A MODEL FOR THE GEOCHEMISTRY OF THE PLATINUM-GROUP ELEMENTS IN MAGMATIC SULFIDE DEPOSITS

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Abstract

Partition coefficients D for Pt and Pd between immiscible silicate and sulfide liquids can be calculated if the Pt and Pd contents of magmatic sulfides and the conjugate silicate melt are known. Calculated values of D, obtained from the concentration of the precious metal in the sulfide melt and its initial concentration in the silicate melt, cover a wide range: from ~300 for sulfides related to komatiites, to 1000 for flood-basalt-related sulfides, and over 100,000 for the J–M Reef of the Stillwater Complex and the UG-2 chromitite of the Bushveld Complex. Partition coefficients may be expected to change with the temperature and composition of the melt, but not by the two or three orders of magnitude implied by these calculations. If D is very high, the separation of an immiscible sulfide liquid depletes the silicate melt in platinum-group elements (PGE). Here, $Y_i = X_i D_i (R+1)/(R+D_i)$, where R is the mass ratio of silicate to sulfide liquid, Y_i is the concentration of element i in the sulfide liquid and X_i that in the silicate melt. If R is small compared to D_i, Y_i approximates $X_i(R+1)$ and is virtually independent of D_i. The values of D_{Pt} and D_{Pd} are in excess of 100,000 in all melts; the calculated coefficients in most cases are apparent values, controlled by low values of R. For any pair of elements having D_i large as compared to R, the ratio of these elements in the sulfide liquid is equal to that in the conjugate silicate melt. Since, for a given group of magmatic sulfides, PGE ratios do not change as functions of R, partition coefficients for all PGE must be high, of the order of 10^5.

Keywords: platinum-group elements, geochemistry, magmatic sulfides, partition coefficients.

Sommaire

On peut calculer les coefficients de partage D pour le Pt et le Pd entre liquides immiscibles silicaté et sulfuré si l'on connaît le contenu de Pt et de Pd des sulfures magmatiques et du liquide silicaté associé. Les valeurs calculées de D, obtenues à partir de la concentration du métal précieux dans le liquide sulfuré et de sa concentration originelle dans

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le liquide silicaté, s'étalent sur un large domaine: à ~300 pour les sulfures reliés aux komatiites, la valeur de D passe à 1000 pour les sulfures reliés aux basaltes des plateaux et à plus de 100,000 pour le banc J–M du complexe de Stillwater et la chromitite UG-2 du complexe du Bushveld. On peut prévoir un changement des coefficients de partage avec la température et la composition du bain, mais pas de deux ou trois ordres de grandeur comme l'impliquent ces calculs. Si D est très élevé, la séparation du liquide sulfuré immiscible appauvrit le bain silicaté en éléments du groupe du platine (EGP). Ici, $Y_i = X_i D_i(R+1)/(R+D_i)$, où R est le rapport de masse entre les liquides silicaté et sulfuré, Y_i est la concentration d'un élément i dans le liquide sulfuré, et X_i, celle-ci dans le liquide silicaté. Si R est petit par rapport à D_i, Y_i tend vers $X_i(R+1)$ et devient virtuellement indépendant de D_i. Les valeurs D_{Pt} et D_{Pd} dépassent 100,000 dans tous les magmas; les coefficients calculés dans la plupart des cas sont donc des valeurs apparentes, que gouvernent de faibles valeurs de R. Pour n'importe quelle paire d'éléments ayant un D_i élevé par rapport à R, le rapport de ces éléments dans le liquide sulfuré est égal à celui du bain silicaté associé. Puisque, pour un groupe donné de sulfures magmatiques, les rapports de EGP ne changent pas en fonction de R, les coefficients de partage pour tous les EGP doivent être élevés, de l'ordre de 10^5.

(Traduit par la Rédaction)

Mots-clés: éléments du groupe du platine, géochimie, sulfures magmatiques, coefficients de partage.

Introduction

The concentrations of the platinum-group elements (PGE) in magmatic sulfide ores display a remarkable range of values and may vary by orders of magnitude from one deposit to the next. Ores from the Merensky Reef (Bushveld Complex), for example, which have less than 2 wt.% sulfide, only 1/15 to 1/20 that of the Sudbury ore, contain ten times the amount of Pt and Pd of a typical Sudbury deposit. Attempts to model the geochemistry of the PGE in magmatic sulfides, using partition coefficients (D) of 1000 for Pt and 1500 for Pd and assu-

ming that continuous equilibrium is maintained between the sulfide and silicate melts, have been only partly successful (Naldrett *et al.* 1979, Naldrett 1981a). In this paper, the failure of previous models to explain the very high concentrations of PGE in the Merensky Reef, the UG–2 chromite seam (Bushveld Complex) and the J–M Reef (Stillwater Complex) is attributed to the use of partition coefficients that are too low. We suggest that partition coefficients for the PGE may be one to two orders of magnitude higher than previous estimates. Using these higher values for the partition coefficients, a simple equilibrium-model is developed that can explain the wide range of PGE concentration in magmatic sulfides.

