Exploration for magmatic Ni–Cu–PGE sulphide deposits: a review of recent advances in the use of geochemical tools, and their application to some South African ores

W.D. Maier

Department of Geology, University of Pretoria, Pretoria, 0002 Republic of South Africa

S.-J. Barnes

CERM, Université du Québec, Chicoutimi G7H 2B1, Canada

S.A. de Waal

Department of Geology, University of Pretoria, Pretoria, 0002 Republic of South Africa

Most major magmatic Cu-Ni-PGE sulphide deposits are thought to have formed by segregation of an immiscible sulphide melt from a silicate host magma, in response to processes such as magma mixing, rapid cooling, differentiation, and contamination. The metal content of the sulphides is governed by the concentration of the metals in the silicate host magma, the sulphide melt/silicate melt partition coefficients (D values) of the metals, and the R-factor during sulphide segregation. Fractionation between the metals occurs during partial melting of the upper mantle source, crystallization of oxides, platinum-group minerals (PGM), and silicates (mainly olivine and less so orthopyroxene), segregation of sulphide melt, and crystallization of the sulphide melt. The latter process may yield zoned ore bodies consisting of Os, Ir, Ru, Rh, Fe, (Ni)-rich monosulphide solid solution (mss) cumulate ore and fractionated sulphide ore rich in Cu, Pt, and Pd. It is possible to model these processes and thereby to estimate the potential of a magmatic body to host economic Cu–Ni–PGE sulphide deposits. The location of Cu–Ni–PGE sulphide ores may be facilitated by applying a number of geochemical tools. PGE-rich horizons within layered intrusions are particularly difficult to locate because the ore zones are generally thin compared to the thickness of the intrusions. Variation in Cu/Pd ratios of the silicate rocks may delineate the position of some of these horizons, since the strongly chalcophile Pd is preferentially depleted during sulphide segregation, resulting in an increase in Cu/Pd of the subsequently crystallizing overlying cumulates. Cu/Pd ratios may also be applied in sill-like bodies such as the Uitkomst intrusion, Mpumalanga, to estimate the potential for conduit-type deposits, and in lavas where they may help to locate possible Noril'sk-type mineralized feeder zones to basalt flows. Other methods of determining whether igneous bodies have experienced magma mixing and sulphide segregation are based on Ni contents of olivines, Ti contents, and Cr/Fe ratios of spinels, and petrographic features such as the presence of plagioclase inclusions within ferromagnesian phases. Se/S ratios may help to determine whether magmatic sulphide ores underwent post-magmatic (metamorphic or hydrothermal) sulphur loss. They may also discriminate between a magmatic or sedimentary source of the S, and between a magmatic or hydrothermal origin of the metals. Hydrothermal sulphide ores may further be distinguished from magmatic ores by means of significantly higher Cu/Ni and Pd/Ir ratios of the former. Such distinction is important because it would be futile to investigate hydrothermal deposits for magmatic ore zonation.

Die meeste belangrike magmatiese Cu–Ni–PGE-sulfiedafsettings is moontlik deur segregasie van 'n onmengbare sulfiedsmeltsel uit 'n silikaatgasheermagma, in reaksie op prosesse soos magmavermenging, vinnige afkoeling, differensiasie, en kontaminasie, gevorm. Die metaalinhoud van die sulfiede word deur die konsentrasie van die metale in die silikaatgasheermagma, deur die partisiekoëffisiënte van die silikaat-/sulfiedsmeltse (D-waardes) van die metale en die R-faktor gedurende sulfiedsegregasie beheer. Fraksionering tussen die metale vind tydens gedeeltelike smelting van die bokorsbron, kristallisasie van oksiede, platinumgroepminerale (PGM), en silikate (hoofsaaklik olivien en tot 'n mindere mate ortopirokseen), segregasie van sulfiedsmeltsel, en kristallisasie van die sulfiedsmeltsel plaas. Laasgenoemde proses kan gesoneerde ertsliggame oplewer wat bestaan uit 'n vaste oplossing van Os, Ir, Ru, Rh, Fe, en (Ni)-ryke monosulfiede kumulaaterts, en gefraksioneerde sulfiederts wat ryk is aan Cu, Pt, en Pd. Dit is moontlik om hierdie prosesse te modelleer en om die potensiaal van 'n magmatiese liggaam om ekonomiese Cu–Ni–PGE- sulfiedafsettings te huisves, te bepaal. Die opsporing van Cu–Ni–PGE-sulfiedertse kan vergemaklik word deur die toepassing van 'n aantal geochemiese instrumente. Dit is veral moeilik om die ligging van PGE-ryke horisonne binne gelaagde intrusies te bepaal omdat die ertssones gewoonlik dun is in vergelyking met die dikte van die intrusies. Variasie in Cu/Pd-verhoudings van die silikaatgesteentes kan die posisie van sommige van hierdie horisonne afbaken, aangesien die Pd wat sterk chalkofiel is, by voorkeur tydens segregasie uitgeput word, wat 'n toename in Cu/Pd van die oorliggende kumulate wat daarna gekristalliseer het veroorsaak. Cu/Pd-verhoudings kan ook toegepas word in die plaattipe liggame soos die Uitkomst-intrusie, Mpumalanga, om die potensiaal vir toevoerkanaaltipe afsettings te bepaal, en in lawas waar hulle kan help om moontlike Noril'sk-tipe gemineraliseerde voersones na basaltiese vloeie te lokaliseer. Ander metodes om te bepaal of intrusiewe liggame aan magmavermenging en sulfiedsegregasie onderworpe was, is gebaseer op Ni-inhoude van oliviene, Ti-inhoude en Cr/Fe-verhoudings van spinel, en petrografiese kenmerke soos die teenwoordigheid van plagioklaas insluitsels binne ferromagnesiese fases. Se/S-verhoudings kan help om te bepaal of magmatiese sulfiedertse namagmatiese (metamorfe of hidrotermale) S-verlies ondergaan het. Hulle kan ook onderskei tussen 'n magmatiese of sedimentêre bron van die S, en tussen 'n magmatiese of hidrotermale oorsprong van die metale. Hidrotermale sulfiedertse kan verder van magmatiese ertse onderskei word deur middel van aansienlike hoër Cu/Ni- en Pd/Ir-verhoudings van eersgenoemde. Sodanige onderskeiding is belangrik omdat dit futiel sou wees om hidrotermale afsettings vir magmatiese ertssonering te ondersoek.

Introduction

The success of any exploration program for magmatic Cu–Ni–PGE sulphide deposits strongly depends on a good understanding of the origin of such ores. Unfortunately, many aspects of ore formation are still poorly understood. For example, the sulphide melt–silicate melt partition coefficients of the PGE in natural magmas remain ill constrained, partly because the sulphur content of the system strongly influences metal partitioning into sulphide melt (Barnes et al., 1997). Similarly, the role of PGM or PGE metal clusters in concentrating PGE, particularly within sulphur-poor chromitites, remains the subject of vigorous debate (Tredoux et al., 1995). Here, the present models for the origin of magmatic Cu–Ni–PGE sulphide deposits are reviewed, some of the factors that govern the size and grade of the deposits are summarized, a number of geochemical methods to identify exploration targets are discussed, and, finally, the possible application of these methods to a number of South African examples, including layered intrusions (Bushveld, Insizwa), conduit- and dyke-hosted deposits (Uitkomst), deposits associated with lavas (Karoo flood basalts, komatiites), and the Okiep deposits, is considered.

Role of magmatic sulphur

Sulphur is a minor component of the earth's upper mantle (250 ppm, Lorand, 1990). It can be assumed that at the temperatures achieved during partial melting of the upper mantle (> 1100 °C), all sulphides present in the affected portion of the mantle would melt. Thus, sulphur concentrations in magmas derived from the mantle would be expected to range from 2.5% (potassic and ultrapotassic magmas, 1% melting) to 0.05% (komatiites, 50% melting). However, most basalts and komatiites actually contain values in the range 0.01 to 0.2% sulphur. The reason for this is that silicate magmas can only dissolve a limited amount of sulphur. The experimentally determined solubility of sulphur in basaltic magmas lies between 0.05 and 0.26 wt.% (Wendlandt, 1982), with the surplus sulphur segregating out as an immiscible sulphide melt upon melting of the mantle, and possibly remaining in the source.

Central to the formation of economic sulphide deposits is the principle that the solubility of sulphur in basic and ultrabasic magmas decreases with falling temperature (0.04 wt.% sulphur per 100 °C, Wendlandt, 1982) and FeO content of the silicate magma (Haughton et al., 1974). As a result, the S-solubility curve is non-linear (Figure 1). A relatively rapid decrease in sulphur solubility, due to falling temperature *and* FeO content, is observed during olivine and orthopyroxene fractionation, but little variation is seen once plagioclase has appeared on the liquidus. Because plagioclase incorporates little Fe in its structure, the FeO content of the residual magma increases, an effect that tends to balance the decrease in sulphur solubility caused by the continuing decrease in temperature (Czamanske & Moore, 1977; Naldrett & Von Gruenewaldt, 1989).

Why is the non-linear nature of the S-solubility curve of such crucial importance for the formation of economic sulphide deposits? Consider the crystallization of basaltic magma containing approximately 0.1% sulphur (i.e. 0.3% sulphide of composition FeS): as sulphur is not incorporated
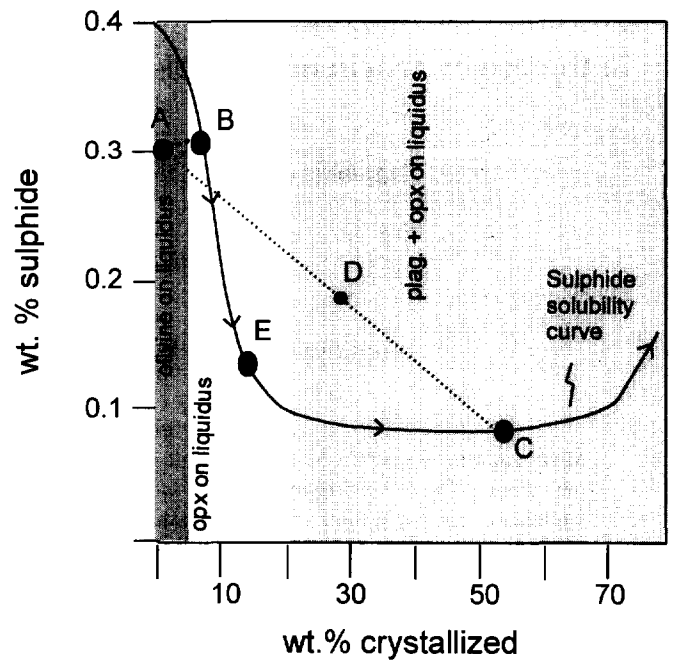

Figure 1 Variation in solubility of Fe-sulphide in differentiating basaltic magma (Figure modified after Naldrett & Von Gruenewaldt, 1989).

into the major rock-forming minerals, its concentration increases initially during crystallization. At some stage determined by the starting composition, sulphur saturation may be reached and a sulphur-rich melt will exsolve from the silicate magma (point B, Figure 1). Due to the strongly chalcophile nature of Fe and the relatively high Fe content of basaltic magmas, this melt will essentially be of FeS composition (Kullerud et al., 1969). As the sulphide melt is relatively dense it may segregate from low-viscosity basaltic magma to accumulate at the base of the magma body, where it will crystallize a sequence of sulphide minerals comprising essentially pyrrhotite, chalcopyrite, pentlandite, and pyrite (Kullerud et al., 1969).

With continued crystallization (path B–C, Figure 1), minor segregation of sulphide melt will continue, causing relatively small amounts of sulphide to be dispersed throughout the crystallizing rock. For large amounts of sulphide melt to segregate it appears to be essential that the silicate magma penetrates the field of sulphur supersaturation more thoroughly. Several mechanisms have been proposed to this effect:

(i) magma mixing (Irvine et al., 1983; Campbell et al., 1983). Mixing of relatively primitive, hot, and FeO-rich magma (point A, Figure 1) with differentiated, cooler, and FeO-poor magma (point C, Figure 1) may produce hybrids that fall into the field of S-supersaturation (point D, Figure 1). This model could explain the lack of sulphide-enriched horizons in the Lower and Lower Critical Zones of the Bushveld Complex. There the resident magma may have been relatively undifferentiated (perhaps point E, Figure 1), and mixing of replenishing magma with resident magma would have led to little or no S-supersaturation. Further up in the sequence, within the Upper Critical Zone, the resident magma was probably more differentiated (point C, Figure 1), and magma mixing would have caused extensive sulphide segregation;

(ii) a relatively rapid drop in temperature, that is, supercooling of the magma. This mechanism could be particularly significant at the margins of intrusions, where cooling occurs by heat conduction to the country rocks. Increased sulphide contents are, for example, observed at the contact of the Bushveld Complex with its floor rocks (Liebenberg, 1970), at the bottom of lava flows (komatiites: Lesher, 1989; MORB: Mathez, 1976), and at the margins of dykes intruding the Karoo sediments. A rapid decrease in temperature has also been proposed to yield the sulphide-enriched zones of the Great Dyke of Zimbabwe (Prendergast & Keays, 1988).

(iii) relatively rapid differentiation of mildly sulphur undersaturated or saturated silicate magma. During the formation of massive chromite or magnetite layers, the FeO content of the magma falls sharply. The ensuing decrease in sulphur solubility may lead to S-supersaturation and sulphide segregation (Haughton et al., 1974). This may explain the elevated sulphide contents of some Bushveld chromitites, particularly the UG2 (Gain, 1985).

(iv) magma contamination. Changes in the concentration of SiO_2, Al_2O_3, MgO, CaO, as well as the oxygen fugacity have a distinct effect on sulphur solubility (Naldrett, 1989). For example, assimilation of felsic, siliceous country rock material may lower the sulphur solubility of basaltic magma, thereby causing sulphide segregation (Irvine, 1975). Assimilation of S-bearing country rock (Lesher & Campbell, 1993) or transfer of sulphur from country rocks into the magma by volatiles (Ripley & Alawi, 1988) may significantly raise the sulphur content of basaltic magma and thereby lead to enhanced sulphur supersaturation. The former mechanism appears to be more relevant in the case of larger intrusions (Bushveld, Duluth), while the latter may be envisaged for smaller bodies that cool relatively fast (Uitkomst, Okiep).

