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Platinum Metals in Magmatic Sulfide Ores

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Summary. Platinum-group elements (PGE) are mined predominantly from deposits that have formed by the segregation of molten iron-nickel-copper sulfides from silicate magmas. The absolute concentrations of PGE in sulfides from different deposits vary over a range of five orders of magnitude, whereas those of other chalcophile elements vary by factors of only 2 to 100. However, the relative proportions of the different PGE in a given deposit are systematically related to the nature of the parent magma. The absolute and relative concentrations of PGE in magmatic sulfides are explained in terms of the degree of partial melting of mantle peridotite required to produce the parent magma and the processes of batch equilibration and fractional segregation of sulfides. The Republic of South Africa and the U.S.S.R. together possess more than 97 percent of the world PGE reserves, but significant undeveloped resources occur in North America. The Stillwater complex in Montana is perhaps the most important example.

World demand for the six transition elements that comprise the platinum-group elements (PGE) (Pt, Pd, Rh, Ru, Ir, and Os) currently exceeds 210,000 kilograms annually, and this rate is expected to double by the year 2000 (*1*). Although recycled metal satisfies a small proportion of this demand, almost 90 percent of total consumption is newly mined material. The Republic of South Africa and the U.S.S.R. together account for 92 percent of the mine production, and 7 percent comes from Canada. The United States and Japan are responsible for more than 60 percent of the consumption of PGE. The main uses of PGE in the past have been as catalysts in the chemical and petroleum refining industries, in electrical components, in jewelry, and in medical and dental applications. The production of automobiles that incorporated catalytic converters in their exhaust systems began in 1974, and this is now the largest single use of PGE in the United States. As automobiles with catalytic converters are scrapped in increasing numbers, reclamation of the PGE will tend to moderate the demand for new metal. It seems likely that fuel cells will play a part in supplying future electrical energy requirements, and, because such fuel cells contain substantial quantities of Pt catalysts, their widespread use would have a significant positive impact on the demand for PGE (*2*).

The PGE are primarily siderophile, tending to associate with the other transition metals Fe, Ni, and Co in iron meteorites and, presumably, in the earth's core. In the range of oxygen and sulfur fugacities prevalent in the crust and upper mantle, however, the PGE commonly exhibit chalcophile behavior. Mafic and ultramafic igneous rocks are the most PGE-rich of the common crustal rocks (*3*). These rocks, or their parent magmas, are the source of the PGE in most ores. Weathering of the rocks and the concentration of native alloys derived from them have given rise to the alluvial deposits responsible for minor production in Colombia, the U.S.S.R., and the United States (the mine at Goodnews Bay, Alaska, ceased operation in 1976). However, more than 99 percent of primary PGE production comes from sulfide ores that are almost certainly of magmatic origin. In this article, we document the abundance of PGE in a wide range of magmatic sulfide deposits and examine the implications of the data for models of the formation of the ores and also for estimates of the reserves and resources of this important group of metals.

Magmatic Sulfide Deposits

The formation of a magmatic sulfide deposit consists of the following steps: (i) the generation of a mafic or ultramafic magma within the mantle; (ii) ascent of the magma into the crust; (iii) cooling and the onset of crystallization within or on the crust preceded, accompanied, or succeeded by the segregation of immiscible sulfide into which Ni, Cu, Co, and the PGE partition readily and which thus acts as a collector for these elements; (iv) concentration of sulfides, commonly by gravitational settling (specific gravity of the sulfide liquid $\simeq 4$, specific gravity of the silicate magma $\simeq 2.7$ to 3.1); (v) crystallization of the sulfide liquid into the major sulfide minerals pyrrhotite, chalcopyrite, pentlandite, and pyrite, all of which may contain PGE in solid solution, accompanied or followed by the crystallization of discrete PGE minerals; and (vi) redistribution of the metals of the ore, including PGE, by hydrothermal processes after crystallization but not necessarily complete cooling; some deposits have originated hydrothermally rather than just being modified in this way, but these are relatively uncommon [for example, the Mooihoek pipe in the Bushveld complex in South Africa and the New Rambler Mine in Wyoming (*4*)].

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Magmatic sulfide deposits fall into two main categories with respect to the PGE: those in which the PGE are the principal products extracted from the ore and those in which Ni and Cu are the most important products and the PGE are by-products. The former usually consists of sparsely disseminated sulfides that occur at particular stratigraphic horizons within large, generally tholeiitic, layered intrusions. The latter includes many individual deposits associated with a variety of mafic and ultramafic rock types. Because of their association with specific rock types occurring within specific tectonic regimes, the magmatic sulfide deposits are conveniently classified according to their petrotectonic setting (*5*). The following four settings account for more than 95 percent of the known Ni-Cu sulfide ores:

1) Setting I, noritic rocks associated with an astrobleme (the scar resulting from meteorite impact). The only example of this type is the Sudbury mining camp in Canada.

2) Setting II, intrusive equivalents of flood basalts associated with intracontinental rifting. Important examples include the Noril'sk camp of Siberia (*6*) and the as yet undeveloped deposits at the western edge of the Duluth complex in Minnesota (*7, 8*).

3) Setting III, rocks emplaced during the early stages of formation of Precambrian greenstone belts and comprising two main types: A, tholeiitic intrusions such as those hosting the ores of the Pechenga Ni camp in the Kola peninsula, U.S.S.R. (*9*), and Lynn Lake, Manitoba, Canada; and B, komatiitic lavas and intrusions, in particular the more ultramafic variants. Ultramafic komatiites (*10*), extruded at temperatures of 1500° to 1600°C, are restricted to the Archean and are hosts to important sulfide deposits in the Abitibi region of Ontario and Québec, Zimbabwe Rhodesia (*11*), and, in particular, the Kambalda camp of Western Australia (*12*). Rocks believed to be komatiitic (*13*) are hosts to the deposits in the Thompson area of Manitoba and to rich deposits, as yet unmined, in the Ungava peninsula of Québec.

