

Magmatic Ni-Cu versus PGE deposits: Contrasting genetic controls and exploration implications

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ABSTRACT

Both Ni-Cu and PGE deposits are associated with mafic and ultramafic rocks, but the former often occur in dynamic magmatic systems such as lava channels and magma conduits whereas the later occur in larger layered intrusions. The contrasting modes of occurrence appear to be related to different degrees of preferential partitioning of the metals (PGE versus Cu and Ni) into segregating sulfide liquid and different concentration processes of the sulfide liquid during the formation of the ores.

Primary magmas derived from partial melting of the upper mantle are fertile in PGE, Ni and Cu only when the molten sulfides are completely dissolved in the magmas. This requires a high degree of partial melting of the mantle, perhaps higher than 30 percent. The partial melts usually have basaltic to komatiitic compositions, and are unlikely to achieve sulfide saturation during ascent to the crust. Fractional crystallization and crustal contamination are the most important processes known to have induced sulfide saturation in magma upon intrusion. Sulfide liquid segregated in a large chamber may achieve high R-factors required for the formation of reef-type PGE deposits. Crustal assimilation appears to be most effective in dynamic lava channels and magma conduits. A large volume of sulfide liquid segregated from magma in such dynamic environments often has a lower R-factor, and relatively lower metal concentrations. Such metal-poor sulfide liquid needs to be deposited in restricted localities, and/or to be upgraded in metals by reacting with new surges of magma, to become a Ni-Cu sulfide deposit.

Because of their extremely high partition coefficient between sulfide liquid and magma, PGE will become significantly depleted in magma even at small amounts of sulfide segregation. Copper, on the other hand, will be much less depleted because of its relatively low partition coefficient. Thus, Pd/Cu ratios in whole rocks can be used to detect PGE mineralization associated with small sulfide segregation in large layered intrusion. The whole rock Cu/Zr ratio is sensitive to large amounts of sulfide liquid segregation from magma and thus is a useful tool for Ni-Cu exploration. Nickel contents of olivine can also be used to identify Ni depletion in magma associated with large amounts of sulfide segregation.

Introduction

Magmatic sulfide deposits can be divided into two sub-types according to metal production, *i.e.* Ni-Cu deposits and PGE (platinum-group elements) deposits. Nickel and copper may be the by-products of PGE deposits, and PGE may be the by-products of Ni-Cu deposits. Examples of Ni-Cu deposits include the Kambalda deposit in western Australia (Lesher, 1987), the Jinchuan deposit in western China (Chai and Naldrett, 1992), the Noril'sk deposit in Siberia, Russia (Duzhikov *et al.*, 1992; Naldrett *et al.*, 1996), the Voisey's Bay deposit in northern Labrador, Canada (Li and Naldrett, 1999) and the Uitkomst deposit in South Africa (Gauert *et al.*, 1995). All these deposits occur in dynamic magmatic systems such as lava channels and magma conduits. The Ni-Cu deposits at Sudbury, Canada, are related

to a unique astrobleme event (*i.e.* meteorite impact fusion, see Grieve *et al.*, 1991 and references therein), and are not relevant to our understanding of other Ni-Cu deposits formed by continental magmatism. Important PGE deposits occur in large layered intrusions. These include the UG-2 chromitite and Merensky Reef of the Bushveld Complex in South Africa (Eales and Cawthorn, 1996 and references therein), the J-M Reef of the Stillwater Complex in Montana, USA (McCallum, 1996 and references therein), and the Main Sulfide Zone of the Great Dyke in Zimbabwe (Wilson *et al.*, 1989).

Critical to the understanding of the different occurrences of Ni-Cu and PGE deposits are the different geochemical behaviours of Ni and Cu versus PGE in related igneous processes, particularly their different

degree of preferential partitioning into sulfide liquid segregated from magma and their different compatibility with respect to other phases during partial melting of the upper mantle and subsequent magma differentiation. Therefore, this review begins with a summary of existing knowledge on these subjects. Nickel, copper and PGE are closely associated with sulfides, so a second section focuses on the processes of sulfide segregation and concentration during magma differentiation. A third matter concerns the development of new exploration techniques for both types of deposits.

Sulfur solubility in magma

Experiments by Maclean (1969), Shima and Naldrett (1975), and Carroll and Rutherford (1988) have demonstrated that for f_{O_2} below QFM (the quartz-fayalite-magnetite buffer) sulfur is present in magma predominantly as FeS according to the reaction:



At equilibrium, the relationship of the mole fraction of FeS (N_{FeS}) with other variables is described by the expression:

$$\ln N_{\text{FeS}} = K + \frac{1}{2} (\ln f_{\text{S}_2} / \ln f_{\text{O}_2}) + \ln a_{\text{FeO}} - \ln r_{\text{FeS}} \quad (2)$$

where r_{FeS} is the rational activity coefficient for FeS in the melt, K is the equilibrium constant, and f_{S_2} and f_{O_2} are the fugacities of sulfur and oxygen, respectively. Sulfide liquid saturation occurs when the activities of FeS and FeO in the sulfide melt and the silicate melt are equal. The solubility of S is therefore mainly a function of a_{FeO} in the melt. If the activity coefficient of FeO and the ratio of $f_{\text{S}_2}/f_{\text{O}_2}$ are assumed to be constant over the range of interest, then a_{FeO} is proportional to N_{FeO} , and the sulfide solubility is dependent only on the concentration of FeO and temperature.