Partition coefficients

Apart from Fe, there are a number of other metals, including Ni, Cu, and the PGE, that are strongly chalcophilic. In multi-phase systems such as crystal-bearing magmas, the affinity of an element for any phase can be expressed in terms of its partition coefficient (D) into this phase. For example, the D value of an element between sulphide melt and silicate melt (with the two phases being in equilibrium) is defined as (Naldrett, 1989):

$$D_{sul/sil} = \frac{\text{concentration of element in sulphide melt}}{\text{concentration of element in silicate melt}} \quad (1)$$

D values may be determined by experiment, in which crystallizing magmas are chilled and the composition of sulphide and silicate glass are analysed by microprobe or other microanalytical equipment. For the PGE, the results obtained vary between 2000 and 200 000, depending on analytical conditions (see Fleet et al., 1996, for a summary of recent experimental data), indicating that the PGE are extremely chalcophilic. $D_{sul/sil}$ values of Cu and Ni are 200 – 1400 and 200 – 500, respectively, for basaltic magma (Francis, 1994). Alternatively, determination of the D value may be based on empirical observations. In many natural examples of sulphide ores, it appears that the PGE are, on average, approximately 100 000 times more concentrated in the sulphides than in the coexisting silicates (Peach & Mathez, 1996). If this ratio rep-

resents equilibrium between sulphide melt and silicate melt, the D of the PGE between sulphide melt and silicate melt appears to be approximately 100 000.

Equation (1) is useful in making rough predictions about metal concentrations of sulphides that crystallized from magmas of known composition. 'Standard' basaltic magmas contain approximately 100 ppm Cu and Ni (Karoo, Deccan, Parana, Snake River flood basalts, Thompson et al., 1983; Marsh et al., 1997). Magmatic sulphide ores crystallizing from such magmas therefore contain around 2 – >10 wt.% Cu and 3 – 4 wt.% Ni.

Parental magmas to the Bushveld Complex are significantly more Ni-rich (330 ppm Ni, 60 ppm Cu, B1 magma of Harmer & Sharpe, 1985). Thus, Bushveld sulphides have Ni/Cu ratios of around 2 (Naldrett et al., 1986). The massive sulphides at the base of the Uitkomst Complex (Figure 2) contain 2% Ni, 1% Cu, and 6 ppm Rh + Pt + Pd (Anonymous, 1997), and thus also have Ni/Cu ratios of 2, supporting the assertion that the Complex is of Bushveld lineage (Gauert et al., 1995). Interestingly, the intrusion is trough-shaped (1 km wide, 12+ km long, and 800 m thick) and thus has been interpreted to be a conduit to an unexposed or eroded larger layered intrusion (Gauert et al., 1995). This possibility will be explored in a later section.

Komatiitic magmas have significantly more Ni than basalts (c. 1000 ppm), but $D_{sul/sil}$ values for Ni in these magmas are lower, at about 100 (Naldrett, 1989). As a result, sulphide ores associated with komatiite flows have up to around 10% Ni (Keays et al., 1982). Hence, if Ni grades of more than 3 – 4% are required to make a deposit economically feasible, exploration has to concentrate on komatiites.

It may also be of use to estimate the metal content of the silicate magma from which a known sulphide body is derived. To do this by means of equation (1), one has to have a rough idea of the bulk composition of the sulphides, which in many cases may be unobtainable. If possible, such modelling may yield information about the geotectonic setting of the magmatism and thereby provide further exploration guidelines. For example, many island arc and back-arc tholeiitic basalts are
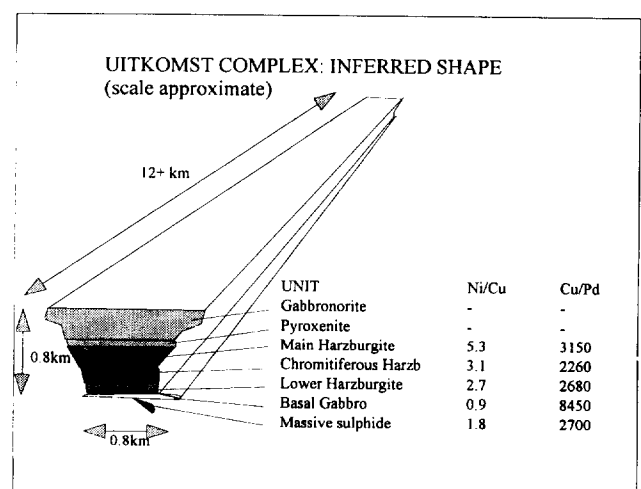

Figure 2 Schematic shape of the Uitkomst intrusion (Ni/Cu and Cu/Pd ratios of individual units are compiled from the data of Anonymous, 1997).

distinctly depleted in Ni, as compared to MORB or continental flood basalts (Wilson, 1989), possibly a result of olivine fractionation during ascent (Wilson, 1989).

It must be kept in mind that the above modelling is simplistic. For example, in the Bushveld Complex, there is significant variation in absolute and relative metal concentrations between closely associated ore bodies such as the UG2 chromitite and the Merensky Reef (Naldrett et al., 1986), and even within individual ore bodies (UG2; Peach & Mathez, 1996). Metal contents of sulphides are not only governed by the D values but also by a number of other factors, some of which are still incompletely understood. For example, the ratio of silicate melt to sulphide melt during sulphide segregation (R-factor, to be discussed below) strongly influences the metal enrichment of the sulphide melt (Campbell & Naldrett, 1979). Furthermore, other phases such as PGM (Merkle, 1992), spinel (Oshin & Crocket, 1982), olivine (Lee & Tredoux, 1986), and perhaps even metal clusters (Ballhaus et al., 1994; Tredoux et al., 1995) also appear to concentrate the PGE. Finally, post-depositional redistribution of the PGE by means of migrating late-stage melt (Mathez, 1995) or magmatic fluids (Boudreau & McCallum, 1992) may play an as yet unquantified role. Our incomplete understanding of metal concentration in magmatic environments is exemplified by the UG1 and UG2 chromitites. As Eales et al. (1993a) pointed out, both layers are of similar thickness, are hosted by similar lithologies, have similar compositions, and are vertically separated by as little as 20 m of silicate rocks. Yet, the UG1 contains minor PGE only, whereas the UG2 is the largest PGE deposit on Earth.

R-factor

Differing PGE contents may in part be explained by variable R-factors during sulphide segregation (Campbell & Naldrett, 1979). A high R-factor signifies that relatively few sulphide droplets are segregating through the silicate magma (Figure 3). In contrast, a low R-factor means that many sulphide droplets segregate through the silicate magma. In the latter case, the sulphide melt will more effectively deplete the limited amount of metals in the magma, but at the same time will be relatively less metal-enriched than sulphide melt that segregated under high R-factor conditions. The apparent D value has in effect become smaller, which illustrates that equation (1) should not be used in isolation. R-factors during sulphide segregation are generally estimated in the following way:
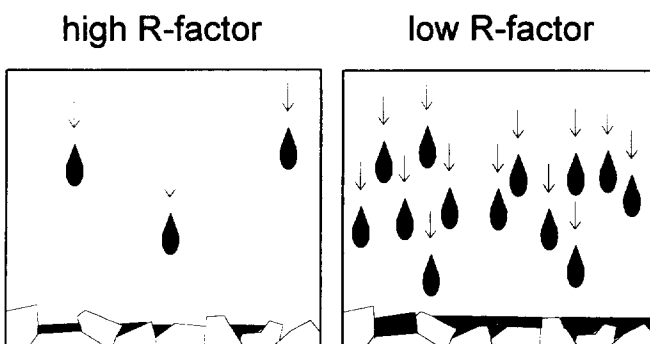

Figure 3 Schematic diagram showing sulphides segregating at high and low R-factor conditions.
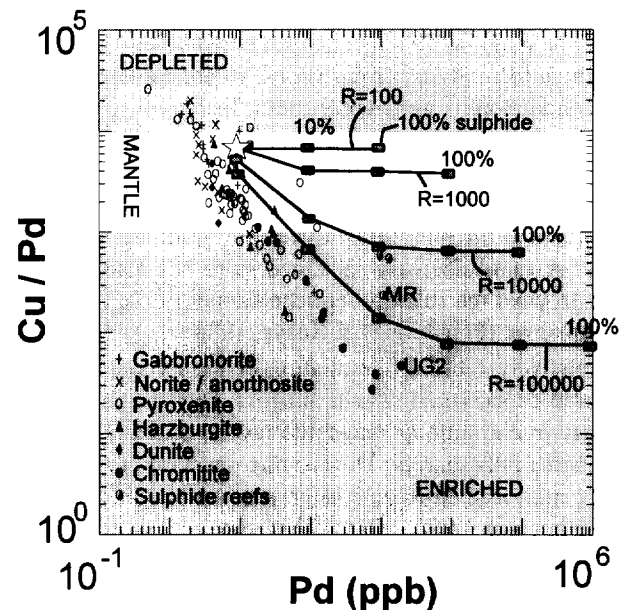

Figure 4 Plot of Cu/Pd versus Pd showing compositional variation of rocks in the Bushveld Complex. Tie-lines are mixing lines between sulphide and silicate melt at various R factors. Star symbol represents model parental silicate melt (from Davies & Tredoux, 1985, and Harmer & Sharpe, 1985). MR = Merensky Reef (Figure from Maier et al., 1996b).

$$C_C = \frac{C_L \times D \times (R + 1)}{(R + D)} \qquad (2)$$

where C_c and C_L are the concentrations of the metal in the sulphide and initial silicate melts, respectively, and $D = D_{sul/sil}$. This may be rearranged to:

$$R = \frac{C_L D - C_C D}{C_C - C_L D} \qquad (3)$$

A graphical method to determine R-factors by means of Cu, Pd, and sulphide contents of rocks has been developed by Barnes et al. (1993) and was applied to Bushveld cumulates by Maier et al., (1996b) (Figure 4).

Importantly, the Ni and Cu content of the sulphides does not depend as much on the amount of sulphides segregating as does the PGE content, because the D value of Cu and Ni with respect to sulphide melt is smaller than that of the PGE. One may say that relatively small amounts of segregating sulphides (high R-factor) do not significantly deplete the silicate melt in the relatively moderately chalcophilic Cu and Ni, but small amounts of sulphide melt do strongly deplete the magma in the extremely chalcophilic PGE. Only a relatively large amount of sulphides (low R-factor) will create a notable depletion of the magma in Cu and Ni as well (Figure 5), but this in turn will result in relatively low bulk-PGE contents of the sulphides (Figure 6). The implication is that PGE are likely to be no more than a by-product in large sulphide deposits.

Figure 7 schematically illustrates how different R-factors during sulphide segregation may result in variable metal concentrations in closely associated sulphide-bearing rocks, as defined by contrasting mixing lines for PGE-rich and PGE-poor sulphides. The result may be scatter in binary sul-
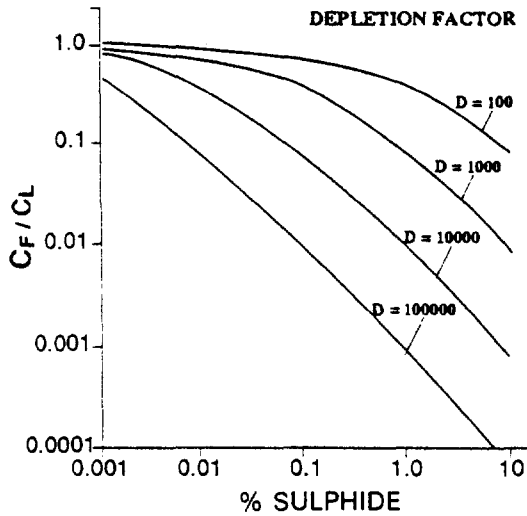
Figure 5 Element depletion (C_F/C_L) in magmas experiencing sulphide removal, as a function of $D_{sul/sil}$. C_F = concentration of element in fractionated magma. C_I = concentration of element in initial magma (after Barnes et al., 1993).

Figure 7 Schematic diagram showing PGE/S ratios of sulphide formed at variable R-factors.

phur/metal variation plots such as observed in S-bearing silicate rocks of the Bushveld Complex (Figure 8). In layered intrusions, variation in R-factors may be a common phenomenon. If the density of the compositionally stratified resident magma (Irvine et al., 1983) changes with differentiation, replenishing magma may intrude at variable levels of neutral buoyancy in the chamber (Campbell et al., 1983). Sulphide melt may then segregate through a magma column of variable thickness.

It has been recognized for some time (Stanton, 1972; Naldrett et al., 1996a) that sulphides deposited within magma conduits may equilibrate with large quantities of streaming magma. The composition of such sulphides can be modelled by means of a zone-refining equation.

It is clear that application of relevant R-factors and D values is esential for meaningful modelling. Significantly, equation (2) may be simplified when D is very much greater than
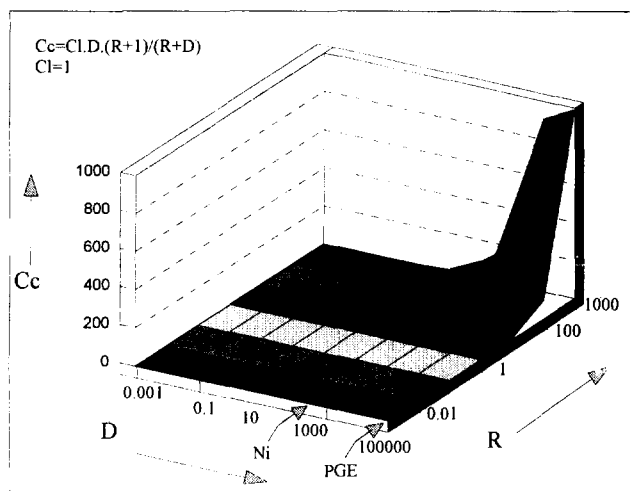
R (Campbell & Barnes, 1984), such as usually in the case of the PGE:

$$C_C = C_L \times (R + 1) \tag{4}$$

Thus, knowing D and either C_L or C_C, and applying equation (1) to obtain the unknown parameter, an estimate of R may be obtained. By means of such modeling, it has been possible to establish the flow direction of the streaming magma (Naldrett et al., 1996a), as the latter will become progressively depleted in PGE with distance from the feeder. Application of this

Figure 6 Element enrichment in segregating sulphide melt (C_C) as a function of R and $D_{sul/sil}$.

