THE COMPOSITION OF Ni-SULFIDE ORES, WITH PARTICULAR REFERENCE TO THEIR CONTENT OF PGE AND Au

A.J. NALDRETT, E.L. HOFFMAN, A.H. GREEN, CHEN-LIN CHOU AND
S.R. NALDRETT

Department of Geology, University of Toronto, Toronto, Ontario M5S 1A1

R.A. ALCOCK

INCO Metals Ltd., Mississauga, Ontario L5K 1Z9

ABSTRACT

Sulfides associated with 'classic' Archean peridotitic komatiite flows have characteristic levels of PGE and Au close to average levels in chondrites. Sulfides associated with mafic rocks at Sudbury also have characteristic values, but with higher levels of Au, Pt and Pd and much lower levels of Ru, Ir and Os. Other mafic-associated deposits are also characterized by high (Pt+Pd): (Ru+Ir+Os) ratios, although absolute levels may vary greatly. These observations reflect contrasting compositions of the associated silicate magmas which, in turn, are attributed to variations in the amount of olivine incorporated during magma genesis. The great variation in the absolute concentrations of the noble metals, together with coincident variations observed in the Cu and Ni levels observed in the sulfides of deposits associated with apparently similar rock types, may reflect a number of processes. Among these are: (1) Depletion of magma in chalcophile metals through fractional crystallization under sulfide-saturated conditions, with the resultant removal of sulfides as well as silicates prior to separation of the main ore. (2) Reaction of a fixed mass of sulfide with a variable mass of silicate magma. The ore of the Pipe deposit (Manitoba nickel belt), for instance, shows unusual metal values. While displaying the flat profile typical of 'classic' komatiite deposits, it contains only ⅓ of the Ni, ⅕ of the Cu and 1/10 of the Pt and Pd characteristic of these deposits. Here, the metal values suggest the second model: the magma:sulfide ratio was much smaller than in komatiite deposits, which is explicable if the Pipe ores were formed by the localized assimilation of barren country rock sulfide.

SOMMAIRE

Les sulfures associés aux coulées de komatiites péridotitiques archéenes classiques possèdent des teneurs caractéristiques en éléments du groupe du platine et en or, semblables aux teneurs moyennes des chondrites. Dans les roches mafiques de Sudbury, les sulfures ont aussi des valeurs caractéristiques, mais avec beaucoup plus d'Au, Pt et Pd et beaucoup moins de Ru, Ir et Os. D'autres gisements associés aux roches mafiques montrent aussi un rapport (Pt + Pd): (Ru + Ir + Os) élevé, mais avec des teneurs variables pour chaque métal. Les observations ci-dessus reflètent la différence de composition entre les magmas silicatés associés, différence qui s'explique par la quantité variable d'olivine incorporée durant la formation des magmas. La grande variation de concentration absolue des métaux nobles, comme celle de Cu et Ni dans les sulfures des gisements associés à des roches du même type, peut s'expliquer par deux (parmi plusieurs) processus: (1) Appauvrissement du magma en éléments chalcophiles, par cristallisation fractionnée, lors d'une saturation en sulfures, ce qui élimine tant sulfures que silicates avant la séparation du minerai principal. (2) Réaction entre une masse fixe de sulfure et une masse variable de magma silicaté. Par exemple, le minerai du gisement Pipe (ceinture nickelifère du Manitoba) possède des teneurs en métaux anomales. Bien que montrant le profil en palier typique des gisements komatiitiques classiques, ce minerai ne contient qu'un tiers du Ni, un cinquième du Cu et un dixième de (Pt + Pd) caractéristiques de ces gîtes. Dans ce cas, suivant le 2ᵉ processus, le rapport magma:sulfure était beaucoup plus faible que dans les gissements komatiitiques, ce qui s'expliquerait si les minerais du gisement Pipe résultaient d'une assimilation localisée, par un volume restreint de magma, des sulfures stériles de la roche encaissante.
(Traduit par la Rédaction)

INTRODUCTION

Very little information is available in the literature about the platinum-group-element (PGE) content of nickel–copper sulfide ores (Naldrett & Cabri 1976). In part, this is due to the unwillingness of producers to publish data on grades and in part to the difficulty of analyzing for these elements, particularly Ru, Os and Ir, at the levels at which they commonly occur.

The sulfide ores in which they are concentrated are regarded as direct segregations from mafic and ultramafic silicate magmas. Processes involved in the formation of an eventual ore are therefore: (1) formation of the host

magma as a result of partial melting in the mantle, (2) introduction and crystallization of the magma, (3) segregation and concentration of a sulfide liquid, coupled with partitioning of metals such as Ni, Cu, Co and PGE into the sulfide phase, and (4) redistribution of the metals as a result of later postconsolidation processes. The concentration of metals is a function of all of these processes, those listed under (2) and (3) often occurring together. Provided that the effect of (4) is known to be small or can be minimized by careful sampling of a given deposit, the concentrations of different metals in the sulfides can provide important constraints on models of ore genesis. It has been shown that the ratios of Ni, Cu and Co in many ores are in line with a) predictions made on the basis of experimental data on partitioning between sulfide and silicate melts and b) concentrations of these metals in silicate melts (Rajamani & Naldrett 1978). PGE are particularly important to study in this regard as they seem to partition into the sulfide phase approximately 10 times as readily as Ni, Cu and Co (W.H. MacLean, pers. comm.). In consequence, a given mass of sulfide will cause a much more obvious depletion of PGE in a given mass of magma than will be the case for Ni, Cu and Co, with important implications for genesis and for prospection.

The sparsity of high-quality analytical data on systematically collected samples representative of a wide range of deposits led to the inception of an analytical project in late 1975. Two years were spent in developing analytical procedures (Hoffman *et al.* 1978); since that time analytical work, including Ni, Cu, Co, S, Se, Sb, As, Pb, Zn, Cd, Ag, PGE, Au and δ^{34}S determinations, has been initiated on samples from 14 deposits. This paper is concerned with the results obtained for Ni, Cu, Co, S, PGE and Au from the first 8 deposits studied.

