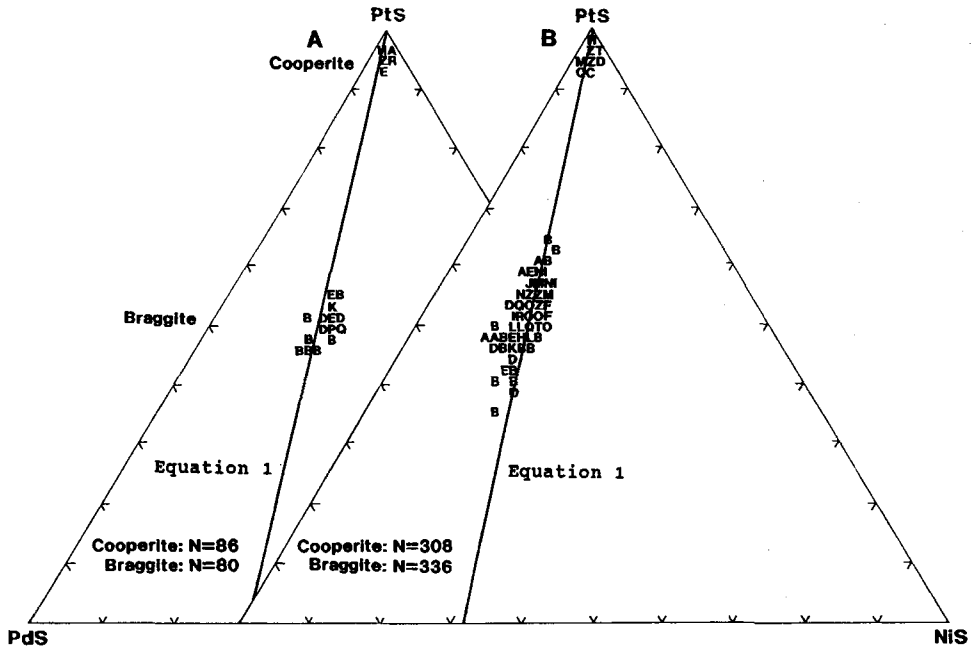
FIG. 2. Compositional variation of discrete (A) and coexisting (B) braggite and cooperite from the Merensky Reef in the PtS–PdS–NiS diagram (in mol. %; A = 1 observation, B = 2 observations, etc., Z = 26 and more). Equation 1 is graphically represented by the solid line.

grains from the Merensky Reef based on 810 analyses. The fields of the discrete (Fig. 2A) and the coexisting grains (Fig. 2B) show a complete overlap. The range in the PdS component of the individual braggite grains, however, is smaller (45–55 mol. %) than that of braggite coexisting with cooperite. Here the PdS content ranges from 35 to 65 mol. %. This difference is likely to be due to the smaller number of individual grains analysed.

When compared to compositions of braggite and cooperite from various other localities (Fig. 1), the compositional range of the two minerals observed in this investigation is seen to be more restricted and better defined. Figure 1 indicates a range of 28–90 mol. % PdS in braggite and up to 20 mol. % PdS in cooperite. In this investigation, a maximum of 8 mol. % PdS was observed in cooperite.

It is also evident from Fig. 2 that braggite contains significantly more Ni than the cooperite. A clearly visible miscibility gap, as previously described by Cabri et al. (1978), exists between the two minerals, most likely because of the different crystallography of the two minerals. Cooperite belongs to space group $P42/mmc$ and braggite to $P42/m$ (Bannister and Hey, 1932). This miscibility gap between coexisting braggite and cooperite (Fig. 2) is much larger than is indicated in literature analyses (Fig. 1). If the possibility of mixed analyses is excluded, the mineral compositions that lie inside the gap probably represent grains that formed at high temperatures which permitted a higher degree of solid solution. Fast cooling or different degrees of postmagmatic overprinting (e.g. through hydrothermal fluids) may have a profound effect on the exsolution and the development of a clear miscibility gap. The difference in the miscibility gaps of Figs. 1 and 2 implies that these gaps depend on the temperature at which equilibration ceases (see discussion below).