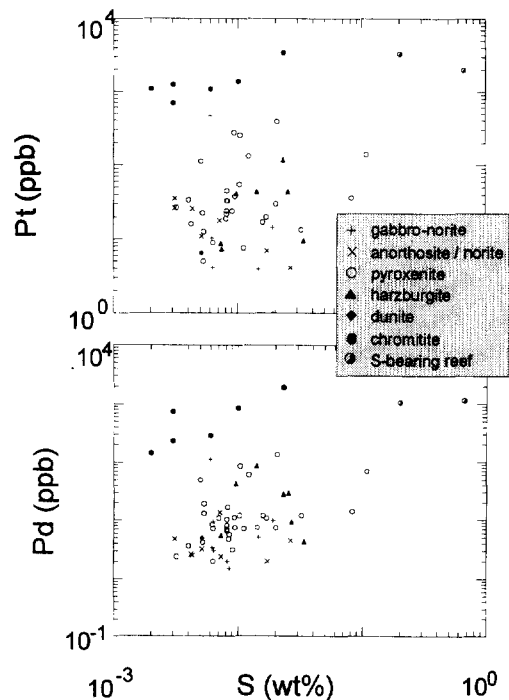Figure 8 Binary variation diagrams, of Pt and Pd versus sulphur in rocks from the Lower, Critical, and Main Zones of the Bushveld Complex (data from Maier & Barnes, 1998).
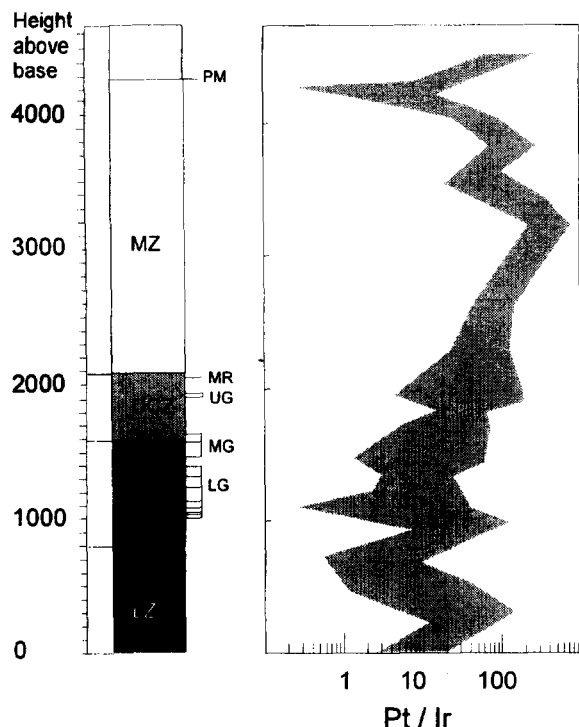
Figure 9 Pt/Ir ratio in the Lower, Critical, and Main Zone of the Western Bushveld Complex at Union Section (data from Maier & Barnes, 1998).

modelling may also be of merit in dyke-like bodies (i.e. the Uitkomst Intrusion, Mpumalanga).

Notably, equation (2) may equally be simplified if R is very much greater than D, to essentially yield a version of equation (1):

$$C_C = C_L \times D \qquad (5)$$

This stresses the point that the concentration of metals with moderately high to low D values into sulphide melt is relatively less affected by variation in R factors.

Fractionation of Ni, Cu, and the PGE

Fractionation is another important process to yield variation in relative metal abundances in sulphide ores. Fractionation of the metals considered here may be caused by a number of contrasting processes. Initial fractionation may occur during partial melting of the upper mantle. Retention of a sulphide melt in the source will concentrate the PGE over Cu and Ni. S-undersaturated second-stage melts that are able to dissolve the surplus sulphides could therefore be significantly enriched in PGE and less so in Cu and Ni (Hamlyn & Keays, 1986).

Following partial melting of the upper mantle, further fractionation of the metals occurs during cooling of the magma, by means of the incorporation of Ni (and perhaps Ir, Lee & Tredoux, 1986) into olivine, Os, Ir, Ru, and Ni into chromite (Oshin & Crockett, 1982) and high-temperature PGM, such as laurite (Merkle, 1992), and Ru and Rh into magnetite (Capobianco & Drake, 1990). It is not clear yet whether the PGE enter the spinel structure as a solid solution or as discrete PGM or alloys (Keays & Campbell, 1981). This fractionation of the IPGE (Os, Ir, Ru) and Rh from Pt and Pd

during silicate, oxide, and PGM crystallization is expressed, for example, by increasing Pt/Ir ratios with height in the Bushveld Complex (Figure 9).

Sulphide melt segregation is believed to cause little fractionation amongst the PGE, based on the presently available experimental data. Due to similar $D_{sul/sil}$, all PGE will be equally depleted in the silicate melt. However, there will be strong fractionation of the PGE from Cu and Ni, due to the much larger partition coefficients of the PGE. Thus, Ni and Cu will be much less depleted in the silicate melt from which the sulphide melt has been extracted.

Finally, fractionation of Cu, Ni, and the PGE occurs during crystallization of the sulphide melt. Sulphide melt, like silicate magma, crystallizes over a temperature interval. The first phase to crystallize is monosulphide solid solution (mss), which is essentially FeS that recrystallizes to pyrrhotite at a lower temperature (Kullerud et al., 1969). Mss incorporates little Cu into its structure ($D_{mss/sulf}$ of Cu is between 0.05 and 0.2, based on experimental and empirical data of Barnes et al., 1997 and Naldrett et al., 1997) and, as a consequence, the Cu content of the fractionating sulphide melt will increase upon cooling. At c. 90% crystallization (assuming average natural sulphide compositions, Naldrett, 1969), the Cu content of the sulphide melt reaches 30%, resulting in the crystallization of intermediate solid solution (iss), later to be recrystallized to chalcopyrite (Kullerud et al., 1969). Ni is equally rejected by mss in komatiite-related ores ($D_{mss/sulf}$ around 0.6, Barnes et al., 1997), but appears to be mildly compatible with respect to mss in most tholeiitic intrusions (Barnes et al., 1997). In part, this may be a temperature effect, that is, Ni partitioning into mss increases with falling temperature (Barnes et al., 1997).

Alternatively, the relatively Ni-poor nature of mss in komatiitic ores may be explained if lava flows lose sulphur to the atmosphere as Ni becomes incompatible into mss at low sulphur contents of the sulphide melt (Barnes et al., 1997). At the same time, the fractionating sulphide melt will become enriched in Ni, resulting in the crystallization of pentlandite at lower temperatures (Naldrett et al., 1997). Further pentlandite and pyrite will exsolve from the cooling pyrrhotite at around 250 °C (Craig, 1973), yielding the assemblage po + pent + cp + py common to natural magmatic sulphide ores. The PGE show contrasting behaviour, with Pt and Pd ($D_{mss/sulf}$ 0.01 – 0.5) being incompatible into mss, and Os ($D_{mss/sulf}$ 4.3), Ir ($D_{mss/sulf}$ 0.3 – 10), Ru ($D_{mss/sulf}$ 4.2), and Rh ($D_{mss/sulf}$ 0.2 – 8) being compatible (Fleet et al., 1993; Barnes et al., 1997).

If sulphide melt and mss are physically separated, for example by sinking of mss, or entrapment of fractionated sulphide melt by streaming magma in conduits, the resulting ore bodies may be zoned into an Os–Ru–Ir–Rh-rich portion representing cumulate mss and a Cu–Pt–Pd-rich portion representing later, more fractionated sulphide melt. Ni zonation tends to be minor, due to the average $D_{mss/sulf}$ of Ni approaching unity.

Metal ratio diagrams

An understanding of the Cu, Ni, and PGE zonation of ore bodies such as Sudbury and Noril'sk (Naldrett et al., 1997) is
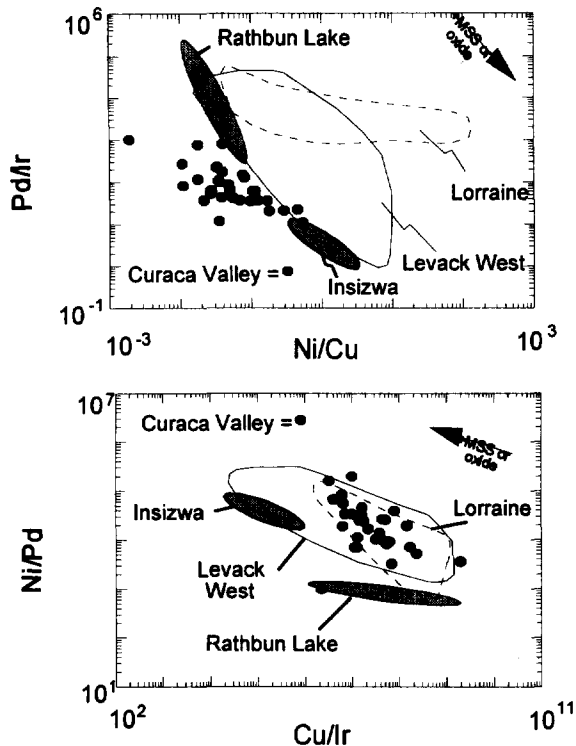
Figure 10 Metal ratio diagrams of Pd/Ir versus Ni/Cu and Ni/Pd versus Cu/Ir for Cu-sulphide ores from the Curaca Valley, Brazil (Maier, unpubl. data), and compositional fields of ores from Insizwa (data from Lightfoot *et al.*, 1984), Levack West (Sudbury Complex, data from Hoffman *et al.*, 1979), Lorraine Mine (Abitibi subprovince, data from Barnes *et al.*, 1993), and Rathbun Lake (Ontario, data from Rowell & Edgar, 1986) .

of considerable significance in exploration. It has been shown by Barnes *et al.* (1988) that metal ratio plots of Pd/Ir versus Ni/Cu and Ni/Pd versus Cu/Ir (Figure 10) are useful tools in determining whether sulphide ores may have undergone mss fractionation. The latter will result in increasing Pd/Ir and Cu/Ir ratios and decreasing Ni/Cu and Ni/Pd ratios of the fractionating sulphide melt, thus defining mixing lines in such plots. Such mixing lines are observed in a number of ore deposits (Figure 10), amongst them the Insizwa Complex, the Canadian Sudbury Complex, the Curaca Valley Cu-sulphide bodies of Brazil, and Lorraine mine in the Abitibi subprovince, Canada. Some of these deposits (Sudbury, Insizwa) have distinct Os–Ir–Ru–Rh–(Ni)- and Cu–Pt–Pd–(Au)-enriched portions (Naldrett *et al.*, 1982; Lightfoot *et al.*, 1984), but others, such as the Cu-rich ores of the Curaca Valley and the genetically apparently related Okiep district (for which PGE data are not yet available), are relatively homogeneous (Maier & Barnes, 1996). Thus, the trends in the metal ratio diagrams defined by the Curaca Valley ores may be a result of other processes. For example, olivine and chromite fractionation, as well as hydrothermal mechanisms of mineralization may equally produce linear trends of one kind or another as shown by the Rathbun Lake occurrence, Canada (Figure 10) (Rowell & Edgar, 1986). Clearly, metal ratio plots have to be applied in combination with other tools that may discriminate magmatic and hydrothermal deposits by means of lithological and compositional data.

Spider plots

To compare sulphide ores that underwent different degrees of fractionation, noble metal concentrations are generally compared (normalized) to either chondrite (Naldrett *et al.*, 1979) or model mantle (Barnes *et al.*, 1988). These are plotted in order of increasing melting temperature (Figure 11). In such diagrams, colloquially referred to as 'spider' plots (Wood *et al.*, 1979), the mantle and primary partial mantle melts have an essentially flat pattern. Sulphide segregation will deplete all PGE evenly resulting in little fractionation, but crystallizing olivine, oxide, some high-temperature PGM, and mss preferentially incorporate Os–Ir–Ru–Rh. In theory, this may result in negative slopes in olivine–oxide cumulates, and in positive slopes in more fractionated rocks. Spider plots from the Bushveld Complex (Figure 11) are increasingly fractionated with height, reflecting the continuing extraction of Os–Ir–Ru–Rh from the magma. However, even the lowermost ultramafic silicate cumulates and chromitite layers do not have negative slopes, indicating the presence of Pt–Pd-enriched phases (BMS, PGM, alloys). In contrast, spider
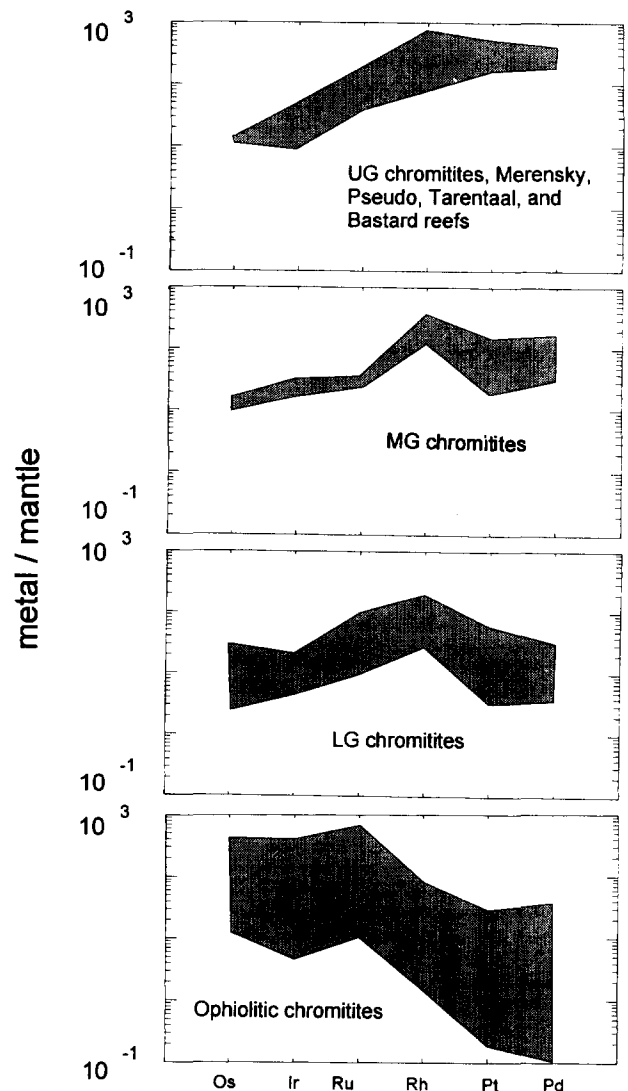

Figure 11 Mantle normalized PGE 'spider' diagrams for rocks from the Bushveld Complex and ophiolitic chromitites (data from Scoon & Teigler, 1994; Barnes *et al.*, 1985; Maier & Barnes, 1998).

plots of chromitites from ophiolites generally do have negative slopes, that is, Os–Ir–Ru are strongly enriched over the mantle. Hence, chromitites in ophiolites and layered intrusions may be of fundamentally different origins. Many of the former could be restites from mantle melting (Tredoux *et al.*, 1995) enriched in Os, Ir, and Ru due to the highly refractory nature of the host mineral chromite. In contrast, the latter are magmatic precipitates containing appreciable amounts of Pt- and Pd-bearing BMS, PGM, and alloys.