BRIEF DESCRIPTIONS OF DEPOSITS

The deposits studied, together with those for which sufficient data exist in the literature for meaningful comparisons to be made, can be subdivided into (1) deposits associated with 'classic' Archean komatiitic rocks, typified by those of Kambalda, W. Australia, (2) those associated with ultramafic rocks believed to be komatiitic, such as Pipe in the Manitoba nickel belt and Donaldson West in the Proterozoic Ungava nickel belt, and (3) deposits associated with gabbroic rocks, including Little Stobie and Levack West orebodies at Sudbury, the sulfide zones in the Espedalen intrusion,

Norway, the ores at Noril'sk, W. Siberia, and those of the Merensky Reef.

'Classic' Archean komatiite-related deposits

Langmuir. This area covers two deposits, Langmuir Nos. 1 and 2. The samples included in this suite are from the larger of the two, the No. 2 deposit, the only one mined to date. Sulfides occur predominantly within a depression, in part the result of contemporaneous faulting at the base of an ultramafic lava flow. Massive, net-textured and weakly disseminated ore types are present, together with sulfides that appear to have been remobilized and redeposited in zones of brecciation and shearing within overlying ultramafic rocks. The predominant ore mineralogy is pentlandite–pyrrhotite–chalcopyrite; zones rich in pyrite and millerite that are commonly associated with magnetite are attributed to alteration.

Mt. Edwards. This deposit has been described by the staff of INAL (1975). It consists of two sulfide lenses, one at the base of a sequence of ultramafic lava flows and the other 100 m above the base. The dominant mineralogy is pentlandite, pyrrhotite and minor chalcopyrite. The deposit is associated with an anticlinal structure that represents the northern extension of the Widgiemooltha dome, a structure lying 40 km southwest of Kambalda, W. Australia; several Ni sulfide orebodies and numerous prospects occur around this dome.

Kambalda. This camp consists of more than 20 deposits distributed around the Kambalda dome, 50 km south of Kalgoorlie, W. Australia. Numerous descriptions of the deposits exist, including those of Woodall & Travis (1969), Ewers & Hudson (1972), Ross & Hopkins (1975), and Ross & Keays (1979). Three quarters of the ore occurs within irregularities at the base of a sequence of lava flows. The irregularities are commonly trough-shaped, the troughs being bounded by faults that have been active both before and after extrusion of the ore-bearing flows. Within many of the ore deposits, a zone of massive pyrrhotite–pentlandite–pyrite–chalcopyrite ore occurs in sharp contact with the basaltic footwall and is overlain by net-textured ore, overlain in turn by sulfides, weakly disseminated in peridotite.

Other deposits associated with ultramafic rocks

Pipe. This deposit occurs in the Manitoba nickel belt, described by Peredery (1979). The belt itself, thought to be Archean in age, consists of a highly folded and metamorphosed sequence of gneisses overlain by psammitic and

pelitic sediments. Spinifex-bearing pyroxenitic komatiites occur in association with basalts within the sedimentary pile. Lower in the stratigraphy, close to the sediment–gneiss boundary, small lenses of peridotite (interpreted as boudinaged portions of larger intrusions) occur, not infrequently associated with large concentrations of Ni-bearing sulfides. At Pipe, ore occurs as a massive sheath enclosing one end of the peridotite and as zones of disseminated sulfide within it.

Donaldson West. This deposit was selected as representative of those of the Raglan–Cross Lake greenstone belt of the Ungava peninsula. Within the belt, concentrations of nickel sulfides occur within embayments at the base of lenses of peridotite which intrude close to the contact of a sequence of middle Proterozoic (~ 1.8 Ga) pelitic and calcareous sedimentary rocks with an overlying sequence of magnesian basalts (Wilson *et al.* (1969). Donaldson W. ore consists of zones of intermixed massive and net-textured disseminated ore comprising the minerals pyrrhotite, pentlandite and chalcopyrite. In general, the proportion of massive sulfide increases towards the base of the deposit.

Deposits associated with mafic rocks

Little Stobie #1 and 2 and Levack West. These three Sudbury deposits are described by Hoffman *et al.* (1979); they are not described further here.

Espedalen. Discontinuous zones of sulfide displaying marked interstitial magmatic textures have been intersected in a gabbro–anorthosite-pyroxenite complex lying just east of the Precambrian Jotunheim complex. The Espedalen complex is thought to be allochthonous, and its age is uncertain; it may have been emplaced during the same time as the Jotunheim complex of central Norway (Battey & McRitchie 1973, Englund 1973). The principal concentrations of sulfides discovered to date occur in a gabbro- and pyroxenite-rich portion of the complex and define an irregular zone extending for several kilometres.

Noril'sk (-Talnakh-Octyabr'sk). These deposits constitute the largest Ni-sulfide camp in the USSR, and although tonnage figures are not published, they probably represent the second largest camp in the world (after Sudbury). Sulfides are associated with a series of subvolcanic intrusions feeding the lower Triassic members of a sequence of Permo-Triassic flood basalts. Sulfur isotope ratios are highly anomalous and are taken to indicate that much of the sulfur has been obtained as a result of the

magma ingesting a high proportion of underlying Devonian evaporite. Ore occurs (1) disseminated within the intrusions themselves, (2) as concentrations within and close to the base of the intrusion, (3) disseminated within footwall rocks to the intrusions, and (4) as rich veins extending away from the contact to the underlying footwall rocks. The analytical data used in this paper have been obtained by apportioning the total amount of metal in the ores as given by Newman (1973) amongst the 6 PGE according to the ratios given by Smirnov (1977).

Merensky reef. The ores of the reef, their mineralogy and the geology of the host rocks have been discussed recently by Vermaak (1976) and Vermaak & Hendriks (1976). Most of the metal concentrations occur in a 5–10 cm seam rich in sulfides and chromite; the seam is associated with a mafic pegmatite forming the base of a cyclical magmatic unit near the top of the critical zone of the Bushveld complex. Sulfides include pentlandite and chalcopyrite, together with a large number of sulfide, arsenide, sulfosalt and native PGE minerals. Unlike the other deposits under discussion, in which massive sulfides and sulfide-rich disseminations make up the majority of the ore and in which Ni and Cu are the major products, the sulfides in the Merensky reef are very sparse, Ni and Cu are relatively unimportant by-products, and the value of the ore is based largely on its PGE content. The widespread occurrence of the reef throughout much of the Bushveld complex, its restriction to a specific zone within the magmatic stratigraphy, its continuity and the high tenor of PGE minerals are all remarkable. Ores of the Bushveld complex account for approximately 45% of the world's and 90% of the western world's production of PGE.

