MODELS FOR THE CONCENTRATION OF PGE IN LAYERED INTRUSIONS

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ABSTRACT

The variation in sulfur solubility with fractionation of the magma of a layered intrusion is such that the mixing of this magma with new inputs of fresh primitive magma at an early stage, well before plagioclase has appeared on the liquidus, may induce chromite saturation but will not give rise to sulfide saturation. However, sulfide saturation may result from such mixing if the resident magma is crystallizing or close to crystallizing plagioclase as a cumulate phase; sulfide-enriched, and therefore Pt- and Pd-enriched layers may result in this way. This accounts for the distribution of Pt and Pd in chromitites and sulfide-bearing "reefs" in the Bushveld and Stillwater complexes. The "reefs" are interpreted as the consequence of "batch segregation" of sulfide; the sulfide batches are thought to have developed from their source magma in turbulent plumes and subsequently to have been held in suspension by turbulent convection, which has provided the opportunity for very complete equilibration between sulfides and magma. Straightforward crystallization of a magma may give rise to the segregation of sulfide at any stage in the fractionation of a layered intrusion, depending on how close the magma was to saturation initially, but the amount of sulfide segregating in this way is unlikely to greatly exceed 2 wt.% of the cumulate silicates crystallizing at the same time. Sulfides that are thought to have segregated as a result of this process form Sulfide zones 1(iii), 2 and 3 in the Great Dyke of Zimbabwe. Magma mixing is thought to have played a role in the genesis of the Main Sulfide Zone of the Great Dyke [zones 1(i) and 1(ii)]. Field relations at the Robie deposit, Lac des Iles Complex, in Ontario, indicate that the host gabbros to this ore have undergone partial melting and brecciation. High (Pt + Pd)/(Ru + Ir + Os) and Pd/Pt ratios, such as those characterizing this deposit, have been interpreted in the past as the result of hydrothermal deposition of PGE, but it is proposed that they are the consequence of zone refining accompanying the partial melting of the gabbro.

Keywords: layered intrusion, PGE, platinum, palladium, nickel, magmatic sulfide, sulfide saturation, chromitite, constitutional zone refining, Merensky Reef, Bushveld Complex, Stillwater Complex, Great Dyke of Zimbabwe.

INTRODUCTION

The aim of this paper is to suggest a unifying magmatic model to explain the different types of PGE concentrations that are known to have developed in layered intrusions. Factors controlling the PGE content of a magmatic sulfide liquid include the PGE
content of the silicate magma, the partition coefficients of the different PGE between coexisting sulfide liquid and silicate magma and the magma/sulfide ratio (R) of the equilibrating liquids (Naldrett 1989).

With respect to the PGE content of the magma, this varies widely from a few tenths of a ppb to several tens of ppb for Pt and Pd, depending on whether or not sulfides remained behind in the mantle residuum during partial melting (Hamlyn et al. 1985, Naldrett & Barnes 1986) or whether or not sulfides segregated from the magma either during its ascent into the crust or (as is suggested by the data of Prendergast & Keays 1989 and Wilson et al. 1989) for the Great Dyke of Zimbabwe that are discussed below) during subsequent cooling.

Partition coefficients between sulfide liquids and silicate magmas are believed to be high (10^4 to 10^5) for all of the PGE (Campbell et al. 1983, Campbell & Barnes 1984, Peach et al. 1989), but there is some evidence, particularly from the Great Dyke (see below), that they vary for the different PGE.

The high partition coefficients for PGE have been used by Campbell et al. (1983) to develop the idea that the high PGE tenors of sulfides of deposits of the type under discussion here are the consequence of the equilibration of sulfide liquid involved in their formation with a much greater proportion of silicate magma than has been the case for other magmatic ores. They gave the name "R Factor" to the ratio between the amount of magma and amount of sulfide liquid involved in this equilibration.

In this paper we first discuss the variation in sulfur solubility in the magma of a layered intrusion as it fractionates and show how sulfide saturation can be attained as the consequence of the crystallization of silicates. We then show how the mixing of two batches of the same magma at different stages of fractionation can induce or suppress sulfide segregation. These ideas (first proposed by Naldrett & von

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**Fig. 1.** Schematic diagram illustrating the variation in the solubility of iron sulfide with the fractionation of what Cawthorn & Davies (1983) considered the best representative (a sample of chilled marginal material) for the magma responsible for the Lower Zone of the Bushveld Complex. Variations in solubility are based on the data of Haughton et al. (1974), Buchanan & Nolan (1979) and Buchanan et al. (1983) and the compositional calculations of Barnes & Naldrett (1986). From Naldrett & von Gruenewaldt (1989).
Gruenewaldt 1989) are used to explain PGE concentrations (or the lack of them) associated with chromitite layers in the Bushveld and Stillwater complexes and with sulfide zones in the Great Dyke of Zimbabwe. The same ideas, coupled with the R factor argument, are then used to explain the PGE content of chromite-poor, sulfide-bearing “reefs” such as the Merensky and J-M Reefs, also of the Bushveld and Stillwater, respectively. Finally, a non-stratiform ore zone within the Lac des Iles Complex is discussed in terms PGE partitioning during the partial melting of gabbroic cumulates and subsequent saturation of the partial melt in sulfide, a process that McBirney (1987) and Brügmann et al. (1989) have referred to as constitutional zone refining.