Cu/Pd ratios: a potentially useful exploration tool

To determine whether an igneous body has experienced sulphide segregation or not is of considerable use for an exploration programme. Barnes *et al.* (1993) showed that Cu/Pd ratios of silicate rocks in the Munni Munni Complex of Australia show a distinct increase in the vicinity of the PGE-rich horizon (Figure 12). This was interpreted as a result of sulphide segregation. The Cu/Pd ratio is much lower in the segregating sulphide melt than in the host silicate magma, because $D_{sul/sil}$ of Pd far exceeds that of Cu. In contrast, the residual silicate melt will have elevated Cu/Pd ratios, and rocks that crystallize from such a residual silicate magma equally have high Cu/Pd ratios. In fact, as primary mantle magmas have Cu/Pd ratios of approximately 6500 (Barnes *et al.*, 1988), rocks with Cu/Pd ratios below that value should contain Pd-rich sulphides, while rocks with Cu/Pd ratios above 6500 may have crystallized from magma that has lost Pd as a result of a sulphide segregation process.

This method may be of considerable importance for PGE exploration in layered intrusions (Bushveld, Molopo Farms, Great Dyke), particularly since it may be relatively easily applied. Many exploration programs routinely analyse for Cu, Pt, and Pd. To test the merit of the method, Maier *et al.* (1996b) conducted a detailed study on the Bushveld Complex. They observed a similar pattern as in the Munni Munni Complex, with the main shift in Cu/Pd (and Cu/Pt) occurring in the vicinity of the economically important UG2 chromitite and Merensky Reef (Figure 13). The Lower and Critical Zones have ratios below 5000 (confirming the presence of minor sulphides), while the Main Zone values plot mostly around 10000 (suggesting sulphide extraction).
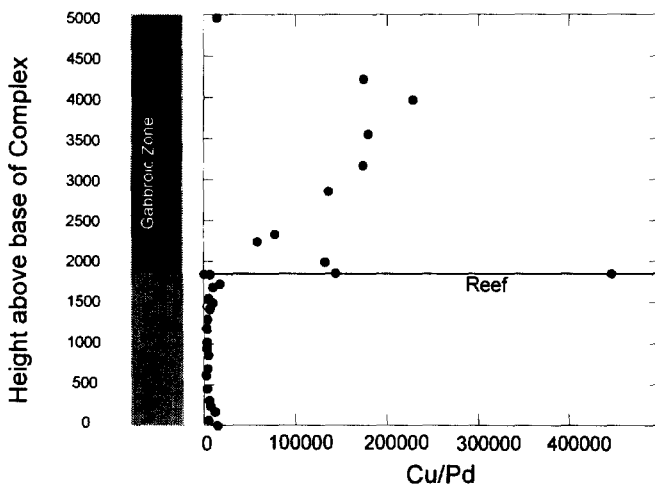

Figure 12 Variation in Cu/Pd ratio with height in the Munni Munni intrusion, Western Australia (data from Hoatson & Keays, 1989).
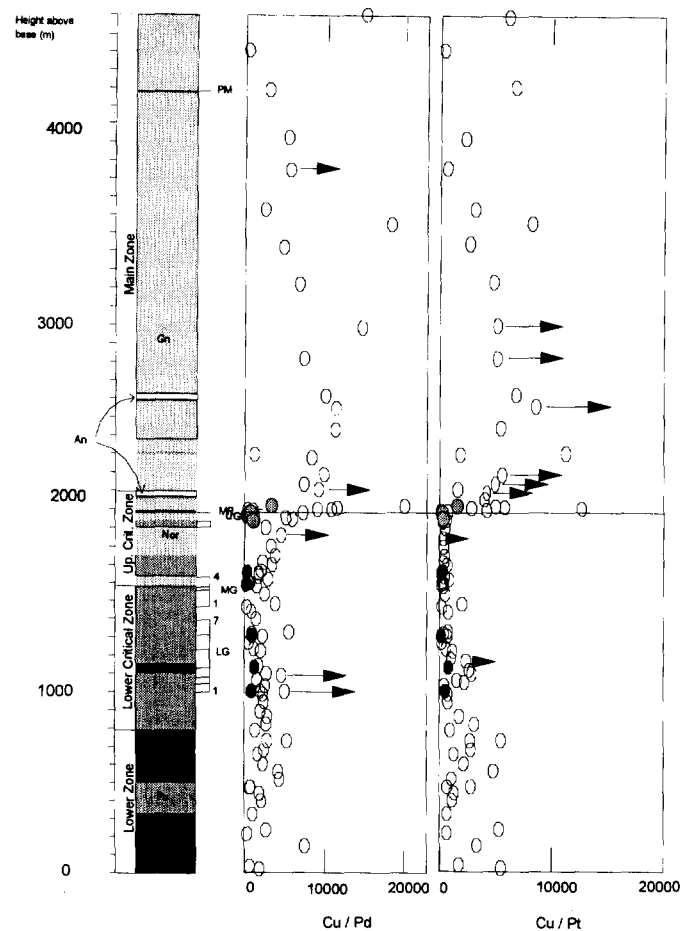

Figure 13 Cu/Pd ratios through the Lower, Critical, and Main Zones of the Western Bushveld Complex at Union Section (Figure from Maier *et al.*, 1996b; open circles = silicate rocks; shaded circles = sulphide-bearing reefs; solid circles = chromitites).

Cu/Pd ratios also highlight the conduit-type nature of the Uitkomst Complex (Figure 2). The massive sulphides have low Cu/Pd ratios, while the overlying gabbro-hosted disseminated sulphides have Cu/Pd ratios above mantle values, reflecting the depletion of the magma in response to the sulphide segregation. However, the Cu/Pd ratio of the gabbro is only marginally above the mantle (compare with Bushveld and Munni Munni), which may be explained by a model having replenishing magma continously streaming through the conduit. The harzburgites in the central portion of the intrusion have low Cu/Pd ratios indicating that they crystallized from undepleted magma. By implication, they are not directly related to the gabbros but crystallized from magma streaming through the conduit. Furthermore, it appears that the individual harzburgite units represent separate intrusions with sulphides which show no sign of Pd depletion in response to the sulphide segregation events of the underlying units. This highlights the difficult task of locating sulphide ores in conduits by means of geochemical tools. In the case of the Uitkomst Complex, the lack of Pd depletion may indicate the potential for further sulphide bodies associated with the conduit.

The Uitkomst Complex is not the only mafic–ultramafic intrusion in the floor of the Eastern Bushveld Complex. Peri-

dotite sills of up to 300 m in thickness have been intersected by boreholes drilled near Machadadorp, some 40 km to the east of the southeastern lobe of the Complex. The sills contain up to 5% sulphides (po, cp) and 0.5 ppm Pt + Pd. The Pt/Pd ratio of the ore is <1, that is in the range of the Uitkomst ores, but significantly lower than the Bushveld ores. Based on these preliminary data and the fact that the bodies lie on the same set of lineaments as the Uitkomst Complex, it appears possible that the Machadadorp and Uitkomst intrusions are comagmatic. Interestingly, average Cu/Pd ratios in the former are relatively high for a sulphide-bearing rock at around 10 000, suggesting that the parental magma had previously experienced sulphide segregation (at Uitkomst?) and was thus depleted in PGE.

It would be interesting to determine, in this context, whether Cu/Pd ratios show lateral variation in mineralized intrusions. Should the answer be positive, the method may be useful to locate the magmatic feeder zones. Based on the limited published data, it appears that Cu/Pd ratios of the UG2 increase with distance from a putative feeder at Union Section in the western Bushveld Complex (Maier & Bowen, 1996). Recent work on the Duluth Complex (Theriault, unpubl. data) shows a similar pattern.

Sulphides in lavas

In general, modern basaltic lavas have less potential for economic sulphide deposits than intrusions. This is mainly a result of the high cooling rate of lavas which leads to (i) a rapid increase in viscosity preventing accumulation of sulphide melt, and (ii) suppressed differentiation preventing mixing of magmas of contrasting compositions. Furthermore, sulphur may be lost to the atmosphere by means of devolatization.

In sharp contrast, many ultramafic lavas from the Archaean (komatiites within greenstone belts) commonly host massive Ni-sulphide deposits. This is presumably because they were hotter (extrusion temperature of c. 1650 °C, Green et $al.$, 1975). As a result they are less viscous, allowing for accumulation of potential sulphide melt, and they have an enhanced capacity to assimilate sulphur-bearing country rocks (Lesher & Campbell, 1993). The komatiites of the Barberton Mountainland form an exception in that they do not host significant Ni-sulphide ores. They are somewhat older than komatiites from Western Australia and eastern Canada, but it is unclear if the absence of Ni deposits is related to this factor (see Arndt et $al.$, 1997, for a discussion). A review of komatiite-associated sulphide deposits may be consulted in Lesher (1989).

Komatiite-hosted sulphide ores are particularly Ni-rich because ultramafic magmas represent relatively large degrees of partial melting of the mantle (Arndt & Lesher, 1992). With increasing degrees of partial melting, the relative proportion of olivine in the melt increases because olivine is the most abundant refractory phase in the upper mantle (around 65 vol.%, Maaløe & Aoki, 1977). Olivine is also the main carrier for Ni in igneous rocks (besides sulphides) ($D_{ol/sil}$ of Ni is 9 – 15, Beattie et $al.$, 1991), incorporating up to 0.5 wt.% NiO in its structure. On the other hand, because of the strong affinity of Ni for olivine, as little as 5% fractional crystallization of olivine from basaltic magma will deplete its Ni content by

around 50%. Therefore, one generally does not find Ni-rich sulphides associated with differentiated igneous rocks.

Equation (2) may be used to estimate R-factors during sulphide segregation from komatiite lavas: assuming a $D_{sul/sil}$ of c. 100 for Ni, a Ni content of approximately 1000 ppm in ultrabasic magmas, and an average Ni content of approximately 4 – 7 wt.% in natural sulphide ores associated with komatiites, one can estimate the R-factor at c. 100. This compares to an estimated R-factor of around 100 000 for the UG2 and Merensky Reefs (Figure 4). Due to this relatively low R-factor, PGE are generally a byproduct in sulphide deposits associated with lava flows, e.g. Kambalda (Keays et $al.$, 1981).

Cu/Pd ratios in lavas

Determination of whether a komatiite flow has undergone sulphide segregation or not should also be possible by applying the Cu/Pd method. The Chukotat Group in the Cape Smith fold belt, Quebec (Figure 14) may be considered as an example. It consists of flows of komatiitic basalts interlayered with more differentiated pyroxene- and plagioclase-phyric basalts of MORB composition (Barnes & Picard, 1993). Ni–Cu rich sulphides are found at the base of the lowermost flow. Cu and Ni contents show little systematic variation through the sequence and are of little exploration value in determining whether sulphide segregation occurred, much the same as in the Bushveld Complex. Apparently, the sulphide melt did not sufficiently deplete the magma in Cu and Ni. In contrast, the
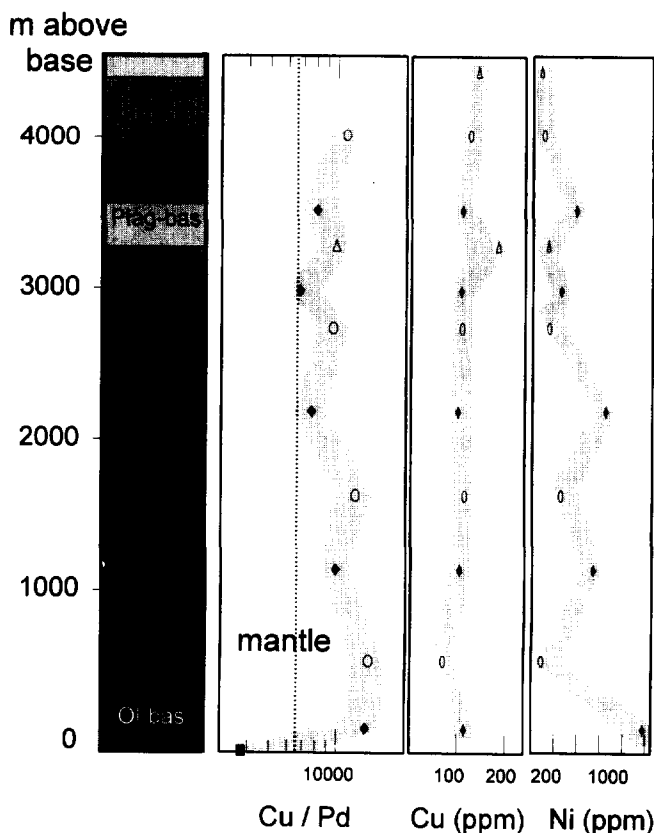

Figure 14 Cu/Pd ratios, and Cu and Ni contents from olivine-, pyroxene-, and plagioclase-phyric komatiitic and MORB basalts of the Chukotat Group, Cape Smith Fold Belt, Quebec, Canada (data from Barnes & Picard, 1993).
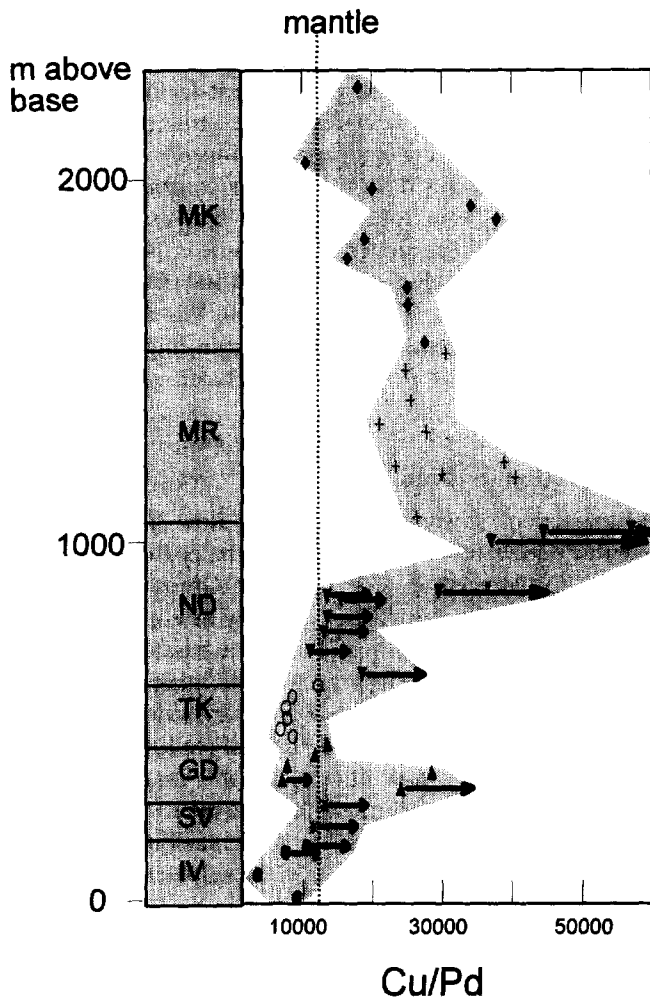
Figure 15 Cu/Pd ratios in basalt flows from the Siberian Trap. Iv = Ivakinsky suite; Sv = Syverminsky suite; Gd = Gudchichinsky suite; Tk = Tuklonsky suite; Nd = Nadezhdinsky suite; Mr = Morongovsky suite; Mk = Mokulaevsky suite (data from Brügmann *et al.*, 1993).

