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Highly siderophile and strongly chalcophile elements in magmatic ore deposits

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INTRODUCTION

An ore deposit by definition must be economically viable, that is to say it must contain sufficient material at high enough grade to make it possible to mine and process it at a profit (Bates and Jackson 1987). This requires the elements to be collected and concentrated by some phase and for them to be deposited close to the surface of the earth. At the oxygen fugacities found in the crust native Fe is not normally stable and thus the highly siderophile elements (defined as Ru, Rh, Pd, Re, Os, Ir, Pt and Au) cannot behave as siderophile elements except in rare cases such as on Disko Island (Klöck et al. 1986) where the magma is sufficiently reduced for native Fe to be present. However, if mafic magmas become saturated in a base-metal-sulfide liquid the highly siderophile elements behave as highly chalcophile elements (Table 1). Thus these elements are generally found in association with base-metal-sulfide minerals which crystallized from a magmatic sulfide liquid, namely pyrrhotite, pentlandite, chalcopyrite, cubanite +/-pyrite. An exception to this is Au. Although Au is strongly chalcophile and is produced as a by-product from many platinum-group element (PGE) deposits (Table 2) most primary Au deposits consist of native Au (Groves et al. 1998). These will not be discussed in this chapter.
There are many PGE-deposits (i.e., accumulations of PGE minerals and base metal sulfides containing PGE; Bates and Jackson, 1987) around the world, but most of these do not constitute PGE ore deposits because they are either too small or their grade is too low, or other political or infrastructure factors prevent the economic exploitation of the deposit (Bates and Jackson, 1987). For the purpose of this work we have defined PGE ore deposits as those which have significant production (>2% of the annual world production) of Pt or Pd (Fig. 1, data from Cowley 2013 and Mudd 2012). Aside from these deposits Pt and Pd are also produced as by-products from many magmatic Ni-deposits. But the amount from each deposit is small, and in total for all deposits is ~2% of annual world production (Fig. 1). They will not be discussed further, but the behavior of the PGE in these types of deposits is similar to their behavior in the Noril’sk and Sudbury deposits and more details on them can be found in Naldrett (2011).

Platinum deposits in zoned complexes, also known as Alaskan or Uralian complexes are not currently mined and will not be covered here. Information on these types of deposits is provided by Augé et al. (2005) and Anikina et al. (2014). Finally a small quantity of Pt (~2%, Cowley 2013) is produced from alluvial deposits, information on these can be found in Weiser (2002) Tolstykh et al. (2004).

The majority of the World’s Pt and much of its Pd are produced from the Bushveld Complex of South Africa (Figs. 1 and 2). These resources are present in three deposits; the UG2 reef, the Merensky reef and the Platreef (Table 2). The next most important source of Pd and Pt (Fig. 1) is as a by-product of nickel mining in the Noril’sk area of Russia. These Ni deposits occur in three sub-volcanic intrusions; Noril’sk 1, Talnakh and Kharaelakh (Fig. 3). In fact the Noril’sk deposits produce most of the World’s Pd, although that the actual Pd resources are less than those of the Bushveld Complex (Fig. 1, Table 2).

In addition to the Bushveld Complex there are three intrusions that are primary producers of Pt and Pd; the Great Dyke of Zimbabwe, the Stillwater Complex of United States and the Lac des Iles Complex of Canada (Figs. 4, 5, 6). The ore deposits in these intrusions are the Main Sulphide Zone, the JM reef and the Roby and Offset Zones respectively (Table 2).

In the past the Sudbury Igneous Complex, Canada, (Fig. 7) produced a significant amount of Pt and Pd as a by-product of Ni mining (Table 2). The Sudbury Igneous Complex (Fig. 7) is a unique structure formed as a result of a meteorite impact, which flash melted a mixture of Archean and early Proterozoic crust (Dietz 1964). However, current production is low (Fig. 1) and these resources are now largely mined out. Nonetheless an example of the Sudbury ores will be discussed because in terms of resources it originally represented a major source of PGE (Table 2).

**CLASSIFICATION OF THE DEPOSITS**

Broadly speaking the deposits may be classified based on their location in an intrusion and the amount of base metal sulfide minerals (BMS) present. There are three broad groups; stratiform or reef deposits, contact deposits and Ni-sulfide deposits.

**Reef or stratiform deposits**
Most primary PGE-deposits (the UG2, the Merensky, the JM reefs and the Main Sulphide Zone) take the form of laterally extensive narrow (stratiform) layers, of 1 to 3 m thickness, that contain 3-15 ppm (1 µg g⁻¹) Pt+ Pd and occur within the Bushveld, Stillwater and Great Dyke layered intrusions respectively (Fig. 8). (Workers on economic deposits express the grade of a deposit in g tonne⁻¹ or as ppm: 1 g tonne⁻¹ = 1 ppm = 1 µg g⁻¹, this chapter will use ppm). In some places the PGE enriched layer widen to 10-20 m in structures which are termed pot-holes at the Bushveld reef (Viljoen 1999) and ballrooms in the JM reef (Zientek et al. 2002). With the notable exception of the UG2 reef, the reefs contain a small amount (0.5-3 wt %) of BMS. Base metal sulfides are present in the UG2 reef, but the amount is so low (<0.1 wt %) that there are no visible BMS in hand specimen. The reefs are present in a variety of rock types. In the case of the UG2 the host is a massive chromitite with interstitial orthopyroxene and plagioclase (Barnes and Maier 2002a, Mathez and May 2005). The rock types in the Merensky reef vary from thin chromitite seams, through coarse grained melanorite to anorthosite (Kruger and Marsh 1985; Barnes and Maier 2002b). The JM reef comprises troctolite, olivine gabbro and anorthosite (Barnes and Naldrett 1985; Zientek et al. 2002; Godel and Barnes 2008). The host rock of the Main Sulphide Zone is described as a plagioclase orthopyroxenite or bronzitite (Oberthür 2002; Wilson and Brown, 2005).

Contact deposits.

The term contact deposit has been used to refer to deposits of variable width that are composed of disseminated BMS found at the margins of intrusions. The Platreef, which occurs along the northern edge of the Bushveld Complex (Figs. 2 and 8), falls into this group. Strictly speaking the deposit should not be referred to as a reef because it is not a narrow zone but rather 50 to 100 m thick with variable distribution of PGE across the zone. There is a great deal of variation in the rock types from pyroxenite to gabbronorite with minor anorthosite and peridotites and included in these are xenoliths of the country rocks (Kinnaird 2005; Maier et al. 2008; McDonald and Holwell 2011). The combination of extreme variations in grain size and textures, the mixture of rock types, and presence of xenoliths with reaction rims around them, produced a heterogeneous zone referred to as varitextured.

Eckstrand (2005) suggested that the Roby Zone of the Lac des Iles Complex should be classified with the Platreef. The Roby, Offset and Twilight zones consist of varitextured gabbro and they occur at the contact between the margins of the intrusion and the homogeneous east gabbro (Fig. 6). Other authors classify the Lac des Iles deposits as a magmatic breccia e.g., Lavigne and Michaud (2001).

Ni-sulfide deposits

In the Noril’sk area the ores take a number of forms; disseminated BMS, massive BMS, vein/ breccia/ cupriferous BMS, and low-S-high-Pd-Pt ore (Distler 1994; Torgashin 1994; Sluzhenikin et al. 2014). Each type will now be briefly described. The disseminated ore is the main ore type of the Noril’sk 1 intrusion (Sluzhenikin et al. 2014). It occurs in the lower parts of the intrusion (Fig.9a) in a varitextured gabbro. Russian geologists use the term taxitic for this type of texture. The BMS occur both as interstitial amorphous patches and as globules (referred to as droplet ore). The droplets are 1-4 cm in size and zoned with pyrrhotite-rich bases and chalcopyrite or cubanite (CuFe₂S₃) rich tops (Czamanske et al. 1992; Barnes et al. 2006) (Fig 10).
The main ore type in the Talnakh and Kharaelakh intrusions is massive BMS which occurs at the lower contact between the intrusions and the country rock (Fig. 9b). In many cases there is a narrow zone of hornfels between the massive BMS and the intrusion. The massive BMS show a mineralogical zonation similar to that observed in the droplet ore (Fig. 9b). The lower parts and the margins are rich in pyrrhotite and the top or central parts are rich in a number of Cu-rich sulfide minerals from chalcopyrite to talnakhite \([\text{Cu}_9(\text{Fe}, \text{Ni})_{8}\text{S}_{16}]\) (Torgashin 1994).