One way of representing S solubility with equation (2) would be to use regular solution theory in order to obtain expressions for activity coefficients, in conjunction with the standard state properties of FeO and FeS liquids. This procedure requires the evaluation of a large number of regression coefficients (see Ghiorso and Sack, 1995). A relatively simple, empirical regression equation calibrated using sulfide saturated oceanic basalts has been given by Li *et al.* (2001):

$$S = 1431 + 221 \times (\text{FeO} - 9) + 5 \times (T - 1200) \quad (3)$$

where S is in ppm, FeO is in mole percent, and T is temperature in degree centigrade. The second term of the equation describes the effect of FeO content and the third term describes the effect of temperature, in which 9 and 1200 are chosen to represent the intermediate values of FeO content and temperature of a basaltic magma, respectively. This equation is applicable to basaltic systems at constant total pressure.

Pressure has a negative effect on the solubility of S in magma (Wendlandt, 1982; Mavrogenes and O'Neill, 1999). As a result, primary mantle magmas will be likely S-undersaturated upon intrusion (Mavrogenes and O'Neill, 1999), and for sulfide saturation to occur, other processes are required.

Partitioning of Ni, Cu and PGE between sulfide and silicate melts

Nickel, copper, and PGE are chalcophile elements and strongly partition into a sulfide liquid that segregated from magma. The degree of such preferential partitioning can be described in terms of a partition coefficient (D) between the co-existing melts:

$$D^{\text{sul. liquid/sil. melt}} = \frac{\text{concentration of element in sulphide melt}}{\text{concentration of element in silicate melt}} \quad (4)$$

The experimental D values for PGE vary around 10^4 to 10^5 (Bezmen *et al.*, 1994; Peach *et al.*, 1994; Fleet *et al.*, 1996; Crocket *et al.*, 1997), which are similar to the empirical values of the MORB samples (Peach *et al.*, 1990). The D values for Cu and Ni are much lower than that of PGE, ranging from 200 to 1400 and from 200 to 500, respectively, and strongly depend on oxygen fugacity (Naldrett, 1989; Peach and Mathez, 1993; Gaetani and Grove, 1997).

When a very small amount of immiscible sulfide liquid segregated from a silicate melt, the concentration of any metal in the sulfide liquid (C_c) is related to its concentration in the silicate melt (C_i) after the attainment of equilibrium by the partition coefficient ($D^{\text{sul. liquid/sil. melt}}$) by the expression:

$$C_c = C_i \times D, \quad (5)$$

which is a rearrangement of equation (4). It is often more useful to be able to model the composition of the sulfide liquid in terms of the initial composition of the silicate magma (C_i). In this case the concentration of an element in the sulfide liquid is best described by the expression given by Campbell and Naldrett (1979):

$$C_c = \frac{C_i D (R + 1)}{(R + D)}, \quad (6)$$

where R is the mass ratio of silicate melt to sulfide liquid.

The R -factor, as it has been formulated, is largely applicable to describe the PGE concentration by sulfide liquid segregation from magma. A high R -factor means that relatively less immiscible sulfide liquid and a low R -factor means that more immiscible sulfide liquid segregated from the magma. The effect of the R -factor on metal tenors in the sulfide is much larger for PGE than for Ni and Cu because the former have much higher D values. R -factors for typical reef-type PGE deposits such as the Merensky Reef and the J-M Reef are estimated to be higher than 10^5 . Estimated R -factors for Ni-Cu deposits are as low as a few hundred (Naldrett, 1989).

Fertile parental magma

Primary magmas often form by melting of the upper mantle related to mantle plumes or subduction. The mineralogy of the upper mantle typically comprises olivine, orthopyroxene and clinopyroxene with minor garnet, spinel, amphibole and mica, and trace phases such as carbonate, apatite, sphene, perovskite and sulfide minerals. Nickel, copper and PGE are mainly hosted by sulfide minerals. Some PGE such as Ir, Os, Ru may also be hosted by spinel (Capobianco and Drake, 1990). Nickel is also hosted by olivine. The melting behaviour of the upper mantle is complex, depending on depth of melting and composition. In general, the first partial melts extract most phases of the upper mantle. With the increase of partial melting, phases of lower abundance and refractivity may become completely consumed and subsequent melts will become relatively enriched in components from relatively more abundant and refractory phases such as olivine, orthopyroxene and clinopyroxene. Hence, magma of high degree-partial melting will be enriched in MgO and diluted in alkaline components. Sulfide minerals have lower melting temperatures than most silicates and would mostly melt during the early stage or a small degree of partial melting. Because of their high solubility in a sulfide liquid, most of the PGE in the upper mantle will be dissolved in an initial sulfide liquid during partial melting. Final distributions of the PGE are controlled by the physical distribution of the initial sulfide liquid. Typical upper mantle is estimated to contain about 0.07 % sulfides (mainly pyrrhotite, Lorand, 1990). The solubility of sulfide in a silicate melt under upper mantle condition is between 0.1-0.2% (Mavrogenes and O'Neil, 1999). As a result, only when partial melting of the upper mantle reaches about 30% will the molten sulfide become completely dissolved in the silicate melt (Barnes and Maier, 1999). If the degree of partial melting is smaller, the molten sulfide may not all be dissolved in the silicate melt, and the undissolved portion may remain in the upper mantle because of its higher density relative to the silicate melt. In this case, most of Ni, Cu, and PGE will stay behind in the upper mantle because they partition strongly into the sulfide liquid, and the silicate melt will be poor in these metals. In contrast, magmas formed by a large degree of partial melting such as komatiitic and high-MgO basaltic magma that can dissolve all molten sulfide will be rich in these metals (Keays, 1995). A high degree of partial melting that can dissolve all sulfide is thus important for the formation of PGE deposits.