Cu/Pd ratios of the rocks overlying the sulphide horizon are much higher than the mantle ratio, indicating that a sulphide segregation process may have occurred and that at least the lower flows are derived from a common subvolcanic chamber.

The Noril'sk Cu–Ni–PGE sulphide deposits of Siberia are hosted by sill-like intrusive bodies thought to represent feeder zones for extensive flood basalt volcanism (the Siberian Traps) (Naldrett *et al.*, 1996a). The basaltic suite comprises seven main members. The IV, SV, and GD suites (Figure 15) show large internal compositional heterogeneity (Lightfoot *et al.*, 1990) and are believed to have crystallized from different parental magmas, representing variable degrees of partial melting and crustal contamination. This may explain the variation in Cu/Pd, with minor sulphides probably having segregated from the SV and some of the GD magmas. The overlying TK to MK suite is not comagmatic with the underlying lavas, which explains the resetting of the Cu/Pd ratio to mantle values at the base of the TK lavas. The individual members of the suite may, however, be internally related by some kind of an assimilation fractional crystallization (AFC) process (Brügmann *et al.*, 1993). Substantial sulphide melt

probably segregated from early ND magmas, as indicated by the sharp increase in Cu/Pd ratio from the TK suite throughout the ND suite. This interpretation is in line with the findings of Brügmann *et al.* (1993), and Naldrett *et al.* (1996a). The gradual decrease in Cu/Pd ratio throughout the MR and MK suites may then be interpreted as a result of the streaming of magmas over increasingly PGE-rich sulphides in the conduit zones, causing increasingly less depletion in Pd in the basalts.

In a South African context, Cu/Pd ratios may prove to be useful in determining whether portions of the Karoo flood basaltic sequence have suffered sulphide segregation. This may then potentially facilitate target selection of feeder zones or magma conduits hosting sulphide enrichments, analogous to the Noril'sk, Uitkomst, and, perhaps, the Canadian Voisey's Bay occurrences (Naldrett *et al.*, 1996b).

Olivine as a tracer for sulphide segregation

Amongst methods to estimate whether igneous rocks have experienced sulphide segregation, comparison of olivine compositions has been the most widely used in the past. This is because the Ni content of the silicate magma may fall sharply upon sulphide segregation. Ni-bearing silicate minerals crystallizing from such Ni-depleted magma (essentially olivine) would therefore have relatively low Ni contents. Ideally, the sulphide-bearing horizon may be pinpointed if expo-
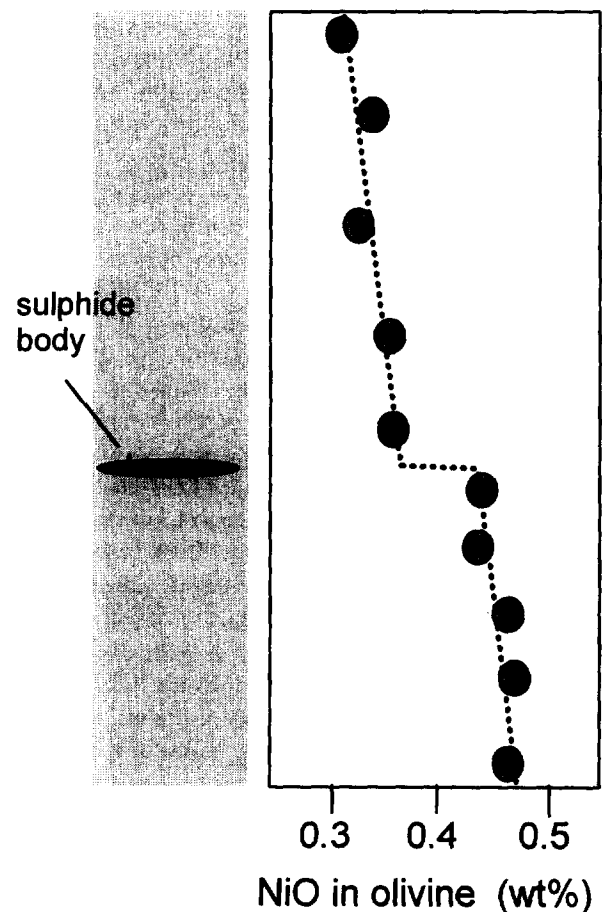

Figure 16 Schematic diagram, showing possible variation in NiO content of olivine within an intrusion, as a result of sulphide extraction from silicate magma.

sure is abundant (Figure 16). However, the method will only work at low R-factors, because the Ni depletion of the magma will otherwise be insignificant (Campbell & Barnes, 1984). It is interesting to note, in this regard, that the sulphide-enriched Lower Harzburgite and Chromitiferous Harzburgite Units of the Uitkomst Intrusion contain olivine with NiO contents of below 0.2 wt%, whereas in the unmineralized Upper Harzburgite Unit, NiO contents of olivine increase to 0.36 wt% (Van Zyl, 1996). Again, this pattern suggests that the individual harzburgite units crystallized from streaming flows of undepleted magma.

If exposure is limited and only a few samples are available for analysis, one has to compare the composition of the olivines to those of other intrusions. In doing this, it is of help to know that Ni and MgO contents of olivines vary in unison, that is, both decrease with falling crystallization temperature (Hart & Davis, 1978). Natural olivines, therefore, define a distinct compositional field on a plot of Fo versus Ni content (Figure 17). One of the most important processes to disturb this relationship is sulphide segregation, depleting the magma from which the olivines crystallize in Ni but not in MgO. Hence, olivines that crystallize from such magmas may plot outside the compositional field defined by olivines that crystallize from undepleted magmas (Figure 17).

This method has been applied to propose concealed deep-seated Ni-deposits below the Insizwa intrusion (Lightfoot et al., 1984) and the Norwegian Rana intrusion (Barnes, 1987), because the olivines at the base of these intrusions are thought to be depleted in Ni relative to Fo contents. These models may be independently assessed once complete metal contents of the parental magmas are available (in the Insizwa case presumably basalts of Karoo composition): deep seated
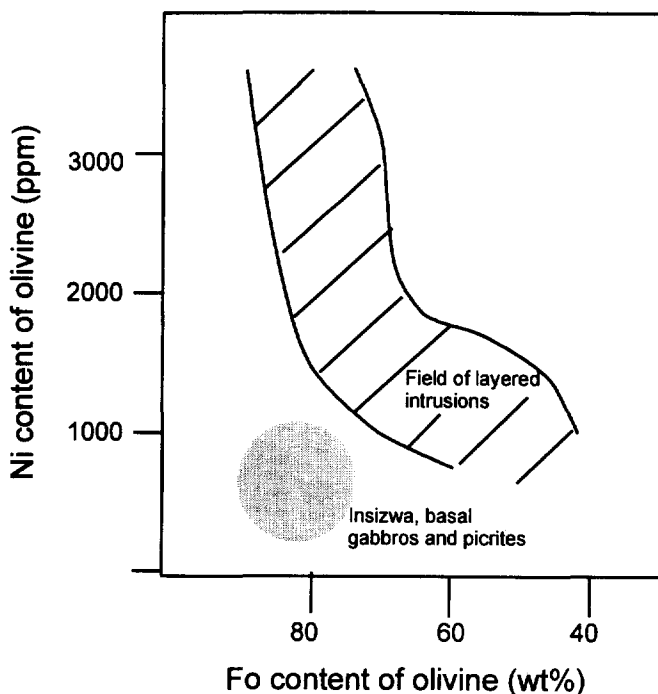
sulphide segregation will increase the Ni/Cu ratio (due to relatively higher $D_{sul/sil}$ values of Ni than Cu) and dramatically decrease the PGE content of the silicate magma. These modified metal patterns should be evident in ores segregating from such depleted magma (i.e. the Waterfall Gorge deposit).

Other guidelines for the exploration of magmatic sulphide deposits

It was discussed earlier that sulphide segregation may occur as a result of magma mixing. Evidence for magma mixing in the rock record would therefore be of interest for the exploration geologist. Isotopic heterogeneities are obvious tracers (Kruger & Marsh, 1982) but are only sensitive to mixing of magmas of distinct lineages. Mixing of differentiated and primitive magma of the same lineage will not be evident in the isotopic record, as heavy isotopes, in particular, are not fractionated during magmatic processes.

Major- and trace-element patterns of cumulate rocks may be difficult to interpret, due to equilibration of cumulates with percolating interstitial melt (Barnes, 1986; Mathez, 1995) or late stage fluids (Boudreau & McCallum, 1992). Chilled margins or comagmatic sills are less sensitive to these processes but are often not exposed to analysis.

Eales et al. (1993b) have proposed that corroded inclusions of plagioclase in orthopyroxene and olivine, which are characteristic of the Bushveld Upper Critical Zone and also of the rocks in the vicinity of the J-M reef of the Stillwater Complex (Boudreau, 1988), are a result of resorption of suspended plagioclase by hot, undifferentiated, replenishing magma, and subsequent entrapment by crystallizing ferromagnesian phases. However, it is not yet clear to what degree cumulus textures are modified during compaction, creep, and recrystallization (Means & Park, 1994).

The extent of mixing between compositionally contrasting magmas is partly governed by density and temperature differences between the mixing partners (Campbell et al., 1983). If the replenishing magma is denser than the fractionating resident magma, it may intrude the chamber along its floor and relatively little mixing will occur. This scenario may apply during the initial stages of crystallization of a basaltic resident magma, that is, during fractionation of relatively dense olivine, which, in spite of the effect of cooling, leads to a relatively rapid decrease in magma density (Naldrett et al., 1986) (Figure 18). However, once the cooling resident magma begins to fractionate light plagioclase, its density rises rapidly to eventually surpass that of any undifferentiated replenishing magma (Figure 18). The latter will then intrude as a fountain or a plume (Campbell et al., 1983), providing optimum conditions for thorough mixing, and possibly sulphide segregation. This model could explain why in the Bushveld, Stillwater, and the northern Finnish Penikat intrusion (Alapieti & Lahtinen, 1986), the PGE reefs occur some 400 – 500 m above the first occurrence of cumulus plagioclase, rather than near the base of the intrusions. It must be pointed out that, in some cases, notably the Great Dyke of Zimbabwe (Prender-
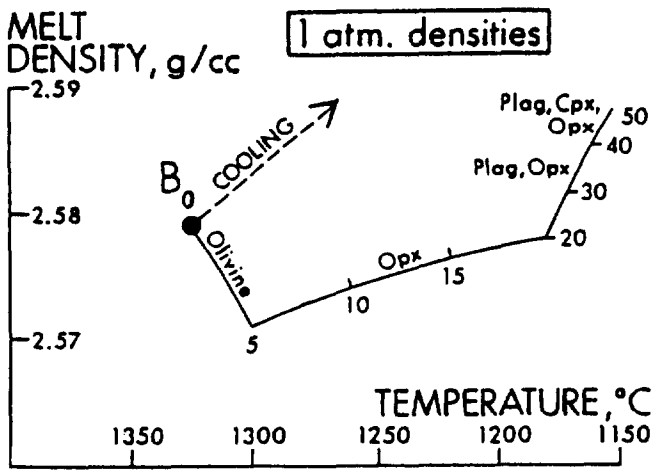

Figure 17 Binary variation diagram of Ni versus Fo content of olivine. Compositional fields cover layered intrusions, and basal gabbros and picrites from the Insizwa intrusion, Eastern Cape (modified after Lightfoot et al., 1984).

Figure 18 Density variations in fractionating magma of B₀ Bushveld parental composition (at 5 – 50% crystallization, 1 atmosphere confining P, modified after Naldrett *et al.*, 1986).

gast & Keays, 1988) and the Munni Munni intrusion of Australia (Barnes *et al.*, 1992), the main sulphide zones lie above thick ultramafic sequences and cannot be explained by the above model. One explanation would be that the 'reefs' may reflect the intrusion of light magma of distinct lineage. However, in the Great Dyke, the available Sr-isotopic data fail to support the presence of distinct magmatic lineages (Hamilton, 1977), and instead, sulphide segregation may be related to a combination of differentiation and relatively fast cooling, perhaps a function of the geometry of the Complex (Prendergast & Keays, 1988).

Importantly, the appearance of cumulus plagioclase on the liquidus may not always be evident in the cumulate record. Plagioclase has a relatively low density and if it floats, cotectic orthopyroxene may form monomineralic cumulates. Such pyroxenites may, however, be discriminated by means of lower Al contents of the orthopyroxenes, a result of the competition for Al between plagioclase and pyroxene (Eales *et al.*, 1994). Hence, study of orthopyroxene compositions by microanalytical equipment may provide information about the likelihood of magma mixing upon replenishment. Amongst other compositional traits that indicate the state of differentiation of the magma (particularly by means of comparison with other intrusions, Figure 19), one may mention Ti contents and Cr/Fe ratios of chromite (which increase with differentiation, Teigler & Eales, 1993), Mg# of both whole-rock compositions and ferromagnesian phases, and An contents of plagioclase (which decrease, Wager & Brown, 1968).

Evaluation of ores that underwent S-loss by means of Se/S ratios

Some PGE-rich deposits, in particular chromitites in layered intrusions and

ophiolites are relatively poor in sulphur. Ophiolitic chromitites mainly contain Os–Ir–Ru which are known to be compatible into chromite (Agiorgitis & Wolf, 1977; 1978). Chromitites from layered intrusions, however, tend to be enriched in Rh–Pt–Pd as well (Scoon & Teigler, 1994). The question therefore arises if the latter are controlled by sulphides, particularly in the LG chromitites of the Bushveld Complex which have sulphur contents below 0.02 wt.% (Scoon & Teigler, 1994). Rh–Pt–Pd and sulphur show a distinct correlation in chromitites and associated silicate rocks in parts of the Critical Zone (Figure 20), suggesting that in both lithologies these metals are somehow coupled to sulphur contents. This has previously been suggested by Von Gruenewaldt *et al.* (1986) and Naldrett & Lehmann (1987), based on petrographical and mass balance considerations. According to these authors, the chromitites have lost much of their initial magmatic sulphur as a result of subsolidus equilibration between sulphides, chromite, and interstitial melt.