SAMPLE COLLECTION, PREPARATION AND ANALYTICAL METHODS

Between 10 and 40 samples were selected from each deposit, the number depending on the diversity of ore types within a given deposit and on the availability of material. Experience has shown that 6–10 samples of each compositionally distinct ore type are required for meaningful conclusions to be drawn about their PGE content. In most cases, the samples were 1–2 kg in size and were carefully selected by mine geologists to be representative of a given area of each deposit.

All samples were crushed, ground, mixed and split under carefully controlled conditions by INCO Metals Ltd. using a combination of jaw crusher and swing mill that had been proved

TABLE 1. SENSITIVITY, PRECISION AND ACCURACY
FOR ANALYSIS OF PGE + Au IN PPB

	Au	Pd	Pt	Rh	Ru	Ir	Os
Detection Limit	0.1	5	5	1	3	0.1	2
Average &(Std. Dev.) for 22 replicate analyses of 1 sample	42(6)	320(40)	290(30)	135(7)	150(20)	75(5)	30(3)
Recommended values for standard PTC (McAdam et al. 1973)	650	12,700	3,000	620			
Our average values for PTC	590	12,800	2,900	620	590	200	340

(Hoffman 1978) to cause minimal contamination. A 0.5 kg split was subjected to the final pulverization (95% −100 mesh) and stored in sealed bags at −20°C to avoid oxidation.

Analyses for Ni, Cu, Co and S were undertaken by INCO Metals Ltd. using atomic absorption (Ni, Cu, Co) and a LECO titrator (S) or using XRF (X-ray Assay Laboratories). Analysis for PGE and Au involved a combination of fire assay and neutron activation on at least duplicate 50 g aliquots. The method was developed specifically for this study and is described briefly by Hoffman et al. (1979) and in more detail by Hoffman et al. (1978). Detection limits are 0.1 ppb for Ir and Au, 1 ppb for Rh, 2 ppb for Os, 3 ppb for Ru and 5 ppb for Pd and Pt. An indication of the precision and accuracy of the technique is given in Table 1.

TABLE 2. CONCENTRATION OF METALS IN DIFFERENT DEPOSITS, CALCULATED TO METAL CONTENT IN 100% SULFIDE AND AVERAGED

Type of Deposit	Deposit	No. of Samples	Ni	Cu	Co wt.%	Pt	Pd	Rh	Ru ppb	Ir	Os	Au	Reference
"Classic" Archean komatiites	Langmuir	.42	12.70	0.51	0.25	628	1,182	195	626	201	336	94	This study
	Mt. Edward	6	11.30 (.69)	1.31 (.29)	0.27 (.007)	421 (47)	1,063 (175)	162 (34)	488 (168)	121 (30)	141 (50)	67 (9)	This study
	Kambalda	?	12.10	0.84		<730	1,314		803	219	402	402	Keays et al. 1976
Other ultramafic rocks (presumed komatiitic)	Pipe	26	3.96 (.13)	0.16 (.016)	0.16 (.003)	54 (7)	122 (14)	35 (1.6)	217 (22)	55 (3)	107 (10)	57 (11)	This study
	Donaldson W.	23	15.50 (.31)	3.71 (.26)	0.23 (.007)	4,131 (682)	15,530 (3886)	801 (103)	1,979 (350)	324 (53)	382 (55)	462 (94)	This study
Sudbury	Levack W.	25	5.60 (.17)	3.70 (.66)	0.13	1,154 (108)	1,253 (225)	186 (32)	60 (14)	47 (11)	22 (4)	150 (43)	Hoffman et al. 1979
	Little Stobie #1	23	3.60 (.08)	4.40 (.65)	0.19 (.003)	1,946 (415)	2,108 (344)	119 (12)	123 (16)	61 (6)	29 (3)	733 (180)	Hoffman et al. 1979
	Little Stobie #2	11	4.00 (.18)	3.67 (.54)	0.17 (.004)	2,081 (275)	3,132 (250)	303 (28)	247 (40)	113 (14)	46 (7)	859 (314)	Hoffman et al. 1979
Other gabbro-related deposits	Espedalen	6	6.65 (.43)	2.01 (.48)		330 (84)	246 (36)	36 (17)	48 (16)	26 (9)	27 (10)	278 (71)	This study
	Noril'sk (Oktyabr'sk)	?	7.60	10.90		13,700	36,000	2,240	1,500	1,500	950	1,600	Naldrett & Cabri 1976 Smirnov 1977
	Merensky	?	10.90	4.65	0.18	258,800	102,000	17,000	21,000	4,300	3,500	21,000	Naldrett & Cabri 1976
Average chondrite						1,500	1,200	200	1,000	500	700	170	McBryde 1972 Crocket 1974

(Figures in parentheses are standard errors of the mean)

PRESENTATION OF RESULTS

We have chosen to present our results (Table 2) in terms of concentrations of metals recalculated to their levels to be expected in ore composed of 100% sulfide. This is because our sampling was not designed to determine the grade of any given deposit but merely to be representative of certain major ore types in different areas of each of the deposits studied. In some samples sulfide content was greater than that of 'average' ore, in others less. Calculation to 100% sulfide is based on the assumption that all of the metals were introduced in the ore magma and thus gives a guide as to their concentration in this magma. An error is introduced into our calculations if metals have been remobilized selectively during or subsequent to crystallization of the ore magma and either removed from the ore or concentrated in specific ore types, e.g., in low-grade ore. The reader should bear this in mind when evaluating our

results. Data from the literature on the Merensky reef, Noril'sk and Kambalda are included in Table 2 for comparison. The PGE and Au content of different deposits are compared in graphical form in Figures 1 to 3. In these the data of Table 2 are normalized with respect to their average abundance in chondritic meteorites [McBryde (1972) for PGE, Crocket (1974) for Au]. This method of presentation is used because it tends to smooth out irregularities in the profile for each deposit.

Figure 4 shows all of the individual analyses obtained for the Pipe deposit together with the mean for each element. Despite the scatter in the data, the profile as defined by the means (and as used in Fig. 1) is characteristic of the deposit as a whole. Standard errors of the mean are relatively small and indicate a strong probability that the profile is representative of the deposit.