**Sulfide Solubility, Magma Mixing, Sulfide Segregation and Chromitite Genesis**

On the basis of experimental data, Naldrett & von Gruenewaldt (1989) estimated how the solubility of sulfur was likely to have varied in the magma of the Bushveld Complex as it fractionated. Their estimate, shown in Figure 1, is not necessarily very accurate, but they argued that the concave upward shape was definitely established, even though the absolute levels of saturation of sulfide in the magma might vary by a factor of 2 or more. Crystallization of an initial magma not saturated in sulfur, such as at point A, would follow a path A-B and attain sulfide saturation at B. Further crystallization would cause the magma to move down the saturation curve, segregating sulfide. The early sulfides would be PGE-rich, but because of the strong partitioning of PGE into sulfide, the magma would become rapidly depleted in PGE, and late-segregating sulfides would thus be poor in PGE. None of the sulfides forming in this way would necessarily be associated with the base of a cyclic unit, since sulfide saturation would be attained as the consequence of straightforward crystallization, not as the consequence of a process initiating a cyclic unit.

Field relations and mineralogical data (Jackson 1961, von Gruenewaldt 1979) and, more recently, isotopic studies (Kruger & Marsh 1982, Sharpe 1985, Lambert et al. 1989) have shown that large layered intrusions are not the result of single, one-shot injections of magma, but are the result of repetitive inputs.

Returning to Figure 1, suppose that at an early

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![Figure 2](image_url)  
**Fig. 2.** Phase relations in the system olivine-silica-chromite as determined by Irvine (1977) and illustrating the consequence of mixing primitive magma (A) with well-fractionated (D) and slightly fractionated (B) variants of the same primitive magma.
stage, when the resident magma in the chamber had achieved sulfide saturation but was still in the orthopyroxene field, a fresh input of magma A entered the chamber and became mixed with that resident there. The mixture would lie somewhere on the sulfide-unsaturated side of the saturation curve and, during continued crystallization, sulfide segregation would cease. On the other hand, if the resident magma had fractionated sufficiently that it lay in the gabbro field at a point such as D, and was therefore crystallizing plagioclase-bearing cumulates, the addition of more magma A could cause the resulting hybrid to lie at a point such as AD, on the sulfide-saturated side. Under these circumstances, sulfides would segregate in a greater proportion relative to silicates than would have been the case if the magma were merely crystallizing down the sulfide-saturation curve.

Turning to the presence or otherwise of sulfides in chromitites, Irvine (1977) showed that the mixing of two magmas, one that had reached a higher degree of fractionation than the other, could inhibit the fractional crystallization of silicate minerals such as olivine and orthopyroxene and permit the crystallization of chromite alone. He proposed this as the mechanism by which layers of massive chromitite can develop, without dilution by cumulate silicates. It can be seen from Figure 2 (after Irvine 1977) that the mixing of liquid A with liquid D, one on the olivine–chromite cotectic and the other in the orthopyroxene field, may, provided that points on the mixing line lie above the liquidus surface, give rise to a hybrid magma such as AD, which, on cooling, will intersect the liquidus in the chromite field. Thus it will crystallize chromite alone while it moves to point X on the olivine–chromite cotectic, at which stage it will continue to crystallize chromite and olivine. Murck & Campbell (1986) showed that the decrease in the solubility of Cr in basaltic magma in equilibrium with chromite per degree centigrade
fall in temperature is greater at high (1300–1400°C) than at low (1100–1200°C) temperature. Because of this concave-upward curvature of the solubility curve, the mixing of two magmas at different temperatures saturated (or nearly saturated) in chromite places the resultant mixture above the saturation curve, which suggests that point AD in Figure 2 is likely to lie above the liquidus.

Fig. 4. The Great Dyke of Zimbabwe, showing the location of Cyclic Unit I in the Darwendale Subchamber. After Wilson et al. (1989).
Irvine’s (1977) suggestion is consistent with observations on chromitites in layered intrusions. Most of these are very extensive, stratabound formations that, in the Bushveld Complex, occur at the base of well-defined cyclic units and, in the Stillwater Complex, at or near the base of similar cyclic units. Textural evidence from underlying rock units pointing to the common cotectic crystallization of chromite with olivine or orthopyroxene indicates that the magmas previously in the chambers were saturated with respect to chromite.