PARTITION COEFFICIENTS FOR Pt AND Pd

Although partition coefficients for the PGE between immiscible sulfide and silicate liquids are known to be high (Naldrett 1981a, Keays & Campbell 1981), the precise values are uncertain. Ideally, partition coefficients should be measured experimentally, but the experimental determination of high partition-coefficients is extremely difficult. Assume, for example, that D_{Pd} for the partitioning of Pd

between immiscible sulfide and silicate liquids is 10,000. If the Pd content of the sulfide melt is 10%, the Pd content of the silicate liquid will be only 10 ppm, well below the detection limit of the electron probe. Experiments of this type have been carried out by W.H. MacLean (pers. comm., 1976); although these did not yield a value for D_{Pd}, they did show that D_{Pd} is in excess of 1,000. Attempts to measure D_{Pt} by separating the sulfides from the quenched glass have also been unsuccessful (A.J. Naldrett, pers. comm., 1976). Here, the problem is to extract a glass completely free of sulfides, since a trace of Pt-rich sulfide in the glass will invalidate the analysis of the glass.

An alternate approach is to calculate D_{Pt} and D_{Pd} from the Pt–Pd content of natural magmatic sulfides and the silicate liquids from which they are believed to have crystallized. The Pt–Pd content of magmatic sulfides can be determined by analysis of the sulfides. Some difficulties are encountered in obtaining a representative sample of a trace element in a sulfide orebody, but these can be minimized by using a large weight of sample and by analyzing numerous samples (Naldrett *et al.* 1979, Naldrett 1981a). Estimates of the Pt–Pd content of the silicate melt from which the immiscible sulfides separated are not so

TABLE 1. PARTITION COEFFICIENTS[†] FOR Ni, Cu, Pt AND Pd CALCULATED FROM THE METAL CONTENT OF SULFIDE ORE AND ESTIMATES OF THE METAL CONTENT IN THE SILICATE MELT FROM WHICH THEY SEPARATED

	Initial conc. in silicate liquid (ppm)*				Conc. in sulfide liquid (ppm)				Calculated D = D^a				Ref.
	Ni	Cu	Pt	Pd	Ni	Cu	Pt	Pd	Ni	Cu	Pt	Pd	
Pipe	1500	50	.005	.0075	40000	1600	.05	.12	27	32	11	12	7
Archean Komatiites													
Fisher	1500	50	.005	.0075	140000	11600	1.8	2.2	93	232	360	295	8
Lunnon	1500	50	.005	.0075	122000	10000	1.5	1.6	81	200	290	216	8
Juan	1500	50	.005	.0075	144000	9700	1.3	1.9	96	194	268	252	8
Mt. Edwards	1500	50	.005	.0075	113000	13100	.42	1.1	75	262	84	141	7
Langmuir	1500	50	.005	.0075	146000	6700	.89	1.6	97	134	178	213	7
Proterozoic Komatiites													
Katiniq	900	150	.005	.01	105000	31000	3.3	6.7	116	206	664	671	7
Donaldson West	900	150	.005	.01	155000	37000	4.1	15.5	172	247	826	1550	7
Ni-Cu-Dominant Gabbros													
Strathcona	240	170		.0012	36000	28000	.42	.37	150	165		308	6
Levack West	240	170		.0012	57000	37000	1.15	1.25	238	218		1042	7
L. Stobie 1	240	170		.0024	38000	44000	1.9	2.1	158	259		880	7
L. Stobie 2	240	170		.0024	40000	36000	2.1	3.2	167	212		1315	7
Talnakh	280	440	.014	.024	76000	109000	13.7	36	271	247	978	1500	1
Pt-Pd-Dominant Gabbros													
Merensky			.040	.016	109000	46000	258	102			6450	6375	2,3
UG-2			.040	.016			4850	4900			1.2×10^5	3.1×10^5	2,3,4
J-M. Reef	250	200	.012	.055	78000	50000	1900	6500	312	250	1.6×10^5	1.2×10^5	4,5

† The partition coefficients calculated by this method are apparent partition coefficients (D^a, see text). References: 1. Naldrett (1981a), 2. Naldrett & Cabri (1976), 3. Sharpe (1982), 4. Naldrett (1981b), 5. S. Barnes (unpubl. data), 6. Naldrett *et al.* (1982), 7. Naldrett & Duke (1980), 8. Ross & Keays (1979). Note: The calculation of the metal content of the sulfide liquid is based on the sulfur content of the ore. If the ores have lost S, D^a values will be high.
* Initial concentrations in the silicate liquid are taken from Naldrett (1981a).

straightforward. In some instances, the Pt–Pd content of the silicate liquid can be obtained from quenched liquids, *e.g.*, the chilled margin of a layered intrusive complex or the top of a komatiite flow. In other cases, the Pt–Pd content of the silicate liquid must be estimated from typical abundances of these elements in the magma type from which the sulfide liquid separated.

Concentrations of Ni, Cu, Ir, Pt and Pd for some typical magmatic sulfides, together with estimates of the concentration of these elements in the silicate melt from which they separated, are given in Table 1. Also listed in Table 1 are partition coefficients calculated from these data. Errors in these calculated partition-coefficients, which arise mainly from the estimate of the precious-metal content of the silicate melt, are likely to be large. The values given are believed to be accurate to within ± 50% in most cases, but in some instances the error may be as high as 100%.