Inter-element relations of coexisting cooperite and braggite (Merensky Reef)

Cooperite and braggite have distinct compositional ranges, which make differences in their inter-element relations likely. The spot analyses taken from 36 coexisting grains of cooperite and braggite of the Merensky Reef were averaged for each phase in each grain. As the elements Pt, Pd, and Ni are the only elements, apart from S, that are always present in quantities above the detection limits, their inter-element relations will be discussed first.

Braggite. A Spearman correlation coefficient (Table 3) of $r = -0.8569$ between Pt and Pd (see also Fig. 3A) indicates a substitution of Pt and Pd.

TABLE 3. Spearman correlation coefficients (error probabilities underneath) calculated from analyses in at. % (N = 36) of braggite coexisting with cooperite of the Merensky Reef.

	Pd	Ni	Pd + Ni
Pt	−0.85689	−0.65611	−0.94826
	0.0001	0.0001	0.0001
Pd		0.30888	0.95084
		0.0668	0.0001
Ni			0.56113
			0.0004

Pt and Ni also show a negative correlation, with a coefficient $r = -0.6561$ (Fig. 3B). A rather weak positive correlation of $r = 0.3089$ (Fig. 3C) between Pd and Ni indicates that the inter-element relations are not restricted to a 1:1 substitution of Pt and Pd. If a coupled substitution of Pt for Pd + Ni is assumed and tested for the degree of correlation, the correlation coefficient improves to −0.9483 (Fig. 3D). The small deviation from an ideal relation is likely to be caused not by an even more complex substitution involving additional elements, but rather by the unavoidable analytical uncertainties. A least-squares fitting of the data leads to Equation 1 (at the 95% confidence level) for the substitution of Pt by Pd + Ni in braggite in atomic proportions.

$$Pt = (0.68 \pm 0.03) \times Pd + (0.32 \pm 0.03) \times Ni \quad (1)$$

The same relation (without the error margin) can be derived graphically by drawing a line in Fig. 2 from the PtS-corner through the mean of the braggite population to the PdS–NiS join.

Fe and Cu show a fairly weak positive correlation ($r = 0.5879$; N = 10) within the braggite when present in quantities above the detection limit (Table 1). In eight grains, only Fe was detected and in three grains only was Cu detected.

Cooperite. For cooperite (Table 4), the Spearman correlation between Pt and Pd is well developed ($r = -0.7663$), whereas correlations between Ni and Pt ($r = -0.3776$) and Ni and Pd ($r = 0.4224$) are weaker. If the same type of coupled substitution as shown for braggite is assumed and the correlation between Pt and Pd + Ni is tested, a marginally higher coefficient results than that between Pt and Pd alone ($r = -0.7866$). This indicates that Pt, here also, is most likely to be substituted by Pd + Ni. However, due to the lower concentrations of Pd and Ni in cooperite (i.e., larger relative analytical uncertainty) and the restricted compositional range, the correlation coefficients for cooperite are less clearly defined
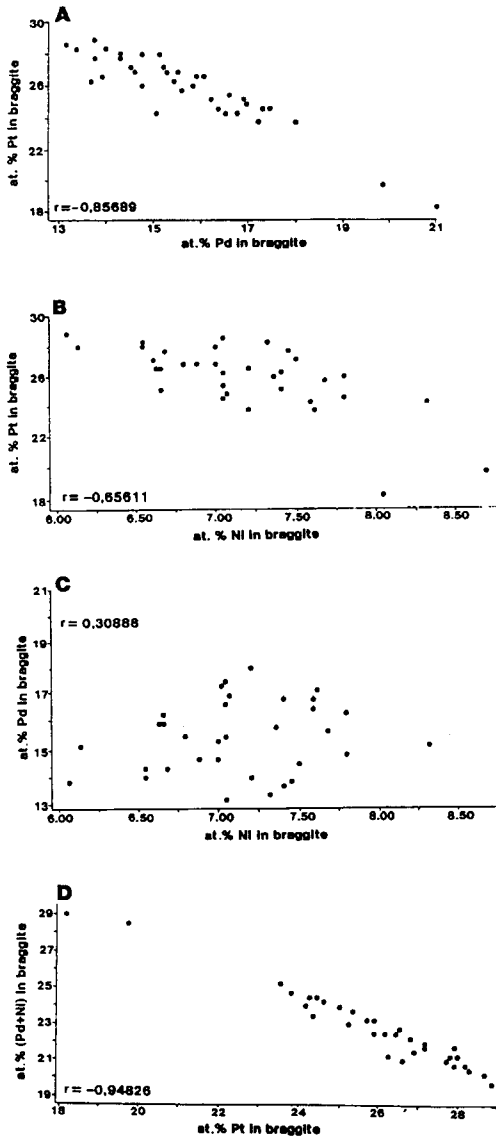
FIG. 3. Scatter plots (in atomic per cent) of Pt versus Pd (A), Pt versus Ni (B), Pd versus Ni (C), and Pt versus Pd + Ni (D) in braggite from the Merensky Reef.