It should be pointed out that the immediate parental magmas for both Ni-Cu and PGE deposits do not need to be the primary partial melts of the upper mantle. They can be the differentiated liquids of primary magmas that have not experienced significant chalcophile depletion *en route* to the crust. Early sulfide segregation during magma ascent is the main cause for chalcophile depletion in magma before reaching upper crustal levels. The impact of early sulfide segregation on

chalcophile metal depletion in magmas is much more significant for PGE than for Ni and Cu. Olivine crystallization can cause nickel depletion, coupled with a slight enrichment of PGE and Cu in the residual magma, producing a fractionated magma that is not favourable for Ni deposits, but may still be capable of forming PGE and Cu mineralization. A lack of large volumes of such fractionated magma, however, often limits the formation of significant PGE and Cu sulfide ore bodies during the late stages of crystallization.

Onset of sulfide immiscibility and segregation

The foregoing discussions on the solubility of S in magma indicate that, upon ascending to the crust, oxidation as well as falling temperature and FeO content may induce sulfide saturation in magma. These are intrinsic variables of the magma and are directly related to important igneous processes such as crystallization, magma mixing and crustal contamination. Thus, in this section we have chosen to examine the inter-relationships of these processes. Rather than summarizing existing models, however, we shall explore the relationships between the above-mentioned igneous processes and segregation and concentration processes of the sulfide melt that are critical to the understanding of different magmatic systems for both Ni-Cu and PGE deposits.

The effect of crystallization on S-solubility

Primary magmas derived from the upper mantle start to crystallise different phases such as olivine, orthopyroxene, clinopyroxene, plagioclase, etc. according to their solidus temperatures which in turn depend on the pressure and composition of the magmas. For example, if the magma is relatively rich in calcium, clinopyroxene may crystallize before orthopyroxene. If the magma is relatively rich in SiO₂, olivine crystallized earlier may be converted to orthopyroxene. The details of crystallization sequences can be determined by high temperature experiments or by thermodynamic calculations.

Li *et al.* (2001) have used the silicate liquid model of Ghiorso and Sack (1995) to calculate the intrinsic variables of a basaltic magma represented by the chilled margin composition of the Bushveld Complex (B1 magma of Harmer and Sharpe, 1985). The results are applicable not only to the Bushveld Complex but also other large layered intrusions, and thus are summarised below. Under the conditions of QFM-1 and 100 bars, olivine crystallizes between 1358 and 1312 °C, followed by orthopyroxene between 1312 and 1301 °C, then by orthopyroxene plus spinel between 1301 and 1166 °C. Plagioclase starts to crystallize at 1166 °C and clinopyroxene starts to crystallize at 1158 °C. This crystallization sequence is in excellent agreement with that observed in the Lower and Critical Zones of the Bushveld Complex, bearing in mind the numerous reversals in crystallization sequence within this sequence

that are interpreted to be the result of magma replenishments to the chamber (*e.g.* Eales *et al.*, 1990).

Cawthorn (personal communications) pointed out that we mistyped one value in our calculation of S solubility of a fractionated magma (point C in Figure 4 of Li *et al.*, 2001), resulting in a slight change of the S solubility curve. A corrected curve is now shown in Figure 1a. Its petrological implication is summarized below. During the crystallization of olivine and orthopyroxene S solubility decreases rapidly due to the large decrease in temperature coupled with a minor decrease in FeO content in the magma. During the crystallization of plagioclase, the FeO content in the residual magma rises markedly and the rate of change of temperature is much slower. Consequently, the S solubility increases slightly. This trend continues until clinopyroxene joins plagioclase on the liquidus during the later stages of crystallization. Consider an initial magma input to the chamber corresponding to point A (Figure 1a) that contains ~900ppm S which is within the range of S contents in the chilled B1 marginal samples and sills of the Bushveld Complex (Davies and Tredoux, 1985). As the magma crystallizes, its S content will rise along the path A to S (Figure 1a), reaching sulfide saturation after about 20 percent crystallization. Further crystallization will cause sulfide saturation and immiscible sulfide droplets will form. If the immiscible sulfide droplets settle out of the magma once they form (*i.e.* fractional segregation), the content of S dissolved in the residual magma will decrease along the solubility curve from S to B. After the magma has reached point B, the solubility curve turns slightly upward due to plagioclase crystallization. Because the rate of increase in S solubility is lower than the rate of increase in S content in the residual magma, the residual magma still remains sulfide saturated. Additional crystallization after point R causes a small decrease in S solubility in the residual magma, and the residual magma continues to remain sulfide saturated thereafter.

The effect of magma mixing on S-solubility

Li *et al.* (2001) and Naldrett and von Gruenewaldt (1989) suggested that mixing of resident magma with primitive replenishing magma may cause sulfide saturation at the level of the Merensky Reef, but Cawthorn (1999) argued that such mixtures would be sulfide undersaturated. It has since been pointed out to us by Cawthorn (personal communication) that the arguments from both sides were based on a flawed comparison of magma formed by mixing with magma formed by fractionation. To evaluate the effect of magma mixing on S-solubility, the content of S in the hybrid magma must be compared to the S solubility of the hybrid magma itself, but not to that of a fractionated magma with the same Zr content (as used by Li *et al.*, 2001) or MgO content (as used by Cawthorn, 1999). We have used MELTS (Ghiorso and Sack, 1995) to calculate the liquidus temperatures of end member magmas and their hybrids. We have then used equation (3) above to