RESULTS

When discussing the data in Table 1, it is convenient to divide the deposits into four geochemical groups: Archean komatiites, Proterozoic komatiites, Ni–Cu-dominant gabbroic sulfides and Pt–Pd-dominant gabbro-hosted sulfides. The Pipe deposit in the Manitoba Nickel Belt is associated with a narrow, metamorphosed peridotite sill and forms a fifth class that must be discussed separately.

The following generalizations can be made:
1) With two exceptions, Pipe and Langmuir (Ontario), D_{Cu} shows a limited range, varying from 194 to 264 for silicate compositions that range from komatiite to gabbro. 2) D_{Ni} shows a systematic change with the chemical composition of the silicate melt (Rajamani & Naldrett 1978, Campbell *et al.* 1979). It varies between 75 and 97 for Archean komatiites, 116 and 172 for Proterozoic komatiites and 158 and 312 for both types of gabbroic deposits. 3) D_{Pt} and D_{Pd} are the same within the accuracy of the calculation. D_{Pt} and D_{Pd} are about 250 for Archean komatiites, 800 for Proterozoic komatiites, 1,000 for Ni–Cu-dominant gabbroic deposits and over 5,000 for Pt–Pd-dominant deposits, reaching a maximum of 160,000 for D_{Pt} in the J–M Reef of the Stillwater Complex. 4) All partition coefficients for Pipe are very low.

Partition coefficients may change with temperature and the $f(O_2)/f(S_2)$ ratio of the melt. Campbell *et al.* (1979) have shown that γ_{NiO} increases with decreasing temperature and increasing acidity of the silicate liquid. Since D_{Ni} is proportional to γ_{NiO}, D_{Ni} can be expected to increase by about the observed amount between a komatiite with an MgO content of 32% and a liquidus temperature of 1600°C and a gabbro with less than 10% MgO and a liquidus temperature of less than 1200°C (Rajamani & Naldrett 1978, Campbell *et al.* 1979). It

could be argued that the variations in temperature and melt composition may be responsible for similar changes in D_{Pt} and D_{Pd}, causing them to change from 250 in komatiites to about 1,000 in gabbros. However, this approach cannot be used to explain the change in D_{Pt} and D_{Pd} from about 1,000 for Ni–Cu-dominant gabbroic sulfides to over 100,000 in Pt–Pd-dominant sulfides, since both have separated from silicate melts of similar composition.

DISCUSSION

The apparent partition-coefficients in Table 1 have been calculated from equation (1)

$$D^a_i = Y_i/X^o_i \qquad (1)$$

where Y_i is the concentration of the element *i* in the sulfide liquid, X^o_i is its initial concentration in the silicate liquid and D^a_i is the Nernst distribution coefficient. Equation (1) assumes that the reservoir of silicate liquid is infinite, so that separation of the immiscible sulfide liquid does not deplete the silicate liquid in *i*. If the silicate reservoir has a restricted volume, equation (1) is no longer valid, and Y_i should be calculated from the Nernst distribution law,

$$Y_i = D_i X^f_i \qquad (2)$$

where X^f_i is the final concentration of *i* in the silicate liquid after separation of the sulfide liquid. X^f_i is rarely known, but Y_i can still be calculated from

$$Y_i = \frac{X^o_i D_i (R + 1)}{(R + D_i)} \qquad (3)$$

where R is the mass ratio of silicate to sulfide (Campbell & Naldrett 1979).

If the sulfides are added to the silicate liquid, by assimilation from the country rock, for example, equation (3) should be replaced by

$$Y_i = \frac{X^o_i D_i R}{(R + D_i)} \qquad (3a)$$

The effect of R on Y_i for a wide variety of partition coefficients is illustrated in Figure 1. If R lies between 1/10 and 10 × D_i, Y_i is strongly dependent on R, but if R is greater than 10 × D_i, further increases in R have little effect on Y_i. If R is less than 10 × D_i, equation (1) yields apparent partition-coefficients that are less than the true partition-
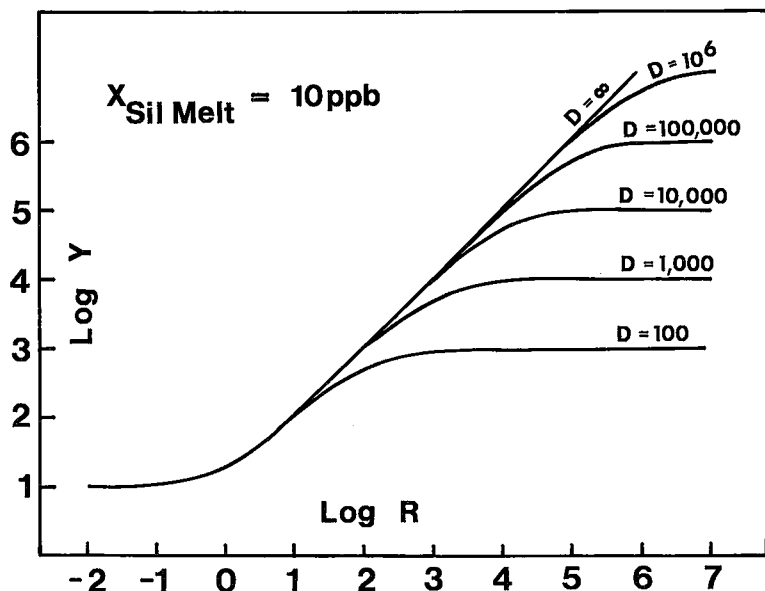
FIG. 1. The effect of variations in the silicate/sulfide ratio R on the precious metal content of a sulfide liquid (Y) for different values of D. The concentration of the precious metal in the silicate liquid is assumed to be 10 ppb. Note that if R is less than a tenth of D, Y is virtually independent of D. D^a is the apparent distribution-coefficient and is equal to Y_i/X_i.

coefficients as defined by equation (2). The lower the value of R, the lower the apparent partition-coefficient. A simple example serves to illustrate this point.