It is important to note that the mixing of fresh primitive magma with that resident in an intrusion can give rise to chromitite formation regardless of the degree of fractionation of the resident magma, whereas extensive segregation of sulfide will only occur as a consequence of this type of mixing close to or after the stage at which plagioclase saturation has been achieved by the resident magma.

**ASSOCIATION OF PGE WITH CHROMITITES**

In Figure 3, the PGE contents of the different chromitite layers of the Bushveld and Stillwater complexes are plotted against the stratigraphic position of the chromitites in terms of the distance above and below the level in the intrusion at which plagioclase first enters as a cumulus phase. Naldrett & von Gruenewaldt (1989) pointed out that it is only those chromitites occurring close to or above where plagioclase is present as a cumulate phase that are particularly enriched in PGE. They showed that all of the chromitites contain modest levels of Ru, Ir and Os, which is understandable in view of the

![Diagram showing stratigraphy of the Ultramafic Sequence of the Great Dyke in the Darwen-dale Subchamber with special reference to Cyclic Unit 1. After Wilson (1982).](image-url)
MODELS OF PGE IN LAYERED INTRUSIONS

FIG. 6. Vertical variations in chalcophile elements and chalcophile element ratios, together with the Mg# of coexisting orthopyroxene, in a transect through sulfide zones I(i), I(ii), I(iii), 2 and 3 in the Darwendale subchamber of the Great Dyke, based on data from two drill holes AW-1 and AW-2 presented by Wilson et al. (1989). Zone 1 extends from 5 to 8.5 m, Zone 2 from 15 to 20 m and Zone 3 from 40 to 50 m.

Apparent compatibility of these elements in chromite. The much higher total PGE concentrations in certain chromitites is due to their much higher concentrations of Pt, Pd and Au. Naldrett & von Gruenewaldt demonstrated that the reason for this is the appreciable (several tenths of 1 percent) sulfide in these chromitites. The answer to the question as to why sulfides accumulate only in these particular chromitites lies in the discussion of the previous section.

Magma mixing can give rise to chromitites whether the resident magma is saturated in plagioclase or not. Accepting that sulfide solubility varies as predicted in Figure 1, chromitites that have formed by mixing of primitive magma with that crystallizing orthopyroxene or olivine (i.e., those of the Lower Group of the Bushveld Complex and most of those of the Stillwater Complex) are interpretable as the result of the mixing of a liquid such as A with one lying between B and Y in Figure 1; no sulfide immiscibility, and thus no Pt, Pd and Au enrichment, are to be expected in this case. Those such as the Bushveld Upper Group are interpretable as the result of the mixing of A with D, and larger than cotectic proportions of Pt and Pd and Au-enriched sulfides are possible. It should be noted that since the resident magma involved in the mixing has fractionated

FIG. 7. Schematic summary of aspects of the cyclical variation in element concentrations and ratios exhibited by each of the sulfide zones in the Great Dyke. The vertical axis represents vertical height. In the second column showing Pt and Pd in sulfides, the solid line refers to Pt and the dashed line to Pd. From Wilson et al. (1989).
Fig. 8. Model of the variation in the concentrations and the ratios of chalcophile elements in typical sulfide zones of the Great Dyke as a consequence of fractional segregation of sulfide. No data are available on the PGE content of the Great Dyke magma, so that typical values for continental flood basalt of 10 ppb Pt and 5 ppb Pd were assumed. Partition coefficients of $10^{4.3}$ and $10^{5}$ were assumed for Pt and Pd, respectively. In order to facilitate comparison with the observed data, the results of the calculation expressed by the figure have been modified in that the bases of the sulfide zones have been made gradational. The first 0.001% of sulfide to segregate has been intermixed with 3 m of cumulates, the second 0.001% with 2 m and each of the remaining ten 0.001% of sulfide each with 1 m of cumulates. As described in the text, sulfide segregation is believed to have been halted as a consequence of the introduction of new magma. At this stage, the magma resident in the chamber was essentially devoid of PGE, as shown by the very low PGE content of sulfide segregating toward the top of each mineralized zone. As new magma (containing the original concentration of PGE) enters and mixes with that in the chamber, the PGE content of the resulting hybrid increases. Eventually crystallization of silicates (which is believed to occur while the new influx is occurring) brings the magma in the chamber back to the sulfide-saturation curve, sulfides start to segregate, and the whole process recommences, as shown at the top of the figure. The extent to which the magma in the chamber (and thus any sulfide to equilibrate with it) is enriched in PGE depends on the percentage of new magma that is introduced. This diagram applies particularly to Sulfide zones 1(iii), 2 and 3. Modified after Wilson et al. (1989).
down the sulfide-saturation curve, sulfides will have segregated from it during this fractionation and will have left it essentially devoid of PGE. All of the PGE concentrated by the sulfides resulting from the magma mixing must, therefore, have come from the new input of unsaturated, primitive magma that was involved in this mixing.