DISCUSSION OF RESULTS

Figure 1 illustrates PGE and Au profiles for

deposits associated with Archean komatiites, including data for the Kambalda camp (Keays & Davison 1976) for which Rh analyses are unavailable. Looking first at the 'classic' flow-related deposits, the profiles are characterized by a gentle positive slope from Os to Pd, save that Pt falls somewhat below the line, followed by a decrease to Au for all of the deposits except Kambalda. The similarity in values for these deposits from widely different areas is regarded as remarkable and characteristic for deposits of this type.

As outlined previously, the Pipe deposit differs in its stratigraphic, structural and metamorphic setting and in the absence of any evidence suggestive that it is a flow. The profile for Pipe is broadly similar to those of the 'classic' komatiite deposits just discussed in that it shows a gentle positive slope, but differs markedly in that, with the exception of Au, PGE concentrations are a factor of 3 to 10 times lower. Reference to Table 2 shows that Ni and Cu are about 3–5 times lower than in 'classic' komatiites, whereas Co is 1½ times lower.

Data for the Sudbury deposits, presented and discussed by Hoffman et al. (1979), are sum-

FIG. 1. Noble-metal data, recalculated to concentration in 100% sulfide for each sample, and averaged for each of the 'classic' Archean komatiite deposits, Kambalda, Langmuir and Mt. Edwards and for the Pipe deposit of the Manitoba nickel belt. Data are presented normalized with respect to average abundances in chondrites.
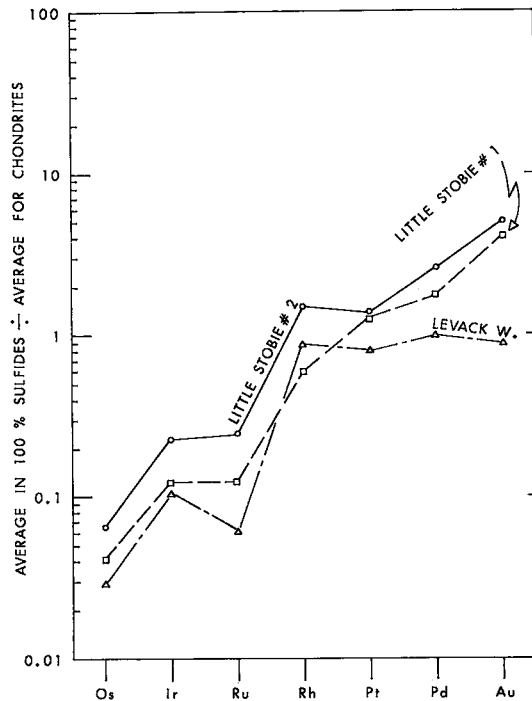

FIG. 2. Noble-metal data for each of the three Sudbury deposits studied, Little Stobie #1 and 2 and Levack West. See legend to Figure 1 for details of presentation of analytical data.
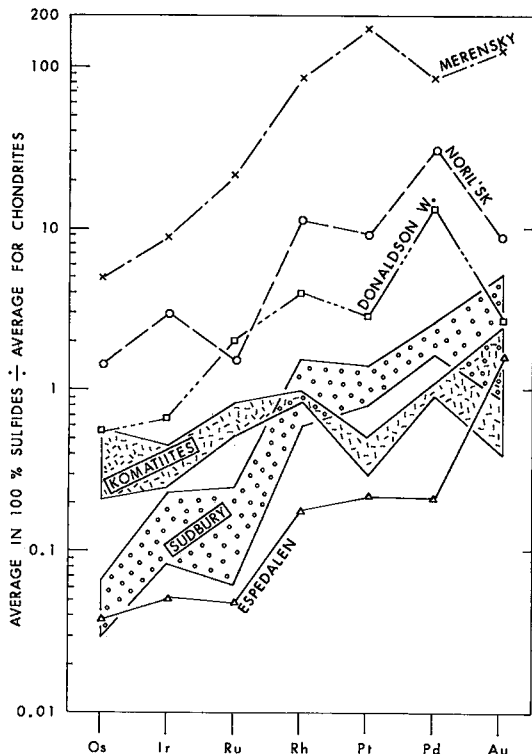
FIG. 3. Noble-metal data for the Merensky, Noril'sk, Donaldson West and Espedalen ores compared with that shown in Figures 1 and 2 for 'classic' Archean komatiites and Sudbury.

FIG. 4. Plot of all of the data obtained for the Pipe deposit together with the arithmetic means and standard errors of the means for each element.

marized in Figure 2. Here the profile is one of a steep positive slope from Os to Au. In Figure 3, hatched areas representing the fields established for Sudbury and the 'classic' komatiite deposits are compared with each other and with other deposits. The Sudbury field, with its high concentration of Au, Pd, Pt and Rh and low concentration of Ru, Ir and Os, is completely different to the gently sloping profile of the komatiites.

The Espedalen ore is distinctly lower than Sudbury, particularly in Pt and Pd, but is similar in the generally steep positive slope of the trend from Os to Au. The Merensky reef, as pointed out earlier, is much more enriched in PGE than the other deposits; it is also characterized by a steep positive slope, although it differs from the Sudbury profile in that the trend does not extend to Pd and Au.

As mentioned earlier, the Noril'sk data are drawn from the literature; because of our assumption that all ore contains the tenor of 9.6 g/t reported by Newman (1973), they are regarded as distinctly less reliable than the other
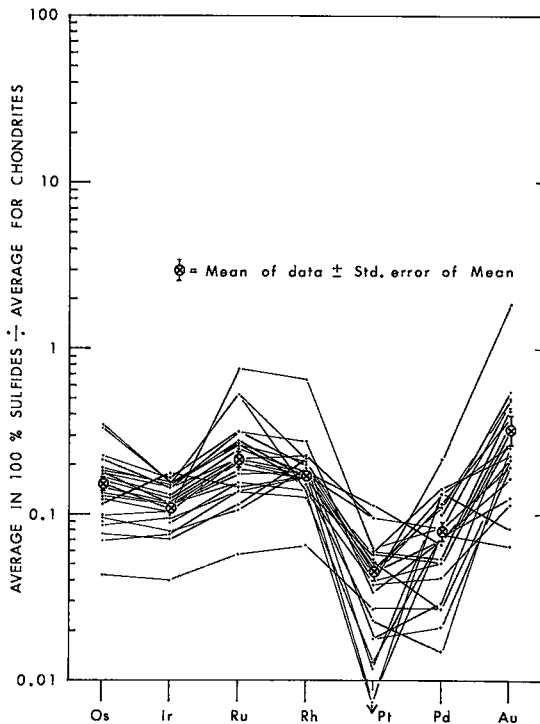
data discussed in this paper. Nevertheless, the extremely PGE-rich nature and the trend of a steep positive slope similar to the other gabbro-related deposits is undoubtedly characteristic of Noril'sk.