Consider a melt that contains 10 ppb of a trace element and that precipitates an immiscible sulfide liquid. Assume that D, the partition coefficient for the trace element between the sulfide and silicate liquid, is 100,000. Y_i, the concentration of the trace element in the sulfide liquid calculated from equation (3) for various values of R, is listed in Table 2. If $R = \infty$, the concentration of the trace element in the sulfide liquid is 1,000,000 ppb, but if R falls below $10 \times D_i$, Y_i begins to decrease. The depletion in the trace-element content of the sulfides with decreasing R is accompanied by a corresponding decrease in the trace-element content of the silicate liquid as defined by equation (2). Equation (1) does not recognize this depletion. Distribution coefficients calculated from equation (1) are therefore apparent and are designated D^a. Apparent distribution-coefficients calculated by dividing Y_i by 10 (the original concentration of the trace element in the silicate liquid) are also listed in Table 2. D^a_i is less than D_i, especially if R is less than $10 \times D_i$. Notice that if R is less than $D_i/10$, D^a_i is approximately equal to R (i.e., below $R = 10,000$ in Table 2).

Campbell & Naldrett (1979) used equation (3) to explain the low Ni, Cu and Co contents of the Pipe ores. They showed that if R is low for Pipe (about 30), the depleted base-metal geochemistry of the sulfides can be successfully explained. Naldrett et al. (1979) and Naldrett (1981a) have used this principle to model a wide range of komatiitic and Ni–Cu-dominant gabbroic deposits for Ni, Cu, Co, Pt and Pd. In this model, partition coefficients for Ni are assumed to vary with temperature and composition,

TABLE 2. Y_i AND D^a_i (THE APPARENT DISTRIBUTION COEFFICIENT) FOR DIFFERENT VALUES OF R, ASSUMING D_i = 100,000 AND X_i = 10

R	Y_i	D^a_i
∞	1,000,000	100,000
10^7	990,099	99,010
10^6	909,090	90,909
10^5	500,000	50,000
10^4	90,918	9,092
10^3	9,911	991
10^2	1,009	101
10	110	11

from 100 in a komatiite with 27% MgO to 275 in a basaltic magma. D_{Cu}, D_{Pt} and D_{Pd}, are assumed to be independent of temperature and composition. The values used are 250, 1000 and 1500, respectively. The success, simplicity and internal consistency of the model suggest that the approach taken is basically sound.

Attempts to extend the model to Pt–Pd-dominant gabbroic sulfides, using the partition coefficients recommended by Naldrett (1981a), have been unsuccessful. The problem is that apparent partition-coefficients for Pt–Pd-dominant sulfides are well above 1500 (Table 1). Variations in R can explain why the apparent partition-coefficients for Pt and Pd fall below 1000 and 1500, respectively (as, for example, at the Pipe and Kambalda deposits), but cannot explain the very high apparent values of D_{Pt} and D_{Pd}, for the Merensky Reef, UG–2 chromite seam (Bushveld Complex) and J–M Reef (Stillwater Complex).

Solution

If R is small compared with D_i, it can be shown from equation (3) that

$$Y_i \approx X_i(R+1) \qquad (4)$$

Two points follow from equation (4).

(i) If R is small compared to D_i, Y_i is a function of R and is virtually independent of D_i. For practical purposes, equation (4) can be used if R is less than $D/10$. Note that in Figure 1, it is virtually impossible to distinguish between Y_i for D values of 10^4, 10^5, and 10^6 if R is less than 10^3 and, in general, difficult to distinguish between different values of D where R is less than D.

(ii) It follows from equations (1) and (4) that if R is small compared to D, the apparent distribution-coefficient calculated from equation (1) is approximately equal to $R+1$. This point was illustrated in connection with Table 2.

Our solution to the problem is simple. We suggest that D_{Pt} and D_{Pd} are high, of the order of 10^5 for all types of magmatic sulfide deposits, and that the partition coefficients in Table 1 for komatiitic and Ni–Cu-dominant gabbroic deposits, calculated from equation (1), are apparent partition-coefficients controlled by the R factor. We suggest that the apparent success of the Naldrett (1981a) model, using D_{Pt} and D_{Pd} values of 1000 and 1500, respectively, stems from the fact that if R is less than D, it is difficult to distinguish between different values of D. Equation (4) can also be used to obtain a value of R. Estimates of R for most magmatic sulfide deposits are less than 10^4 (Naldrett 1981a). If the values for D_{Pt} and D_{Pd} are greater than 10^5 as we suggest, $D_{Pt,Pd}$ is much greater than R, and it follows from

equation (4) that R is approximately equal to $D^a_{Pt,Pd}$.