Sulphur loss of magmatic sulphide ores is commonly evaluated by means of Se/S ratios (Peck & Keays, 1990). Se is strongly chalcophilic ($D_{sul/sil} = 1770$, Peach *et al.*, 1990), but a relatively immobile element (Howard, 1977). Hence, Se/S ratios of sulphide ores may increase in the event of sulphur loss. It has to be borne in mind that high Se/S values are not necessarily proof of sulphur loss. The data of Eckstrand *et al.* (1989) and Theriault *et al.* (1997) show that Se/S ratios of magmatic sulphides vary widely, presumably as a result of variation in Se content of the parental silicate magma, and variable R-factors during sulphide segregation. In other words, Se is affected by many of the same factors as Cu or the PGE. It can be readily demonstrated that a typical value for Se/S in magmatic sulphides is not applicable. The Se/S ratio in the mantle is approximately 160×10^{-6} (Taylor & McLennan, 1985). As both S and Se are principally hosted by sulphides, Se/S of primary magmas may fall into the same range.
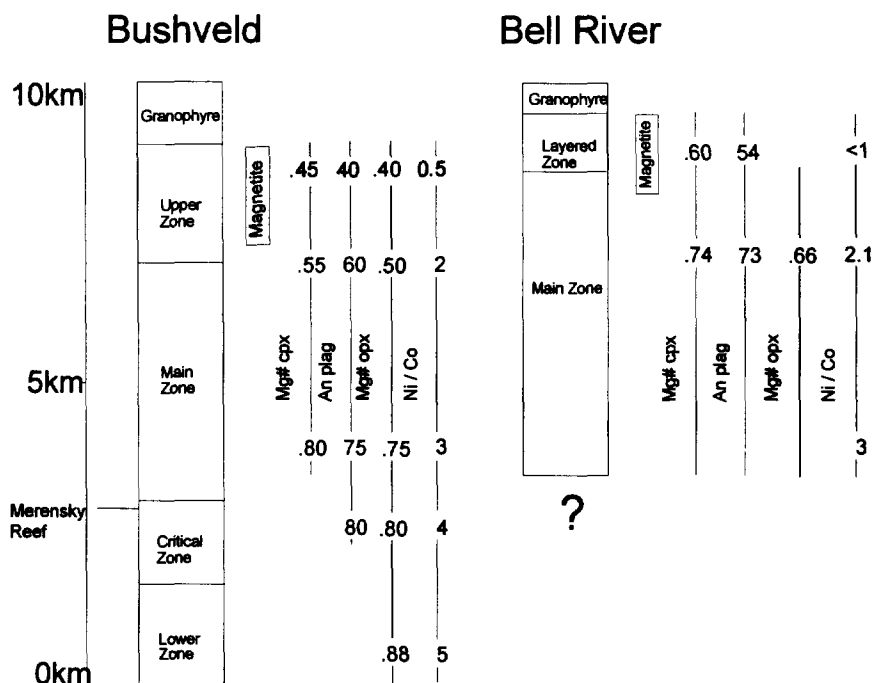

Figure 19 Comparison of stratigraphic and selected compositional variation in the Bushveld Complex and the Bell River Complex of Quebec, Canada (from Maier *et al.*, 1996a).
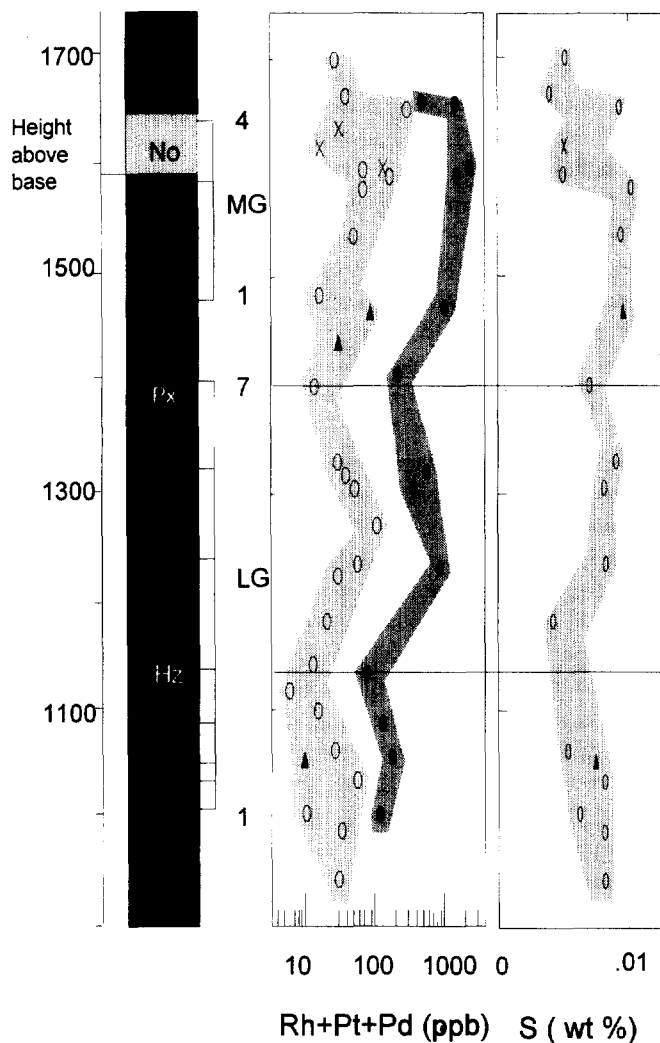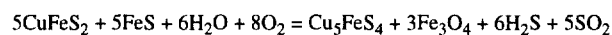
Figure 20 PGE and S contents of silicate rocks (data from Maier & Barnes, 1998) and chromitites (data from Scoon & Teigler, 1994) in parts of the Critical Zone of the Western Bushveld Complex at Union Section.

Barnes, 1996) transforming an original magmatic ore dominated by po + cp into a bn–cp–mag assemblage, according to the following equation:

$$5CuFeS_2 + 5FeS + 6H_2O + 8O_2 = Cu_5FeS_4 + 3Fe_3O_4 + 6H_2S + 5SO_2$$

In the Curaca Valley, the relative amount of sulphur lost may be quantified if we estimate (by means of Figure 21) that the original Se/S ratios fell within the mantle range (160×10^{-6}). Thus:

$$S_{lost} = S_{Original} - S_{left} \tag{i}$$
$$S_{left} = S_{present} \times \text{mass correction (M)} \tag{ii}$$
$$S_{Original} = (Se/160 \times 10^{-6}) \text{ mass correction (M)} \tag{iii}$$

where $M = 100/[100 + (Se/160 \times 10^{-6}) - S_{present})$

Substituting (iii) into (i) and (ii) gives:

$$S_{lost} = (Se/160 \times 10^{-6}) \times M - S_{present} \times M \tag{iv}$$
$$\% \, S_{lost} = (S_{original} - S_{left}) \times 100/S_{original} \tag{v}$$

and substituting (ii) and (iii) into (v) gives:

$$\% \, S_{lost} = [(Se/160 \times 10^{-6}) - S_{present}(\text{in ppm})] \times 100/(Se/160 \times 10^{-6}) \tag{vi}$$

It thus appears that the Curaca Valley ores could have lost between 30 and 95% of their original magmatic sulphur (Figure 22) (Maier & Barnes, 1996). Similar estimates have been proposed for the Okiep ores (Cawthorn & Meyer, 1993).

High Se/S ratios have also been invoked to suggest that the sulphides of the Uitkomst Complex are of predominantly magmatic origin (Kenyon et al., 1986). This is because sedimentary rocks tend to have relatively low Se/S ratios. However, more recent S-isotopic studies (Gauert et al., 1996) indicate that c. 10% of the sulphur is derived from the sedimentary country rocks.

Assuming that Se has not been mobile and that the original sulphur content of the sulphides was approximately 38 wt.%, the original metal content of ores may be calculated by applying a recalculation factor of $38000/S_{present}$. Average PGE contents, normalized to 100% sulphides, may then be compared to those from other sulphide deposits. The above procedure is,

Segregating sulphide melt will be essentially mss and have about 38 wt.% S, while Se contents are governed by the R-factor. At high R factors (equation 5) the maximum Se content of the sulphides is $1770 \times C_L$. In primitive magmas C_L is approximately 3 – 5 times mantle (assuming 20 to 30% partial melting necessary to consume all sulphides in the mantle). As the mantle contains around 0.04 ppm Se (Taylor & McLennan, 1985), Se contents of the silicate magma will be between 0.12 and 0.2 ppm, yielding maximum Se contents of the sulphide melt of 350 ppm, and Se/S ratios of up to 930×10^{-6}. At relatively low R, equation (2) applies. For R = 100, Se in the sulphide melt may be up to 19 ppm, and Se/S up to 50×10^{-6}. Hence, most ore deposits have Se/S ratios between 50 and 930×10^{-6}.

Nevertheless, due to the R-factor dependency, Se/S ratios and noble metal contents show a well-defined correlation (Figure 21) which allows the relative Se enrichment and, hence, S-loss of an ore, to be broadly quantified.

In both the Curaca Valley and the Okiep district, the ore has Se/S ratios of up to 5000×10^{-6}, far exceeding the range of magmatic values. This has been explained as a result of metamorphic sulphur loss (Cawthorn & Meyer, 1993; Maier &
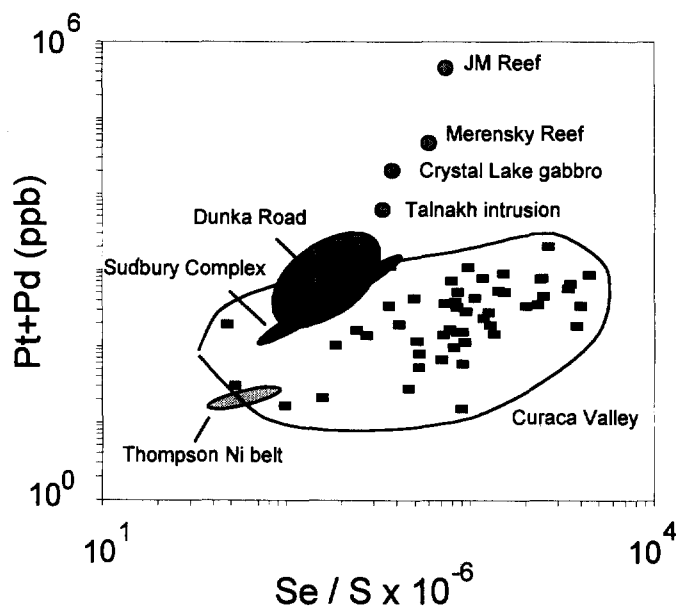

Figure 21 Binary variation diagram of Pt + Pd versus Se/S ratios in a number of magmatic sulphide deposits (unpubl. data of Eckstrand in Thériault et al., 1997), and rocks from the Curaca Valley, Brazil (Maier, unpubl. data).
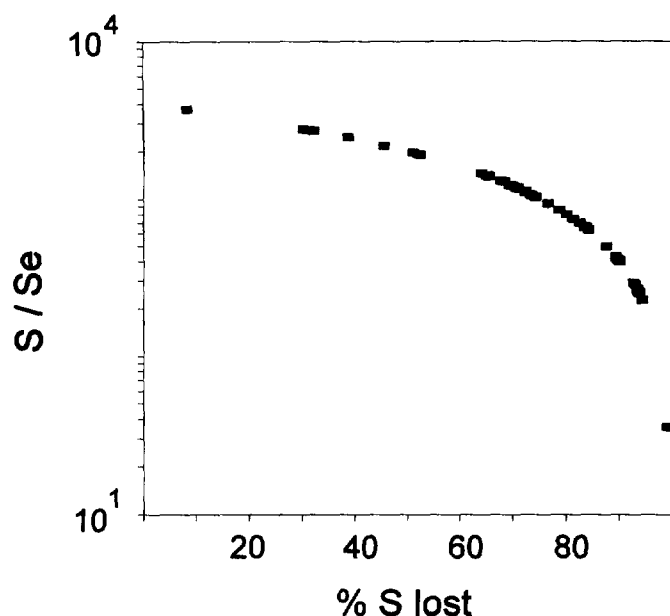
Figure 22 S/Se ratios of samples from the Curaca Valley plotted versus calculated proportion of wt.% S lost (data from Maier & Barnes, 1996).

of course, not without danger, in that it is based on a hypothetical Se/S ratio. This may lead to magnification of errors. Furthermore, the PGE (particularly Pd and perhaps also Pt) may have been mobile (Wood, 1987) which is not accounted for here.

Distinguishing between magmatic, metamorphic, and hydrothermal sulphides

Determination of whether sulphide ores are of magmatic or hydrothermal origin is of considerable importance. As an example, one may consider the Okiep deposits. These are highly unusual with respect to most other magmatic deposits, in that the sulphide assemblage contains abundant bornite, yielding high Cu/S ratios (up to 3) and Cu/Ni ratios (averaging 74). Bornite is absent in most other magmatic ores, but is a common constituent of hydrothermal ores such as Cu-porphyries (McMillan & Panteleyev, 1988). Nevertheless, since the Okiep ores are exclusively hosted by mafic–ultramafic rocks, magmatic models of origin are generally preferred (McIver et al., 1983; Cawthorn & Meyer, 1993) and the presence of bornite is explained by metamorphic S-loss of an originally magmatic pyrrhotite-rich ore (Cawthorn & Meyer, 1993). Based on this model, the ore could be the Cu-rich end-member of an mss fractionation process, in which case exploration should aim to locate possible unexposed refractory Os–Ir–Ru–(Ni) ore bodies. Maier & Barnes (1996) supported this model for the Curaca Valley ores of Brazil, which, in addition to being bornite-rich and having high Se/S ratios and magnetite contents, have Pt and Pd contents up to 2 ppm and Os–Ir–Ru contents of up to 30 ppb. These PGE concentrations would appear to be too high for most hydrothermal deposits (but see McCallum et al., 1976; Rowell & Edgar, 1986; McDonald et al., 1995). One problem with the magmatic model is that there are no refractory ore bodies exposed anywhere in the Curaca Valley. However, a showing of

Ni-rich sulphide ores in rocks apparently related to the Koperberg suite has been described by Hamman et al. (1996). Thus, it appears possible that sulphide segregation occurred at depth, followed by physical separation of mss cumulate ore from fractionated Cu-rich sulphide melt by the ascending silicate magma.