To summarize the PGE and Au data as presented to this stage, deposits related to gabbroic or noritic rocks are characterized by a high ratio of (Pd+Pt) : (Os+Ir+Ru) and a high ratio of Au:(Os+Ir+Ru), whereas deposits related to ultramafic rocks are characterized by much lower values of these ratios. In the cases quoted, the host rocks of a given type are thought to be typical of the initial magma, i.e., the mafic rocks have crystallized from mafic magmas and ultramafic rocks from ultramafic magmas. The generalizations with regard to metal ratios seem to apply despite variations of several orders of magnitude in the levels of PGE in deposits of a given type, i.e., the slope of a profile seems more characteristic of the host-magma type than its absolute level. A possible explanation for the difference between the slopes of the profiles of the ultramafic-related and mafic-related deposits is suggested by the observation of Ross & Keays

(1979) that Ir is 100 times more highly concentrated in olivine than is Pd. It would seem reasonable on the basis of their chemical similarity that Os and Ru resemble Ir in their behavior and are thus also concentrated in olivine. The location of Pt, Pd and Rh in the mantle source-rocks of igneous magmas is uncertain but as these elements do not seem to partition into olivine, it is likely that they are present largely in accessory phases such as sulfides and spinels. A gabbroic magma, resulting from a relatively low degree of partial melting, will incorporate much of the sulfide and spinel present in its source region but little of the olivine and, if the distribution of PGE is as suggested above, will be relatively rich in Pt, Pd and Rh and poor in Ru, Ir and Os. A magma such as a peridotitic komatiite, resulting from a high degree of mantle melting and incorporating a much higher proportion of olivine would be expected to have the higher proportion of Ru, Ir and Os relative to Pt and Pd that we observe in ore deposits of this association.

Reference to Table 2 reinforces the well-established dictum that deposits associated with gabbroic magmas have high Cu/Ni ratios and those with ultramafic magmas low values. As olivine concentrates Ni strongly and does not concentrate Cu, the reason suggested for the difference in the slopes of the PGE profiles certainly explains much of the difference in Cu/Ni ratios. However, it does not account for the great difference in the absolute levels of the elements. Reasons for these differences are discussed in the following section.

The Donaldson West deposit seems to be an exception to the rules just established. Naldrett & Cabri (1976) classified the deposit as komatiitic; Schwarz & Fujuwara (1977) and Arndt et al. (1979) provide further documentation for this point of view, and yet the Os–Pd profile in Figure 3 is steeply positive. Although classified as komatiitic, spinifex textures involving olivine have not been observed in any of the rocks of the Raglan–Cross Lake belt. The absence of spinifex texture suggests that the initial magma, although magnesian, was not nearly so magnesian as that of magmas from which 'classic' komatiite deposits have developed. [This statement stems from the fact that spinifex texture is regarded as the consequence of the crystallization of a lava that has become supersaturated due to supercooling (Donaldson 1974, 1976, Walker et al. 1976, Arndt et al. 1977). Supercooling of komatiite lava is thought to result from the relatively rapid cooling of a flow in which heterogeneous nucleation is retarded due to the absence of phenocrysts. The high temperatures and silica-poor compositions of Archean peridotitic lavas result in the magma having a very low viscosity which, in turn, leads to the rapid settling out of any suspended crystals. Nucleation then tends to occur on material forming the upper crust of the flow with olivine crystals growing downwards into the supersaturated lava and giving rise to the spinifex texture.] The Proterozoic Raglan–Cross Lake belt may represent a link between Archean ultramafic magmatism and the typical basaltic magmatism of recent times. The PGE and Au profile of Donaldson West and its relatively high Cu:Ni ratio (Table 2) are consistent with this view.

POSSIBLE EXPLANATIONS OF VARIATION IN ABSOLUTE CONCENTRATION OF METALS IN NI SULFIDE ORES

The large variation in the PGE content of nickel sulfide ores evident from the preceding section is also reflected in the Ni, Cu and Co content of some deposits. For example, the ultramafic-related Pipe deposit is compared to the composition of a typical 'classic' Archean komatiite ore in Table 3. The differences shown here are unexpected in that Pipe is associated with komatiitic rocks believed to have formed from a magma similar to that responsible for the 'classic' komatiites (Peredery 1979).

Possible explanations for variations of this kind fall into three main areas: (1) post-consolidation processes have modified the composition of some ores drastically; (2) there is a great variation in the chalcophile-metal content of otherwise similar magmas, reflected in the ores separating from them; (3) some process, as yet unspecified, affects the partitioning of metals from two similar magmas so that they give rise to ores of different compositions.

With respect to explanations relating to type (1), Hoffman et al. (1979) have suggested that diffusion along a thermal gradient can produce considerable zoning within a deposit; despite the evidence that these processes have occurred at Levack West and to a lesser extent at Little Stobie #1, the PGE profiles at Sudbury are

TABLE 3. COMPARISON OF PIPE ORE WITH TYPICAL ARCHEAN KOMATIITE ORE

| | wt.% | | | ppb | | | | | |
	Ni	Cu	Co	Pt	Pd	Rh	Ru	Ir	Os
Pipe	3.96	0.16	0.16	54	122	35	217	55	107
Typical komatiite	11.6	1.0	0.26	610	1200	180	640	160	300

distinct and form a coherent group. It is possible that metamorphic fluids have remobilized and drastically altered the PGE content of the ore at Pipe, but it is much harder to envisage this operating in the case of Ni. Pipe contains ⅓ of the Ni at Kambalda, so that if the ores were identical originally, an enormous amount (equal to ⅔ of the original Ni) has been removed from the Pipe ore, without leaving evidence in the form of compositional gradients. Although we believe that remobilization of metals may be important for some ores, we think that some other processes must control composition in other ores and we include Pipe in this latter class.