Table 1. Petrotectonic setting of the magmatic sulfide deposits referred to in this article. The PGE determinations have been carried out at the University of Toronto for all deposits except those marked with an asterisk, for which data have been taken from other sources, and those in italics, for which no data are included.

Setting I
  Little Stobie 1 (Sudbury, Ontario)
  Little Stobie 2 (Sudbury, Ontario)
  Levack West (Sudbury, Ontario)
Setting II
  Minnamax (Duluth complex, Minnesota)
  *Noril'sk (Siberia, U.S.S.R.)
Setting IIIA
  Montcalm (Timmins, Ontario)
  Lynn Lake (Manitoba)
  Pechenga (Kola peninsula, U.S.S.R.)
Setting IIIB
  Langmuir (Timmins, Ontario)
  Mount Edward (Western Australia)
  *Kambalda (Western Australia)
  Donaldson West (Ungava, Quebec)
  Katiniq (Ungava, Quebec)
  Pipe (Thompson, Manitoba)
Setting IV
  Råna (Norway)
Setting uncertain
  *Stillwater (Montana)
  *Bushveld (South Africa)
  Espedalen (Norway)

4) Setting IV, tholeiitic intrusions, generally synorogenic, are hosts to deposits of lesser importance in Phanerozoic orogenic belts [for example, the Råna deposit, Norway (*14*)].

Figure 1 shows the amount of Ni contained in past production and known resources of deposits in each of these four petrotectonic settings. In Table 1 we classify the deposits discussed in this article according to their settings. Although the Sudbury camp (setting I) has dominated past production of Ni-Cu sulfide ores, it is evident that deposits associated with komatiites (setting IIIB) and particularly those hosted by the intrusive equivalents of flood basalts (setting II) will have greater relative importance in the future. These Ni-Cu sulfide deposits currently account for more than half of world PGE production. There are two important examples of magmatic sulfide deposits in which the PGE are the principal metals of interest. The Bushveld complex of South Africa, which is the source of 46 percent of PGE production, is emplaced in a cratonic environment but there is no close association with flood basalts. The tectonic setting of the Stillwater complex in Montana, which contains significant undeveloped deposits, is uncertain since only a small portion of the original host rocks is preserved and the remaining boundaries of the intrusion are faults and unconformities of very much younger age.

Data on PGE

The almost complete absence of reliable published data on the concentrations of PGE in Ni-Cu sulfide ores led to the inception of this study. Analysis for the full range of PGE based on the use of earlier techniques presented problems inasmuch as the detection limits for Ru, Ir, and Os were not low enough for our purpose. Neutron activation gamma-ray spectrometry is much more sensitive, but the small sample size (typically less than 500 milligrams) was a limiting factor. The distributions of PGE in ores are very heterogeneous, and earlier experience had indicated that a sample size of at least 50 grams was necessary to overcome this problem.

Method of analysis. We developed a Ni sulfide fire assay method (*15*), adapting the procedure described by Robert *et al.* (*16*). We produced Ni sulfide assay buttons by utilizing Ni already present in the sample; these buttons were crushed and leached with hydrochloric acid, and the leach residue was analyzed by neutron activation. Every sample has been analyzed in duplicate, and, where duplicate analyses did not agree to within 20 percent, replicate analyses were performed until satisfactory agreement was obtained. Information on detection limits, precision, and accuracy is given by Hoffman *et al.* (*15*), and the sampling procedures are the same as those described by Naldrett *et al.* (*17*). In addition to the concentrations of Pt, Pd, Rh,

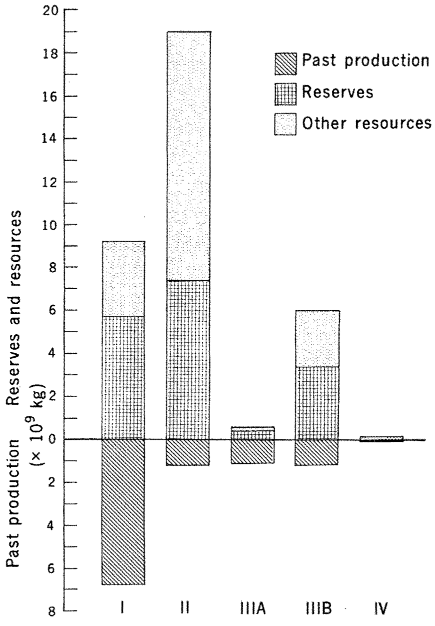

Fig. 1. Quantity of Ni metal contained in total past production, present reserves, and other identified resources of magmatic sulfide deposits. The deposits are classified according to their petrotectonic settings as described in the text. Reserves comprise known ores that are currently minable at a profit, whereas other resources include those known deposits that are not economically viable at present but which are likely to undergo development in the foreseeable future. The other resources present at Sudbury (setting I) and at Noril'sk (included in setting II) are not known but have been conservatively estimated to be one-half of the reserves.

Ru, Ir, Os, and Au determined by the fire assay and neutron activation method, the results reported below include the concentrations of Ni and Cu determined by x-ray fluorescence and Co analyses by atomic absorption.

Analytical results. It is beyond the scope of a study of this kind to determine the precise grade of PGE within any given ore deposit, as this would require many thousands of analyses of the deposit. Since the deposits are believed to have been formed by the segregation and crystallization of a sulfide liquid, it has been our aim to characterize the composition of this liquid. We have assumed that pyrrhotite, pentlandite, and chalcopyrite are the only sulfide minerals present and have then used the concentrations of Ni, Cu, and S in each sample to recalculate the analyses on the basis of 100 percent sulfide. There is an uncertainty in our assumption that the PGE content of each of a series of samples from a given deposit is directly proportional to the sulfide content of the sample in question. The fact that our results are calculated as arithmetic means rather than as averages weighted according to the proportions of different ore types in each deposit introduces another uncertainty. However, the numbers of samples of each ore type generally reflect the proportions present within the ore body. When an ore type that we know is present in insignificant amounts has PGE values that would greatly distort the deposit mean, we have omitted it from the calculation. We have found it necessary to do this with only five samples out of the several hundred studied so far.