than they are for braggite. A formula for the substitution, calculated as for the braggite (at the 95% confidence level), would be:

$$Pt = (0.45 \pm 0.09) \times Pd + (0.55 \pm 0.09) \times Ni \quad (2)$$

Spearman correlation coefficients (Table 4) imply a negative correlation ($r = -0.5077$)

between Co and Pt and positive correlations between Co and Pd ($r = 0.3670$), and between Co and Ni ($r = 0.5297$). This suggests a possible substitution of Co for Pt. Rhodium correlates positively with Pt ($r = 0.4336$) and negatively with Pd ($r = -0.4755$), indicating a substitution of Rh for Pd. The correlation between Rh and Ni is very poor. We may therefore be dealing with a more complex systematic substitution of Pd + Ni + Co for Pt + Rh, but our data do not permit a more rigorous evaluation of this aspect. A further positive correlation is indicated between the amounts of Fe in cooperite and Ni in coexisting braggite ($r = 0.4990$, N = 23).

Dependence of braggite compositions on BMS assemblages (UG-2)

From the UG-2 of the Bushveld Complex, we selected samples in which cooperite, braggite, and vysotskite occur in two different BMS assemblages. In one assemblage, the Ni-bearing phase is pentlandite and in the other one millerite with only traces of pentlandite. The distinct associations indicate different activity of NiS and could therefore be expected to have an effect on the Ni-proportion of Pt–Pd–Ni sulphides. In the UG-2, the average grain sizes of braggite, cooperite and vysotskite are smaller ($\pm$ 5µm in diameter) than in the Merensky Reef (often > 100 µm in diameter). Compositional heterogeneity could therefore not be observed to the same degree as in the Merensky Reef. Analyses of cooperite, braggite, and vysotskite coexisting with pentlandite are presented in Fig. 4. Spearman correlation coefficients (Table 5) between Pt, Pd, Ni and Pd + Ni indicate the same coupled substitution of Pd + Ni for Pt as for the braggite of the Merensky Reef (Table 3), which also coexists with pentlandite. Mathematically, the Pd/Ni ratio is also very similar to that of the Merensky Reef (Equation 3).

$$Pt = (0.67 \pm 0.06) \times Pd + (0.33 \pm 0.06) \times Ni \quad (3)$$

Figure 4 indicates that the trend established for braggite continues right down to vysotskite and that there is no significant difference between the Merensky Reef and UG-2 trends.

In contrast, Fig. 5 shows compositions of cooperite, braggite, and vysotskite from the UG-2 in association with millerite. The analyses all plot on the Ni-poor side of the trend established for the pentlandite association (Equations 1 and 3). For the millerite association the Pd/Ni ratio can be expressed as follows:

$$Pt = (0.75 \pm 0.10) \times Pd + (0.25 \pm 0.10) \times Ni \quad (4)$$

TABLE 4. Spearman correlation coefficients from analyses of cooperite (in at. %), coexisting with braggite of the Merensky Reef. Error probabilities and the number of observations underneath.

