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

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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 chalcophilic 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 magmatische Cu–Ni–PGE-sulfiidesettings is moontlik deur segregasie van ’n onmengbare sulfiidsmeltel uit ’n silikaatsandermagma, in reaksie op prosesse soos magmavermenging, vinnige afkoeling, differentiasie, en kontaminasie, geverm. Die metaaihoud van die sulfiide word deur die konsentrasie van die metale in die silikaatsandermagma, deur die partisiekoeffisientie van die silikaat-/sulfiidsmeltel (D-waardes) van die metale en die R-faktor gedurende sulfiidsegregasie beheer. Fraksionering tussen die metale vind tydens gesediere sulfiidkristallisering van die boksersbron, kristallisering van oksiede, silikate (hoofsaaklik olivien en tot ’n mindere mate ortopirokseen), segregasie van sulfiidsmeltel, en kristallisering van die sulfiidsmeltelplaas. Laasgenoemde proses kan gesoneerde ertsliggame oplewer wat bestaan uit ’n vaste oplossing van Os, Ir, Ru, Rh, Fe, en (Ni)-ryke monosulfiide kumulaaterts, en gefraksioneerde sulfiiderts wat ryk is aan Cu, Pt, en Pd. Dit is moontlik om hierdie prosesse te modelleer en om die potensiaal van ’n magmatische liggaam om ekonomiese Cu–Ni–PGE-sulfiidesettings te huuisse, te bepaal. Die opsporing van Cu–Ni–PGE-sulfiidertse kan vergemaklik word deur die toepassing van ’n aantal geochemiese instrumente. Dit is veral moeilik om die ligging van PGE-rykte horizonne binne gelaagde intrusies te bepaal omdat die etsoones gewoonlik dun is in vergelyking met die dikte van die intrusies. Variasie in Cu/Pd-verhoudings van die silikaatsandermeltel kan die posisie van sommige van hierdie horizonne afbaken, aangesien die Pd wat sterk chalcophil is, by voorkeur tydens segregasie uitgeput word, wat ’n toename in Cu/Pd van die oorliggende kumulaat wat daarna gekristalliseer het veroorsaak. Cu/Pd-verhoudings kan ook toegespas word in die plaattipe liggame soos die Uitkomst-intrusie, Mpumalanga, om die potensiaal vir toevoer-kanalitipe afsettings te bepaal, en in lavas waar hulle kan help om moontlike Noril’sk-tipe gemineraliseerde voerones na basaltiese vloeie te lokalisieer. Ander metodes om te bepaal of intrusiewe liggame aan magmavermenging en sulfiidsegregasie onderworpe was, is gebaseer op Ni-inhoudre van oliviene, Ti-inhoudre en Cr/Fe-verhoudings van spinel, en petrografiese kenmerke soos die teenuweheid van platigklaas insluituises binne ferromagnesiense fase. Se/S-verhoudings kan help om te bepaal of magmatische sulfiidertse namagmatische (metamorfe of hidrotermale) S-verliese ondergaan het. Hulle kan ook onderskei tussen ’n magmatische of sedimentêre bron van die S, en tussen ’n magmatische of hidrotermale oorsprong van die metale. Hidrotermale sulfiidertse kan verder van magmatische ertsdeurderski en deur middel van aansienlike hoë Cu/Ni- en Pd/Ir-verhoudings van eersgenoemde. Sodanige onderskeiding is belangrik omdat dit futil sou wees om hidrotermale afsettings vir magmatische ertsseering 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 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;
Chromitiferous coexisting silicates empirical observations. In many natural examples of sulphide Alternatively, determination of the D value may be based on mental data), indicating that the PGE are extremely between sulphide melt and silicate melt. The former mechanism appears to be more relevant in the case of larger intrusions (Uitkomst, 1995). This possibility will be explored in a later section.

Komatititic magmas have significantly more Ni than basalts (c. 1000 ppm), but \( D_{\text{Ni/sil}} \) 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 obtanifiable. 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

\[
D_{\text{Ni/sil}} = \frac{\text{concentration of element in sulphide melt}}{\text{concentration of element in silicate melt}}
\]

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. \( D_{\text{Ni/sil}} \) 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 represents equilibrium between sulphide melt and silicate melt, the D of the PGE between sulphide melt and silicate melt appears to be approximately 100 000.