Vein/breccia/cupriferous ore occurs in the country rock both above and below the intrusions and it also occurs cross-cutting the intrusions (Fig. 9b, Torgashin 1994; Sluzhenikin et al. 2014). The vein ore consists mainly of Cu-rich BMS and takes two forms. In some cases it consists of veins 2 to 10 cm wide containing massive BMS with sharp contacts with the host rock. In other cases, such as at the Oktrabr’yysk deposit (Fig. 9b), the vein ore occurs towards the top of the intrusion and in the overlying country rocks as a network of fine anastomosing veins. This ore is referred to as breccia or cupriferous ore.

The low-S-high-Pd-Pt ore is not common. It occurs as narrow discontinuous layers towards the top of some intrusions (Distler 1994; Sluzhenikin 2011; Sluzhenikin et al. 2014). The host rock type is gabbronorite with disseminated chromite (Fig. 9a). Generally the rocks contain \(\sim 1\) wt % BMS.

The traditionally the Sudbury ores have been divided into contact ores and offset ores (Ames et al. 2007; Farrow and Lightfoot 2002). The contact ores consist of massive BMS and disseminated BMS found at the contact between the intrusion and the country rocks and include the chalcopyrite-rich massive BMS veins which occur in fractures immediately beneath the contact ores. The offset ores are found in quartz diorite dikes (Grant and Bite1984; Lightfoot et al. 1997). These dikes are 50 to 100 m wide and extend for several kilometers into the country rocks. The dikes are thought to represent injections of the differentiated impact melt into the country rocks. Massive BMS occur both at the center and on the margins of the dikes, and occur where the dikes widen. More recently a new category of deposits has been described in the country rocks; these are low-S-high-Pd-Pt deposits (Pentek et al. 2008; Tuba et al. 2014).

**MINERALS HOSTING THE PLATINUM-GROUP ELEMENTS**

**Base metal sulfides**

The highly chalcophile nature of the PGE suggests that they should partition into a sulfide liquid and therefore could be present in the BMS (pyrrhotite, pentlandite, chalcopyrite, pyrite) formed from this liquid. It has long been established that Pd, Rh and Ru can be present in pentlandite (Cabri 1992 and references therein). However, until the advent of laser ablation ICP-MS analysis it was difficult to obtain in situ concentrations of all the PGE in BMS. As discussed below there is now rapidly growing literature on PGE contents of the BMS. We have chosen to represent examples where both whole rock and mineral analyses are available from the same samples. This section is not intended as a complete inventory of all the analyses available.

In order to facilitate comparison of the mineral data with the whole rock data the mineral data will be presented in the same fashion as the whole rock PGE data, namely normalized to primitive mantle and plotted in order of compatibility. More details on the reason for this choice of this are outlined below in the section on whole rock geochemistry.
Pentlandite is the BMS with the highest PGE and Re contents (Table 3). All of the pentlandites show similar patterns with an increase in concentration from Re to Pd and strong negative Pt anomalies (Fig. 11). Pentlandites from the JM reef are richest in all of the PGE. The other reefs and Noril’sk pentlandites contain an order of magnitude less PGE. Pentlandites from McCreedy East and the Roby Zone contain 3 orders of magnitude less Os, Ir, Ru and Rh than the JM reef pentlandites (Fig. 11, Table 3). The whole rock concentrations of these elements are low at McCreedy and Roby Zone (Table 4). The magmas that formed the Sudbury deposits and Roby Zone are thought to have been andesitic in composition and thus contained less Os, Ir, Ru and Rh than the picritic to basaltic magmas that formed the other deposits. Thus there are less of these elements in the sulfides. Pyrrhotite is the next most important host of PGE and Re. Pyrrhotites from the reefs and Noril’sk have higher concentrations of all the PGE than those from McCreedy East or Roby Zone and once again reflect the difference in whole rock concentrations (Table 4, Fig.12). Rhenium, Os, Ir, Ru and Rh are present at approximately similar mantle normalized concentrations and these decrease for Pt and Pd (except at the JM reef where the pyrrhotite appears to contain some Pd). McCreedy East and Roby Zone pyrrhotites have similar mantle normalized patterns but at lower levels. The concentrations of all of the PGE are low in all of the chalcopyrite and the patterns are approximately flat. Complete PGE analyses are available for pyrite from McCreedy East and in the Roby Zone. It occurs in two forms; in essentially igneous assemblages, where it makes up less than 5% of the BMS, and in altered assemblages where it appears to have replaced pyrrhotite and is the most common sulfide present (Dare et al. 2011; Djon and Barnes 2012). The pyrites show similar patterns to the pyrrhotite patterns both in level and shape (Fig.11), except that the pyrites from the unaltered assemblage at McCreedy East are richer in Ir, Os and Ru and Rh than the pyrrhotite. Pyrite is present in the Main Sulfide Zone and the Platreef and is known to contain PGE (Oberthür et al. 1997) however complete PGE analyses are not available at present.

Platinum-group minerals

A detailed list of the 109 known platinum-group minerals (PGM) may be found in Cabri (2002) and PGM are also described in another chapter of this publication (O’Driscoll and González-Jiménez 2015). Here only a brief mention of the main types of PGM found in PGE deposits will be presented. For the Merensky and UG2 reefs reviews of the PGM are provided by Kinloch (1982), McLaren and de Villiers (1982) and Cawthorn et al. (2002). Platinum and Pd are mainly hosted by Pt and Pd sulfides (cooperite and braggite), the next most common hosts of Pd and Pt are bismuthotellurides (merenskyite, kotulskite michenerite, moncheite). Arsenides and stannides (sperrylite and rustenburgite) are minor hosts of Pt. Close to the potholes the mineralogy is different with FePt alloys being common and sulfides less common (Kinloch 1982; Cawthorn et al. 2002). In the case of the Platreef the mineralogy is similar, but bismuthotellurides are more common than sulfides (Holwell and McDonald 2007). The common PGM of Rh and Ir are sulfarsenides (hollowingworthite-irarsite series). In the UG2 reef Junge et al. (2014) found that Os and Ru are mainly found in laurite, Pt is present in Pt-Fe alloy and cooperite-braggite whereas Pd, Rh and are largely present in pentlandite. In contrast Penberthy et al. (2000) in their study of the reef report Rh and Ir occur as sulfides in combination with Cu and Pt in malantite-cuprorhodosite.
In the JM reef of the Stillwater complex the PGM mineralogy is similar to that of the
Merensky reef consisting of Pd and Pt sulfides followed by Pd-Pt bismuthotellurides (Zientek et
al. 2002; Godel and Barnes 2008). In contrast the Pd and Pt PGM of the Main Sulfide Zone of
the Great Dyke are largely bismuthotellurides with sulfide making up <13% of the PGM.
Arsenides of Pt, Rh and Ir are common throughout the complex, but are more common in the
southern part of the Dyke than the northern part (Oberthür 2002).

There is a large literature on PGM of the Noril’sk-Talnakh ores. Kozyrev et al. (2002)
gives an overview and Sluzhenikin et al. (2011) an update. The PGM present are similar to those
reported from the PGE reef deposits. The main PGM from the ores of the Noril’sk 1 intrusion
are Pt and Pd stannnides (rustenburgite and atokite), FePt alloys (isoferroplatinum), Pt, Rh, and
Ir arsenides, (sperrylite and hollingworthite). The composition of the PGM in the massive ores
varies with the type of ore. The pyrrhotite (Cu-poor ore) contains mainly FePt alloy and
sperrylite. The Cu-rich ore contains a wider variety of PGM, mainly Pt sulfide, Pt arsenide, Pt
stannide (rustenburgite and niggliite), FePt alloy, Pd stannides (atokite and paolovite) and Pd
bismuthide (sobolevskite).