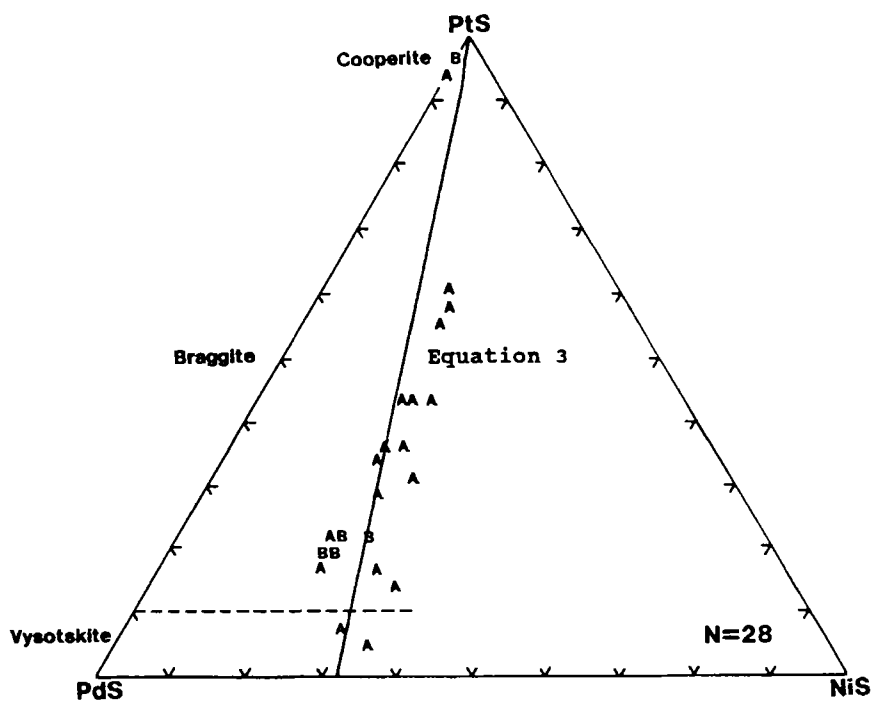|	Pd	Ni	Co	Rh	Pd + Ni
Pt	−0.76628	−0.37761	−0.50769	0.43357	−0.78662
	0.0001	0.0232	>0.0638	0.1591	0.0001
	36	36	14	12	36
Pd		0.42239	0.36703	−0.47552	0.96834
		0.0103	0.1967	0.1182	0.0001
		36	14	12	36
Ni			0.52967	0.18881	0.54100
			0.0514	0.5567	0.0007
			14	12	36
Co				0.20000	
				0.5796	
				10	

FIG. 4. Compositional variation of 28 cooperite, braggite and vysotskite grains from the UG-2 associated with pent landite (in mol. %, A = 1 observation, B = 2 observations). Equation 3 is graphically represented by the solid line.
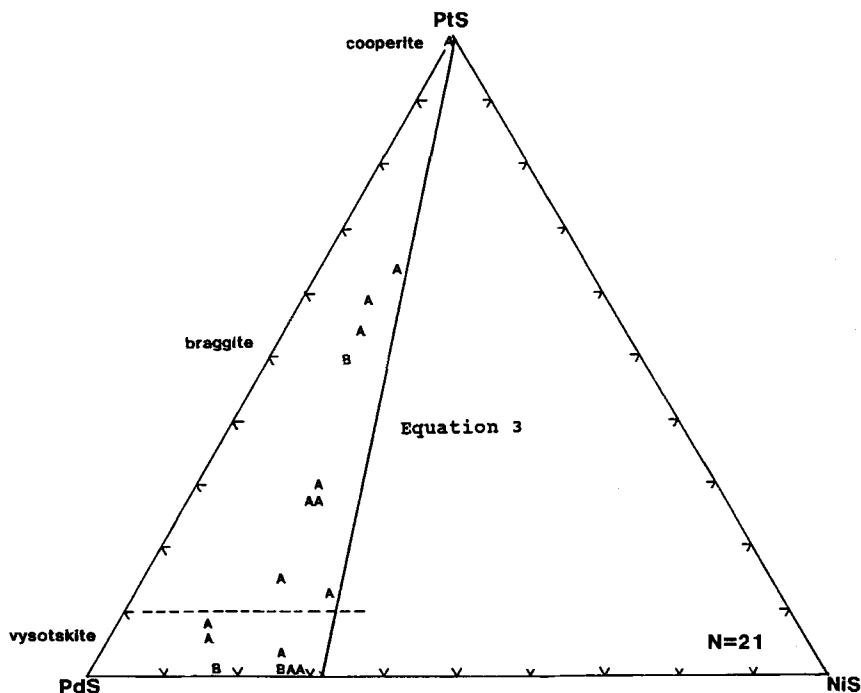
FIG. 5. Compositional variation of 21 cooperite, braggite and vysotskite grains from the UG-2 associated with miller ite (in mol. %, A = 1 observation, B = 2 observations). Equation 3 is graphically represented by the solid line.