EXAMPLES

The Sudbury deposits

Naldrett et al. (1982) have developed a multistage model to explain the Ni, Cu, Co and Pd content of four of the Sudbury ore deposits. The model assumes that each of the deposits comes from a common source-magma. This source-magma fractionates various amounts of sulfide or olivine (or both) to form the parent magmas from which the individual deposits form. The final step in the calculation is to assume a value for R and to calculate the composition of the sulfides using D values of 1500, 275, 250 and 80 for Pd, Ni, Cu and Co, respectively. The results for the final step in Naldrett's calculation are listed in Table 3. Also listed in Table 3 are the results of a similar calculation in which D_{Pd} is assumed to be 100,000. The R factors for this second calculation were obtained from the apparent partition-coefficients in Table 1 and thus differ from Naldrett's. All other assumptions are the same. Notice that the values for Ni, Cu and Co are 20%, 10% and 15%, respectively, less than the Naldrett values. The close agreement between the calculated value of Pd for $D_{Pd} = 100,000$ and the actual value is an artifact of the calculation. Since the errors in estimating the base-metal content of silicate liquid and the D for each metal are likely to be in excess of 20%, the two models are indistinguishable. A fit equal to that obtained by Naldrett could be obtained by making an appropriate increase in the assumed base-metal content of the silicate melt or in the D values used in the calculation. If the higher value is used for D_{Pd}, the amount of sulfide fractionation required by the Naldrett model to lower the Pd content of the melt prior to formation of the ore deposit is appreciably less.

Other Ni–Cu-dominant deposits

The type of modeling applied to the Sudbury

TABLE 3. MODELED Ni, Cu AND Co CONTENTS OF SULFIDES FROM FOUR SUDBURY ORE DEPOSITS ASSUMING D_{Pd} OF 1500 AND 100,000

	Levack West			Strathcona			Little Stobie No. 1			Little Stobie No. 2		
D_{Pd}	Obs.[a]	1500[b]	10^5	Obs.[a]	1500[b]	10^5	Obs.[a]	1500[b]	10^5	Obs.[a]	1500[b]	10^5
R		4500	1042		442	308		1900	880		8830	1315
Ni	5.7	5.5	4.6	3.6	3.6	3.1	3.8	3.6	3.1	4.0	4.0	3.4
Cu	3.7	3.6	3.3	2.8	2.4	2.2	4.4	4.0	3.8	3.6	4.4	4.1
Co	0.16	0.17	0.15	0.15	0.14	0.13	0.19	0.17	0.16	0.17	0.17	0.16
Pd	1253	1350	1240	372	410	370	2120	2020	2104	3170	3090	3130

a. Obs.: observed values for the deposit from Naldrett (1981a)

b. Value of D_{Pd} assumed by Naldrett (1981a)

deposits has been extended in a more general way to the remainder of the Ni–Cu-dominant deposits listed in Table 1. Our simple approach assumes that no sulfide or silicate fractionation has occurred prior to precipitation of the sulfide ore deposit. The first step is to calculate a value for R. R can be calculated if the true distribution-coefficient (D_i) and the apparent distribution-coefficient (D^a_i) are known, where

$$D^a_i = Y_i / X^o_i \qquad (5)$$

If equation (5) is substituted into equation (3), it can be shown that

$$R = \frac{D_i(D^a_i - 1)}{(D_i - D^a_i)} \qquad (6)$$

Two series of calculations have been made; the first assumed a D_{Pd} value of 1500, the second a value of 120,000. The D^a_{Pd} values used are the calculated D_{Pd} values listed in Table 1. The R factors, calculated from equation (6), are listed in Table 4. From these two sets of R factors, two sets of Ni and values have been calculated using the X_i values from Table 1 and the appropriate D_i. The results are given in Table 4.

The difference between the Ni and Cu values calculated from both models is less than 20% in all cases; in most instances, both models yield values that are in close agreement with the observed values. Given the difficulties in estimating the Ni and Cu content of the silicate melt and the appropriate value for D_i, the agreement between observed and calculated

values is as good as can be expected. Pd values have been omitted from Table 3 because the method of calculating R insures that the calculated Pd values will agree closely with the observed values. If Pt is used instead of Pd, results similar to those listed in Table 4 are obtained.

The difference between the observed and calculated values for Ni and Cu in the Pipe deposit is over 100% and requires special comment. Better agreement can be obtained if the R factor is increased to 30. This would imply that the estimate of the Pd content of the Pipe magma is too high by a factor of three. The Pd could be reduced to the required level if the magma fractionated a small amount of sulfide prior to formation of the ore deposit.