If the magma overlying the cumulates has fractionated nearly to the point of appearance of plagioclase (point C in Fig. 1), the mixture can be slightly oversaturated in sulfide, but only at low ratios of A to C; the smaller possible degree of oversaturation and the low ratio of A to C at which it can be achieved mean (because all of the PGE must have come from the primitive magma “A”) that the enrichment of the resulting chromitite in PGE may be less than in the case of mixing A and D. The intermediate concentrations of Pt and Pd characterizing the Bushveld Middle Group chromitites are, therefore, explicable in the light of this intermediate case, since they occur just a few meters above or below the incoming of cumulus plagioclase.

The Stillwater “A” chromitite appears to be an exception to the model proposed above, until it is appreciated that the Stillwater Complex, like most other layered intrusions, shows a reversed fractionation at its base. The “A” chromitite lies only a few meters above the first incoming of cumulate olivine, in a region where the mafic minerals have a much lower Mg/Fe ratio than they have higher in the sequence, and not far above the norites of the basal zone. An input of primitive magma at an early stage such as this thus mixes with a relatively fractionated magma and, under these conditions, can give rise to sulfide segregation in addition to chromitite formation.

**Physical Interaction of Mixing Magmas and Genesis of PGE Reefs**

Campbell et al. (1983) investigated the likely physical interaction between fresh magma inputs and resident magma. They showed, using hydrodynamic equations, that mixing is likely to be turbulent and have the form of a fountain or plume; the turbulence would give rise to significant entrainment and mixing of resident magma within the input. The physical form of the input will depend on its density relative to that of the resident magma. If the resident magma is less dense, the input will have the

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**Fig. 9.** Schematic diagram showing how the solubility of sulfide in the magma of the Great Dyke is likely to vary with fractional crystallization, and mixing with more and less fractionated derivatives of the magma. This diagram is modified to reflect the more primitive nature of the Great Dyke from that presented as Figure 1. After Wilson et al. (1989).
form of a turbulent fountain, and the hybrid of fresh and resident magma will accumulate at the interface between magma and the pile of cumulate crystals; if the resident magma is denser than the input, the input will rise through the resident magma as a turbulent plume, entraining and mixing with resident magma as it rises. In the case of the plume, if, as is thought likely, the resident magma is stratified in a series of layers of differing density, the hybrid magma forming the plume will continue to rise until it reaches its own density level, at which point it will spread out as a turbulently convecting layer. Barnes & Naldrett (1985) showed that the crystallization of olivine would lower the density of a primitive magma such as that responsible for the Lower Zone of the Bushveld Complex; crystallization of orthopyroxene would cause relatively little change in density. However, once plagioclase joined orthopyroxene on the liquidus, the density of the fractionating magma would start to rise, eventually exceeding that of the original primitive input. Turbulent plumes are thus likely later in the crystallization of a layered intrusion, after plagioclase-bearing cumulates have been forming for some time. Campbell et al. (1983) suggested that if sulfides formed in the hybrid during the turbulent mixing, they would find themselves in the ideal environment in which to develop a high R factor, and thus become very enriched in PGE.

Naldrett et al. (1986) argued that the cyclic units that host the PGE-bearing "reefs" in the upper part

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**Fig. 10.** Geological map of the Lac des Iles Complex. From Sutcliffe & Sweeney (1985).
of the Critical Zone of the Bushveld Complex are the consequence of inputs of fresh primitive magma. The “reefs” occur at the base of these cyclic units, and the sulfides within them are characterized by very high PGE-tenors (600 g/t in the Merensky Reef compared to 20 g/t immediately overlying the Reef) and more primitive Ni/Cu ratios (2.3 in the Merensky Reef compared to 1.3) than in the small amounts of sulfide in the rocks above and below them. The boundaries between the high-tenor “reefs” and the adjacent rocks are extremely sharp. They concluded that the sulfides segregated from their source magma in a batch that formed as a result of magma mixing in a turbulent plume. The batch of sulfide liquid subsequently became well equilibrated with a large mass of this magma in a turbulently convecting layer. The

![Fig. 11 A] Gabbro showing weak modal layering in the proportions of mafic and felsic minerals. B) Varitextured gabbro containing fragments of anorthosite and melanocratic to leucocratic gabbro; most of the fragments, and in particular the leucocratic variants, show signs of partial digestion by, and incorporation into the surrounding gabbroic matrix. C) Gabbro megabreccia. D) Partially digested anorthositic fragments in gabbro megabreccia. E) A pyroxenitic dyke which, outside the varitextured zone, is a parallel-sided discordant unit but here, inside the zone, shows scalloped margins and splits into a series of smaller stringers and, in places (F), discrete fragments, connected by small “stringers” of pyroxene-rich material.
sulfide liquid then settled from this layer, together with associated silicates and entrained magma, to form the reefs. They showed that many other aspects of the geology of the Merensky Reef could be explained using a model of this kind.