In considering explanations coming under types (2) and (3), distribution coefficients between sulfide and silicate melts become very important ($D_i^{S/L}$ = wt. % metal i in sulfide melt/wt. % metal i in silicate melt). These have been studied experimentally by MacLean & Shimazaki (1976) and Rajamani & Naldrett (1978). The latter authors showed that for Ni the distribution coefficient was relatively insensitive to variations in the compositions of the sulfide melt but varied as a function of the composition of the silicate melt, largely due to the variation in the activity coefficient of NiO in the silicate melt (Campbell *et al.* 1979). In this paper, we follow Rajamani & Naldrett and use a value of 100 for $D_{Ni}^{S/L}$ in an ultramafic melt containing 27% MgO, increasing to 275 in a basaltic melt containing 8% MgO. On the basis of experiments and crystal-field theory, Rajamani & Naldrett concluded that Cu is unlikely to show very much variation, and thus we use a constant value of 250 for Cu in all melts. Experimental data for Pd are rare; we regard the unpublished results of MacLean (pers. comm.) on a synthetic FeO–SiO₂ melt approximating a gabbroic composition of $D_{Pd}^{S/L}$ > 1000 as the most reliable. We have assumed a value of 1500 for Pd, in reasonable agreement with the value of 2000 predicted by Keays & Campbell (pers. comm.) on the basis of their work on the Jimberlana intrusion. Pt is known to be somewhat less chalcophile than Pd; thus we have assumed a slightly lower value of 1000. No experimental data exist as to how $D_{Pt}^{S/L}$ and $D_{Pd}^{S/L}$ vary with changing magma composition. Ross & Keays (1979) have compared the composition of the spinifex-textured portion of Kambalda lava flows with the composition of the ore and concluded that values of $D^{S/L}$ for Pt and Pd are of the order of 100–300. We hold some reservations concerning the assumption inherent in their argument, that the Pt and
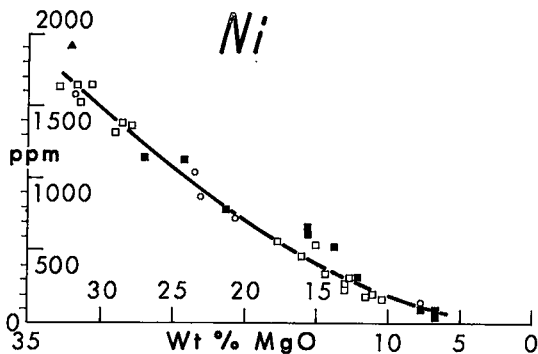

FIG. 5. Plot of Ni *vs.* MgO for komatiitic rocks thought to represent liquid compositions (*i.e.*, exhibiting spinifex texture and no phenocrysts).

Pd concentrations of the spinifex zones are equivalent to those of the silicate liquids with which the ores equilibrated. We believe it likely that a significant amount of olivine may have crystallized from the komatiite magma both during flow and after it reached its final resting place, altering its composition appreciably. Nevertheless, doubt exists as to the correct values of $D^{S/L}$ for PGE; the following discussion should be viewed in this light.

With regard to explanations of type (2), calling upon metal-depleted magmas, Figure 5 is a plot of Ni *vs.* MgO for a number of komatiitic rocks from around the world that are thought to represent liquid compositions. The correspondence is remarkable, with most samples falling within 100–150 ppm of the line. There is little evidence for the existence of liquids showing significant Ni depletion amongst these samples.

However, using computer modeling, Duke & Naldrett (1978) have drawn attention to the fact that a differentiating magma may become significantly depleted in chalcophile elements if it is saturated in sulfide; therefore, liquid sulfides in addition to silicates are separating from it as it crystallizes. Turning to the specific problem of the Pipe ore, Figure 6, based on their program, illustrates how Ni, Cu, Co and Pt of the sulfide phase would vary, assuming that a magma containing 27% MgO, 1200 ppm Ni, 45 ppm Cu, 65 ppm Co and 0.7 ppb Pt (assuming $D_{Pt}^{S/L}$ = 1000) or 7 ppb Pt (assuming $D_{Pt}^{S/L}$ = 100) fractionated under sulfide-saturated conditions. Before fractional crystallization the metal content of the sulfides would have been very similar to the values given in Table 3 for a typical 'classic' komatiite ore. After approximately 21% crystallization, the Ni value would have dropped to the level found at
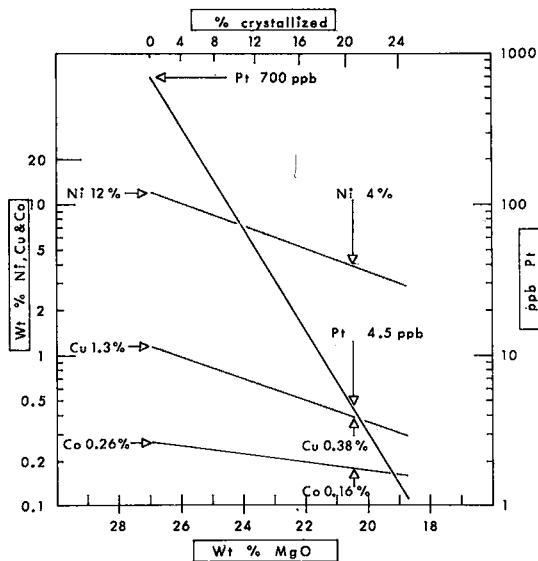
FIG. 6. Result of computer modeling of the composition of the sulfides segregating as a result of the fractional crystallization of a sulfide-saturated komatiitic magma containing 27 wt. % MgO, 1200 ppm Ni, 45 ppm Cu, 65 ppm Co and 0.7 ppb (D=1000) or 7 ppb (D=100) Pt.

Pipe, i.e., 4.0 wt. %. Cobalt would have dropped from 0.26 to the value of 0.16%, also characteristic of the Pipe ore. Assuming a value of $D_{Pt}^{S/L}$ of 1000, Pt would have dropped to 4.5 ppb, a factor of 10 lower than actually observed at Pipe, ruling out fractional crystallization of a sulfide-saturated magma as a possible mechanism. However, if the value of $D_{Pt}^{S/L}$ is of the order of 100, the modeling predicts that Pt concentration would be around 240 ppb, i.e., nearly 5 times higher than observed. Intermediate values of D would produce intermediate values of Pt in the sulfide phase, much closer to the observed value at Pipe. In view of the uncertainty about D values for Pt in ultramafic melts, one cannot rule out fractional crystallization as a method for producing magmas depleted in this or similar metals. Looking at Cu, however, the model predicts a value of 0.38 wt. %, twice as much as is present; for this reason, we do not rule out fractional crystallization entirely, but we downplay it as the explanation for Pipe and look to an explanation of type (3).