The means of sample data recalculated to 100 percent sulfide are given for a series of deposits in Table 2 together with the standard errors of the means. The means, normalized on the basis of the elemental abundances in type 1 carbonaceous chondrites (C1), are shown in Figs. 2 through 5. The normalization produces trends which, when the elements are plotted in the order of their melting points, are much more regular than those that would be obtained if the unnormalized data were plotted. We used elemental abundances in C1 chondrites because they are believed to be the best available indication of cosmic abundances. The actual numerical data used for the normalization are included in Table 2. The standard errors of the deposit means are relatively large. We believe that this reflects the redistribution of elements within the deposits after emplacement of the sulfide liquid by such processes as fractional crystallization of the sulfide, diffusion of elements in response to thermal

Table 2. Concentrations of metals in magmatic sulfide deposits. Analyses have been recalculated to reflect the concentration of metal in the sulfide fraction and averaged; the standard errors of the means are given in italics.

Deposit	Samples (No.)	Ni	Cu	Co	Pt	Pd	Rh	Ru	Ir	Os	Au	(Pt + Pd)/ (Ru + Ir + OS)	Source
		Percent by weight			Parts per billion								
Langmuir	31	14.60	0.67	0.27	890	1,600	230	760	240	414	181	1.8	(*17*)
		1.31	*0.12*	*0.02*	*138*	*300*	*32*	*123*	*31*	*73*	*59*		
Mount Edward	6	11.30	1.31	0.27	421	1,060	162	490	120	140	67	2.0	(*17*)
		0.69	*0.29*	*0.01*	*47*	*175*	*34*	*168*	*30*	*50*	*9*		
Kambalda	?	12.10	0.84		< 730	1,314		803	219	402	402	< 1.4	(*39*)
Pipe	26	3.96	0.16	0.16	54	122	35	217	55	107	57	0.5	(*17*)
		0.13	*0.016*	*0.003*	*7*	*14*	*1.6*	*22*	*3*	*10*	*11*		
Donaldson West	23	15.50	3.71	0.23	4,130	15,530	800	1,980	320	380	460	7.3	(*17*)
		0.31	*0.26*	*0.007*	*682*	*3,886*	*103*	*350*	*53*	*55*	*94*		
Katiniq	23	10.50	3.11	0.21	3,320	6,710	640	1,364	230	350	260	5.2	This study
		0.36	*0.83*	*0.005*	*434*	*462*	*61*	*206*	*30*	*45*	*64*		
Levack West	21	5.18	7.72		1,154	1,253	186	60	47	22	150	19	(*40*)
		0.31	*1.95*		*108*	*225*	*32*	*14*	*11*	*4*	*43*		
Little Stobie 1	23	3.83	4.41	0.19	1,930	2,120	120	120	62	29	862	19	(*40*)
		0.08	*0.65*	*0.003*	*415*	*344*	*12*	*16*	*6*	*3*	*23*		
Little Stobie 2	11	4.00	3.60	0.17	2,130	3,170	300	250	110	46	860	13	(*40*)
		0.18	*0.65*	*0.004*	*871*	*829*	*28*	*40*	*14*	*7*	*314*		
Espedalen	6	6.65	2.01		330	250	36	48	26	27	280	5.7	(*17*)
		0.43	*0.48*		*84*	*36*	*17*	*16*	*9*	*10*	*71*		
Montcalm	21	4.31	1.38	0.24	58	17	2.4	3.7	0.7	< 1.5	82	> 13	This study
		0.21	*0.22*	*0.014*	*7*	*3*	*0.29*	*0.56*	*0.09*		*12*		
Minnamax	22	3.91	17.20	0.37	2,640	8,840	120	120	48	< 53	1,170	> 52	This study
		0.32	*1.6*	*0.082*	*950*	*4,534*	*24*	*26*	*10*	*13*	*292*		
Noril'sk-Talnakh		7.60	10.90		13,700	36,000	2,240	1,500	1,500	950	1,600	13	(*6, 18*)
Merensky Reef		10.90	4.65		258,000	102,000	17,000	21,000	4,300	3,500	21,000	13	(*13*)
Stillwater		4.50	4.00		≃ 300,000	≃ 1,000,000							(*13, 19*)
Average type C1 chondrite					1,020 (*41*)	545 (*44*)	200 (*43*)	690 (*43*)	540 (*44*)	514 (*42*)	152 (*42*)	0.9	

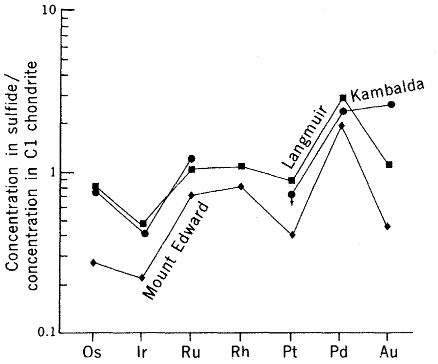

Fig. 2. Average chondrite-normalized PGE and Au concentrations in the sulfide fraction of ore deposits associated with classic, ultramafic komatiites.

gradients, and hydrothermal activity. However, we are concerned here with inter-, rather than intradeposit, variations and thus are more interested in how well our mean represents a given deposit than in how close the analysis of any one sample is to the deposit mean.

Data for three komatiite-related deposits are illustrated in Fig. 2, and Fig. 3 shows data for three Sudbury deposits. The sulfides of komatiitic affinity are characterized by a relatively flat pattern with concentrations generally within a factor of 2 of their chondritic abundances, whereas the Sudbury ores are characterized by a pattern sloping steeply upward from left to right with Pd about four times, Pt about twice, and Ru, Ir, and Os about one-tenth their abundance in C1 chondrite. Data for three deposits of gabbroic affinity (Espedalen, Montcalm, and Minnamax) are compared with the fields defined by the Sudbury and komatiite data in Fig. 4; also shown are data for the Merensky Reef in the Bushveld complex (*13*), the picritic gabbro hosted deposits of Noril'sk-Talnakh in Siberia [overall grade taken from Newman (*18*), proportioned according to the ratios of the metals given by Glazkovsky *et al.* (*6*)], and Pt and Pd in the Johns-Manville Company zone of interest in the Stillwater complex in Montana [the data from Conn (*19*) were recalculated to 100 percent sulfide on the basis of an estimate of 1.5 percent sulfide in the ore zone (*20*)]. These gabbro-related deposits all have steeply sloping PGE patterns similar to those characteristic of Sudbury, but the concentrations of the PGE vary enormously among the deposits; for example, Pt in the Montcalm sulfides is only 1/30 that at Sudbury, whereas the Noril'sk sulfides have six times as much Pt as those at Sudbury and the Merensky sulfides 120 times as much.