calculate the solubility of S in the hybrid magmas. The results are shown in Figure 1b. Line 1 represents the solubility of S in the hybrid magmas formed by mixing of resident magma (a residual magma formed by 30% crystallization of B1 magma, and represented by point R in Figure 1a) with variable amounts of primitive magma (B1 magma of Harmer and Sharpe, 1985) under the same conditions as those used in the modeling of crystallization above (100 bars, QFM-1 buffer). Line 4 represents the contents of S in the hybrid magmas. It should be pointed out that the hybrid magmas are all supersaturated with solid phases, *i.e.* the mixing temperatures are lower than their liquidus temperatures, up to ~10 °C. When the amounts of new input are less than 70 weight %, the hybrid magmas are supersaturated with olivine. When the amounts of new input are between 70 to 40 weight %, the hybrid magmas are supersaturated with orthopyroxene. When the amounts of new input are below 40, the hybrid magmas are super saturated with orthopyroxene and spinel. If the compositions of the hybrid magmas are adjusted for crystallization resulting from super cooling, the solubility of S in the hybrid magmas will decrease slightly, between 1 to 5 ppm. It is seen from Figure 1b that the solubility of S in the hybrid magmas is always higher than their S contents. Thus, mixing of resident magma with B1 magma does not appear to yield sulfide saturation. Instead, Cawthorn (1996) suggested replenishment with mafic magma parental to the Critical Zone (B2 magma of Harmer and Sharpe, 1985). Line 2 in Figure 1b is calculated for the mixing of resident magma with B2 magma under the same conditions. The liquidus temperatures of the hybrids in this case are always slightly lower than their mixing temperatures (up to 3 °C), *i.e.* the hybrid magmas are slightly superheated. Compared to the previous example, the solubility of S in the hybrid magmas in this case is slightly lower, but still higher than the S contents in the hybrids even if the content of S in the B2 magma is assumed to be the same as in B1 (~900ppm S). In reality, the S content of B2 magma may be much lower (Davies and Tredoux, 1985). This suggests that replenishment with B2 magma does not result in sulfide saturation either. Kruger (1992) suggested that relatively dense B3 magma replenishing the chamber at the level of the Merensky Reef pooled at the bottom of the chamber and cooled the supernatant resident magma, resulting in super saturation of sulfide in the latter, but this model has to be questioned on geochemical grounds; Maier and Barnes (1999) showed that all cumulate rocks below the reefs are highly enriched in PGE relative to the parental magmas and thus the resident magma should have been depleted in PGE.

A further possibility is that the new input was more oxidized due to crustal contamination in a staging chamber (Maier *et al.*, 2000), and thus had much less FeO. Line 3 is calculated for a more oxidized B2 magma (at QFM versus QFM-1). The resulting hybrid magmas

in this case have slightly lower S solubility, but still higher than the contents of S in the mixed magmas.

It is important to point out that in a binary plot of S solubility versus mixing proportion, sulfide saturation will not occur during magma mixing unless both end members are sulfide saturated. This is because the S solubility line of mixed magma remains straight with changing composition and temperature of two end members. Thus, replenishment with any S under-saturated magma does not result in sulfide saturation in the hybrids and it appears that the mechanism for the PGE mineralization of the Merensky Reef needs to be re-examined.

Crustal contamination

Contamination of basaltic magma with siliceous crustal rocks can result in sulfide super-saturation even if the crustal rocks do not contain sulfide because the

contamination can lower both the content of FeO and temperature in the resulting hybrid, and thus lower the ability of the hybrid to dissolve sulfides (Irvine, 1975; Li and Naldrett, 1993). In addition, contamination may have involved the ingestion of crustal sulfur from country rocks. The isotopic signature of the sulfide ores at Noril'sk (Grinenko, 1985), Uitkomst (Gauert *et al.*, 1995) and Voisey's Bay (Ripley *et al.*, 1999) indicates that addition of crustal sulfur was involved in the genesis of these deposits. Bulk assimilation is not the only mechanism for magma to gain crustal sulfur from country rocks. If the sulfides in the country rocks occur as pyrite, sulfur may be relieved to magma through the conversion of pyrite to pyrrhotite during contact metamorphism. This process is believed to be important for the formation of disseminated sulfides in the basal unit of the Duluth Complex (Ripley and Alawi, 1986).

Sulfide deposition

In a large layered intrusion, the sulfide droplets that segregated from magma will eventually settle out of the magma and be deposited on the floor of the magma chamber to form a sulfide zone once magma convection eases and the gravity force takes control. In a magma conduit system, sulfide deposition is mainly controlled by fluid dynamics. Favourable environments for sulfide deposition are the wider parts of a magma conduit and its entry to a large magma chamber where the velocity of magma suddenly decreases. The Voisey's Bay Ni-Cu deposit is a good example for the formation of a Ni-Cu deposit in a dynamic magma conduit system (Li and Naldrett, 1999). The first wave of magma carried a large volume of sulfide liquid through a conduit and deposited it in the wider part within the conduit and the entrance of the conduit to an upper chamber. The sulfide was subsequently upgraded in Ni and Cu by a new surge of magma relatively undepleted in chalcophile elements magma using the same conduit.

Similarly, the Noril'sk deposits are also related to a magma conduit system where large volumes of magmas have passed through (*e.g.* Naldrett *et al.*, 1996). The Noril'sk ores, however, contain much higher PGE because, firstly, their parental magmas were more primitive and hence contained much higher PGE and, secondly, the relevant R-factors during sulfide segregation were much higher.

New exploration techniques

Calculation of the composition of sulfide liquid

Sulfide ores are often diluted with silicates and/or oxides, and whole rock assay values of Ni, Cu and PGE do not represent their concentrations in the sulfide portion. To understand the quality of bulk sulfide and its genesis we need to know the concentrations of Ni, Cu and PGE in the sulfide liquid. Suppose we have found disseminated sulfides at an early stage of exploration, we need to know the concentrations of Ni, Cu and PGE in the sulfide portion in order to evaluate whether or not we should continue our search for zones of higher