A further problem in applying a primary magmatic model to the origin of the Okiep and Curaca Valley ores is the extremely high Cu/Ni ratio in both ores (around 40 in the Curaca Valley, Maier & Barnes, 1996, and 70 at Okiep, Cawthorn & Meyer, 1993). Most fractionated ores known elsewhere, such as Cu-rich stringers in the footwall of the Sudbury intrusion (Hoffman et al., 1979) or gabbro-hosted ores at Stormyrplutten, Norway (Larsen & Grenne, 1995) have Cu/Ni ratios not exceeding 35 (Table 1). An exception is the recently discovered Platinova PGE Reef of the Skaergaard Intrusion (Anderssen et al., 1998), where Cu/Ni ratios reach values comparable to those at Okiep and in the Curaca Valley. This is explained by the fact that the Platinova ore is hosted by gabbronorite. Cu-rich sulphides are not uncommon in differentiated rocks such as gabbronorites and diorites, for example at St. Charles, Québec (Lister, 1966). Apparently, the Skaergaard intrusion failed to experience major sulphide segregation until a relatively late stage. It is difficult, at this stage, to understand how this may relate to the origin of the Curaca Valley and Okiep ores, since the latter are hosted by pyroxenite.

Keays et al. (1982) have suggested that Pd/Ir ratios of sulphide ores may discriminate between magmatic and hydro-

Table 1 Cu/Ni and Pd/Ir ratios in some magmatic and hydrothermal sulphide ores

	Cu/Ni	Pd/Ir
Magmatic ores		
Bushveld[1]		
Lower Zone (average silicate rocks)	0.02	9.3
LCZ (average silicate rocks)	0.02	4.3
UCZ (average silicate rocks)	0.07	7.3
Main Zone (silicate rocks)	0.36	45
Levack West massive sulphides[2]	0.25	9.2
Levack West Cu stringers[2]	11 (up to 48)	5159
Stormyrplutten[3]	36	35
Platinova Reef, Skaergaard[4]	up to 100	nd
Curaca Valley[5]	40	72
Okiep[6]	74	nd
Hydrothermal ores		
Kambalda footwall veins[7]	0.08	696
Waterberg dykes[8]	nd	851
New Rambler mine[9]	nd	>1800
Rathbun Lake[10]	41	52645

1. Maier & Barnes (1998); 2. Hoffman et al. (1979); 3. Larsen & Grenne (1995); 4. Anderssen et al. (1998); 5. Maier & Barnes (1996); 6. Cawthorn & Meyer (1993); 7. Lesher & Keays (1984); 8. McDonald et al. (1995); 9. McCallum et al. (1976); 10. Rowell & Edgar (1986). nd = not determined

thermal modes of origin, due to the enhanced mobility of Pd relative to Ir (Wood, 1987). They argued that hydrothermal ores generally have Pd/Ir ratios in excess of around 100, with magmatic ores being relatively less Pd enriched and thus having lower Pd/Ir ratios. However, while it is accepted that hydrothermal ores invariably have elevated Pd/Ir ratios, magmatic ores clearly have highly variable Pd/Ir ratios, reaching values of several 1000 in the Sudbury intrusion (Table 1) (Hoffman et al., 1979). The Curaca Valley ores have average Pd/Ir ratios of 70, supporting a magmatic origin of the PGE.

Conclusions

Whilst the understanding of the concentration of Ni, Cu, and the noble metals in sulphide ores is still incomplete, there exist now a number of techniques that may facilitate exploration for such deposits. These include metal ratio diagrams, Cu/Pd, Pd/Ir, Cu/Ni, and Se/S ratios, as well as isotopic, petrographic, and lithological studies of ores and their host rocks. Calculations applying metal contents of parental silicate magmas, published D values, and R-factors during sulphide segregation may yield useful estimates of the composition of ores that may be hosted by an igneous body, and thus facilitate target selection. Due to the variability of natural deposits application of any one single method will be of limited value, but a combined analysis of lithological, petrographical, and geochemical patterns should offer valuable guidelines for an exploration programme.

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References

Agiorgitis, G. & Wolf, R. (1977). The distribution of platinum, palladium and gold in Greek chromites. Chem. Erde, 36, 349–351.

---- & ---- (1978). Aspects of osmium, ruthenium and iridium contents in some Greek chromites. Chem. Geol., 23, 267–272.

Alapieti, T.T. & Lahtinen, J.J. (1986). Stratigraphy, petrology, and platinum-group element mineralization of the early Proterozoic Penikat layered intrusion, northern Finland. Econ. Geol., 81, 1126–1136.

Anderssen, J.C., Rasmussen, H., Nielsen, T.F.D. & Ronsbo, J. (1998). The triple group and the Platinova gold and palladium reefs in the Skaergaard Intrusion: Stratigraphic and petrographic relations. Econ. Geol., 93, 488–509.

Anonymous (1997). Nkomati — South Africa's first primary nickel mine. S. Afr. Min. Coal, Gold & Base Metals, July, 27–31.

Arndt, N.T. & Lesher, C.M. (1992). Fractionation of PGE by olivine and the origin of Kambalda komatiites, Western Australia. Geochim. Cosmochim. Acta, 56, 4191–4204.

----, Naldrett, A.J. & Hunter, D.R. (1997). Ore deposits associated with mafic magmas in the Kaapvaal Craton. Mineralium Deposita, 32, 323–334.

Ballhaus, C., Ryan, C.G., Mernach, T.P. & Green, D.H. (1994). The partitioning of Fe, Ni, Cu, Pt and Au between sulphide, metal and fluid phases: a pilot study. Geochim. Cosmochim. Acta, 58, 811–826.

Barnes, S.-J. (1987). Unusual nickel and copper to noble-metal ratios from the Rana Layered Intrusion, northern Norway. Norsk Geol. Tidskr., 67, 215–231.

---- & Picard, C.P. (1993). The behaviour of platinum-group elements during partial melting, crystal fractionation, and sulphide segregation: An example from the Cape Smith Fold Belt, northern Quebec. Geochim. Cosmochim. Acta, 57, 79–87.

----, Naldrett, A.J. & Gorton, M.P. (1985). The origin of the fractionation of platinum group elements in terrestrial magmas. Chem. Geol., 53, 303–323.

----, Boyd, R., Korneliussen, A., Nilsson, L.-P., Often, M., Pedersen, R.B. &

Robins, B. (1988). The use of mantle normalization and metal ratios in discriminating between the effects of partial melting, crystal fractionation and sulphide segregation on platinum group elements, gold, nickel and copper: examples from Norway. In: Pritchard, H.M., Potts, P.J., Bowles, J.F.W. & Cribb, S.J. (Eds.), Geo Platinum 87. Elsevier, London, 113–143.

----, Couture, J.-F., Sawyer, E.W. & Bouchaib, C. (1993). Nickel–copper occurrences in the Belleterre–Angliers belt of the Pontiac subprovince and the use of Cu–Pd ratios in interpreting platinum-group element distributions. Econ. Geol., 88, 1402–1418.

----, Makovicky, E., Makovicky, M., Rose-Hansen, J. & Karup-Moller, S. (1997). Partition coefficients for Ni, Cu, Pd, Pt, Rh, and Ir between monosulphide solid solution and sulphide liquid and the formation of compositionally zoned Ni–Cu sulphide bodies by fractional crystallization of sulphide liquid. Can. J. Earth Sci., 34, 366–374.

Barnes, S.J. (1986). The effect of trapped liquid crystallization on cumulus mineral compositions in layered intrusions. Contr. Miner. Petrol., 93, 524–531.

----, Keays, R.R. & Hoatson, D.M. (1992). Distribution of sulphides and PGE within the porphyritic websterite zone of the Munni Munni Complex, Western Australia. Austr. J. Earth Sci., 39, 289–302.

Beattie, P., Ford, C. & Russell, D. (1991). Partition coefficients for olivine-melt and orthopyroxene-melt systems. Contr. Miner. Petrol., 109, 212–224.

Boudreau, A.E. (1988). Investigations of the Stillwater Complex IV: The role of volatiles in the petrogenesis of the J-M reef, Minneapolis Adit Section. Can. Miner., 26, 193–208.

---- & McCallum, I.S. (1992). Concentration of platinum-group elements by magmatic fluids in layered intrusions. Econ. Geol., 87, 1830–1848.

Brügmann, G.E., Naldrett, A.J., Asif, M., Lightfoot, P.C., Gorbachev, N.S. & Fedorenko, V.A. (1993). Siderophile and chalcophile metals as tracers of the evolution of the Siberian Trap in the Noril'sk region, Russia. Geochim. Cosmochim. Acta, 57, 2001–2018.

Campbell, I.H. & Barnes, S.J. (1984). A model for the geochemistry of the platinum-group elements in magmatic sulfide deposits. Can. Miner., 22, 151–160.

---- & Naldrett, A.J. (1979). The influence of silicate: sulfide ratios on the geochemistry of magmatic sulfides. Econ. Geol., 74, 1503–1505.

----, ---- & Barnes, S.J. (1983). A model for the origin of the platinum-rich sulphide horizons in the Bushveld and Stillwater Complexes. J. Petrol., 24, 133–165.

Capobianco, C.J. & Drake, M.J. (1990). Partitioning of Ru, Rh, and Pd between spinel and silicate melt and implications for platinum-group element fractionation trends. Geochim. Cosmochim. Acta, 54, 869–874.

Cawthorn, R.G. & Meyer, F.M. (1993). Petrochemistry of the Okiep copper district basic intrusive bodies, northwestern Cape province, South Africa. Econ. Geol., 88, 590–605.

Craig, J.R. (1973). Pyrite–pentlandite assemblages and other low-temperature relations in the Fe–Ni–S system. Am. J Sci., 273A, 496–510.

Czamanske, G.K. & Moore, J.G. (1977). Composition and phase chemistry of sulfide globules in basalt from the mid-Atlantic ridge rift valley near 37°N. Lat. Bull. geol. Soc. Am., 88, 587–599.

Davies, G. & Tredoux, M. (1985). The platinum-group element and gold contents of the marginal rocks and sills of the Bushveld Complex. Econ. Geol., 80, 838–848.

Eales, H.V., Botha, W.J., Hattingh, P.J., De Klerk, W.J., Maier, W.D. & Odgers, A.T.R. (1993a). The mafic rocks of the Bushveld Complex: a review of emplacement and crystallization history, and mineralization in the light of recent data. J. Afr. Earth Sci., 16, 121–142.

----, Maier, W.D. & Teigler, B. (1993b). Corroded plagioclase feldspar inclusions in orthopyroxene and olivine of the Lower and Critical Zones, Western Bushveld Complex. Mineral. Mag., 55, 479–486.

----, Teigler, B., De Klerk, W.J. & Maier, W.D. (1994). Nature and origin of orthopyroxenites in the western Bushveld Complex, in the light of compositional data. S. Afr. J. Geol., 97, 399–407.

Eckstrand, O.R., Grinenko, L.N., Krouse, H.R., Paktunc, A.D., Schwann, P.L. & Scoates, R.F.J. (1989). Preliminary data on sulphur isotopes and Se/S ratios, and the source of sulphur in magmatic sulphides from the Fox River Sill, Molson Dykes and Thompson nickel deposits, northern Manitoba. Spec. Pap. geol. Surv. Can., 89-1C, 235–242.

Fleet, M.E., Chryssoulis, S.L., Stone, W.E. & Weisener, C.G. (1993). Partitioning of platinum-group elements and Au in the Fe–Ni–Cu–S

system: experiments on the fractional crystallization of sulfide melt. *Contr. Miner. Petrol.*, **115**, 36–44.

----, Crocket, J.H. & Stone, W.E. (1996). Partitioning of platinum-group elements (Os, Ir, Ru, Pt, Pd) and gold between sulfide liquid and basalt melt. *Geochim. Cosmochim. Acta*, **60**, 2397–2412.

Francis, D.M. (1994). Chemical interaction between picritic magmas and upper crust along the margins of the Muskox Intrusion, N.W.T. Canada. *Spec. Pap. geol. Surv. Can.*, **92–12**, 94 pp.

Gain, S.B. (1985). The geologic setting of the platiniferous UG2 chromitite layer on Maandagshoek, Eastern Bushveld Complex. *Econ. Geol.*, **80**, 925–943.

Gauert, C.D.K., De Waal, S.A. & Wallmach, T. (1995). Geology of the ultrabasic to basic Uitkomst complex, eastern Transvaal, South Africa: an overview. *J. Afr. Earth Sci.*, **21**, 553–570.

----, Jordaan, L.J., De Waal, S.A. & Wallmach, T. (1996). Isotopic constraints on the source of sulphur for the base metal sulphides of the Uitkomst Complex, Badplaas, South Africa. *S. Afr. J. Geol.*, **99**, 41–50.

Green, D.H., Nicholls, I.A., Viljoen, M. & Viljoen, R. (1975). Experimental determination of the existence of peridotite liquids in earliest Archean magmatism. *Geology*, **3**, 11–14.

Hamilton, J. (1977). Strontium isotope and trace element studies on the Great Dyke and Bushveld mafic phase and their relation to early Proterozoic magma genesis in southern Africa. *J. Petrol.*, **18**, 24–52.

Hamlyn, P.R. & Keays, R.R. (1986). Sulfur saturation and second-stage melts: application to the Bushveld platinum metal deposits. *Econ. Geol.*, **81**, 1431–1445.

Hamman, J.N., Rozendaal, A. & Jordaan, W. (1996). Gabbro-norite hosted Ni–Cu–(Co) sulphide mineralization in southern Namaqualand and its relationship to the cupriferous Koperberg Suite of the Okiep Copper District, South Africa. *S. Afr. J. Geol.*, **99**, 153–168.

Harmer, R.E. & Sharpe, M.R. (1985). Field relations and strontium isotope systematics of the eastern Bushveld Complex. *Econ. Geol.*, **80**, 813–837.

Hart, S.R. & Davis, K.E. (1978). Nickel partitioning between olivine and silicate melt. *Earth Planet. Sci. Lett.*, **40**, 203–219.

Haughton, D.R., Roeder, P.L. & Skinner, B.J. (1974). Solubility of sulfur in mafic magmas. *Econ. Geol.*, **69**, 451–467.

Hoatson, D.M. & Keays, R.R. (1989). Formation of platiniferous sulphide horizons by crystal fractionation and magma mixing in the Munni Munni layered intrusion, West Pilbara Block, Western Australia. *Econ. Geol.*, **84**, 1775–1804.

Hoffman, E.L., Naldrett, A.J., Alcock, R.A. & Hancock, R.G.V. (1979). The noble metal content of ore in the Levack West and Little Stobie mines, Ontario. *Can. Miner.*, **17**, 437–451.

Howard, J.H. (1977). Geochemistry of selenium: formation of ferroselite and selenium behaviour in the vicinity of oxidizing sulfide and uranium deposits. *Geochim. Cosmochim. Acta*, **41**, 1665–1678.

Irvine, T.N. (1975). Crystallization sequences in the Muskox intrusion and other layered intrusions: II Origin of chromitite layers and similar deposits of other magmatic ores. *Geochim. Cosmochim. Acta*, **39**, 991–1020.