Data for other deposits related to magmas believed to have been komatiitic but differing in some respects from the "classic" komatiites discussed above are plotted in Fig. 5. These include the Katiniq and Donaldson West deposits in the Ungava peninsula and the Pipe Mine near Thompson, Manitoba. Pipe ore has the relatively flat pattern characteristic of the deposits hosted by classic komatiites, but the concentrations of Pt and Pd are about an order of magnitude lower than the komatiitic sulfides, and the abundances of Ru, Ir, and Os are lower by factors of 2 to 4. The Ni and Cu contents of the Pipe sulfides are also several times lower than those of the komatiitic deposits. The PGE patterns of the Katiniq and Donaldson West deposits have rather steep slopes and in this respect are more similar to the patterns of the Sudbury sulfides than to those of the classic komatiites. However, although these ores are believed to have segregated from komatiitic magmas, it is thought that the magmas were much less ultramafic than classic komatiite liquids. For example, it has been suggested that the maximum magnesium oxide content of the parent magmas of the Ungava deposits was about 16 percent (by weight) (*21*), whereas the concentrations in the magmas that gave rise to the Kambalda ores were probably between 20 and 26 percent (*22*).

Discussion

General observations. The study of the compositions of magmatic sulfide ores is in its early stages, and a detailed interpretation of the data at the present time would be unwise. However, the following general features warrant discussion.

1) The chondrite-normalized PGE patterns of magmatic sulfides are systematically related to the composition of the igneous host rocks. In particular, the (Pt + Pd)/(Ru + Ir + Os) ratios are lowest in sulfides associated with rocks that have crystallized from the most ultramafic magmas. The sulfides associated with peridotitic komatiites, which have crystallized from magmas containing more than about 20 percent MgO, have (Pt + Pd)/(Ru + Ir + Os) ratios of 2.0 or less. Ratios of 13 or more are characteristic of magmatic sulfide deposits related to gabbroic rocks that have crystallized from magmas containing less than about 12 percent MgO (the Espedalen deposit is an apparent exception with a ratio of 5.7). The (Pt + Pd)/(Ru + Ir + Os) ratios of 5.2 and 7.3 in the two Ungava deposits thus seem to be consistent with the idea that their parent magmas contained about 16 percent MgO.

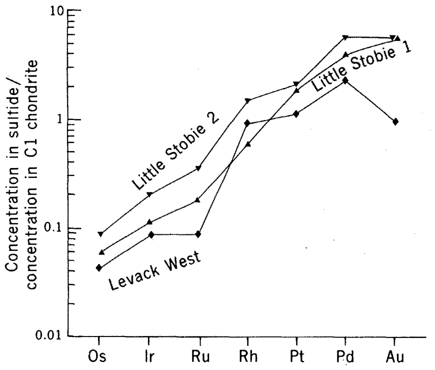

Fig. 3. Average chondrite-normalized PGE and Au concentrations in the sulfide fraction of ores from Sudbury, Ontario.

2) Despite the similarity of the PGE patterns for deposits of a particular magmatic association, the absolute PGE concentrations vary greatly in a way that shows no obvious relationship to magmatic affiliation. A number of processes may operate to redistribute metals within an ore body after emplacement of the molten sulfide, but, although these processes may be responsible for many of the variations within a given deposit, they cannot account for the variations of PGE concentrations among deposits of the same magmatic association. We will argue below that the observed variations in the abundances of PGE and other metals in magmatic sulfide ores in large part reflect differences in the concentrations of these elements in the silicate magma from which the sulfide segregated and also the relative amount of magma with which the sulfide equilibrated.

Variation of PGE concentration in magmas with the degree of partial melting in the mantle. There is little doubt that the parent magmas of the sulfide deposits in question were ultimately derived by partial melting of mantle peridotite, and it is relevant to consider how the PGE would behave during this process. Ross and Keays (*22*) have found Ir and Pd concentrations of 5.7 and 0.21 parts per billion (ppb), respectively, in olivines from Western Australian komatiites, whereas rocks representing the parent liquid composition contain about 1.4 and 10 ppb, respectively. These and other data (*3*) indicate that Ir partitions into olivine in preference to silicate liquid but that Pd concentrates in the liquid relative to olivine. It seems reasonable on the basis of similarities of other chemical properties to assume that the behavior of Pt is similar to that of Pd, whereas Ru and Os exhibit the behavior of Ir. Little is known of the abundance and distribution of the PGE in the mantle. However, it is likely that the PGE are concentrated in sulfide minerals (and possibly spinel) that are generally present in minor quantities in mantle peridotite. This concentration would be less pronounced for Os, Ir, and Ru owing to their stronger affinity for olivine, the most abundant mineral. During partial melting, the sulfides and spinel would be consumed early, whereas olivine would be the most refractory phase. Once the sulfides have dissolved in the melt, Pt and Pd would be concentrated in the silicate liquid fraction but Ir, Ru, and Os would partition into the olivine in the solid residuum. Thus melts resulting from low degrees of partial melting would contain much of the available Pd and Pt but smaller proportions of the Ir, Ru, and Os, whereas more advanced melts, incorporating more olivine, would be richer in Ir, Ru, and Os. The composition of the silicate melt would be reflected in any sulfide liquid that subsequently segregated from it, and this may account in part for the high (Pt + Pd)/(Ru + Ir + Os) ratios in deposits related to basaltic magmas as compared to those related to komatiitic magmas. This effect would be compounded if, as indicated by data on rare-earth and other trace elements, the ultramafic komatiites are generated in a part of the mantle that has undergone an earlier, limited partial melting (*23*) and which is therefore depleted in Pt and Pd.