Farrow and Lighfoot (2002) summarize the PGM mineralogy at Sudbury as follows. The
PGM assemblage at Sudbury is dominated by Pt and Pd bismuthotellurides. The next most
commmon group of Pd minerals is antinomides (sudburyite and mertierite). Apart from the
bismuthotellurides Pt is hosted mainly by sperrylite in deposits on the south side of the Sudbury
intrusion and by the stannide niggliite in deposits from the north side of the intrusion. Rhodium
and Ir occur as hollingworthite and irarsite in deposits from the south side of the intrusion.

Chromite

Experimental work has shown that Os, Ir, Ru and Rh are compatible in both magnetite
and chromite whereas Pd, Pt and Re are not (Capobianco et al. 1994; Righter et al. 2004; Brenan
et al. 2012). Laser ablation work has shown that in volcanic rocks the IPGE and Rh are present in
chromite phenocrysts in solid solution (Locmelis et al. 2011; Pagé et al. 2012; Park et al. 2012)
whereas the concentrations of Pd, Pt and Re are less than detection levels. Furthermore
chromites in the marginal rocks of the Bushveld contain IPGE and Rh apparently in solid
solution (Pagé and Barnes 2013). All of the volcanic chromites contain 5 to 100 ppb (ng g\(^{-1}\))
each of Os, Ir and Rh and 100 to 500 ppb Ru and thus could be a significant host for these
elements in ore deposits. However we have analyzed the chromites from the UG2 and
Merensky reefs and they contain less than detection levels of all the PGE and Re (Godel 2007)
and do not appear to host the IPGE and Rh.

Mass Balance

The proportion of each element in each mineral is important both for petrogenetic studies
and for metallurgical work. Petrogenetic studies concentrate on how each element came to be
hosted in each mineral. These studies require textural information and are necessarily concerned
with individual hand-specimen sized samples. Metallurgical studies consider the mill feed and
report on large bulk samples and focus on maximizing the recovery of the economically
important elements (mainly Pt and Pd). The methodology required to optimize the results is
different for the different types of study. This chapter is concerned with the petrogenesis and will
consider the results based on individual samples and their textures.
Although to date the petrogenetic studies have been based on small sample sets they do show similar trends (Fig. 13). Rhenium, Os, Ir, Ru and Rh are hosted in large part by a combination of pentlandite and pyrrhotite in the unaltered ores and by pyrite and pentlandite in altered ores. Pentlandite is the only base metal sulfide mineral to host significant amounts of Pd. The amount of Pd hosted by the pentlandite versus the amount of Pd in PGM is variable, at some deposits (Noril’sk 1, Merensky and JM reefs) most of the Pd is in the pentlandite. In contrast in the Roby Zone most of the Pd is in PGM. In all cases that have been examined so far very little of the Pt and Au are present in BMS. In most cases the Pt is present in platinum-group minerals. Detailed studies of Au minerals were only made at McCreedy East and Noril’sk and in these cases Au was found to be present largely as native Au (Dare et al. 2011, 2014; Sluzhenikin 2011) with minor amount as electrum.

**GEOCHEMISTRY**

**Introduction**

The grade of Pt and Pd in the PGE dominated deposits are in the 2 to 15 ppm range with Ni and Cu values of ~ 1000 ppm (Table 2). The concentrations of Au and the remaining PGE are generally at the 0.01 to 0.5 ppm level (Tables 2 and 4). Within the deposits the concentrations may vary considerably. In Ni sulfide deposits the combined Ni and Cu concentrations are generally around 2 wt % (Table 2). The Pd and Pt contents can vary from quite low values such as those found at Sudbury, <1 ppm to the high values found in the Noril’sk deposits, 4 ppm Pd+Pt.

**Normalization to mantle or chondrite?**

The PGE data are generally presented on a line graph where the metals have been divided by mantle or chondrite values. Traditionally the order of the elements is from relatively compatible elements on the left side (Ni, Os, Ir, Ru, Rh) to relatively incompatible on the right side (Pt, Pd, Au, Cu). This is in contrast to the practice in lithophile element geochemistry where the incompatible elements are plotted on left side and compatible on the right. The choice of whether to normalize to chondrite or mantle values depends on the specific application of the diagram. During separation of the earth’s core from the mantle, PGE partitioned preferentially into the Fe-Ni core, leaving the mantle depleted in PGEs relative to Ni and Cu (Walker 2009). Therefore, the patterns for all mantle-derived magmas normalized to chondrite values tend to be depleted in PGEs relative to Ni and Cu. Consequently, normalizing the data to chondrite values always produces trough patterns depleted in PGE.

Nickel and PGE deposits are thought to form when a sulfide liquid segregates from mantle derived magma (Naldrett 2004). Therefore normalization to primitive mantle values is more useful in deducing the history of the formation of a deposit. The PGEs have much higher partition coefficients between silicate and sulfide liquid than Ni or Cu (Table 1). Therefore, the first sulfide liquid to segregate from a magma will be rich in PGE, and if normalized to mantle values, will have normalized Ni values approximately in line with Os and Ir, and normalized Pd values in line with Cu (e.g., disseminated BMS from the Kharaelakh and Talnakh intrusions, Fig. 13). The silicate liquid from which this sulfide liquid segregated will be PGE-depleted and any sulfide liquid that subsequently forms from it will also have a PGE-depleted pattern and not be capable of forming a PGE ore deposit. In order to avoid confusion between depletion due to
core separation and depletion due to sulfide segregation we normalize data to primitive mantle values (Lyubetskaya and Korenaga 2007).

**Recalculation to 100 % Sulfides or whole rock.**

On mantle-normalized diagrams, metal values can be plotted as whole-rock values, however in Ni-deposits the sulfide contents vary from 1 to 90 %. Therefore in order to compare rocks with different sulfide contents many authors recalculate the metal abundances to 100 percent sulfide (i.e., the metal tenor of the sulfide). The mineralogy observed in a magmatic sulfide under crustal conditions is essentially pyrrhotite, pentlandite, and chalcopyrite (+/- minor pyrite +/- cubanite). In rocks where the bulk of the BMS are pyrrhotite, pentlandite, and chalcopyrite, the concentration of an element in the sulfide fraction maybe calculated using the formula

\[ C_{(100 \text{ percent sul})} = C_{wr} \times \frac{100}{[2.527 \times S + 0.3408 \times Cu + 0.4715 \times (Ni-Ni_{sil})]} \] (1)

Where \( C_{(100 \text{ percent sul})} \) = concentration of an element in 100 percent sulfide; \( C_{wr} \) = concentration of the element in the whole rock; \( S, Cu, \) and \( Ni \) = concentration of these elements in the whole rock, in weight percent, \( Ni_{sil} \) = Ni in silicates and oxides.

This calculation is useful for Ni-deposits and for the Ni-deposits the mantle normalized whole rock values have been recalculated to 100 % sulfides. However, its application to PGE dominated deposits with their low S content is questionable because at many localities the presence of metal alloys or abundant millerite and bornite or the alteration of pyrrhotite and pentlandite (e.g. in the UG2 and Merensky reef, Li et al. 2004; High Grade Zone Lac des Iles, Djon and Barnes 2012) suggest that the assemblages do not represent primary igneous BMS. Furthermore, the S content of reef rocks are very low thus the recalculation factors are large which magnifies errors. Therefore we will not recalculate data from PGE dominated deposits to 100 % BMS.