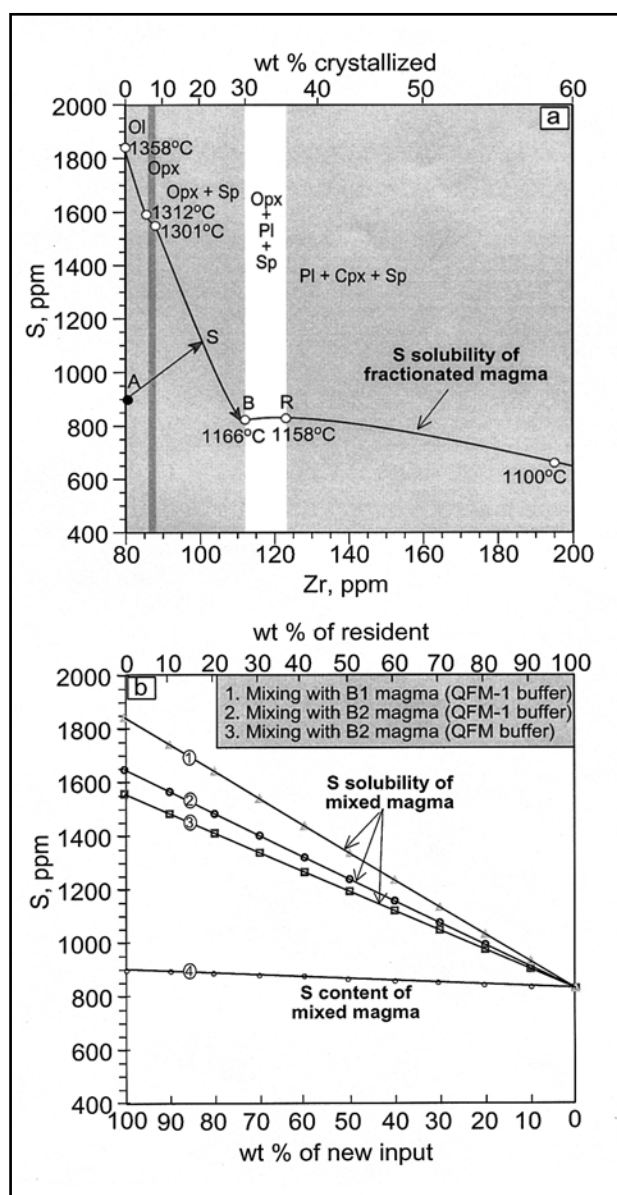


Figure 1. S-solubility of magma formed by fractionation and mixing. See text for discussion.

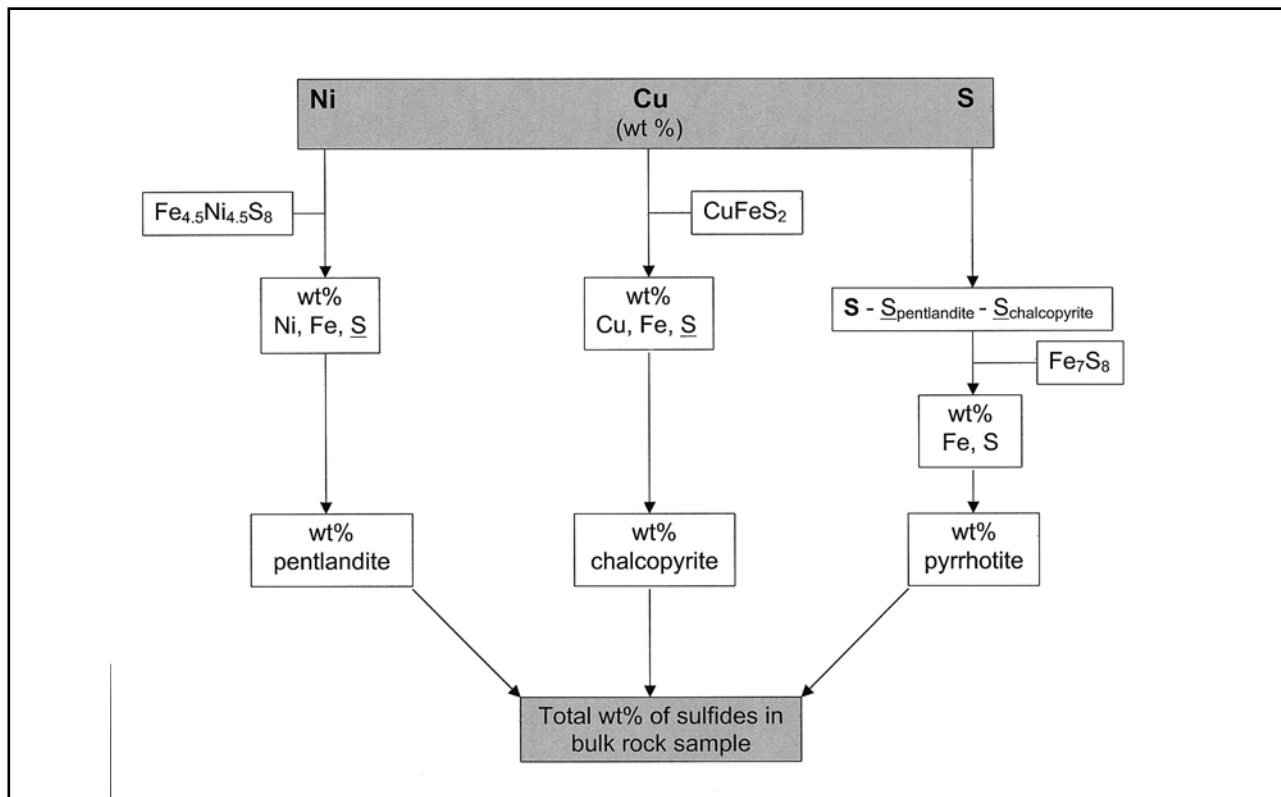


Figure 2. Procedure of estimating sulfide content in rock sample using whole rock assay

sulfide concentration. Further exploration may not be warranted if the potential massive sulfide zones do not yield economic grades of metals. As we have discussed above with respect to genetic processes, we need to know the composition of the sulfide liquid in order to understand the genetic controls such as the composition of the parental magma. Thus, the recalculation may assist in a model-driven approach to exploration target evaluation.