In the investigated samples, the millerite occurs as grains of up to several hundred μm with rare pentlandite inclusions. Phase relations within the Fe–Ni–S system do not change significantly between 600 and 300°C (Vaughan and Craig, 1978). Pentlandite exsolves from the monosulphide solid solution (mss) below 610°C (Kullerud, 1963). For bulk sulphide compositions signifi-

TABLE 5. Spearman correlation coefficients from analyses of braggite of the UG-2 in association with pentlandite (in atomic per cent, N = 25, error probabilities underneath).

	Pd	Ni	Pd + Ni
Pt	−0.8608	−0.6508	−0.9762
	0.0001	0.0004	0.0001
Pd		0.3377	0.9054
		0.0988	0.0001
Ni			0.6139
			0.0011

cantly more Ni-rich than normal magmatic sulphides, the mss can be expected to decompose below 300°C and millerite should coexist with an Fe-rich and a S-rich phase. However, this was not observed in the samples investigated. Naldrett and Lehmann (1988) and Naldrett et al. (1989) demonstrated that the Fe content in BMS assemblages can be reduced through absorption of Fe by chromite, as was suggested by Von Gruenewaldt et al. (1986). Merkle (1992) showed that hydrothermal fluids can have an even more pronounced effect and lead to further reduction in the proportion of sulphidic Fe.

In localized areas of chromitite layers, the loss of Fe may progress to such a degree, that we are effectively dealing with the pure Ni–S system. The Fe-loss results in a relative increase in S and at temperatures above 379°C, $Ni_{1-x}S$ should crystallize instead of stoichiometric millerite. With cooling of the system below 379°C millerite is the stable phase, which should exhibit exsolution of a S-richer phase if it had formed from the non-stoichiometric $Ni_{1-x}S$ (Kullerud and Yund, 1962). Exsolutions, which should easily be observed due

TABLE 6. $K_D^{braggite/cooperite}$ with respective standard deviations (s_{KD}), 68% confidence level.

	atomic		mass	
	K_D	s_{KD}	K_D	s_{KD}
Pt	0.54	0.05	0.69	0.04
Pd	15.81	5.48	19.92	6.84
Ni	5.93	0.85	7.49	1.18

to the large size of the millerite grains, were not once encountered in the samples investigated.

The phase relations in the systems Fe–Ni–S and Ni–S discussed above indicate that we are dealing with millerite that formed at temperatures below 379°C. It can be assumed that the PGM which coexist with millerite are in equilibrium with millerite and reflect the compositional characteristics of PGM formed, or equilibrated, at temperatures below 379°C. The NiS-activity, in an environment in which only millerite forms, is higher than that of an environment where pentlandite is present. The braggite and vysotskite grains in association with millerite, however, contain less NiS than those occurring together with pentlandite. This indicates that temperature of formation or equilibration, rather than Ni-activity, is the dominant factor for the Ni-concentration within braggite and vysotskite.