**Fractional Segregation of Sulfide**

In the Darwendale Subchamber (Wilson & Prendergast 1989), in the northern part of the Great Dyke of Zimbabwe, 2000 m of ultramafic rocks are overlain by 1120 m of gabbro (Fig. 4). Fourteen cyclic units are recognized in the ultramafic succession, of which the six in the upper succession show a complete progression from a basal chromitite, through dunite, harzburgite and olivine orthopyroxenite to a well-developed orthopyroxenite layer at the top (Fig. 5). Their origin is interpreted as due to repeated injections of primary magma followed by fractionation and differentiation (Wilson 1982).

The uppermost cyclic unit, Cyclic Unit 1, contains several zones of sulfide mineralization, to which Wilson *et al.* (1989) gave the names Zone(s) 1(i), 1(ii), 1(iii), 2 and 3 (Fig. 6). The sulfide mineralization is disseminated, amounts to a maximum of 8% sulfide by volume in Zone 1 [the Main Sulfide Zone or MSZ of Bichan (1969) and Prendergast (1988)], and occurs interstitially to the main silicate minerals. Sulfide Zones 2 and 3 are more attenuated than Zone 1 and extend over up to 80 m, but they contain a maximum of less than 2% sulfide by volume (Wilson *et al.* 1989).

Wilson *et al.* (1989) have shown that there are a number of systematic variations in element concentrations and ratios that characterize each of the cycles (Fig. 6) which, when the effects of overlapping cycles are eliminated, correspond to the scheme shown in Figure 7 and have the following features: 1) The Pt and Pd concentrations in the small amounts of sulfide contained in the rocks underlying each sulfide zone increase as the zone is approached. 2) The Pt and Pd contents of the sulfides drop sharply as the percentage of sulfide within the rock increases upward into each sulfide zone. The drop is distinctly

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**Fig. 12.** Geological map of part of the gabbroic portion of the Lac des Iles Complex showing the location of the varitextured gabbro and megabreccia. A, B, C, etc. refer to mineralized zones outlined by Gunnex Ltd. (Pye 1968). After Macdonald (1985) and Macdonald *et al.* (1989).
sharper for Pd than for Pt. 3) Because of the more rapid drop of Pd than Pt, the Pd/(Pd + Pt) ratio also drops sharply as the sulfide content increases at and just above the base of a zone. 4) The Cu content of the sulfides remains relatively constant, showing no systematic trends, but because of the drop in Pt the Cu/(Cu + 1000 x Pt) ratio rises sharply once the sulfide content of the rock increases at the base of a zone. 5) The Pt and Pd contents of the sulfide remains low, once this drop has occurred within any given zone, but once the sulfide content of the rock decreases at the top of a zone, Pt and Pd in the sulfides start increasing. 6) The bases of the sulfide zones either coincide with or occur a very short distance above maxima in the Mg/Fe ratio of orthopyroxene.

Prendergast (1988) and Prendergast & Keays (1989) have documented very similar variations in Pt, Pd, Ni and Cu concentrations in the Wedza sub-chamber of the Great Dyke.

The systematic and smooth way in which Pd and Pt decrease upward in the sulfides of a zone in the Great Dyke is very different to the abrupt upper limits of the Merensky and J-M Reefs and is difficult to explain in terms of the segregation of a batch of sulfide liquid of uniform composition. It is reminiscent of the partitioning of elements into a phase that is continuously being removed from the magma, in this case sulfide. This hypothesis has been tested by modeling the behavior of Pd, Pt and Cu for simple Rayleigh fractionation assuming Pd, Pt and Cu concentrations typical for continental flood basalt (10 and 5 ppb and 180 ppm, respectively: Crocket 1981) and sulfide/silicate partition coefficients of 10^2, 10^4.5 and 250, respectively. In order to facilitate comparison with the observations, the base of each sulfide zone has been made gradational in the model. The results are shown in Figure 8, where it is seen that a reasonable match exists between observations and model.

The model of ore formation favored by Wilson et al. (1989) is that, initially, a column of magma of the order of tens to hundreds of meters high became saturated in sulfide; sulfides fractionally segregated from this and settled to become mixed with orthopyroxene cumulates on the chamber floor. Eventually, for reasons discussed below, the segregation ceased, by which stage the magma column had become in most cases extremely depleted in PGE. The data indicate that, before sulfide segregation started again, the resident magma overlying the cumulate pile became enriched once more in PGE; since this enrichment was accompanied by an increase in the magnesium number (Mg#) of orthopyroxene, it is likely that it was due to mixing of the resident magma with a fresh input of primitive, PGE-rich magma.