Data on the abundance of PGE in basalts are few and limited mainly to Pd and Ir. Crocket (*3*) reported that mid-ocean ridge basalts contain an average of 0.7 ppb Pd and 0.06 ppb Ir but cautioned that these averages represent upper limits because the concentrations in many samples were below the analytical detection limits. Continental flood basalts are much richer in these elements, containing an average of 6 ppb Pd and 0.1 ppb Ir. The mid-ocean ridge basalts are typically depleted in light relative to heavy rare-earth elements and have low concentrations of other incompatible elements, indicating that they were generated in a part of the mantle from which an earlier partial melt fraction had been extracted. Removal of Pd from the source region during an earlier partial melting episode may account for the lower Pd concentrations and Pd/Ir ratios of the mid-ocean ridge basalts as compared with the continental flood basalts which, according to trace element data (*24*), were derived from undepleted mantle.

Relationship between the PGE content of silicate magma and immiscible sulfide. The distribution of a metal between sulfide and silicate liquids coexisting at equilibrium may be expressed in terms of the partition coefficient *D*, the concentration of the metal in the sulfide divided by its concentration in the silicate. The values of *D* for Ni, Cu, and Co that prevail in basaltic systems are reasonably well established, and some typical figures are as follows: Ni, 275; Cu, 245; and Co, 80 (*25*). Although precise determinations of *D* for Pt and Pd have not yet been achieved, the best currently available estimates are 1000 for Pt and 1500 for Pd (*17, 26*). In general, partition coefficients vary as a function of temperature, pressure, and the bulk compositions of the two phases. However, experimental studies (*25, 27*) indicate that rather small changes in the values of *D* for Ni, Cu, and Co may be expected within the range of temperatures and bulk compositions encountered in basaltic magmas, and a variation of at most a factor of 2 or 3 is possible between basaltic and ultramafic liquids. There is little reason to believe that the partition coefficients of the PGE would vary by factors greater than those of the other chalcophile elements. In other words, the range of several orders of magnitude in the concentrations of PGE in magmatic sulfides cannot be explained as being due mainly to equilibration under different conditions of temperature, pressure, and the chemical potentials of components other than the PGE.

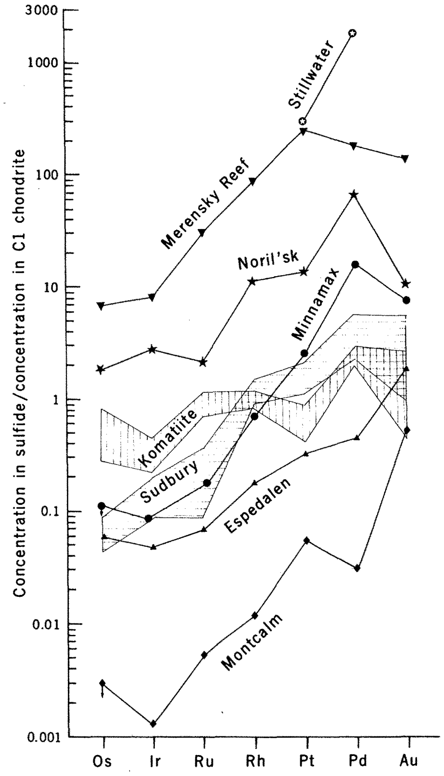

Fig. 4. Average chondrite-normalized PGE and Au concentrations in the sulfide fraction of some deposits related to gabbroic rocks. The shaded areas are the fields defined by the data illustrated in Figs. 2 and 3.

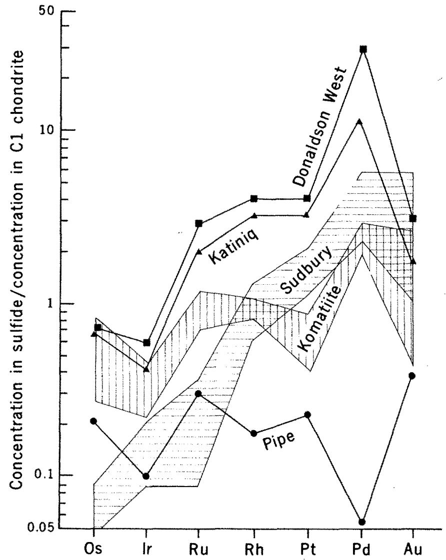

Fig. 5. Average chondrite-normalized PGE and Au concentrations in the sulfide fraction of some deposits related to ultramafic rocks.

The analyses in Table 2 suggest that the PGE contents of magmatic sulfides are generally consistent with the knowledge, albeit rather limited, of the *D* values of the PGE and their concentrations in magmas. For example, the concentration of Pd in rocks representative of magma compositions ranges from less than 0.1 ppb to about 30 ppb (*3, 22*). If these limits are multiplied by 1500, the inferred value of *D*, the range of Pd concentrations of molten sulfides in equilibrium with these magmas is from 150 to 45,000 ppb.

Magmatic sulfides with very low PGE values. The sulfides from the Pipe and Montcalm deposits have PGE concentrations that are very low in comparison to other deposits of their respective types. Such low abundances imply either that the parent magmas were generated in parts of the mantle that contained anomalously low concentrations of PGE or that PGE were removed from the magmas subsequent to their generation. There are two processes whereby the mantle may be depleted in PGE. The evidence discussed above indicates that partial melting followed by the extraction of a molten silicate fraction can deplete the residuum in Pt and Pd but not in RU, Ir, and Os. The solid fraction would also be enriched in Ni and depleted in Cu. Therefore, subsequent partial melts and their derivative sulfides would be relatively Ni-rich and would have high Ni/Cu and low (Pt + Pd)/(Ru + Ir + Os) ratios. Alternatively, Naldrett (*28*) has described a process by

Table 3. World production, reserves, and other resources of PGE for 1977 by country (*1*). The U.S. production is a by-product of Cu refining.