Partition coefficients

Partition coefficients can only be estimated from coexisting phases that are in equilibrium, therefore only the analytical results obtained from samples of the Merensky Reef can be used. As discussed above, the spot-analyses of the grains of coexisting braggite and cooperite were averaged. From these averages, partition coefficients (K_D) were calculated (Table 6).

The element concentrations, and from them the partition coefficients, can also be derived by linear regression in the form of

$$\text{atomic \% in braggite} = a + b \times \text{atomic \% in cooperite} \quad (5)$$

where a is the intercept and b the slope of the regression line. In Table 7 the respective values for a and b for Pt, Pd and Ni, with their standard errors, are presented together with Spearman correlation coefficients. As the values of the 36 grains used for calculations in Table 7 are already mean values of a number of spot analyses, the standard deviations indicated in Table 7 might in actual fact be conservative, because the means on which the calculations are based already do have a variance. Rh and Co seem to have a higher affinity for cooperite than for braggite. Rhodium was detected only three times in braggite, and Co twice compared with 12 and 14 times respectively in cooperite. For individual pairs of cooperite and braggite, the $K_D^{cooperite/braggite}$ of Rh and Co were calculated from the available analytical results, as well as the lower limit of detection (LLD) (Table 1) for those mineral pairs where the respective concentrations of the elements were below the LLD for one of the minerals. Involvement of the LLD for one of the minerals, mostly braggite, results in minimum values for the K_D. The estimated $K_D^{cooperite/braggite}$ for Rh was determined to be >1.11 (by mass) and >1.40 (atomic ratio). For Co the $K_D^{cooperite/braggite}$ was estimated >1.17 (mass ratio) and >1.46 (atomic ratio). For Fe and Cu no systematic behaviour was detected. The ratios of these two elements between braggite and cooperite vary from 0.07 to 7.00 by mass for Fe and 0.17 to 4.49 by mass for Cu, indicating that these elements do not have a preferred affinity for any one of the two minerals.

Implications for phase relations

Skinner et al. (1976) reported ternary phase relations for the system Pt–Pd–S at 1000°C and Cabri et al. (1978) at 800°C. Three phases could be distinguished — a solid solution between Pt and

TABLE 7. Spearman correlation coefficients r with error probabilities e_r and slopes b and intercepts a of regression lines with standard error s_b and s_a for the concentration in atomic per cent Pt, Pd and Ni between braggite and cooperite.

	r	e_r	b	s_b	a	s_a
Pt	0.3426	0.0408	0.94	0.54	−18.63	25.49
Pd	0.4860	0.0027	1.97	0.63	13.52	0.74
Ni	−0.0378	0.8266	−0.51	0.69	7.80	0.85

Pd and two sulphides. The first sulphide is a solid solution with a structure identical to cooperite, extending from PtS to $(Pt_{0.7}Pd_{0.3})S$ at 1000°C and to $(Pt_{0.54}Pd_{0.46})S$ at 800°C (Fig. 6). At 1000°C the braggite-like phase ranges from $(Pt_{0.4}Pd_{0.6})S$ to $(Pd_{0.84}Pt_{0.16})S$ but does not reach the composition PdS. At 1000°C PdS is not stable but the upper stability limit of PdS is not clear; temperatures of 912°C (Skinner et al., 1976) and 970°C (Barin et al., 1977) are reported. At 800°C the braggite-like solid solution ranges from PdS to $(Pd_{0.76}Pt_{0.24})S$.

The Ni-free projected data from our samples of the Merensky Reef, as well as the UG-2, indicate cooperite to range from PtS to $(Pt_{0.94}Pd_{0.06})S$ and braggite from PtS to $(Pt_{0.74}Pd_{0.26})S$ in the case of the UG-2. It can be assumed that the 'freezing in' temperature of this system lies well below 800°C. Looking at the compositional ranges at the different temperatures it seems unusual that the stability field for cooperite should be larger at a lower temperature. The solid solution ranges, as well as the positions of the miscibility gaps require further investigation.