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:

\[
R = \frac{C_L D - C_{D} D}{C_D - C_{L} D} \tag{3}
\]

where \(C_C\) and \(C_L\) are the concentrations of the metal in the sulphide and initial silicate melts, respectively, and \(D = D_{\text{sub/sil}}\). This may be rearranged to:

\[
C_C = \frac{C_L x D x (R + 1)}{(R + D)} \tag{2}
\]

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 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).
Figure 5 Element depletion \( \left( \frac{C_F}{C_L} \right) \) in magmas experiencing sulphide removal, as a function of \( D_{\text{sil/sul}} \). \( C_F \) = concentration of element in fractionated magma, \( C_L \) = concentration of element in initial magma (after Barnes et al., 1993).

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

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

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).

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 essential for meaningful modelling. Significantly, equation (2) may be simplified when D is very much greater than

\[
C_c = C_L \times (R + 1)
\]

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
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 metals by means of the incorporation of Ni (and perhaps S, based on experimental and empirical data of Barnes et al., 1997 and Naldrett et al., 1997) into olivine, resulting in the crystallization of pentlandite at lower temperatures (Kullerud et al., 1969). Ni is equally rejected by mss in komatiite-related ores (D_{mss/sulf} 4.3), later to be recrystallized to chalcopyrite (Kullerud et al., 1969). Ni partitioning into mss increases with falling temperature, 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 pyrrhotite 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...
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

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**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).

**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., 1993) 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 $D_{silicate/Pd}$ 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 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 continuously 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-
Olivine from basaltic magma will deplete its Ni content by
for Ni in igneous rocks (besides sulphides)
of Ni for olivine, as little as 5% fractional crystallization of
abundant refractory phase in the upper mantle (around 65
east of the southeastern lobe of the Complex. The sills contain
dotite sills of up to 100 m in thickness have been intersected by
dhole 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
Pd/Pt 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 devolatilization.

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.%; Maaße & Aoki, 1977). Olivine is also the main carrier for Ni in igneous rocks (besides sulphides) (D_{olivite} 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_{olivite} 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).](image-url)
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 (Brüggmann 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 Brüggmann 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 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 Brüggmann et al., 1993).

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 \( D_{\text{sil}} \) 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).
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, cementic 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_{Se/V} = 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^-5 (Taylor & McLennan, 1985). As both Se and S are principally hosted by sulphides, Se/S of primary magmas may fall into the same range.

![Figure 18](https://example.com/figure18.png)  
**Figure 18** Density variations in fractionating magma of B_2 Bushveld parental composition (at 5 – 50% crystallization, 1 atmosphere confining P, modified after Naldrett et al., 1986).

![Figure 19](https://example.com/figure19.png)  
**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).
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 to 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 $930 \times 10^{-6}$. 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 $50 \times 10^{-6}$. Hence, most ore deposits have Se/S ratios between 50 and $930 \times 10^{-6}$.

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 $5000 \times 10^{-6}$, far exceeding the range of magmatic values. This has been explained as a result of metamorphic sulphur loss (Cawthorn & Meyer, 1993; Maier & Barnes, 1996) transforming an original magmatic ore dominated by po + cp into a bn–cp–mag assemblage, according to the following equation:

$$5CuFeS_2 + 5FeS + 6H_2O + 8O_2 = Cu_3FeS_4 + 3Fe_3O_4 + 6H_2S + 5SO_2$$

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 ($160 \times 10^{-6}$). Thus:

$$S_{\text{lost}} = S_{\text{original}} - S_{\text{left}}$$  \hspace{1cm} (i)
$$S_{\text{left}} = S_{\text{present}} \times \text{mass correction (M)}$$  \hspace{1cm} (ii)
$$S_{\text{original}} = (Se/160 \times 10^{-6}) \times \text{mass correction (M)}$$  \hspace{1cm} (iii)

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

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

$$S_{\text{lost}} = (Se/160 \times 10^{-6}) \times M - S_{\text{present}} \times M$$  \hspace{1cm} (iv)
$$\% S_{\text{lost}} = ((S_{\text{original}} - S_{\text{left}}) \times 100)/S_{\text{original}}$$  \hspace{1cm} (v)
and substituting (ii) and (iii) into (v) gives:

$$\% S_{\text{lost}} = ((Se/160 \times 10^{-6}) - S_{\text{present}}(\text{in ppm})) \times 100/(Se/160 \times 10^{-6})$$  \hspace{1cm} (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 $38000/S_{\text{present}}$. Average PGE contents, normalized to 100% sulphides, may then be compared to those from other sulphide deposits. The above procedure is,
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 Stormyrpluten, 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 gabbronite. Cu-rich sulphides are not uncommon in differentiated rocks such as gabbronorites and diorites, for example at St. Charles, Quebec (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

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


Determining 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-porphyrines (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
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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