**Mantle normalized plots of reef type deposits.** The mantle normalized metal patterns of the Merensky, the UG2 and the Main Sulfide Zone show strong enrichment in all of the PGE relative to Ni and Cu (Figs. 14a and b) with Pt and Pd (Pd-group PGE, PPGE) 10 to 100 times higher than Cu and Os, Ir and Ru (Ir-group PGE, IPGE) approximately 10 to 100 times higher than Ni giving the overall the patterns an arch shape. Furthermore the PPGE are enriched over the IPGE, with Pd/Ir of 5 to 35 (Figs. 15a and b). There appears to be a relationship with the amount of chromite present and the IPGE plus Rh content of the reefs, with the UG2 reef containing higher levels of IPGE and Rh than the other reefs (Table 4, Fig. 14b) and within the Merensky reef the chromite rich layers are richer in IPGE and Rh than the reef as a whole (Figs. 14a, b). The shape of the JM reef mantle normalized pattern is slightly different (Fig. 14c). It is enriched in PGE relative to Ni and Cu as in the case of other reefs, but is much more enriched in PPGE than IPGE with higher Pd/Ir (660).

Concentrations of the PGE vary across the reefs. In the UG2, the Merensky and the JM reefs the highest PGE concentration tend to be found at towards the upper and lower parts of the reefs (Cawthorn et al. 2002; Maier and Barnes 2008; Zientek et al. 2002). In the Great Dyke the lowest parts of the reef are richest in Pt, followed by Pd, followed by Ni and Cu (Oberthür 2002; Wilson and Brown 2005).
Mantle normalized plots of contact type deposits. The grade and shape of patterns from the Platreef vary along strike, with most deposits not being economic (Kinnaird 2005; Maier et al. 2008). The highest grade mineralization at surface in the Platreef is found at Sandsloot, Overysel and Zwartfontein, and here the shape of the PGE patterns is similar to that of the Merensky reef (Fig. 14a), with enrichment of Pd over Cu and the IPGE over Ni. Some workers have suggested that the Platreef grades into the Merensky reef down dip and into the intrusion (Maier et al. 2008 2013) and thus the similarity in the shape of the patterns is reasonable.

Despite some similarities in the outcrop and textures the metal patterns of the Roby and Twilight Zone of the Lac des Iles Complex do not resemble those of the Platreef (Figs. 14a and c). The Lac des Iles ore zones show a strong enrichment of Pd over Cu, similar to the JM reef of the Stillwater complex and an enrichment of Pd over Pt. The ores are even more depleted in IPGE and Rh than the JM reef resulting in very high (7500) Pd/Ir and Ni is enriched relative to the IPGE (Fig. 14c).

Mantle normalized plots of Ni-deposits. The mantle normalized plots for the disseminated BMS from the Noril’sk area are fairly steep (Fig. 12) with high Pd/Ir (220-350). The concentrations of the metals in the disseminated BMS of the Talnakh and Kharaelakh intrusions and the PGE are not enriched relative to Cu and Ni with Pd approximately in line with Cu and Ir approximately in line with Ni. In contrast the Noril’sk 1 disseminated BMS are richer in PGE than the Talnakh and Kharaelakh BMS by an order of magnitude and show a strong enrichment of Pd over Cu (Fig. 12). The mantle normalized metal patterns for the Sudbury disseminated BMS is similar to the Talnakh and Kharaelakh BMS from Ni to Rh, but not as rich in Pd, Pt and Cu and consequently has lower Pd/Ir (54).

The composition of the massive sulfides at both Noril’sk and Sudbury reflects variations observed in the mineralogy with the ores with high concentrations of chalcopyrite and cubanite being Cu-rich and those rich in pyrrhotite being Cu-poor. The Cu-poor ore is the more common type and is poorer in Pt, Pd and Au (Table 4). Therefore the Cu-poor massive sulfide have flatter mantle normalized metal patterns than the disseminated BMS with Pd/Ir of 30 to 150 and slight negative Pt anomalies (Fig. 12). The Cu-rich massive BMS from both Noril’sk and Sudbury are depleted in IPGE and Rh and enriched in Pt, Pd and Au, consequently the patterns are extremely steep (Fig. 12), with Pd/Ir that exceed 17 000. The vein/breccia samples from the Kharaelakh intrusion have similar compositions to the Cu-rich massive BMS and show extremely steep patterns similar to the Cu-rich massive ores (Fig. 12).

Other chalcophile elements.

Platinum-group minerals host most of the Pt and a substantial amount of the other PGE in all the deposits (Fig. 13; Distler et al. 1994; Barnes et al. 2006; Godel et al. 2007; Barnes et al. 2008; Godel and Barnes 2008; Holwell and McDonald 2007; Dare et al. 2011; Rose et al. 2011; Djon and Barnes 2012; Sluzhenikin et al. 2014). The common PGM contain Te, As, Bi, Sb and Sn (TABS) as major elements and thus may play an important role in collecting PGE. All of these elements are chalcophile, but only Te may be described as strongly chalcophile (Table 1). For the PGE dominated deposits there is very little data available for these elements because of the difficulty in determining them in silicate rocks (They are present only at very low levels,
which requires that the analyses are carried out by solution work; but they are volatile, which
means the dissolution must be done at moderate to low temperatures to prevent loss of these
elements). There has been a large study at the JM reef (Zientek et al. 1990) which gave values in
the 0.01 to 2 ppm range. For the Merensky reef, the UG2, the Platreef and Roby Zone there is a
little data available and these values are also in the 0.1 to 2 ppm range (Table 5). For the Main
Sulfide Zone no data there is no data available. When the elements are normalized to mantle
and plotted in order of compatibility with MORB (Fig. 15a) the patterns increase from
approximately twice mantle at Sn and Sb to around one hundred times mantle at Te. (Fig.15b).

In the massive BMS the concentrations of TABS are higher than in the PGE dominated
deposits and are in the 1 to 100 ppm range (Table 5). As in the case of the PGE there is a
variation in concentrations with ore type - the Cu-rich ores contain higher concentrations of
TABS than the Cu-poor ores. Furthermore, the Cu-rich ores have steep TABS patterns than the
Cu-rich ores (Figs. 15c and d).

INTERPRETATION

Composition of the silicate melt

It is generally accepted that the Ni-sulfide ore deposits are formed by collection of the
metals from a mafic or ultramafic magma by a sul
defide liquid (Naldrett 2004). This model can also be applied to PGE dominated deposits,
although there is a school of thought (e.g. Boudreau and Meurer 1999) that suggests that in the
case of PGE dominated deposits the PGE partition into a late magmatic fluid and that the BMS
and PGM currently found in the deposits precipitate from this fluid. In either case the question
arises as to whether the magmas which formed the deposits were exceptionally enriched in PGE
when compared with most mafic magmas.

The Noril’sk deposits are found in sub-volcanic intrusions of the Siberian flood basalts
and the concentrations of the PGE in Siberian basalts (squares on Fig.16a) are similar to the
concentrations reported for basalts and komatiites from the literature (circles Fig.16). For the
Bushveld there are a series of dykes and sills found around the intrusion that are thought to
represent the initial magmas (Sharpe and Hulbert 1985; Barnes et al. 2010). There is a long
standing unresolved debate as to how much crustal contamination these magmas have
experienced versus how much the sub-continental lithosphere has contributed to the magmas
(Kruger 1994; Harmer and Sharpe 1985; Harris et al. 2005; Richardson and Shirey 2008). The
magmas (stars and crosses on Fig.16b) appear to have Pd contents similar to most basalts and
komatiites. The Pt contents, however, are slightly higher than most basalts and komatiites. The
composition of the sills and dikes associated with Stillwater complex are similar to the Bushveld
magmas in terms of major elements (Helz 1995). Unfortunately many of the samples contain a
large amount of BMS and are thus not suitable for estimating the initial PGE content of the
magmas. Samples with S contents less than 3000 ppm (these include all of the magma types
thought to have formed the Stillwater Complex, Zientek et al. 1986)) have Pt and Pd values in
the 1 to 20 ppb range (crosses on Fig.16c) similar to basalts and komatiites. There are no PGE
analyses of chill rocks for the Great Dyke or Lac des Iles complexes. It has been suggested that
the composition of the Great Dyke magma was komatiite (Wilson and Brown 2005) and the
magma of the Roby Zone was andesitic (Barnes and Gomwe 2011). To summarize, for the
intrusions where data is available there is no evidence that the magmas were particularly
enriched in PGE, although the Bushveld parental magma is slightly richer in Pt than most magmas.