Summary and conclusion

In summary, this investigation yielded the following results:

(1) Natural cooperite, braggite and vysotskite are best represented by the system Pt–Pd–Ni–S. There is a clearly defined miscibility gap between cooperite and braggite, but no evident gap exists between braggite and vysotskite.

(2) Coexisting cooperite and braggite grains permitted an approximation of partition coefficients. The $K_D^{cooperite/braggite}$ in atomic proportions were estimated to be 0.54 for Pt, 15.81 for Pd and 5.93 for Ni. Rh and Co seem to have a higher affinity for cooperite and the $K_D^{braggite/cooperite}$ in atomic proportions are > 1.40 for Rh and > 1.46 for Co. For Fe and Cu no systematic behaviour was detected.

(3) A coupled substitution of Pd + Ni for Pt with a Pd:Ni ratio of approximately 9:11 (Equation 2) is indicated within cooperite. This substitution may also include Rh and Co.

(4) In braggite the same coupled substitution of Pd + Ni for Pt is evident. It has been shown here, that the Pd:Ni ratio can be changed by postmagmatic processes, which are reflected in the BMS assemblages. If the Ni-bearing phase in association with the PGM is pentlandite, the Pd:Ni ratio is about 7:3 (Equations 1 and 3, Figs. 2 and 4). However, if the Ni-bearing phase is millerite, the Pd:Ni ratio changes and the analyses plot on the Ni-poor side of the trend established for the pentlandite association (Equation 4, Fig.
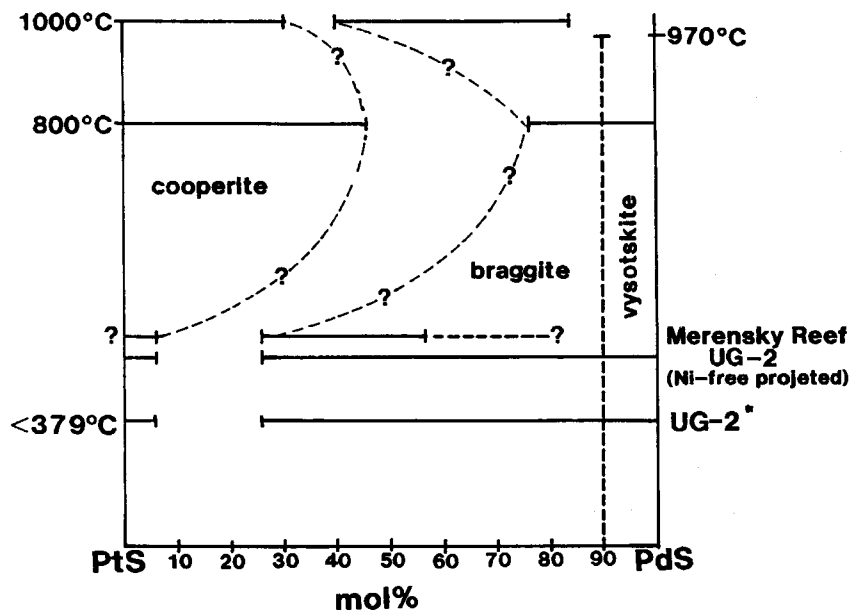

FIG. 6. Stability of cooperite, braggite and vysotskite at 1000°C (after Skinner et al., 1976), at 800°C (after Cabri et al., 1978) and Ni-free projected data from the Merensky Reef and the UG-2 of the Bushveld Complex (*implied by millerite stability).

5). These trends extend right down to vysotskite. The dependence of the Pd:Ni ratio on BMS assemblages indicates that temperature of formation or re-equilibrium rather than the availability of NiS plays the dominant role in the Ni-content of braggite.

(5) The data taken from the literature (Fig. 1) suggest that not all braggites and vysotskites follow the trends derived from our analyses. This, however, could be attributed to variables like temperature of formation and different cooling histories.

(6) The compositional variability of cooperite and braggite/vysotskite at different temperatures (Fig. 6) requires experimental confirmation.

Acknowledgements

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