The model is illustrated in Figure 9 in terms of a sulfide-saturation curve similar to that in Figure 1, but modified to take into account the greater proportion of olivine and lower proportion of orthopyroxene in the Great Dyke, as compared to the Bushveld Complex. The initial magma for the Great Dyke had a composition such as that represented by point A; as it fractionated olivine, it moved along path AB, with its sulfide content increasing. During all of the cyclic units below unit 1 the magma never reached
point B, but was constantly drawn back away from B by new inputs of sulfide-unsaturated magma A; these inputs were responsible for initiating each new cyclic unit, and giving rise to the chromitite layers that mark the bases of the units. Finally, toward the top of cyclic unit 1, the magma reached B and was constrained to move along the saturation curve, segregating sulfide and giving rise to sulfide zone 3. Since the curve is fairly steep in this region, the proportion of sulfide segregating to silicate crystallizing will be higher than it will be at a more advanced stage in the fractionation, where the change in sulfide solubility with fractionation is less. The curve for the Great Dyke (Fig. 9) is highly schematic, but that for the Bushveld Complex (Fig. 1) is somewhat better constrained (see Naldrett & von Gruenewaldt 1989) and indicates that the segregating sulfides may amount to up to 2 wt.% of the cumulate silicates. This estimate compares well with the observed sulfide content of Zones 2 and 3 in the Great Dyke, which contain up to 2 but generally less than 1 wt.% by volume (≈ 1.5 wt.%).

The magma moved down the sulfide-saturation curve, perhaps as far as point C, until mingling with a fresh input of unsaturated magma again pulled it off the curve and sulfide segregation ceased. On the cessation of the new input, continued crystallization of the magma, now enriched in PGE, caused it to move back to the curve to give rise to zone 2 and then, in the same way, to zones 1(iii) and possibly 1(ii). Zone 1(i) and perhaps 1(ii) contain too much sulfide (up to 8 wt.%) to be the result of simple crystallization along the sulfide solubility curve, which would give rise to sulfides in merely the proportions indicated by the curve. Some other, more drastic process that is capable of inducing sulfides to segregate without the simultaneous crystallization of cotectic proportions of silicates must be called upon. In this respect, it is interesting that zone 1(i) occurs very close to the contact with the overlying Mafic Layered Sequence. The geophysical and mass-balance models of Podmore & Wilson (1987) and Wilson & Prendergast (1989) indicate that the dyke is trumpet-shaped in cross section, so that magma at the flanks near the top, i.e., in the flared part of the trumpet, was more exposed to the cooling influence of the wall rocks, and to loss of heat through the roof, than was magma near the axis. Wilson et al. (1989) suggested that more fractionated magma, possibly equivalent to point E in Figure 8, was present near the roof of the Great Dyke, perhaps produced by the simultaneous but more advanced fractionation of a batch of magma in a flanking portion of the Dyke at a level now removed by erosion. There is field evidence of the erosion of websterite cumulates at this level and the filling of the erosion

![Graph showing the covariation of Pt and Pd in both the gabbroic (dark symbols) and ultramafic samples (light symbols) at Lac des Iles. Note that the Pd/Pt ratio of the gabbroic samples is much higher than that of the ultramafic samples, and, unlike the latter, which have a constant ratio of about 1:1, increases with increasing (Pd + Pt). After Brügmann et al. (1989).](image)
channels by magma crystallizing gabbro, indicating that magma currents were operating at this stage. Mixing of a small proportion of this fractionated magma with the more primitive magma responsible for cyclic unit 1, which had by this stage perhaps reached point F, would have constantly tended to pull the mixture into the saturated region of Figure 9, to the right of the sulfide-saturation curve. This mixing would thus have resulted in the segregation of larger amounts of sulfide for the same amount of silicate crystallized than would have been the case for simple crystallization along the saturation curve.

**CONSTITUTIONAL ZONE REFINING AND PGE MINERALIZATION AT LAC DES ILES**

The Lac des Iles Igneous Complex is located in northwestern Ontario, 90 km north of Thunder Bay. It consists (Fig. 10) of a northern ultramafic part, actually made up of at least two intrusive centers, and a southern gabbroic part (Sutcliffe & Sweeney 1985). The exact relationship of the gabbroic to the ultramafic portion is not known, but geochemical data indicate that they are consanguineous. It is likely, therefore, that the gabbro either represents the top of the ultramafic part that has become segregated from it structurally, or, alternatively, that the gabbro has crystallized from fractionated magma that resulted from accumulation of the ultramafic part. The gabbro to the south may, therefore, be regarded as the gabbroic cap to the ultramafic rocks to the north.