ELEMENT RATIOS

The problem of PGE partition-coefficients can also be approached by using element ratios in sulfides. If two elements i and j are considered and if D for both elements is large compared with R, it follows from equation (4) that Y_i/Y_j, the trace-element ratio in the sulfide liquid, is given by

$$\frac{Y_i}{Y_j} = \frac{X_i(R+1)}{X_j(R+1)} = \frac{X_i}{X_j} \qquad (7)$$

That is, the trace-element ratio in the sulfide liquid is equal to that in the silicate liquid from which it separated (Campbell & Naldrett 1979). In practice, equation (7) can be used if R is less than one tenth the lower of the two values of D. The hypothesis presented in this paper requires D_{Pt} and D_{Pd} to be in excess of 100,000. If this is so, equation (7) can be used for all sulfide deposits that have R values of less than 10,000, i.e., all the deposits in Table 1 except for the UG–2 chromite seam and the J–M Reef. The Pd/Pt ratios for all other deposits should be equal to the Pd/Pt ratio of the silicate melt from which they separated.

If R is greater than one tenth the lower of the two values of D, Y_i/Y_j is strongly dependent on R. From equation (3) it can be shown that

$$\frac{Y_i}{Y_j} = \frac{X_i}{X_j} \cdot \frac{D_i}{D_j} \cdot \frac{(R+D_j)}{(R+D_i)} \qquad (8)$$

which can be rearranged as follows:

$$(Y_i/Y_j)/(X_i/X_j) = \frac{D_i}{D_j} \cdot \frac{(R+D_j)}{(R+D_i)} = G \qquad (9)$$

G is the enrichment of the trace-element ratio in the sulfide liquid compared with that in the silicate liquid. G varies between (D_i/D_j) for $R \gg D$ to 1 for

TABLE 4.   N1 AND Cu CONCENTRATIONS IN SULFIDE MELTS OBSERVED AND CALCULATED FROM EQUATION (3)

	Cu			Ni			R Factors*	
	1	2	3	1	2	3	2	3
Pipe	.16	.06	.06	4.0	1.7	1.7	12	12
Archean Komatiites								
Fisher	1.16	.7	.7	14.0	11.8	11.3	367	296
Lunnon	1.0	.6	.6	12.2	10.8	10.3	252	216
Juan	.97	.7	.6	14.4	11.3	10.8	302	253
Mt. Edwards	1.31	.5	.5	11.3	9.2	8.8	156	141
Langmuir	.67	.6	.6	14.6	10.7	10.3	248	213
Proterozoic Komatiites								
Katiniq	3.1	3.1	2.7	10.5	13.8	12.5	1213	675
Donaldson West	3.7	3.7	3.2	15.5	15.7	14.2	>10,000	1571
Ni–Cu-Dominant Gabbros								
Strathcona	2.8	2.6	2.4	3.6	3.9	3.5	387	309
Levack West	3.7	4.0	3.4	5.7	6.1	5.2	3410	1051
L. Stobie 1	4.4	3.8	3.3	3.8	5.8	5.0	2147	887
L. Stobie 2	3.6	4.2	3.6	4.0	6.4	5.5	10,655	1330
Talnakh	10.9	10.8	9.5	7.6	7.7	6.5	>10,000	1519

1. Observed values from Table 1.
2. Calculated values assuming D_{Pd} = 1500.
3. Calculated values assuming D_{Pd} = 120,000.
*   R factors were calculated from equation (6) using the D^a values listed in Table 1 and D_{Pd} values of 1500 (column 2) and 120,000 (column 3). X_i values are also taken from Table 1.

$R \ll D$. Variation in G as a function of R is important only in the region where $D_j/10 < R < 10D_i$.

Application to Sudbury deposits

The hypothesis can be tested where a number of ore deposits have formed from a single magma. The Sudbury ore deposits provide a perfect example. Calculated values of R, based on the apparent distribution-coefficient for Pd (Table 1), range from 308 to 1315. If D_{Pt} and D_{Pd} exceed 100,000, the Pd/Pt ratio should be independent of R and should, therefore, change little from one ore deposit to the next. Values for D_{Cu}, D_{Ni} and D_{Co}, on the other hand, are believed to be 250, 275 and 80, respectively. All of these partition coefficients are greater than one tenth R, so that Pd/Cu, Pd/Ni and Pd/Co ratios are strongly dependent on R and should vary from one deposit to the next. Ratios of Pd/Pt, Pd/Cu, Pd/Ni and Pd/Co for Sudbury ore deposits are given in Table 5. Note that Pd/Cu, Pd/Ni and Pd/Co ratios are highly variable as predicted, all of the ratios varying by at least a factor of 6 between the Strathcona and Little Stobie No. 2 deposits. Variations in the Pd/Pt ratio are small by comparison.

This approach can be used to obtain an indica-

TABLE 5. Pd/BASE METAL ($\times 10^6$) AND Pd/PGE RATIOS FOR SELECTED SUDBURY ORE DEPOSITS*

	Pd/Ni	Pd/Cu	Pd/Co	Pd/Pt	Pd/Rh	Pd/Ru	Pd/Ir	Pd/Os
Strathcona	10	13	248	.89	12	18	31	47
Levack West	22	34	783	1.09	7	21	27	57
Little Stobie #1	55	48	1116	1.10	17	17	35	73
Little Stobie #2	79	88	1865	1.49	10	13	28	69

* Data from Naldrett (1981a).

tion of the value of D for other PGE. Table 5 also gives Pd/PGE ratios for the other PGE. With the exception of Pd/Rh, variations in these ratios are small. This is only possible if all the partition coefficients are greater than $10 \times R$, that is, if they are greater than 10,000. The Pd/Rh ratio does not vary systematically with R, and changes in this ratio are probably due to sampling or analytical error rather than a D value for Rh of less than 10,000.