Country	Production		Reserves		Other resources	
	+ 10^3 kg	Percent of total	× 10^3 kg	Percent of total	× 10^3 kg	Percent of total
Republic of South Africa	91.8	46.1	18,000	72.3	43,540	69.6
U.S.S.R.	90.2	45.3	6,220	25.0	6,220	10.0
Canada	14.6	7.3	280	1.1	220	0.4
Colombia	0.8	0.4	30	0.1	120	0.2
United States	0.2	0.1	30	0.1	9,300	14.9
Others	1.5	0.8	320	1.3	3,110	4.9
Total	199.1	100.0	24,880	100.0	62,510	100.0

which sulfide could be removed from a region of the mantle under certain conditions through the downward percolation of molten droplets. The part of the mantle from which the sulfide was extracted would be depleted in Ni and Cu as well as PGE and would be left with a higher Ni/Cu ratio and a lower (Pt + Pd)/(Ru + Ir + Os) ratio, owing to the preference of olivine for Ni relative to Cu and for Ru, Ir, and Os relative to Pt and Pd. It is unlikely that either of these processes can account for the low concentrations of PGE in the Pipe and Montcalm sulfides because both deposits have Ni/Cu and (Pt + Pd)/(Ru + Ir + Os) ratios similar to other deposits of their respective types. It is more probable that their compositions reflect the subsequent removal of PGE from their parent magmas.

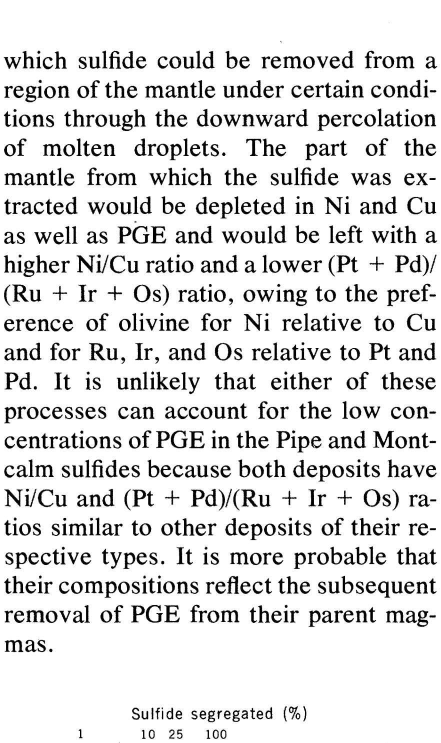

Fig. 6. Variation of the concentration of Ni, Cu, and Pd in sulfide liquid segregating from a gabbroic magma as a function of the ratio *R* = mass of the silicate magma/mass of the sulfide liquid. It is assumed that the magma initially contains 375 ppm Ni, 100 ppm Cu, 7 ppb Pd, and 0.3 percent sulfide in solution. The upper scale indicates the resultant *R* value if 1, 10, 25, or 100 percent of the dissolved sulfide is segregated in a single batch. The vertical dotted line indicates the *R* value required to produce a sulfide liquid containing 17 ppb Pd.

The oxygen fugacity in most terrestrial magmas precludes the presence of metallic phases at near-liquidus temperatures. Accordingly, equilibration with sulfide is the only known mechanism that can effectively remove PGE from these magmas. Removal of metal by sulfide can be viewed in terms of two end-members. The first is the equilibration of a batch of sulfide with the magma as a single event, followed by the concentration of the sulfide as an ore. The second is the segregation and removal of small amounts of sulfide continuously during fractional crystallization of the silicate magma, that is, fractional segregation of sulfide.

Campbell and Naldrett (*29*) have discussed the concept of batch equilibration with special reference to the relationship between sulfide ore composition and the mass ratio of silicate magma to sulfide liquid (*R*). Naldrett *et al.* (*17*) have shown how variations in *R* can account for differences in the compositions of certain ores of komatiitic affinity, and, in particular, have demonstrated that the Pipe deposit may have resulted from the equilibration of a magma with a relatively large batch of sulfide liquid. The applicability of the batch equilibration model to the Montcalm sulfides will be examined below. The gabbro that hosts the Montcalm deposit is poorly exposed, and an estimate of the parent liquid composition may not yet be made from field data. However, the composition of an Fe-rich tholeiitic hyaloclastite [table 6, analysis 1 in (*30*)] is thought to be representative of the compositions of the parent liquids of many gabbroic intrusions and flows in the Archean volcanic successions of northeastern Ontario. This magma is relatively primitive, containing 13.7 percent (by weight) MgO, 375 parts per million (ppm) Ni (*30*), and 7 ppb Pd (*31*). No data on the Cu content of this sample is available, but analyses of similar material indicate that 100 ppm is a reasonable estimate. Experimental studies (*32*) indicate that a gabbroic magma will dissolve about 0.1 percent (by weight) sulfur, which is equivalent to about 0.3 percent Fe monosulfide. The calculated compositions of the sulfide liquids formed if 100, 25, 10, and 1 percent of the total quantity of sulfide dissolved in the magma were instantaneously forced out of solution are illustrated in Fig. 6. The precise reason why sulfides suddenly segregate from a silicate magma to form a magmatic ore is not fully understood, but processes such as assimilation of siliceous country rocks (*33*) or oxidation (*34*) have been suggested. Whatever the process, it is unlikely that all of the dissolved sulfide would segregate at any given instant. Ten percent is perhaps a maximum proportion, in which case the sulfide would contain 7.1 percent Ni, 2.2 percent Cu, and 7200 ppb Pd. If, as is more probable, 1 percent of the sulfide dissolved in the magma were to segregate in a single batch, it would contain 7.5 percent Ni, 2.4 percent Cu, and 10,000 ppb Pd. Although these concentrations are within the range observed in deposits of gabbroic affiliation, they are significantly higher than the 4.3 percent Ni, 1.4 percent Cu, and 17 ppb Pd that we report in the Montcalm sulfides. If 100 percent of the sulfide dissolved in the model gabbro magma separated in one stage, it is evident from Fig. 6 that the sulfide would contain similar amounts of Ni (4.7 percent) and Cu (1.4 percent) to the actual deposit, but the concentration of Pd (1900 ppb) would be more than 100 times greater. An *R* value even lower than that resulting from the separation of 100 percent of the sulfide