The composition of the magmas thought to have formed the intrusions that host the PGE and Ni-deposits range from komatiitic to andesitic. Whereas the Pt and Pd contents of these magmas are fairly similar (1 to 20 ppb, Fig.16a) the IPGE and Rh contents might be expected to be very different because these elements tend to be moderately compatible. Variations in the IPGE and Rh contents of the magmas may explain, in part, the different shapes of the metal patterns from PGE deposits. Komatiites generally have Ir contents in the 1 to 2 ppb range whereas basalts and andesites have much lower contents in the 0.01 to 0.1 range (Fig.16d). Thus komatiitic magmas have Pd/Ir of around 10 and andesitic magmas ratios of 100 to 1000. The BMS that segregate from a komatiitic magma should thus be expected to have a much lower Pd/Ir than the BMS formed from an andesitic magma. This may in part explain why the Great Dyke reef has Pd/Ir of 25 whereas the Lac des Iles deposits have a ratio of ~7000.

Although differences in magma compositions can explain some differences in the metal patterns they are unlikely to explain the enrichment in Os, Ir, Ru and Rh in the chromitite layers of the Merensky reef relative to the silicate parts of the reef because one would expect that the magma composition was similar through-out the reef. The majority of the Os, Ir and Ru in the chromitite are found in laurite (Prichard et al. 2004; Godel et al. 2007; Junge et al. 2014). Many authors suggest that the laurite crystallized from the magma before sulfide saturation occurred and was included in the chromite thereby enriching the chromite layers in these elements (e.g. Merkle 1992). However, the laurite in the Merensky reef is not enclosed in chromite; it is associated with BMS and thus does not support this model (Prichard et al. 2004).

**Saturation of the magma in a sulfide liquid**

Once the magma has been emplaced into the crust it must become saturated in a sulfide liquid (dominantly FeS) in order for it to collect the PGE. Li and Ripley (2009) reviewed the published work on the factors leading to the saturation of magmas in a sulfide liquid. In summary, the factors that lead to the saturation include: i) a rise in pressure, ii) a fall in temperature, iii) a change in magma composition (in particular a drop in Fe-content or an increase in SiO2), iv) an increase in fO2, and v) a decrease in fS2. Li and Ripley (2009) developed an empirical equation to estimate the S concentration of a magma saturated in sulfide liquid,

\[
\ln X_s = -1.76-0.474*(10^4/T)-0.021*P+5.559*X_{FeO}+2.565X_{TiO2}+2.709*X_{CaO} -3.192*X_{SiO2}-3.049*X_{H2O} \tag{2}
\]

where \(X=\) the mole fraction of an element, \(T=\) temperature in Kelvin, \(P=\) pressure in Kb. Li and Ripley (2009) did not find it necessary to include terms for \(fO_2\) and \(fS_2\) because in terrestrial mafic magmas, \(fO_2\) controls the \(fS_2\) and \(fO_2\) is in turn controlled by FeO and temperature. Thus, by including FeO and temperature in equation 2 the effects of changes in \(fO_2\) and \(fS_2\) are taken into account.

Based on recent experimental work Fortein et al. (2015) developed a new equation
\[
\ln S_{\text{ppm}} = 34.784 - 5772.3/T - 17.275 \times X_{\text{FeO}} - 18.344 \times X_{\text{NiO}} - 20.378 \times X_{\text{CaO}} \\
- 25.499 \times X_{\text{SiO}_2} - 20.393 \times X_{\text{H}_2\text{O}} - 27.381 \times X_{\text{Al}_2\text{O}_3} - 22.398 \times X_{\text{MgO}} - 18.954 \times X_{\text{Na}_2\text{O}} - 32.194 \times X_{\text{K}_2\text{O}}
\] (3)

The symbols are the same as for equation 2, but pressure is expressed in GPa. This equation includes more variables for the composition of the magma but both equations give estimates for the concentration of S required to attain sulfide saturation in komatiitic and basaltic magmas.

An important point to note is that S solubility decreases with increased pressure (Mavrogenes and O’Neil 1999). Thus, although a primary magma might be saturated in sulfide liquid when it formed in the mantle, as the magma rises and the pressure decreases the amount of S required to bring about saturation rises, thus primary magmas when they are emplaced in the crust are S undersaturated. Therefore, in order to bring about saturation either the temperature of the magma must drop and/or the composition of the magma must change. As pointed out in Barnes and Lightfoot (2005) ~ 40% crystallization would be required to bring a picrite to sulfide saturation and Barnes et al. (2009) calculate that ~17% crystallization would be required to saturate the initial Bushveld magmas. Li and Ripley (2009) and Ripley and Li (2013) provide detailed calculations on this approach and its implications. The main conclusion are that considerable crystal fractionation would be required and this would lower the amount of Ni available in the magma thus making the formation of Ni-rich magmatic BMS difficult. [The Platina reef of the Skaergaard intrusions may be examples of Ni-poor PGE reef formed from evolved magma (Andersen 2006)]. If we consider intrusions such as the Noril’sk I as closed systems the total amount of S in the magma is too low to produce the amount of S observed in the deposit. Therefore, the systems must have been open and/or S addition must have occurred.

It has long been suggested that reefs in reef type deposits form when the incoming magma mixes with the resident magma. This abruptly changes the composition and temperature of the magma, resulting in sulfide saturation (Naldrett et al. 1986). This model was very popular, being supported by an abrupt change in Sr isotopes and magma composition associated with the Merensky Reef and to some extent the UG2 reef (Kruger 1994). However, it requires that both magmas be very close to S-saturation and it is questionable whether magmas have enough S to generate the reef (Ripley and Li 2013).

To form a magmatic Ni-sulfide deposit contamination of the magma by melts of S-rich crustal rock has long been the accepted model (e.g., Grinenko, 1985; Thériault and Barnes 1998; Lesher and Burnham 2001; Ripley and Li 2003), although, not all authors are in agreement with this (Seat et al. 2009). The contamination model is supported by the S isotopic composition of the ores that indicate the S was derived largely from the crustal rocks (e.g., Noril’sk, Grinenko 1985; Platreef, Holwell et al. 2007; Penniston-Dorland et al. 2008). Assimilation of S-rich crustal rocks will lower the temperature of the magma and increase the S concentrations, thus bringing about S saturation.

It is not possible to examine the process whereby S from the country rock is transferred to the mafic magmas at most ore deposits because, as will be outlined below, after contamination the sulfide liquid is transported from the site of contamination to the site of deposition. The marginal zones of the Duluth Complex have preserved some examples where there are convincing examples of in situ assimilation of black shale, leading to local sulfide saturation (Ripley and Al-Jassar 1987; Thériault and Barnes 1998; Quefferus and Barnes 2015). The mechanism for this assimilation appears to have involved stoping of country rock. The country
rock xenoliths are subsequently heated by magma, causing partial melting and formation of 
granitic melt veins (Thériault and Barnes 1998). The exact mechanism for the transfer of S to 
the melt is still being investigated, but we speculate that the sulfide minerals in the xenolith melt 
and are transferred to the mafic magma by the granitic melt as sulfide droplets. In addition to 
lowering the temperature of the magma and adding S, mixing of the granitic melt into the 
basaltic magma would lower the FeO and raise the SiO2 and H2O content of the melt, thus aiding 
sulfide saturation (see equation 2). The addition of melts of crustal rocks, in particular black 
shale, to the magma could also add some TABS elements as black shales are rich in these 
elements compared with mafic magmas (Table 5, Fig. 15a). Depending on the exact nature of 
the assimilant different elements may be enriched in the sulfide liquid and eventually influence 
exactly which PGM forms. For example it has long been observed that the PGM from ore 
deposits on the south side of the Sudbury Intrusion are rich in As, whereas ore deposits from the 
north side contain PGM rich in Sn (Ames and Farrow 2007). In the south there are Proterozoic 
sediments present, which are rich in As. In the north the host rocks are Archean granite, which 
should contain more Sn than As. The addition of TABS elements from the country rock of the 
Platreef has been used to explain variations in PGM assemblages (Hutchinson and Kinnaird 
2005).