Pt IN SILICATE ROCKS
AS A GUIDE IN EXPLORATION
FOR Ni–Cu-DOMINANT DEPOSITS

A silicate melt that has previously fractionated an immiscible sulfide liquid becomes depleted in chalcophile elements such as Ni, Cu and the PGE. Equations (2) and (3) can be combined to show that
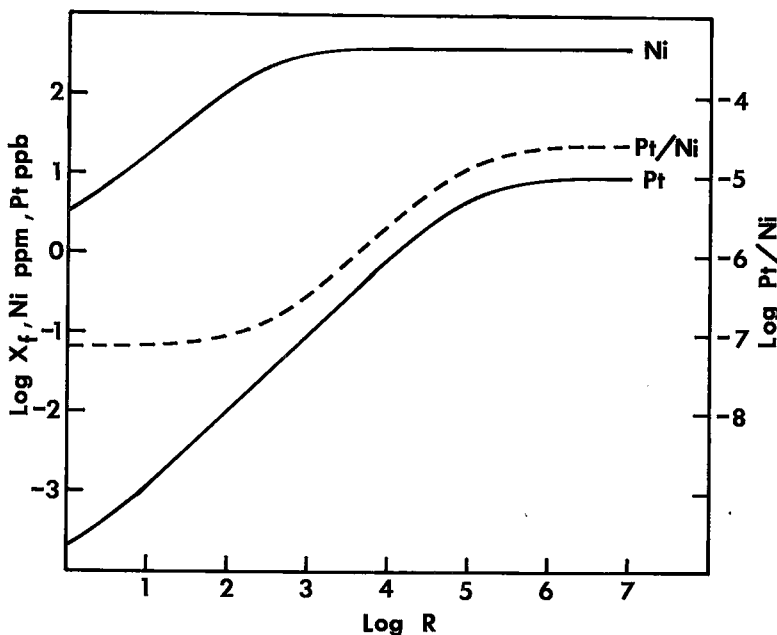

FIG. 2. Variations in the Pt/Ni ratio and Pt and Ni contents of a silicate liquid in equilibrium with an immiscible sulfide liquid, as a function of R. D_{Ni} and D_{Pt} are assumed to be 250 and 100,000, respectively. The Ni and Pt contents of the initial silicate liquid were taken to be 400 ppm and 10 ppb, respectively.

X^f_i, the final concentration of a chalcophile element i in a silicate melt, is given by

$$X^f_i = \frac{X^o_i(R+1)}{(R+D_i)} \qquad (10)$$

Equation (10) has been used to calculate, as a function of R, the Ni and Pt content of a silicate melt that has fractionated an immiscible sulfide liquid. The results are plotted in Figure 2. Note that there is a marked drop in the Ni content of the melt if R is less than 1000. Olivine crystals that crystallize from a Ni-depleted melt will themselves be Ni deficient Thompson (1982) has suggested that the Ni content of olivine can be used as a guide to the identification of silicate melts that fractionated an immiscible sulfide liquid.

Unfortunately, this approach has some important limitations when applied to the exploration of nickel sulfide deposits. In the example illustrated in Figure 2, Ni depletion in the silicate melt does not become significant until the R factor drops below 1000. If the depletion is less than 30%, it would be difficult to distinguish olivine with Ni depletion due to sulfide fractionation from the normal variation in the Ni content of olivine that crystallized from sulfur-unsaturated melts. Further, any depletion in the Ni content of olivine must be accompanied by a corresponding depletion in the Ni content of the sulfides. For example, if the Ni content of olivine is depleted by 50%, the Ni content of coexisting sulfides will be 50% of their value at infinite R. Thus there is a narrow window of R values for which the technique can be successfully used. If R is too large, the composition of olivine coexisting with sulfides will not show sufficient Ni depletion to allow them to be distinguished from normal olivine. If R is too small, the recognition of low-Ni olivine may lead to the discovery of magmatic sulfides, but these sulfides will have a low Ni/S ratio and will thus be uneconomic.

The Pt content of a silicate melt is also depleted by the separation of an immiscible sulfide liquid. The depletion starts at a much higher R value, e.g., at 1,000,000 in the example illustrated in Figure 2. As a consequence, there is a range of R values between 1,000 and 1,000,000 for which the melt is Pt-depleted but not Ni-depleted. We suggest that most Ni-Cu-dominant ores form within this range of R values. The silicates that host such deposits should be characterized by low Pt and low Pt/Ni, but should have normal or only slightly depleted Ni values. Thus the Pt content and Pt/Ni ratio of silicate rocks and minerals is a potentially powerful tool in the exploration for Ni/Cu-dominant sulfide deposits. Its use requires that the value of D_{Pt} be high, but the precise value need not be known.