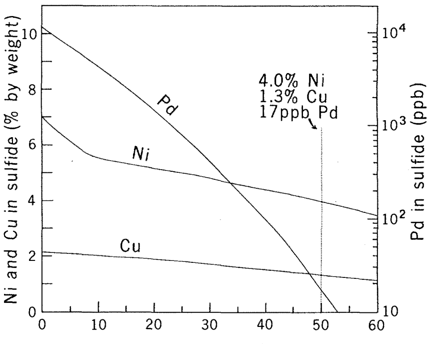

Fig. 7. Variation of the concentration of Ni, Cu, and Pd in sulfide liquid fractionally segregating from a crystallizing gabbroic magma as a function of the percentage of the initial mass of magma that has crystallized. The initial magma composition is the same as that used for the batch equilibration calculation illustrated in Fig. 6. The vertical dotted line indicates the amount of fractional crystallization necessary to produce a sulfide liquid containing 17 ppb Pd.

dissolved in the magma may prevail if, for example, the magma assimilated country rock sulfide (*17*). The *R* value in the model calculation would have to be reduced to 1.5 to produce a sulfide with 17 ppb Pd, and such a low ratio is unlikely in nature. Moreover, the Ni (0.09 percent) and Cu (0.02 percent) contents of the resulting sulfide are very much lower than the observed concentrations. Consequently, we conclude that batch equilibration is not a satisfactory explanation for the very low PGE concentrations in the Montcalm deposit.

Duke and Naldrett (*35*) have stressed the major effect that fractional segregation of sulfide can have on the concentrations of chalcophile metals in a crystallizing, olivine-rich magma. For the present study, their program has been modified to include the fractional removal of plagioclase and pyroxene as well as olivine and sulfide, and to allow the proportions of phases separating to be varied during ongoing fractionation. A calculation was carried out with the use of the same parent magma composition as for the batch equilibration model above, and separating olivine, calcic pyroxene, and plagioclase in proportions consistent with those observed in the cumulate zone of the flow from which the hyaloclastite used as the parent magma composition was collected [figure 12 in (*30*)]. It was assumed that the magma was saturated with sulfide during fractional crystallization, and the variation of the resulting fractionally segregated sulfide is illustrated in Fig. 7. After segregation of 4.2 molecular percent olivine, 37 percent pyroxene, 8.2 percent plagioclase, and 0.45 percent sulfide, the separating sulfide contains 4.0 percent (by weight) Ni, 1.3 percent Cu, and 17 ppb Pd. These concentrations match those in the actual Montcalm sulfide very well. Concentration of sulfides segregating at this stage in the crystallization of the intrusion would therefore account for the composition of the ore, and we conclude that the fractional segregation model is a viable explanation of the origin of the Montcalm deposit.

Magmatic sulfides with very high PGE values. The concentrations of PGE in the Bushveld and Stillwater sulfides are greater than those typical of the Ni-Cu sulfide deposits by one to three orders of magnitude. It follows from the discussion above that the simple magmatic segregation model for the origin of these deposits requires that either the partition coefficients of the PGE or their concentrations in the parent magmas (or a combination of both factors) were 10 to 1000 times higher than usual. We think it is improbable that the partition coefficients that prevailed in the Bushveld and Stillwater magmas were higher than our estimated values by a factor of 10 or more. It is conceivable that regions of the mantle might become enriched in PGE, thereby giving rise to PGE-rich magmas upon partial melting. For example, the process of downward migration of sulfide alluded to above (*28*) could produce zones of sulfide accumulation in the mantle that would be enriched in PGE. Partial melts of such sulfide-rich zones would be expected to carry relatively large amounts of dissolved sulfide and would therefore become saturated with sulfide rather early in their evolution. This model would not seem to account for either the Bushveld or Stillwater deposits inasmuch as each consists of horizons of sparsely disseminated sulfides occurring some distance above the base of a layered intrusion.

Table 4. Estimation of reserves and resources of PGE contained in the most important magmatic sulfide deposits. The recovery of PGE from ores mined primarily for their Ni and Cu is usually much less than 100 percent of the contained metal. The estimates for Sudbury, Thompson, Western Australia, Ungava, and Duluth have been derived by multiplying the PGE/Ni ratios determined in this study by published reserves or resources of Ni (*45*, *46*).

Deposit	Reserves/resources (× 10^9 kg Ni)	Metal ratios (× 10^6)						Reserves/resources of PGE (× 10^3 kg)					
		Pt/Ni	Pd/Ni	Rh/Ni	Ru/Ni	Ir/Ni	Os/Ni	Pt	Pd	Rh	Ru	Ir	Os
Sudbury	5.7 (reserves)	50	55	5.0	3.0	2.0	0.8	286	315	29	17	11	4.6
Thompson	1.6 (reserves)	1.4	3.1	0.9	5.5	1.4	2.7	2.2	5.0	1.4	8.8	2.2	4.3
Western Australia	1.8 (reserves)	6.0	11	1.7	7.0	1.8	3.3	11	20	3.1	13	3.2	5.9
Ungava	0.38 (resources)	32	64	6.0	13.0	2.2	3.3	12	24	2.0	5.0	0.8	1.3
Duluth	8.0 (resources)	68	226	3.0	3.0	1.2	1.4	544	1,808	24	24	9.6	11.2
Merensky Reef	Reserves as presented in Table 3 proportioned according to metal ratios quoted in Table 2.							11,000	4,630	550	1,500	170	140
Noril'sk	Reserves as presented in Table 3 proportioned according to metal ratios quoted in Table 2.							1,550	3,970	250	170	170	109
Stillwater	Resources estimated from Conn (*19*): 11 × 10^9 kg of rock grading 4 ppm Pt, 14 ppm Pd for the two zones of interest investigated by Johns Manville Co. and assuming mineralization continues 300 m downdip.							44	154	Not known			
	Resources if 43-km strike length is similarly mineralized.							280	970	Not known			

A number of processes have been proposed to account for the extremely high PGE tenor of the sulfides of the Merensky Reef of the Bushveld complex. Stumpfl (*36*) has suggested that hydrothermal solutions have upgraded the ores. Hiemstra (*37*) has proposed that Fe-Pt alloy rather than sulfide served as the collector for the PGE. Von Gruenewaldt (*38*) has suggested that the Merensky sulfides have been upgraded after their deposition as a result of interaction with ascending magmatic fluids, compressed out of the underlying pile of cumulates. There is little evidence in favor of any of these hypotheses, and we must conclude that the origin of these magmatic sulfides with very high PGE values remains uncertain.