----, Keith, D.W. & Todd, S.G. (1983). The J-M Platinum – Palladium Reef of the Stillwater Complex, Montana, II: Origin by double-diffusive convective magma mixing and implications for the Bushveld Complex. *Econ. Geol.*, **78**, 1287–1334.

Keays, R.R. & Campbell, I.H. (1981). Precious metals in the Jimberlana Intrusion, Western Australia: implications for the genesis of platiniferous ores in layered intrusions. *Econ. Geol.*, **76**, 1118–1141.

----, Ross, J.R. & Woolrich, P. (1981). Precious metals in volcanic peridotite-associated nickel sulfide deposits in western Australia. II: distribution within the ores and host rocks at Kambalda. *Econ. Geol.*, **76**, 1645–1674.

----, Nickel, E.H., Groves, D.I. & McGoldrick, P.J. (1982). Iridium and palladium as discriminants of volcanic–exhalative, hydrothermal, and magmatic nickel sulfide mineralization. *Econ. Geol.*, **77**, 1535–1547.

Kenyon, A.K., Attridge, R.L. & Coetzee, G.L. (1986). The Uitkomst nickel–copper deposit, Eastern Transvaal. *In*: Anhaeusser, C.R. & Maske, S. (Eds.), *Mineral Deposits of Southern Africa.* Geol. Soc. S. Afr., Johannesburg, **I**, 1009–1017.

Kruger, F.J. & Marsh, J.S. (1982). Significance of $^{87}Sr/^{86}Sr$ ratios in the Merensky Cyclic Unit of the Bushveld Complex. *Nature*, **298**, 53–55.

Kullerud, G., Yund, R.A. & Moh, G.H. (1969). Phase relations in the Cu–Fe–S, Cu–Ni–S, and Fe–Ni–S systems. *Monogr. Econ. Geol.*, **4**, 323–349.

Larsen R.B. & Grenne, T. (1995). Cu–Ni–PGE mineralization hosted by boninitic gabbro, central Norwegian Caledonides: character and tectonic setting. *Trans. Inst. Min. Metal.*, **104**, B87–B98.

Lee, C.A. & Tredoux, M. (1986). Platinum-group element abundances in the Lower and the Lower Critical Zones of the Eastern Bushveld Complex. *Econ. Geol.*, **81**, 1087–1095.

Lesher, C.M. (1989). Komatiite-associated Ni-sulfide deposits. *In*: Whitney, J.A. & Naldrett, A.J. (Eds.), *Ore Deposition Associated with Magmas.* Soc. econ. Geol., Dordrecht, 45–102.

---- & Campbell, I.H. (1993). Geochemical and fluid dynamic controls on the composition of komatiite-hosted nickel sulfide ores in Western Australia. *Econ. Geol.*, **88**, 804–816.

---- & Keays, R.R. (1984). Metamorphically and hydrothermally mobilised Fe–Ni–Cu sulphides at Kambalda, Western Australia. *In*: Buchanan, D.L. & Jones, M.J. (Eds.), *Sulphide Deposits in Mafic and Ultramafic Rocks.* Inst. Min. Metallurgy, Lond., 62–69.

Liebenberg, W.R. (1970). The sulphides in the layered sequence of the Bushveld Igneous Complex. *Spec. Publ. geol. Soc. S. Afr.*, **1**, 108–207.

Lightfoot, P.C., Naldrett, A.J. & Hawkesworth, C.J. (1984). The geology and geochemistry of the Waterfall Gorge section of the Insizwa Complex with particular reference to the origin of the nickel sulfide deposits. *Econ. Geol.*, **79**, 1857–1879.

----, ----, Gorbachev, N.S., Doherty, W. & Fedorenko, V.A. (1990). Geochemistry of the Siberian Trap of the Norilsk area, USSR, with implications for the relative contributions of crust and mantle to flood basalt magmatism. *Contr. Miner. Petrol.*, **104**, 631–644.

Lister, G.F. (1966). The composition and origin of selected iron–titanium deposits. *Econ. Geol.*, **61**, 275–310.

Lorand, J.P. (1990). Are spinel lherzolite xenoliths representative of the sulfur content of the upper mantle? *Geochim. Cosmochim. Acta*, **54**, 1487–1492.

Maaløe, S. & Aoki, K. (1977). The major element composition of the Upper Mantle estimated from the composition of lherzolites. *Contr. Miner. Petrol.*, **63**, 161–173.

Maier, W.D. & Barnes, S.-J. (1996). Unusually high concentrations of magnetite at Caraiba and other Cu-sulphide deposits in the Curaca valley, Bahia, Brazil. *Can. Miner.*, **34**, 717–731.

---- & ---- (1998b). Platinum-group elements in silicate rocks of the Lower, Critical, and Main Zones of the Western Bushveld Complex. *Abstr. 8th int. Platinum Symp.*, Rustenburg, South Africa, 221–223.

---- & Bowen, M.P. (1996). The UG2–Merensky Reef interval of the Bushveld Complex northwest of Pretoria. *Mineralium Deposita*, **31**, 386–393.

----, Barnes, S.-J. & Pellet, T. (1996a). The economic significance of the Bell River Complex, Abitibi subprovince, Quebec. *Can. J. Earth Sci.*, **33**, 967–980.

----, ----, Teigler, B., De Klerk, W.J. & Mitchell, A.A. (1996b). Cu/Pd and Cu/Pt of silicate rocks in the Bushveld Complex: Implications for platinum-group element exploration. *Econ. Geol.*, **91**, 1151–1158.

Marsh, J.S., Hooper, P.R., Rehacek, J., Duncan, R.A. & Duncan, A.R. (1997). Stratigraphy and age of Karoo basalts of Lesotho and implications for correlations within the Karoo igneous province. *In*: Mahoney, J.J. & Coffin, M.F. (Ed.), *Large Igneous Provinces: Continental, Oceanic, and Planetary Flood Volcanism.* Geophys. Monogr., Am. Geophys. Un., **100**, 247–272.

Mathez, E.A. (1976). Sulfur solubility and magmatic sulfides in submarine basalt glass. *J. geophys. Res.*, **81**, 4269–4276.

---- (1995). Magmatic metasomatism and formation of the Merensky Reef, Bushveld Complex. *Contr. Miner. Petrol.*, **119**, 277–286.

McCallum, M.E., Loucks, R.R., Carlson, R.R., Cooley, E.F. & Doerge, T.A. (1976). Platinum metals associated with hydrothermal copper ores of the New Rambler Mine, Medicine Bow mountains, Wyoming. *Econ. Geol.*, **71**, 1429–1450.

McDonald, I., Vaughan, D.J. & Tredoux, M. (1995). Platinum mineralization in quartz veins near Naboomspruit, central Transvaal. *S. Afr. J. Geol.*, **98**, 168–175.

McIver, J.R., McCarthy, T.S. & Packham, B. de V. (1983). The copper-bearing basic rocks of Namaqualand, South Africa. *Mineralium Deposita*, **18**, 135–160.

McMillan, W.J. & Panteleyev, A. (1988). Porphyry Copper Deposits. *In*: Roberts, R.G. & Sheahan, P.A. (Eds.), *Ore Deposit Models.* Geosci. Can. Repr. Ser., **3**, 45–58.

Means, W.D. & Park, Y. (1994). New experimental approach to understanding igneous texture. *Geology*, **22**, 323–326.

Merkle, R.K.W. (1992). Platinum-group minerals in the middle group of chromitite layers at Marikana, western Bushveld Complex: indications for

collection mechanisms and postmagmatic modification. *Can. J. Earth Sci.*, 29, 209–221.

Naldrett, A.J. (1969). A portion of the sytem Fe–S–O between 900 and 1080 °C and its application to sulfide ore magmas. *J. Petrol.*, 10, 171 –201.

---- (1989). Sulfide melts – crystallization temperatures, solubilities in silicate melts, and Fe, Ni, and Cu partitioning between basaltic magmas and olivine. *In*: Whitney, J.A. & Naldrett, A.J. (Eds.), *Ore Deposits Associated with Magmas*. Rev. Econ. Geol., 4, 5–20.

---- & Lehmann, J. (1987). Spinel non-stoichiometry as the explanation for Ni-, Cu-, and PGE-enriched sulphides in chromitites. *In*: Pritchard, H.M., Potts, P.J., Bowles, J.F.W. & Cribb, S.J. (Eds.), *Geo Platinum 87*. Elsevier, Lond., 113–143.

---- & Von Gruenewaldt, G. (1989). Association of platinum-group elements with chromitite in layered intrusions and ophiolite complexes. *Econ. Geol.*, 84, 180–187.

----, Hoffman, E.L., Green, A.H., Chou, C-L. & Naldrett, S.R. (1979). The composition of Ni-sulphide ores, with particular reference to their content of PGE and Au. *Can. Miner.*, 17, 403–415.

----, Innes, D.G., Sowa, J. & Gorton, M.P. (1982). Compositional variations between five Sudbury ore deposits. *Econ. Geol.*, 77, 1519–1534.

----, Gasparini, E.C., Barnes, S.J., Von Gruenewaldt, G. & Sharpe, M.R. (1986). The upper Critical Zone of the Bushveld Complex and the origin of Merensky-type ores. *Econ. Geol.*, 81, 1105–1117.

----, Fedorenko, V.A., Asif, M., Shushen, L., Kunilov, V.E., Stekhin, A.I., Lightfoot, P.C. & Gorbachev, N.S. (1996a). Controls on the composition of Ni–Cu sulfide deposits as illustrated by those at Noril'sk, Siberia. *Econ. Geol.*, 91, 751–773.

----, Keats, H., Sparkes, K. & Moore, R. (1996b). Geology of the Voisey's Bay Ni–Cu–Co deposit, Labrador, Canada. *Explor. Min. Geol.*, 5, 169–179.

----, Ebel, D.S., Asif, M., Morrison, G. & Moore, C.M. (1997). Fractional crystallization of sulphide melts as illustrated at Noril'sk and Sudbury. *European J. Miner.*, 9, 365–377.

Oshin, I.O. & Crocket, J.H. (1982). Noble metals in the Thetford mines ophiolite, Quebec, Canada. Part I: Distribution of gold, iridium, platinum, and palladium in the ultramafic and gabbroic rocks. *Econ. Geol.*, 77, 1556–1570.

Peach, C.L. & Mathez, E.A. (1996). Constraints on the formation of platinum-group element deposits in igneous rocks. *Econ. Geol.*, 91, 439–450.

----, Mathez, E.A. & Keays, R.R. (1990). Sulfide melt – silicate melt distribution coefficients for noble metals and other chalcophile elements as deduced from MORB: implications for partial melting. *Geochim. Cosmochim. Acta*, 54, 3379–3389.

Peck, D.C. & Keays, R.R. (1990). Insights into the behaviour of precious metals in primitive, S-undersaturated magmas: evidence from the Heazlewood River Complex, Tasmania. *Can. Miner.*, 28, 553–557.

Prendergast, M.D. & Keays, R.R. (1988). Controls of platinum-group element mineralization and the origin of the PGE-rich Main Sulphide Zone in the Wedza Subchamber of the Great Dyke, Zimbabwe:

implications for the genesis of, and exploration for, stratiform PGE mineralization in layered intrusions. *In*: Prendergast, M.D. & Jones, M.J. (Eds.), *Magmatic Sulphides – the Zimbabwe Volume*. Inst. Min. Metall., London, 43–69.

Ripley, E.M. & Alawi, J.A. (1988). Petrogenesis of pelitic xenoliths at the Babbitt Cu–Ni deposit, Duluth Complex, Minnesota, USA. *Lithos*, 21, 143–159.

Rowell, W.F. & Edgar, A.D. (1986). Platinum-group element mineralization in a hydrothermal Cu–Ni sulfide occurrence, Rathbun Lake, northeastern Ontario. *Econ. Geol.*, 81, 1272–1277.

Scoon, R.N. & Teigler, B. (1994). Platinum-group element mineralization in the Critical Zone of the Western Bushveld Complex: I. Sulfide poor chromitites below the UG2. *Econ. Geol.*, 89, 1094–1121.

Stanton, R.L. (1972). *Ore Petrology*. McGraw-Hill, New York, 690 pp.

Taylor, S.R. & McLennan, S.M. (1985). *The Continental Crust: Its Composition and Evolution*. Blackwell Sci., Oxford, 312 pp.

Teigler, B. & Eales, H.V. (1993). Correlation between chromite composition and PGE mineralization in the Critical Zone of the Western Bushveld Complex. *Mineralium Deposita*, 28, 291–302.

Thompson, R.N., Morrison, M.A., Dickin, A.P. & Hendry, G.L. (1983). Continental flood basalts...arachnids rule OK? *In*: Hawkesworth, C.J. & Norry, M.J. (Eds.), *Continental Basalts and Mantle Xenoliths*. Nantwich, Shiva, 158–185.

Thériault, R.D., Barnes, S.-J. & Severson, M.J. (1997). The influence of country-rock assimilation and silicate to sulphide ratio (R factor) on the genesis of the Dunka Road Cu–Ni–PGE deposit, Duluth Complex, Minnesota. *Can. J. Earth Sci.*, 34, 375–389.

Tredoux, M., Lindsay, N.M., Davies, G. & McDonald, I. (1995). The fractionation of platinum-group elements in magmatic systems, with the suggestion of a novel causal mechanism. *S. Afr. J. Geol.*, 98, 157–167.

Van Zyl, A.M. (1996). *The sulphides of the Uitkomst Complex, Badplaas, South Africa*. M.Sc thesis (unpubl.), Univ. Pretoria, 122 pp.

Von Gruenewaldt, G., Hatton, C.J., Merkle, R.R.W. & Gain, S.B. (1986). Platinum-group element – chromitite associations in cumulates of the Bushveld Complex. *Econ. Geol.*, 81, 1067–1079.

Wager, L.R. & Brown, G.M. (1968). *Layered Igneous Rocks*. Oliver & Boyd, Edinburgh & Lond., 588 pp.

Wendlandt, R.F. (1982). Sulfide saturation of basalt and andesite melts at high pressures and temperatures. *Am. Miner.*, 67, 877–885.

Wilson, M. (1989). *Igneous Petrogenesis*. Chapman & Hall, Lond., 466 pp.

Wood, D.A., Joron, J.L. & Treuil, M. (1979). A re-appraisal of the use of trace elements to classify and discriminate between magma series erupted in different tectonic settings. *Earth Planet. Sci. Lett.*, 45, 326–336.

Wood, S.A. (1987). Thermodynamic calculations of the volatility of the platinum-group elements (PGE). The PGE content of fluids at magmatic temperatures. *Geochim. Cosmochim. Acta*, 51, 3041–3050.

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