The assumption and procedure used for calculating bulk sulfide composition from whole rock Ni, Cu and S analyses were first introduced by Naldrett and Duke (1980). Typically, a magmatic sulfide melt crystallises primary pyrrhotite, pentlandite and chalcopyrite. Among them pentlandite is the only Ni-bearing mineral and chalcopyrite is the only Cu-bearing mineral. Pyrrhotite is a Fe-sulfide with only minor Ni and trace Cu. If we ignore Ni and Cu in pyrrhotite, we can use the assay values of Ni and Cu in whole rock and standard mineral compositions or actual mineral analysis to calculate the percentage of pentlandite ($\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_8$ or actual mineral analysis) and chalcopyrite (CuFeS_2), respectively, in a given sample. We can then use the balance of S left to calculate the percentage of pyrrhotite (Fe_7S_8) in the sample. The sum of these three minerals represents the total percentage of sulfides in the sample. The metal values in an original assay divided by this value represent their concentrations in 100% sulfide, e.g. contents in original sulfide liquid. Figure 2 is a flow chart summarising the procedure. It should be pointed out that the presence of other Cu-bearing minerals such

as cubanite, and trace to minor amounts of Ni and Cu in pyrrhotite, have little effect on the result of the calculation. Some Ni in an assay may come from silicate minerals such as olivine and orthopyroxene, depending on the contents of these phases in the sample and the analytical methods used. Correction should be applied to the samples in which such contribution cannot be ignored, particularly when the samples contain low amounts of sulfides. In practice, samples containing less than 0.5 wt % S are often excluded in such calculations because of high uncertainty associated with the correction and potential errors propagated from S analyses at low concentration.

Use of Cu/Pd and Cu/Zr ratios

The determination of whether or not an igneous body has experienced segregation of sulfide liquid is of considerable use for exploration target evaluation, particularly for PGE deposits. Maier *et al.* (1996) showed that Cu/Pd ratios of silicate rocks in the Bushveld Complex show a distinct increase in the vicinity of the PGE-rich horizon due to early sulfide segregation (Figure 3). The Cu/Pd ratio is much lower in the segregating sulfide melt than in the host silicate magma, because $D_{\text{sul/sil}}$ of Pd far exceeds that of Cu. In contrast, the residual silicate melt will have elevated Cu/Pd ratios, and consequently cumulate rocks containing trapped residual silicate magma will have high Cu/Pd ratios.

The Cu/Pd ratios can also be used to investigate lava flows that have experienced sulfide segregation. The basalts associated with the Noril'sk deposits of Siberia

provide a good example for such a study. The deposits are hosted by sill-like intrusive bodies thought to represent conduits for extensive flood basalts in the region (Naldrett *et al.*, 1996). The basaltic suite comprises 7 sequences with different Cu/Pd ratios (Figure 4, from Maier *et al.*, 1998). The magmas of the ND sequence may have experienced early sulfide liquid segregation, as indicated by the sharp increase in Cu/Pd ratio in this sequence. The sulfide may have been left behind in the conduits such as those represented by the mineralized Talnakh-type intrusions (Brügmann *et al.*, 1993; Naldrett *et al.*, 1996). The gradual decrease in Cu/Pd ratio throughout the overlying MR and MK sequences may then be interpreted as a result of the streaming of magmas over increasingly PGE-rich sulfide liquids in the conduits.

The Cu/Zr ratios in rocks is governed by similar factors as the Cu/Pd ratio in that we are comparing the concentrations of a relatively highly chalcophile element, copper, with that of a non-chalcophile element, zirconium. These two elements are similarly incompatible during silicate crystallisation. Typical undepleted continental flood basalts have Cu/Zr ratios around unity while lavas depleted in metals due to sulfide segregation have Cu/Zr ratios less than unity (Lightfoot *et al.*, 1994). Such a decrease in Cu/Zr ratios resulting from sulfide segregation has also been observed in the intrusive rocks at Voisey's Bay, Labrador (Li and Naldrett, 1999).

Compared to Cu/Pd ratios, Cu/Zr ratios are less sensitive to small amounts of sulfide liquid segregation and thus are less useful for the detection of reef-type PGE deposits in large layered intrusions.

The above discussion is only applicable to relatively fresh rocks in which the distributions of these elements have not been disturbed by secondary processes such as alteration and metamorphism.

Olivine composition

The content of Ni in olivine is primarily controlled by the composition of magma from which the olivine crystallizes. The most important processes that control the variation of Ni in magma are sulfide segregation and olivine crystallization. The relative impact of these two processes on Ni depletion in magma may be determined from the variation of Ni and forsterite (Mg_2SiO_4) contents in olivine. Sulfide segregation alone will cause Ni depletion in the magma with little change in the FeO/MgO ratio. Consequently, olivine crystallizing after sulfide segregation will be depleted in Ni while its major element composition remains almost unchanged. In contrast, olivine crystallization will decrease the Ni concentration and increase the FeO/MgO ratio in the magma, and olivine crystallizing later will have decreased Ni and forsterite contents.

One can use thermodynamic or numerical calculations to model olivine fractionation. An example of the former approach is to use the silicate liquid model

of Ghiorso and Sack (1995) when the parental magma composition is known.

If the composition of the parental magma is unknown, one can use a numerical method, which only requires knowledge of the Fe-Mg and Fe-Ni exchange coefficients between olivine and magma. Roeder and Emslie (1970) have shown that in the case of olivine crystallizing from basaltic magma the ratio $(\text{FeO/MgO})_{\text{magma}}/(\text{FeO/MgO})_{\text{olivine}}$ is constant with a value of 3.3. We have used the experimental data of basaltic to komatiitic systems (Arndt, 1977; Nabelek, 1980; Seifert *et al.*, 1988; Snyder and Carmichael, 1992) to calibrate the composition dependence of the partition coefficient of Ni between olivine and silicate melts (D):

$$\ln D = 5.67 - 1.38 \ln \text{MgO} - 0.25 (\text{FeO/MgO}) \quad (7)$$

where both FeO and MgO are in wt % concentration in the magma. The influence of temperature on the partition coefficient is not seen by the regression analysis of the experimental data.