The ultramafic part contains apparently stratiform zones of sparsely disseminated sulfides within cumulate silicates that are located at the top of cyclic units; these sulfide zones are not particularly enriched in PGE (Brügmann et al. 1989). The principal PGE mineralization occurs in a series of sulfide-bearing zones in the gabbro to the south.

These gabbro-hosted ore zones are examples of PGE mineralization that is very different to that in the Merensky and J-M Reefs (Macdonald 1988, Macdonald et al. 1989). The zone at Lac des Iles that has been explored and studied most extensively is typical and is known as the Robie zone. It is characterized by extremely fractionated PGE concentrations, with a $(\text{Pt} + \text{Pd})/(\text{Ru} + \text{Ir} + \text{Os})$ ratio of $> 9000$ and a variable but high Pd/Pt ratio of between 10 (average of high values of Brügmann et al. 1989) and 18 (average of data of Naldrett et al. 1980). High values of these ratios have been taken as evidence of hydrothermal transport and deposition of PGE by previous workers, but Brügmann et al. (1989) have proposed that the ore concentration and extreme fractionation of the PGE are the consequence of constitutional zone refining (McBirney 1987) resulting from the partial melting of gabbroic cumulates.

Macdonald (1985) and Macdonald et al. (1989) described the gabbro as noritic to gabbroic to leu-
cogabbroic in composition. Much of it is relatively even-textured, shows weak modal layering (Fig. 11A), and consists of plagioclase, clinopyroxene and variable amounts of orthopyroxene. It is cut by fine-grained pyroxenitic and also felsic dykes. Large areas within the gabbro (Fig. 12) have a variable texture (Fig. 11B), referred to by Macdonald (1985) as “varitextured” gabbro, and, in places (Fig. 12), are very brecciated (Fig. 11C); in fact, many of the varitextured areas are megabreccias of gabbroic fragments cemented by a gabbroic matrix. Rounded fragments of both leucocratic and melanocratic gabbro occur in the megabreccia, as do anorthosite fragments (Fig. 11D). Where it enters the zone of megabreccia, the pyroxenite dyke shows signs of both plastic and brittle deformation, as it breaks up into a series of deformed fragments (Fig. 11E) or, in some places, becomes highly brecciated (Fig. 11F). Coarse veins composed primarily of plagioclase and hornblende, referred to by Macdonald (1985) as pegmatoid, cut the varitextured gabbro (Fig. 13A). In some cases the pegmatoid occurs as clots, and in many cases it is sulfide-rich (Fig. 13B). One of the last events in the ore zone is the formation of pegmatite veins (Fig. 13C and also 11C), which also are rich in sulfide. Some of the pegmatoids can be observed grading into pegmatite. Brügmann et al. (1989) interpreted the varitextured and megabrecciated zones as areas that had undergone partial melting, and the pegmatoid and pegmatite veins as the products of the final crystallization of the resultant partial melt.

Brügmann et al. (1989) studied the distribution of the PGE in the rocks of the Lac des Iles Complex. They found that Pt and Pd are well correlated within their ultramafic samples, with a ratio of about 1. The Pd/Pt ratio in the Robie mineralized zone increases with increasing (Pd + Pt) from about 1 in very weakly mineralized gabbro to 12 in high-grade ore samples (Fig. 14). The ratio is probably highly variable throughout the deposit, since Naldrett et al. (1980) found an average Pd/Pt ratio of 18 for the 20 samples that they analyzed.

Another even more striking difference between the ultramafic and mafic parts is the very much higher Pt/Ir and Pd/Ir ratios of the latter (Fig. 15). The fractionation of Pd with respect to Pt and of both Pd and Pt with respect to Ir is a striking characteristic of the Lac des Iles mineralization, as is shown in Figure 16, in which Lac des Iles is compared with Sudbury and certain PGE-enriched ores. As mentioned above, this has been interpreted as the consequence of hydrothermal activity. However, typical vein-related hydrothermal alteration is absent; sulfides are not associated with veins but are concentrated in specific igneous rock-types including pegmatoids, pegmatites and pyroxenites, as well as being distributed to a lesser extent within the matrix of the varitextured gabbro.