Osmium isotopes are particularly useful for investigating the role of crustal 
contamination. More details on the Os isotopic evidence may be found in the Os isotope section 
below.

Upgrading of the Sulfides

Various equations have been used to model the composition of a sulfide liquid segregated 
from a silicate liquid. The one most commonly used is that of Campbell and Naldrett (1979) 
where the concentration of a metal in a sulfide liquid ($C_S$) is controlled by the concentration of 
the metal in the silicate liquid ($C_L$), the partition coefficient between the sulfide and silicate 
liquids ($D$), and the mass of silicate magma from which the sulfide collects the metal, expressed 
as R (mass ratio of silicate to sulfide liquid).

$$C_S = C_L D(R+1)/(R+D) \quad (4)$$

This equation considers a closed system but as pointed out by Brügmann et al. (1993) in many 
cases, such as where sulfide droplets sink through a magma column or where the silicate magma 
is replenished, a variation of the zone refining equation would be more appropriate to model the 
sulfide liquid composition

$$C_S = C_L(D-(D-1)e^{-(1/DN)} \quad (5)$$

where $N =$ number of volumes of magma with which the sulfide liquid interacted. The results 
are similar using either equation, but the zone refining equation produces slightly higher results 
for elements with high partition coefficients because the liquid does not become depleted in the 
elements.

Lesher and Burham (2001) pointed out that when sulfide saturation occurs due to the 
mixing of the magma with an external source e.g. addition of country rock equation 3 needs to be 
modified and should be
\[ C_S = \frac{D(C_A R + C_A)}{(R + D)} \] (6)

where \( C_A \) is the initial concentration of the element in the assimilated material. Lesher and Burham (2001) also provide equations for cases where more complex processes have occurred and the reader is referred to this article for such modelling.

One difficulty in modelling PGE behavior is that partition coefficients between sulfide and silicate liquids for these elements are not well established. Whereas it is clear from empirical work that the partition coefficients are greater than 10,000, experimental work has yielded mixed results. Early experimental work (e.g., Crocket et al. 1992; Fleet et al. 1999) gave values in the 1,000 to 100,000 range, but these experiments suffered from the presence of PGM nuggets in silicate glass. The exact composition of the silicate glass could not be reliably determined due to a lack of analytical techniques that could determine the PGE concentrations in situ in the glass. Consequently, experimentalists began to estimate the partition coefficients based on the solubilities of the PGE in haplobasalts. These estimates gave very high partition coefficients \( > 10^7 \) e.g., Pruseth and Palme (2004), Fonseca et al. (2011). Recently this approach has been questioned because the haplobasalts did not contain S and Fe. In experiments where S and Fe were added the solubility of the PGE changed (Laurenz et al. 2013) thus making the partition coefficients determined in Fe- and S-free glasses questionable. The latest experiments, which attempt to address some of these problems (Mungall and Brenan 2014) still produce a wide range in partition coefficients, for instance the partition coefficient for Pd varies from 57000 to 536 000 (Table 1). More details on recent experiments can be found in Brenan et al. (2015).

Some workers suggest that PGE are not dissolved in the silicate magmas but rather are present in “clusters” of PGE and semi-metals or S (Tredoux et al. 1995). When a sulfide liquid forms the whole cluster could be included in this liquid and the PGE concentrations of the sulfide liquid will appear be high, although the PGE are still thought to be present in the sulfide liquid as PGE semi-metal clusters. Therefore in the opinion of these authors it is not possible to reliably determine partition coefficients for PGE between silicate and sulfide liquid. Possible clusters of PtAs have been observed in experimental sulfide liquids (Helmy et al. 2013a) and some PGM found within the BMS of the Merensky reef are interpreted as clusters (Wirth et al. 2013). The presence of clusters has also been demonstrated in other areas of geology and their effect on partitioning and crystallization is an active area of research (Teng 2013). At this time a theoretical framework to quantitatively describe the behavior of clusters has yet to be established (Teng 2013). Indeed clusters may simply represent the first stage of nucleation of a phase (Baumgartner et al. 2013). According to Teng (2013) clusters may not represent a paradigm shift, but rather a deeper understanding of how phases form. Therefore, although clusters of PGE and semi-metals may very well exist we do not necessarily think that they negate partition coefficients; presumably with further study just as the effects of S and Fe on PGE solubility have to be investigated the effects of the various semi-metals will be established.

Empirical determinations of PGE partition coefficients based on determinations of PGE concentrations in droplets of BMS from MORB and glass were initially carried out by Peach et al. (1990) and yielded results \( > 12,000 \) for Ir and \( >23,000 \) for Pd. Roy-Barman et al. (1998) report \( \sim 48,000 \) for Os. Patten et al. (2013) used LA-ICP-MS to determine partition coefficients for all the PGE and calculated minimum partition coefficients in the range of 12,000 to 37,300.
summary, at this time it is not possible to say exactly what partition coefficients of the PGE are
beyond observing that they are very high and probably >20 000.

Partition coefficients determined by experimental work show that values for Ni and Cu
vary between ~ 200 and 2000 depending on magma composition, temperature and \( \text{f}_\text{O}_2 \) (Table 1). For the purposes of modelling we shall use empirically determined partition coefficients
determined from MORB sulfide droplets (Patten et al. 2013) of 776 and 1334.

The flood basalts of the Noril’sk area contain ~100 ppm each of Ni and Cu and ~ 10 ppb
Pt and Pd (Lightfoot and Keays 2005). The disseminated BMS recalculated to 100 % sulfides
contain between 12 and 15 % Cu and between 5 and 8 % Ni and 30 to 300 ppm Pd (Table 4). These values show that the enrichment factors (\( C_s/C_L \)) in the BMS are between 500 and 800 for
Ni and 1200 and 1500 for Cu and 3 000 to 18 000 for Pd. The variation in enrichment factors for
the different elements indicates that high R-factors are required to produce the ores. At low R-
 factors e.g. 100 all of the metals are equally enriched at approximately 100 times (Fig.17).

Nickel has the lowest partition coefficient and thus can only be enriched to a maximum ~800
times (i.e., its partition coefficient). In contrast, Pd with a very high partition coefficient can be
enriched to a greater degree provided that the R-factor is high enough, for example an
enrichment factor of ~ 3000 is required to model the disseminated BMS of the Talnakh and
Kharaelakh intrusions. The Noril’sk 1 intrusion disseminated BMS require an R-factor of at
least 30 000 (Fig.17).

Modelling of the Sudbury sulfide liquid is a little more difficult because the nature of the
silicate liquid is not well constrained. Osmium isotopic work (Walker et al. 1991; Dicken et al.
1992) indicates that a large percentage of the melt was continental crust. Assuming that the
initial liquid had the composition proposed by Keays and Lightfoot (2004) of ~ 60 ppm Ni and
Cu and ~ 4 ppb Pd and Pt, the enrichment factors would be ~1000 for the PGE, 605 for Ni and
Cu requiring an R-factor of ~1000.

Difference in the partition coefficient of Pd and Cu into a sulfide liquid may be used to
deduce the R-factor of magma from which a sulfide segregated (Barnes et al. 1993). Assuming a
partition coefficient for Cu of 1 400 and for Pd of 500 000, for R < 3000, Cu and Pd will be
enriched in the liquid almost equally (Fig.17) and the Cu/Pd of the sulfide will be similar in the
silicate thus the mantle normalized patterns will not show an enrichment of Pd over Cu, e.g. the
BMS from Talnakh and Sudbury (Fig.12). For R > 3000, Pd will be enriched more than Cu, and
the mantle-normalized metal patterns will show enrichment in Pd relative to Cu (e.g., Noril’sk 1
disseminated BMS Fig.12).