The exploration application of the modeling results is straightforward. If the degree of Ni depletion in olivine is more significant than the depletion caused by crystallisation of silicate minerals, sulfide segregation may have been involved, and thus effort to look for the sulfide is justified.

It should be pointed out, however, that too much Ni depletion or pervasive Ni depletion in olivine throughout an entire intrusion is not a good exploration indication for the intrusion. Suppose olivine in the intrusion contains only 500ppm Ni, using the intermediate partition coefficients of 10 and 500 for Ni between olivine and a basaltic magma and between sulfide liquid and the magma, respectively, the magma from which the olivine crystallised is estimated to have contained only 50 ppm Ni. The possible sulfide liquid segregated from such magma is estimated to contain less than 2.5 wt % Ni. The quality of such sulfide may not be economically important without subsequent metal upgrading by new surges of magmas.

Metal upgrading processes may occur when new, Ni-undepleted magmas stream over Ni-poor sulfide liquids segregated previously. The reaction of the sulfide with new magma will result in higher chalcophile element contents in the sulfide. As this proceeds, Ni will become enriched in the sulfide and the new magma will lose less Ni to the sulfide. As a result, the last magma will be less Ni depleted, and the olivine crystallizing from it will contain higher Ni. This process has been found to be important for the Voisey's Bay deposit (Li and Naldrett, 1999).

The above discussions only apply to primary olivine that has not undergone compositional modification after crystallisation. In many intrusions there are two re-equilibration processes that may modify the composition of olivine. These are (1) the effect of trapped liquid crystallisation referred as trapped liquid shift (Barnes,

1986), and (2) reaction with trapped sulfide liquid. Trapped liquid shift of olivine composition occurs once a cumulate starts to cool and olivine crystallizes from the intercumulus liquid, nucleating on a core of primary cumulus olivine. The trapped liquid fractionates rapidly, so that the additional olivine becomes much richer in the fayalite (Fe_2SiO_4) component. In the interval taken by any reasonably large intrusion to cool, the relatively rapid rates of diffusion of Fe and Mg within the olivine structure will result in homogenization of the olivine, so that the resulting product will be a homogenous olivine that is significantly richer in fayalite than the original cumulus material. Similarly, the content of Ni in the final product will be lower than the original cumulus phase. If the composition of the cumulus assemblage and the amount of trapped liquid are known, then a correction on the shift can be applied using thermodynamic calculations.

The Fe-Ni exchange reaction between olivine and sulfide liquid occurs when olivines of different composition are immersed in a sulfide liquid of a uniform composition according to the following:



Such reaction results in higher Ni contents in more Fe rich olivine, which is the opposite trend of that produced by normal fractional crystallisation of olivine, and has been seen in the heavily sulfide mineralized rocks of the Voisey's Bay deposit (Li and Naldrett, 1999). Thus sulfide-mineralized samples should be treated separately when one tries to determine different controls on olivine composition.

Nickel depletion in olivine is not sensitive to small amounts of sulfide liquid segregation from magma. Hence, it is not a useful exploration tool for reef-type PGE deposits.

Notably, we are not aware of any example of discovery of a Ni-Cu sulfide deposit using olivine geochemistry alone, but the discussion above serves as a step forward in geochemical exploration.

Summary

Because of their chalcophile affinity, PGE and Cu, and to a lesser degree Ni, are mainly hosted in sulfide minerals in the upper mantle. Sulfide minerals usually