Production, Reserves, and Resources of PGE

World production, reserves, and resources of PGE for 1977, estimated by the U.S. Bureau of Mines, are summarized in Table 3. Most of the South African production is from the Merensky Reef of the Bushveld complex (*38*). Because the PGE are their principal product, the South African mines are able to tailor production to meet demand. The PGE output of the U.S.S.R. comes mainly from the Noril'sk-Talnakh region of Siberia, and Canadian production is largely from Sudbury. In each case, the PGE are by-products of Ni-Cu sulfide mines, and output is therefore determined by the prevailing demand for Ni and, to a lesser degree, Cu. Although

South Africa and the U.S.S.R. produce approximately equal amounts of PGE, the South African ores have a Pt/Pd ratio of 2.5 whereas the ratio in the Noril'sk sulfides is 0.4 (Table 2). Accordingly, South African producers largely control the supply and price of Pt, and the U.S.S.R. is in a similar position with respect to Pd.

South Africa has a much greater share of reserves and resources than of current production. World reserves of PGE are sufficient to satisfy mankind's requirements for many decades, even if the growth in demand should be somewhat greater than the 2.6 percent per year that has been predicted for the remainder of this century (*1*). Nevertheless, because production and reserves are dominated by only two countries, the PGE are considered to be strategic mineral commodities by many industrialized nations. The PGE resources in the Stillwater complex in Montana and the Duluth complex in Minnesota are significant in this context. The economic viability of the Duluth deposits has yet to be demonstrated in the form of a producing mine, but one company (Amax) is engaged in underground exploration and another (Inco) has plans for a surface mine that are currently in abeyance as a result of environmental impact considerations. If large-scale mining does occur, the Duluth ores would become an important source of PGE, albeit one tied to the production of Cu and Ni. The Stillwater deposit grades as high in Pt and four times as high in Pd as the Merensky Reef over a mining width twice as great (2 meters as compared with less than 1 meter). The deposit is of particular interest since it could be mined for PGE alone and its economic viability would not depend upon the world Ni market. Potential obstructions to the development of this deposit include the opposition from an environmental lobby and the fact that the mineralized zone is rather disjointed as a consequence of faulting. It has been estimated that development of the Stillwater deposit would make the United States virtually self-sufficient in Pd and satisfy one-quarter of its demand for Pt (*1*).

The data on the concentrations of Ni and PGE in magmatic sulfides (Table 2) have been combined with published reserves and resources of Ni to yield our estimates of the reserves and resources of the various PGE in Table 4. For this purpose, it has been assumed that the data for the ores that we have studied may be taken as representative of the other deposits in the same camp. For example, the concentrations found in the Pipe ore were used to calculate the reserves of the Thompson camp. These estimates suggest that the proportion of PGE supply derived as a by-product of the mining of Ni-Cu ores will be much less in the future than it is at present.

Conclusions

The following conclusions may be drawn from this study:

1) The PGE concentrations in the sulfide fraction of magmatic sulfide deposits range from 58 ppb Pt and 17 ppb Pd in the relatively massive Montcalm deposit to approximately 300,000 ppb Pt and 1,000,000 ppb Pd in the stratiform, sparsely disseminated sulfides in the Stillwater complex. However, the majority of deposits that we have studied contained from 330 to 4130 ppb Pt and from 250 to 15,530 ppb Pd. Concentrations within and below these ranges may be due to either batch equilibration or fractional segregation of sulfide. The reason for the very high concentration of PGE in sulfides from some deposits remains unclear.

2) Despite the very large range of absolute PGE concentrations, the ratio of (Pt + Pd)/(Ru + Ir + Os) in magmatic sulfides is systematically related to the nature of the parent magma. Thus, sulfides that have segregated from gabbroic or basaltic magmas have ratios of 13 or more, whereas those that segregated from ultramafic komatiite magmas containing more than about 20 percent (by weight) MgO have ratios of 2.0 or less. Deposits associated with magmas of intermediate composition have intermediate ratios. We believe that Ru, Ir, and Os reside primarily in olivine in the mantle, whereas Pt and Pd occur in phases that are largely incorporated in early partial melts, and that the value of the (Pt + Pd)/(Ru + Ir + Os) ratio of the sulfide reflects the degree of partial melting required to produce its parent magma.

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47. Analyses reported in this article have been carried out at the University of Toronto Slowpoke II reactor under the supervision of Dr. R. Hancock and at the counting facilities of the neutron activation laboratory at Erindale College, University of Toronto, supervised by Dr. C. L. Chou. Dr. J. Sowa and S. R. Naldrett performed the analyses, and Drs. R. R. Keays, O. R. Eckstrand, R. I. Thorpe, and G. B. Leech critically read the manuscript. We are most grateful for the assistance of all these individuals. Support has been received from Energy, Mines and Resources Canada grant 222-4-78, Ontario Ministry of Natural Resources grant GR-17, and Natural Sciences and Engineering Council Canada grant A4244, all to A.J.N. The Geological Survey of Canada supported the study as part of project 750034 (J.M.D.). Samples have been provided by Inco Metals Ltd., A/S Sulfidmalm, Geophysical Engineering Ltd., Falconbridge Nickel Mines Ltd., and Amax Exploration Inc. We thank the representatives of these companies for their efforts.