METAL–SILICATE PARTITION-COEFFICIENTS FOR THE PGE

Metal–silicate partition-coefficients for the PGE are important for studies of the earth–moon system, especially in relation to core formation (Ringwood 1979). PGE are known to substitute preferentially into Fe metal where it coexists with sulfides. Partition coefficients for PGE between Fe metal and a eutectic sulfide melt are close to 10 for most PGE, with the exception of Pd, which has a D value of 2.6 (Noddack et al. 1940). If, as argued in this paper, partition coefficients of PGE between immiscible sulfide and silicate liquids are of the order 10^5, partition coefficients for metal – silicate liquid should be close to 10^6.

PGE RATIOS IN KOMATIITES

Most of the PGE in the mantle are believed to be hosted by sulfides (Mitchell & Keays 1981), although some (e.g., Ir and Os) may be held in metallic alloys (Keays & Campbell 1981). If all the sulfide and metallic alloys are removed from the mantle by the melting process, the PGE ratios in the melt should be those of the mantle from which they formed. The higher the degree of partial melting, the more likely this condition will be satisfied. High-Mg komatiites, which are believed to have crystallized from the magmas formed by the highest degree of partial melting, are clearly the rocks most suited to this type of study.

Unfortunately, apart from Pd/Ir ratios, there are virtually no data on the PGE ratios in komatiites. However, the PGE ratios of sulfides associated with komatiites can be used to fill this gap. The R factor for these deposits is less than 300 (Table 4), so that

TABLE 6. Pd/PGE RATIOS FOR SULFIDES FROM ARCHEAN FLOW-RELATED KOMATIITES[**]

	Pd/Pt	Pd/Rh	Pd/Ru	Pd/Ir	Pd/Os
CANADIAN					
Langmuir	1.8	7.0	2.1	6.7	3.9
McWatters	2.1	3.3	1.6	4.3	4.5
Marbridge	2.6	11.5			
WESTERN AUSTRALIA					
Mt. Edwards	2.5	6.5	2.2	8.8	7.6
Nepean	1.6			8.4	
Mt. Windarra	2.5				
Redross				6.5	
Scotia	2.1				
Kambalda Av.			1.6	6.0	3.3
Lunnon*	1.1				
Fisher*	1.2				
Juan*	1.4				
Durkin*	1.3				
McMahon*	1.2				
Ken*	1.7				
Average	1.8	7.1	1.9	6.8	4.8
Av. Cl Chondrite[†]	0.5	2.7	0.8	1.0	1.1

* Kambalda ore shoots.
** Data from Naldrett (1981a) and Ross & Keays (1979).
† Values from Naldrett (1981a).

the PGE ratios in the sulfides should be those of the silicate melt from which they crystallized.

PGE ratios for sulfides from Archean komatiites are listed in Table 6. If the arguments advanced in this paper are correct, the values of the Pd/Ir ratio in Table 6 should be similar to those for Archean komatiites. Ross & Keays (1979) reported the Pd/Ir ratio for seven high-Mg komatiites. The average Pd/Ir ratio for these samples is 8.2, which is in close agreement with an average value of 6.8 for the sulfide ores listed in Table 6.

Table 6 also gives chondritic PGE ratios. Note that the PGE ratios for high-Mg komatiites are not chondritic. There are two possible explanations: (i) the upper mantle is not chondritic, or (ii) a PGE-bearing phase, such as a sulfide or metal alloy, has remained in the mantle after melting.

The occurrence of Os-Ir metal alloys in ultramafic rocks and chromitites (Cabri & Harris 1975, H. Stockman, pers. comm. 1982), presumed to be the residue of partial melting, support the second conclusion. Isotopic studies of $^{181}Os/^{186}Os$ in these alloys by Allègre & Luck (1980) have shown that (i) the mantle has a chondritic Re:Os ratio, suggesting that PGE ratios in the mantle should also be chondritic, and (ii) the samples used in their study fall on a single mantle-growth curve. In this respect, the systematics of the Re-Os system differ from those of incompatible isotopic systems, such as those involving Sr, Nd and Pb. The inference is that Re and Os are behaving as compatible elements during anatexis and that their concentrations in the mantle are not significantly affected by small degrees of partial melting. If PGE ratios are chondritic in the mantle but not in komatiites, the residual phase that retains the PGE in the mantle must survive the high degrees of partial melting required to form komatiites. If this argument is correct, the PGE content of basaltic and komatiitic liquids is controlled by the partition coefficients for each of the elements between the liquid and the residual PGE-bearing phase.

CONCLUSIONS

The PGE content of natural sulfide orebodies and silicate liquids has been used to argue that partition coefficients for the PGE are of the order of 10^5 for immiscible sulfide – silicate liquid partitioning and greater than 10^6 for metal – silicate liquid partitioning. These estimates are, of course, not a substitute for experimentally determined values, but in many applications the absolute value of D does not matter, provided that it is known to be high. For example, in magmatic sulfides, where R is less than $D/10$, the PGE content of the sulfides is a function of R and is virtually independent of D. The silicate melt in equilibrium with these sulfides will be characteriz-ed by low PGE values and by low PGE/Ni ratios. This is potentially a powerful tool in the exploration for Ni-Cu-dominant sulfide deposits. In other applications, for example in predicting the PGE content of a silicate melt in equilibrium with an immiscible sulfide liquid, accurately determined values of D are essential. There is clearly an urgent need for the accurate determination of the values of D for PGE partitioning between immiscible sulfide and silicate liquids and between silicate liquids and metals.

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