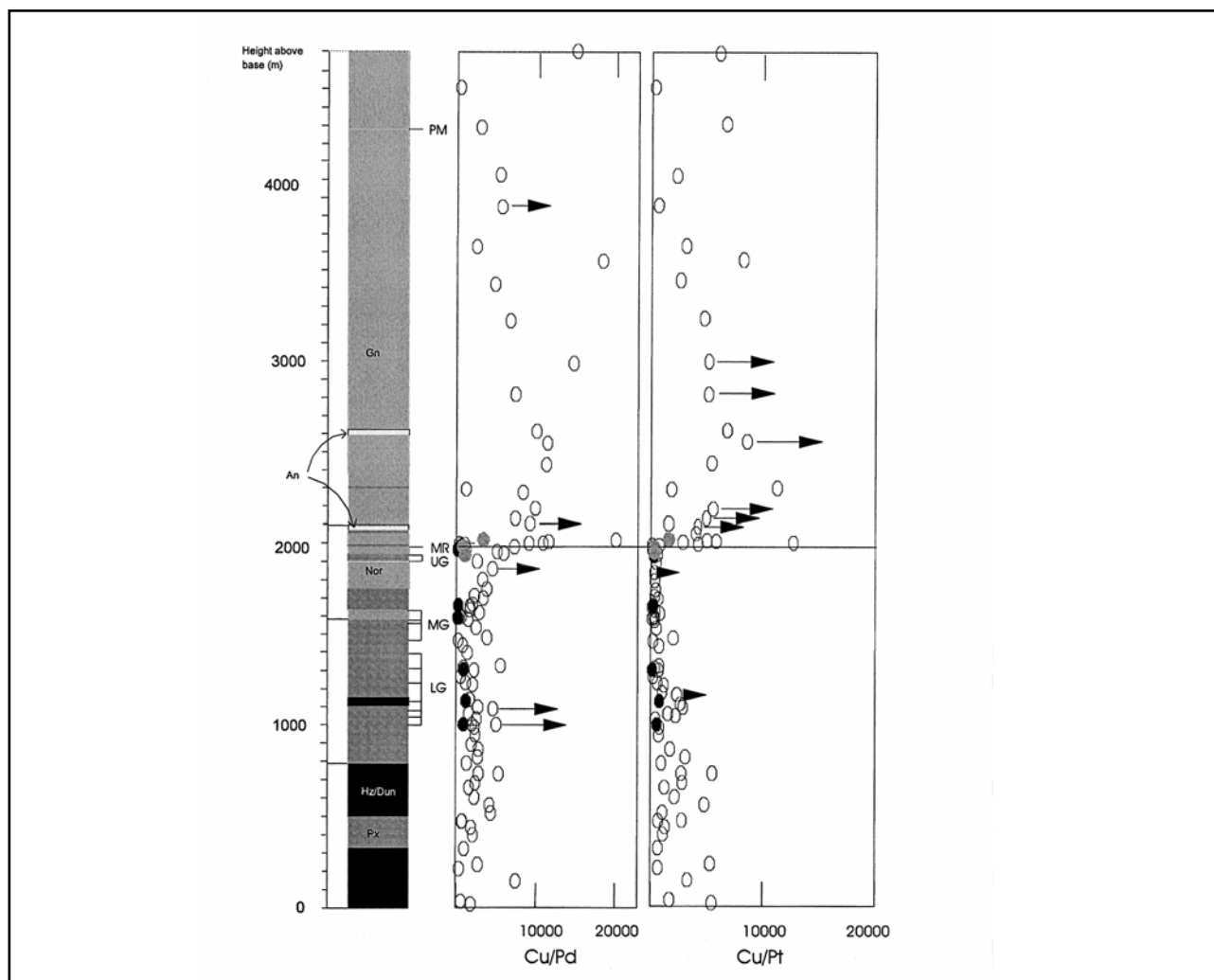


Figure 3. Cu/Pd and Cu/Pt ratios of silicate rocks (open circles), chromitites (solid circles), and sulfide-bearing reefs (shaded circles) in the Lower, Critical, and Main zones at the Union section, Bushveld Complex (from Maier *et al.*, 1996).

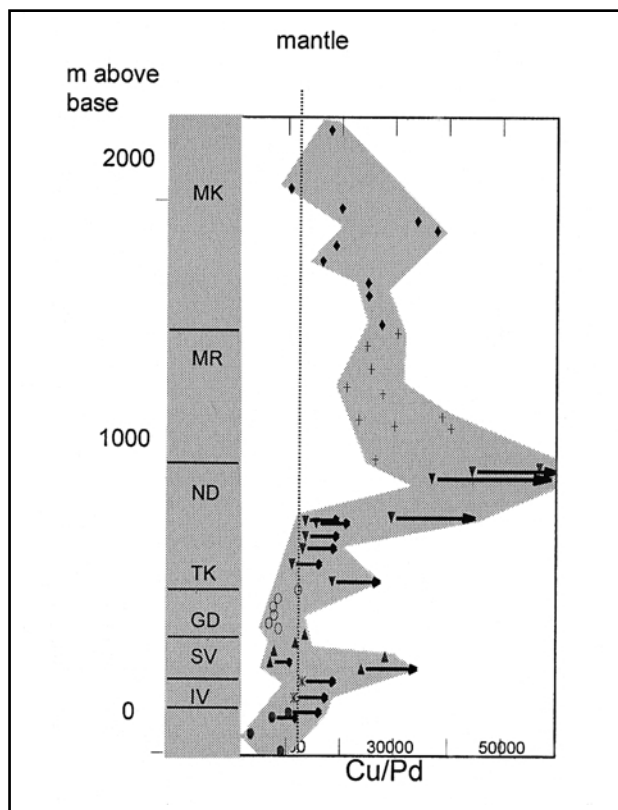


Figure 4. Cu/Pd ratios in the basaltic lavas in the Siberian Trap (figure of Maier *et al.*, 1998 based on the data of Brüggmann *et al.*, 1993).

have lower melting temperatures than most silicate minerals, and will be melted early during partial melting of the upper mantle. Melts generated during a normal course of partial mantle melting are fertile in PGE, Ni and Cu only when the molten sulfides are completely dissolved in the melts. This requires a high degree of partial melting of the upper mantle, perhaps higher than 30 percent. Such primary partial melts usually have basaltic to komatiitic compositions, and are unlikely to achieve significant sulfide super saturation during ascent to the crust. Fractional crystallization and crustal contamination are the most important processes known to have induced sulfide saturation in magma. Sulfide liquid segregated in large chambers may achieve high R-factors that are critical for the formation of reef-type PGE deposits. Crustal contamination, either by way of felsification or addition of crustal sulfur, is most effective in dynamic lava channels or magma conduits. Large amounts of sulfide liquids segregated during this process often equilibrated at relatively lower R-factors and hence have lower metal contents, particularly of PGE. Deposition of the sulfide liquids in limited localities in response to the decrease in magma velocity is an important sulfide concentration process for the Ni-Cu sulfide deposits formed in dynamic magmatic systems.

Because of their extremely high partition coefficients between sulfide liquid and silicate magma, the PGE will become significantly depleted in magma after small amounts of sulfide segregation. In contrast, copper has

a much lower partition coefficient and will be less depleted in magma. Thus, Pd/Cu ratios in whole rocks can be used to detect PGE mineralization associated with small amounts of sulfide segregation in large layered intrusions. Whole rock Cu/Zr ratios are sensitive to large amounts of sulfide liquid segregation. Hence, they are a useful tool in Ni-Cu exploration. The content of Ni in magma can be determined from the content of Ni in the olivine crystallising from it. Therefore, nickel contents of olivine can be used to identify any Ni depletion in magmas from which large amounts of sulfide have segregated.

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