Though favoring for these reasons an igneous origin for the mineralization, Brügmann et al. (1989) noted that Lac des Iles represents a situation very different from that in the Merensky or J-M Reefs. An irregular and definitely not stratabound zone in the gabbro has undergone partial melting and remobilization, leading to the formation of igneous breccia, pegmatoids and pegmatites, the deposition of sulfides and concentration and extreme fractionation of the PGE. They suggested that the gabbro body, containing a small amount of sulfide and associated PGE, underwent remelting due to the introduction of H₂O and other volatiles into largely solidified cumulates. The zone of melting proceeded, probably upward, through the gabbro, propelled by the heat of crystallization at its base, augmented by that from ultramafic (pyroxenitic dykes) that were intruded at this time. The varitextured gabbro is the zone through which the melting front has passed; it consists in part of a residuum of the melting coupled with variable amounts of partial melt that were not completely expelled. The pegmatites and pegmatoids are the final products of crystallization of the melt. As it progressed, the partial melt scavenged the incompatible elements, and dissolved all sulfide present. Elements such as the PGE, which were
associated with the sulfides in the gabbro but which became incompatible when the sulfides dissolved in the partial melt, also dissolved in the melt. Of these, Pt and Pd (and Au), became highly concentrated in the melt. Others, such as Ni, Ru, Ir and Os, which are compatible to varying degrees in mafic silicates (Brügmann et al. 1987, Naldrett & Barnes 1986), were removed, as these silicates crystallized at the base of the zone of partial melting. The process led to an enormous fractionation of the PGE and marked increase in the \((\text{Pt + Pd})/(\text{Ru + Ir + Os})\) ratio. Brügmann et al. (1989) likened the process to the constitutional zone refining described by McBirney (1987). It is suggested that Pt is accepted by mafic silicates more readily than Pd, which accounts for the fractionation observed between these two elements at Lac des Iles.

As it progressed through the body of gabbro, the partial melt became enriched in sulfide (along with incompatible elements including Pd, Pt and Au), finally becoming saturated in sulfide. At this stage it could dissolve no more sulfide; sulfide thus remained behind in the residuum of the partial melting, and essentially all of the PGE in the melt partitioned into this sulfide. The residuum thus became particularly enriched in those PGE, in this case Pd and Pt, which had become concentrated in the partial melt, so forming the ore deposit. In a situation like this, the critical point for the generation of the ore deposit is the stage at which the partial melt becomes sulfide-saturated. The very high partition coefficients of the PGE between sulfide melt and silicate magma cause them to stay with the sulfide, once this exists as a discrete phase, and the ore deposit develops at this site.

**Conclusions**

The types of mineralization discussed in this paper are summarized in Figure 17, which shows a section through a hypothetical layered intrusion. Deep in the ultramafic zone, where mixing of new inputs of primitive magma with resident magma has occurred before sulfide saturation is achievable in this way, massive chromitites that are not enriched in sulfide and thus are poor in Pt and Pd have formed (Fig. 17, example I). These are the equivalents of the chromitites of the Bushveld Lower Zone and most of the

**Fig. 17.** Cross-section through a hypothetical layered intrusion, showing the types of chromitite and PGE-enriched sulfide deposits that can result from fractional crystallization, magma mixing and constitutional zone refining. Mixing of resident with primitive magma before plagioclase has appeared on the liquidus of the former is likely to produce sulfide- and, therefore, PGE-poor chromitites (Example I); fractional crystallization may give rise to a PGE-rich sulfide layer not associated with the base of a cyclic unit (Example II); mixing of resident with more primitive magma after plagioclase is crystallizing from the former may give rise to sulfide- and, therefore, PGE-enriched chromitites or PGE-rich sulfide layers (Example III). Volatile-induced partial melting of cumulates can give rise to constitutional zone refining and the concentration of PGE at the point at which the partial melt becomes saturated in sulfide (Example IV).
Stillwater Complex.

The onset of sulfide saturation due to simple crystallization without magma mixing can give rise to deposits such as Zones 3 and 2 in the Great Dyke (Fig. 17, example II). This can occur at any level in an intrusion, depending on how close the magma was to sulfide saturation initially. These sulfide zones are not likely to be associated with the bases of cyclic units.

Once plagioclase has appeared on the liquidus of the resident magma, which means that this has advanced to the flat part of the sulfide-saturation curve, a fresh input can result in a mixture lying on the saturated side of the curve, forming either a sulfide-bearing and PGE-enriched chromitite or, if the magma mixture is not particularly enriched in Cr, a PGE-rich sulfide layer such as the Merensky Reef (Fig. 17, example III). There is evidence in the Merensky Reef to suggest that mixing in a turbulent plume assisted the sulfides to scavenge PGE from the magma. The relatively fractionated nature of early pulses of magma into the chambers of most layered intrusions means that magma mixing may induce sulfide saturation near the base, as in the Stillwater "A" bronzitite, even though plagioclase does not appear as a cumulate mineral for many thousands of meters in the overlying cumulate succession.

Finally, field relationships within the Lac des Iles Complex indicate that the highly fractionated PGE proportions of the Robie mineralization are unlikely to be the consequence of direct hydrothermal deposition of the ore. It is concluded that constitutional zone refining, brought about by volatile-induced partial melting, can account for many of the features of a deposit such as the Robie zone (Fig. 17, example IV).

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REFERENCES


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