When considering the formation of phase A from a liquid B during cooling, the usual method of calculating the concentration (X_i^A) of a trace element i in A using the partition coefficient D is

$$X_i^A = D \, X_i^B \tag{1}$$

where X_i^B is the final concentration of element i in liquid B. In modeling the composition of Ni sulfide ores expected to form from different silicate magmas, the initial concentration of any element in the magma prior to reaction with a sulfide liquid can be estimated from concentrations in rocks representative of magmas that are not associated with sulfide, but it is much more difficult to estimate the final concentration. Campbell & Naldrett (in prep.) have shown that the initial concentration may be used if equation (1) is modified to read:

$$Y_i^{\text{sulfide}} = \frac{X_i^{\text{silicate}} D \, (R + 1)}{R + D} \tag{2}$$

where X_i^{silicate} is the initial concentration of i in silicate magma (as opposed to the final concentration), Y_i^{sulfide} is the final concentration of i in sulfide melt, D is the partition coefficient of i between sulfide and silicate, i.e., wt. % metal in sulfide melt/wt. % metal in silicate magma, and R is the ratio of the mass of silicate magma to the mass of sulfide melt reaching equilibrium with it. If values of D are small or values of R are large the final concentration is very close to the initial concentration. However, with most metals in ores of this type D is large, ranging from 40 to perhaps 2000 for the metals Co, Ni. Cu, Pt and Pd.

Campbell & Naldrett point out the value of R at which the final concentration is significantly different from the initial concentration and at which therefore Y_i^{sulfide} is affected is a function of D. Where D is small (<10), R can become quite small (~ 100) with little effect on X_i^{silicate}, but where D is large (~ 1000), the effect on X_i^{silicate} (and hence on Y_i^{sulfide}) becomes appreciable where R ~ 10,000. Working entirely independently, W.H. MacLean (pers. comm.) has reached a very similar conclusion on the basis of his experiments.

This point is illustrated in Figure 7 where the Ni, Cu and Co contents of the sulfide phase segregating from a peridotitic komatiite magma containing an initial concentration of 1200 ppm Ni, 45 ppm Cu and 65 ppm Co [from the data of Arndt et al. (1977) and Nesbitt & Sun (1976)] are plotted as a function of log R. The values of D for Ni and Cu are from Rajamani & Naldrett (1978), whereas the value for Co is based on an extrapolation of the experiments of Rajamani & Naldrett.

The points marked K in Figure 7 are typical average values for 'classic' Archean komatiite ores, thought to have segregated from a magma
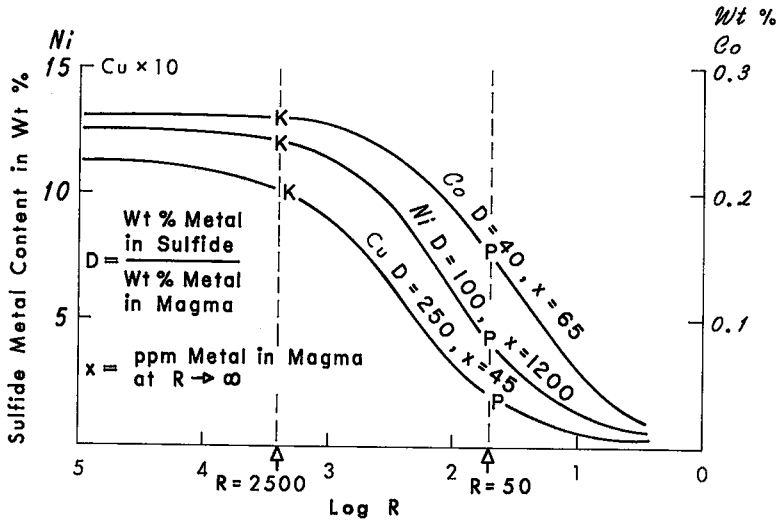
FIG. 7. The Ni, Cu and Co contents of sulfides in wt. % (Y in equations in the text) shown as a function of the magma/sulfide ratio (R) and D, the Nernst partition coefficient. X is the initial concentration (in ppm) assumed for the magma before any metal was depleted significantly by partitioning into sulfide (i.e., at R = ∞). K represents typical values in komatiite-related deposits, P the average of the Pipe data.

of the composition represented in the diagram. They are consistent with a value of R of 2500. The points marked P represent the Pipe analyses and are precisely consistent with segrega-tion from an identical magma, provided that R was 50 instead of 2500.

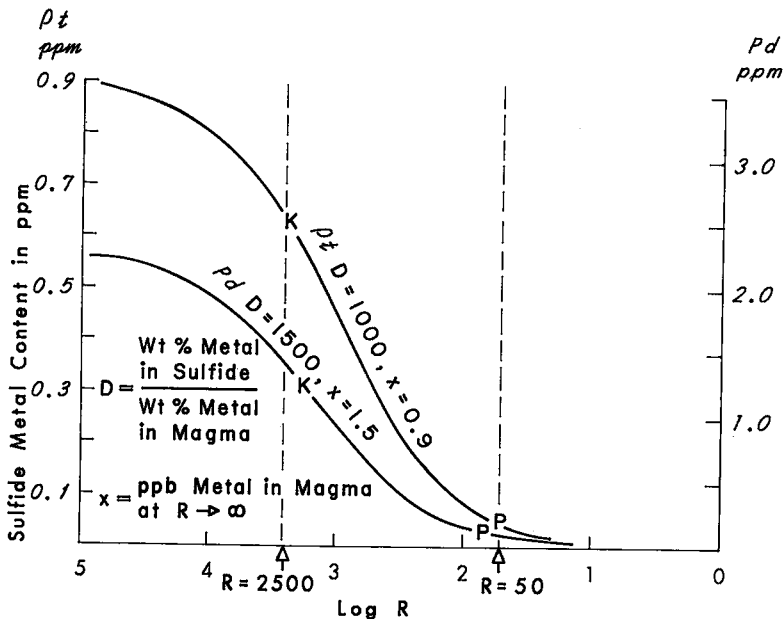Figure 8 is similar to Figure 7, except that Pt and Pd are considered. In this case, the