Recalculating the composition of the PGE-reef deposits to 100 % BMS may lead to errors
due to the mobility of S, however we can use the different Cu/Pd to estimate the R-factors that
would be required to form the deposits assuming that neither element has been mobilized. This
approach is illustrated in Fig.18. The initial silicate magma is assumed to have contained Cu and
Pd contents similar to the B-1 liquid of the Bushveld. When a sulfide liquid segregates from a
silicate liquid the Cu/Pd of the sulfide liquid will depend on the R factor, with low R-factor BMS
having Cu/Pd similar to the silicate liquid, and BMS with R factors > 3 000 having Cu/Pd less
than mantle values. Tie lines have been drawn between the composition of the sulfide liquid at
R=100, 1000, 10 000, 100 000 and a cumulate containing 10 % silicate liquid fraction and 90%
cumulate consisting of silicate and oxide minerals, assuming these contain no Cu or Pd, (Fig.18).
The Cu/Pd of the Platreef (asterisk) ranges from 1 000 to approximately 3 000 suggesting R-factors of 1 000 to 10 000. The Pd content of the rocks ranges from 500 to 1100 ppb. Combining the Cu/Pd with Pd values gives a sulfide content of around 1 % for the Platreef, which is consistent with the amount of BMS observed in the rocks. The Merensky reef (crosses), the Main Sulfide Zone (solid stars) and the Roby Zone (open crosses) all have similar Cu/Pd and Pd contents and plot between R-factors of 10 000 and 100 000, with Pd contents indicating around 1 % BMS. The amount of BMS indicated in each case is consistent with observed amount of BMS in the rocks. For the UG2 and JM reefs the position of the UG2 (Y) suggests sulfide contents of 0.01 to 0.1 % and the JM reef approximately 1 % BMS, consistent with observations, however they would require extreme R-factors of 1 000 000.

The Cu/Pd diagram can also be used for Ni-deposits; sulfide bearing samples from Talnakh and Kharaelek intrusions (triangles and circles on Fig.19) plot close to the R=1,000 line and can be modeled as a mixture of silicate cumulate and ~1 to 100% sulfide liquids formed at an R-factor slightly above 1 000 (Fig.19). The samples from the Noril’sk 1 intrusion (diamonds) have lower Cu/Pd and plot around the R-factor 10,000 mixing line. These observations are consistent with the amount of sulfide present in the rock and did not require that the analyses be recalculated to 100 % BMS. Many of the basalts overlying the intrusions (squares) have Cu/Pd higher than mantle values (7 000) and are depleted in Pd. They plot along the model line (dashed) for a silicate liquid that has segregated co-tectic proportions of sulfide liquid, suggesting that these could be the liquids from which the BMS segregated.

The calculations indicate that if sulfide liquid is the collector of PGE and if the composition of the magmas is similar to normal basalts (an assumption that seems reasonable because the chills and basalts away from the ore deposits resemble normal basalts) then the sulfide liquid must interact with a very large volume of silicate magma. This requirement raises a problem for closed system models. Applying either the Li and Ripley (2009) or Fortin et al. (2015) equation to the average Noril’sk basalt composition indicates that the basalts attained sulfide saturation at ~ 1000 ppm S. If this sulfide segregates from the magma in situ then the R-factor will be ~ 350 (S content at saturation/S content of the sulfide liquid) and yet most deposits require R-factors of >3 000.

The mechanism generally invoked to attain a high R-factor is to argue for an extremely dynamic system. In the case of Noril’sk 1, Talnakh and Kharaelek, the intrusions that contained the BMS can be thought of as conduits through which many pulses of magma may have been transported. In addition the sulfide droplets themselves may have been formed in a lower chamber and been transported; during transport they could have collected some metals from the transporting magma. They could also have been kept in suspension after they were emplaced and collected some metals from the various pulses of magma that passed through the system. Rice and Moore (2001) carried out finite element modelling to demonstrate how sulfide droplets can be held in suspension above an embayment in the footwall of an intrusion.

In the case of the Platreef it is argued that sulfide saturation took place at depth and the BMS liquid were entrained in the magma and emplaced at the margins of the Bushveld Complex (McDonald and Holwell 2007). During transport BMS could have interacted with large volumes of magma. Some authors (Maier et al. 202013 and references therein) suggest that the Platreef changes character down dip and into the intrusion and merges with the Merensky reef away from the margins of the intrusion. We suggest that possibly the magma with entrained sulfide droplets
froze rapidly to form the Platreef at the margins of the intrusion, however further into the intrusion the incoming magma with entrained droplets had more time to interact with the resident magma and thus the sulfide droplets had the opportunity to collect more PGE and thus the Merensky reef has a higher PGE grade than the Platreef.

The UG2 and JM reef both present a challenge to a simple sulfide collection model. Both require extreme R-factors in the $10^5$ to $10^6$ range (Fig.18) which one of the authors (ER) regards as unreasonable. One possible solution is that the sulfide droplets come into contact with sulfide undersaturated magma and party dissolve (Kerr and Leitch 2005). The sulfides could for example form at the top of intrusion and settle downwards into sulfide undersaturated magma (Holwell and Keays 2014). Due to their very high partition coefficients into sulfide liquid the PGE would be preferentially retained in the sulfide liquid. Other processes that could have affected the JM and UG2 reefs are considered in the crystallization of sulfide liquids and sub solidus sections below.

Crystallization of a sulfide liquid

Experimental work has shown that the first phase to crystallize from a sulfide liquid is an Fe-rich monosulfide solid solution (MSS) and the remaining sulfide liquid becomes enriched in Cu (Kullerud et al. 1969; Dutrizac 1976; Ebel and Naldrett 1997; Sinyakova and Kosyakov 2009). When the temperature decreases sufficiently (<900°C), the Cu-rich liquid crystallizes as intermediate solid solution (ISS). The partition coefficient of Ni between MSS and sulfide liquid is dependent on temperature and $f_{S2}$ of the system (Li et al. 1996; Barnes et al. 1997a; Makovicky 2002; Lui and Brenan 2015). At $f_{S2}$ reflecting crustal conditions the partition coefficient increases from ~0.2 at 1100 °C to ~1 at 900 °C. Thus the evolved MSS is richer in Ni than the first MSS.

Natural examples of the crystallization history of sulfide liquids can be observed in sulfide droplets from MORB. Some have chilled sufficiently rapidly for a quench texture of the BMS to be preserved showing an intergrowth of MSS and ISS, with a Ni-rich phase between the MSS and ISS (Fig.20a). If the crystallization of the liquid proceeds more slowly, then the Cu-rich liquid separates from MSS in some cases. Indeed both in MORB droplets and at Noril’sk 1 there are sulfide droplets with Cu-rich tops and Cu-poor bottoms preserving the crystallization history of the sulfide liquid (Figs. 10 and 20b). In the case of some of the massive ores, after initial crystallization of Fe-rich MSS the Cu-rich fractionated liquid migrates away either into the footwall or into the overlying rocks as seen in the veins surrounding both the Noril’sk Intrusions and the Sudbury Igneous Complex. This fractionated liquid crystallizes as an ISS cumulates and can be seen in some MORB droplets (Fig.20c).

Rhenium, Os, Ir, Ru, and Rh substitute into MSS whereas most other elements do not (Table 1). Thus, the MSS cumulates (Cu-poor massive sulfides) are enriched in IPGE and Re relative to the original sulfide liquid and have flatter mantle normalized metal patterns than the disseminated sulfides (Fig.12b). These elements are also concentrated in the lower parts of the Noril’sk sulfide droplets (Fig.10). Most of the elements aside from Cu, Cd and Zn are also incompatible with the ISS (Table 1) therefore Pd, Pt and TABS partition into the last liquid. Because the major elements have all been consumed there is very little of the late liquid and it is
generally trapped in the ISS cumulate (Cu-rich ore). Consequently the Cu-rich ores are normally
enriched in; Pt, Pd and TABS and have mantle normalized metal patterns that are much steeper
than the disseminated ore (Figs.12b and c and Figs 15c and d). The fractionated interstitial liquid
will be enriched in Pt, Pd and TABS. It is possible that the liquid becomes saturated in Pd and Pt
bismuthotellurides, antinomides and stannides. Composite rounded grains of mixtures of
bismuthotellurides and stannides are found interstitial to chalcopyrite in the Cu-rich ore at
McCreedy East (Figs.21 a and b). The composite nature of these grains suggests that they cannot
be exsolutions and they have been interpreted as the product of crystallization from the late
liquid (Dare et al. 2014).