FIG. 8. The Pt and Pd content of sulfide (in ppm) shown as a function of R and D in the same way as Figure 7.

values of 1000 and 1500 used for D for Pt and Pd, respectively, are the estimates based on the data of MacLean (pers. comm.) discussed previously. The values of the initial concentration of Pt and Pd in the silicate melt are not based on measurements but are required if the curves are to pass through the concentrations of these metals in komatiite ores when these are plotted at a value of approximately 2500 for R. The purpose of the diagram is to point out that given these constraints, the measured values of Pt and Pd in the Pipe deposit fall on the same curves as the komatiites if they are plotted at R values of approximately 50. It can be shown easily that values of D of the order of 1000 are required to account for variations in Pt and Pd using this model. If D values are assumed to be significantly below 1000, e.g., closer to 100, and values of X_i raised so that the komatiite ores remain correctly modeled, values of Pt and Pd will be too high by a factor of 4 to 5 in the Pipe ores.

The above exercise serves to point out that the metal content of an ore segregating from a silicate magma of constant initial composition can vary within wide limits depending on the relative proportions of the ore and magma. There is an internal consistency in the measured values for the 'classic' Archean komatiite deposits and Pipe, particularly for Ni, Cu and Co, for which the assumptions made in the case of Pt and Pd were unnecessary; this argues in favor of the hypothesis that differences in magma/sulfide ratio are responsible for the differences between Pipe and the 'classic' komatiite deposits. As we have stated previously, this conclusion is dependent in part on the rather poorly defined values for $D_{PGE}^{S/L}$ in ultramafic melts. Once these have been determined more exactly (which poses severe problems experimentally), arguments of the kind we have undertaken will provide much firmer conclusions as to genesis.

Figure 9 illustrates how widely divergent values of R may have been achieved in the two cases discussed above. The 'classic' komatiite ores are envisaged as resulting from the intrusion of a sulfide-saturated magma that carried sulfides in suspension some distance up the feeder conduit. Turbulence during ascent resulted in the mixing of the sulfides with a large volume of magma. After extrusion, as the lava spread out horizontally, the sulfides settled and became trapped in irregularities on the sea floor. It is suggested that the Pipe ores are the result of the localized assimilation of
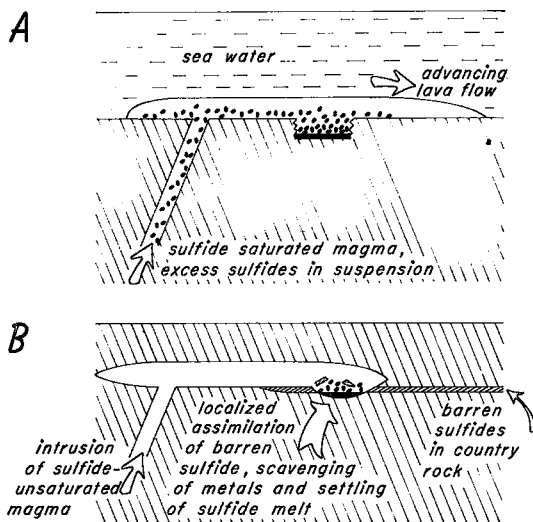

FIG. 9. Schematic diagrams illustrating: A. the settling of sulfides from a sulfide-saturated Archean komatiitic flow carrying excess sulfide; B. the formation of nickeliferous sulfides as a result of assimilation of barren country-rock sulfide by an ultramafic intrusion in the way suggested for Pipe.

non-nickeliferous country-rock sulfide, probably portions of a sulfide iron-formation that is known to exist in the vicinity. This has given rise to a high proportion of sulfide reacting with a local portion of the magma, resulting in ore with relatively low metal values. Support for this conclusion stems from the occurrence of fragments of country rock typically associated with barren sulfide within the ore at Pipe (Peredery, pers. comm.).

Implicit in our model calling upon large variations in R is the fact that where metals have similar values of D, the effect of varying R is to cause variations in the absolute levels of the metals in sulfide ore without changing the ratio of one metal to another greatly. This may account for some of the similarities in the slopes of the PGE profiles between Pipe and the komatiite deposits. However, if differences in D are large, variations in R will cause significant changes in the ratios. For example, Ni has a much smaller D value than that thought most likely to apply for Pt (a value of 100 vs. a value of approximately 1000), thus accounting for the fact that the Pipe ore is only depleted in nickel by a factor of 3 rather than the factor of 10 observed for Pt. Cobalt, with the smallest values of D (40) of the metals investigated, shows the least depletion at Pipe, by a factor of 1½.

This generalization as to the effect of D is only very approximately true for our model involving fractional crystallization of a sulfide-saturated magma. In this case some metals, notably Ni, are removed in the silicates as well as in the sulfides, whereas others, in particular Cu, Pt and Pd, do not partition into the silicates and are removed solely in sulfides. Variation in metal ratios of the ore is thus a function of two sets of partition coefficients in this model.

CONCLUSIONS

The following points are regarded as the most important contributions of this paper.

1. Komatiite-related deposits are characterized by fairly low ratios of (Pt + Pd + Rh) to (Ru + Ir + Os), whereas gabbro-related deposits are characterized by much higher ratios.

2. Whereas this generalization applies to the ratios, the absolute levels of PGE in deposits vary by several orders of magnitude with respect to both komatiite-related and gabbro-related deposits. Cu and Ni also vary in amount in deposits that are related to similar rock types, but not to the same extent as PGE.

3. The higher proportion of Ru, Ir and Os in komatiite-related deposits can possibly be explained in terms of the concentrations of the elements in mantle olivine and the higher proportion of this incorporated in the komatiite melts than in gabbroic melts during mantle melting.

4. The greatly different absolute amounts of PGE, Cu and Ni in otherwise similar deposits can be explained in some cases by postulating that the amount of sulfide reacting with a given magma varies and in others by postulating that some magmas have differentiated to some extent under sulfur-saturated conditions before precipitating an economic concentration of sulfide.

5. The Pipe deposit is significantly poorer in Cu, Ni, PGE and Au than other komatiite-related ores; the metal values there are best explained by postulating that a large amount of sulfide has reacted with a relatively small amount of magma, possibly as a result of assimilation of country-rock sulfide.

ACKNOWLEDGMENTS

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