In some cases the late liquid escapes the ISS cumulate producing a Cu-rich ore depleted in PGE
and TABS and Pd-Pt-TABS-rich liquid. This Pd-Pt-TABS-rich liquid could potentially migrate
into the rocks around the sulfide deposits and form low-S-high-Pd-Pt deposits such as those
found around the Sudbury intrusion (Pentek et al. 2008; Tuba et al. 2014) and in the upper parts
of the Noril’sk intrusions (Sluzhenikin 2011). The Pd-Pt bismuthotellurides which could
crystallize from these liquids solidify at fairly low temperatures (<600 °C, Elliott 1965; Hoffman
and MacLean 1976; Savitsky et al. 1978; Moffatt 1979 a, b). Therefore when there is a structural
adjustment of a cooling cumulate (or possibly even during later metamorphism) the
bismuthotellurides could be readily mobilized and move into fractures and faults and may occur
as isolated grains as seen in the Creighton deposit, Sudbury (Dare et al. 2010 and Fig.21e).
Possibly an extremely fractionated liquid also formed the High Grade zone at Lac des Iles (Djon
and Barnes 2012). One could even suggest that addition of Pd-Pt-TABS liquid to a pre-existing
disseminated sulfide layer formed the JM reef, thus account for the extremely low Cu/Pd ratio
observed in the JM reef, by addition of Pd.

**Late magmatic fluids**

A number of authors (Boudreau et al. 1986; Boudreau et al. 2014; Pentek et al. 2008;
Tuba et al. 2013) favor a role for late magmatic fluids in the formation of PGE-reefs, the Lac des
Iles deposits and the low-S-high-Pd-Pt deposits. In this model late magmatic fluid partly
dissolves magmatic BMS which have already crystallized. Palladium, and to a lesser extent Pt
dissolve into the fluid. The fluid migrates away from the residual BMS and when the physio-
chemical conditions change the fluid deposits the Pd and Pd. In some case the deposition is in
stratiform layers within the intrusion, these are reefs. In some case the Pd and Pt are transported
out of the intrusion and may form low-S-high-Pd-Pt zones surrounding the intrusions. Boudreau
a lesser extent Pt have been added to the JM reef by late fluids. Pentek et al. (2008) Tuba et al.
(2013) argue that the low-S-high-Pd-Pt zones formed around the Sudbury deposits formed in this
way.

Fluids derived from late cooling or metamorphism also result in a change in the BMS
present. At Lac des Iles pyrrhotite and pentlandite are replaced with pyrite and millerite (Djon
and Barnes 2012). The pyrite inherits the PGE that were present in the pyrrhotite and thus
contains Re, IPGE and Rh (Fig.11). Millierite contains some IPGE but does not accept the Pd
thus Pd combines with Te, As and Sb to form isolated PGM grains (Fig.21d). Similar
replacements have been observed in Grasvalley prospect in the Bushveld Complex (Smith et al.
2014). In the case of the Platreef the PGM assemblage in the altered ores is richer in arsenides
and antinomides (Hutchinson and Kinnaird 2005).
**Subsolidus events**

At temperatures <600°C, MSS exsolves to form pyrrhotite and pentlandite +/- pyrite and
ISS exsolves to form chalcopyrite, +/- cubanite +/-pyrite. The sulfide minerals that exsolve from
MSS (pyrrhotite and pentlandite) inherit the IPGE and Re which were in the MSS (Fig.11) and
thus the mass balance indicates that these elements are concentrated in pyrrhotite and pentlandite
(Fig., 13). All of the PGE, Re and Au are incompatible with ISS (Table 1) and thus the
chalcopyrite and cubanite which exsolve from the ISS are poor in highly siderophile elements
(Fig.11).

Significant amounts of Pd are found in pentlandite, which at first glance is surprising because the
partition coefficient of Pd into MSS is 0.1-0.2 (Table 1) and thus one would not expect
pentlandite which is derived from MSS to contain Pd. None the less some Pd will partition pre
into MSS. Dare et al. (2010) postulated that during exsolution of MSS to pentlandite and
pyrrhotite the Pd diffuses along with the Ni into pentlandite. Dare et al. (2010) and Piña et al.
(2012) showed large granular pentlandites, which from at high temperatures, contain more Pd
than small flame pentlandites. They interprets their observation to be the result of the larger
grains, which formed at higher temperature, as having depleting the MSS in Pd before the flame
pentlandite formed. The pentlandite hosts much of the Pd in massive ores because these are
MSS cumulate and thus the contribution of Pd from the Cu-liquid is limited to the trapped liquid
fraction. Consider for example the case where the original sulfide liquid contains 10 ppm Pd,
then the MSS should contain 1ppm. A MSS cumulate with 90 % MSS will then contain 2 ppm
Pd. One ppm of this in the MSS and 1 ppm in the trapped liquid fraction. The Pd in the MSS will
diffuse into pentlandite during exsolution of the MSS and thus 50% of the Pd will be present in
pentlandite.

The diffusion of Pd into pentlandite during exsolution could explain the high Pd content
of the pentlandite formed in MSS cumulates, but it will not explain the tendency for almost 100
% of Pd to be present in pentlandite in BMS thought to represent the sulfide liquid compositions
such as the Noril’sk 1 sulfide droplets (Fig.14). In this case the pentlandite should contain only
10 to 20 % of the Pd. It is possible that not all pentlandite forms by exsolution. Coarse grained
pentlandite occurs between the pyrrhotite and chalcopyrite or cubanite in the droplets (Fig.10).
Makovicky (2002) describes experiments reported by Distler (1977) where the texture was
reproduced in experiments by cooling a sulfide liquid. The “pentlandite” formed by peritectic
reaction between the fractionated liquid and the MSS. They referred to the pentlandite as “high-
temperature” pentlandite. If this is the origin of the coarse pentlandite in the droplets then Pd
could have partitioned into the “high temperature” pentlandite when it formed from the
fractionated liquid.

Not all of the PGE are present in BMS (Fig.13). During cooling and exsolution of the
MSS the solubility of the PGE in the sulfide minerals decreases due the fall in temperature and
the change in S content of the BMS (Makovicky et al.1986; Li et al. 1996) therefore, as the BMS
cool PGM exsolve forming elongate grains within the BMS. For example CuRhPtS exsolutions
develops in pyrrhotite and pentlandite from the Merensky reef (Fig.21c). The formation of PGM
can be enhanced by the circulation of late magmatic fluids or metamorphic fluids which
dissolves some S resulting in a further fall in PGE solubility in the BMS especially at the grain
boundaries (Godel et al. 2007)
Subsolidus processes have also been called upon to explain the low S and Cu contents of the UG2 reef (Naldrett 2011). Naldrett (2011) proposed that originally more BMS were present than are now observed and as the cumulates cooled there was a diffusion of Fe from the BMS into chromite which destabilized the sulfide minerals and resulted in S and Cu loss from the assemblage and in exsolution of laurite from the BMS (Junge et al. 2014). The postcumulate loss of Cu from the UG2 reef could provide a more reasonable explanation for the low Cu/Pd than the very high R-factors suggested by a simple sulfide collection model. Prichard et al. (2004) also suggest S loss explains the PGM mineralogy in the chromite layers of the Merensky reef.

UTILIZATION OF THE Re-Os ISOTOPE SYSTEM IN STUDIES OF MAGMATIC Ni-Cu-PGE ORE GENESIS

Background

Rhenium and osmium may both be concentrated in magmatic sulfide liquids, sulfide minerals or minerals that are strongly associated with sulfides (e.g. arsenides, bismuthinides, tellurides), and hence the Re-Os isotope system has been extensively utilized in studies of sulfide ore genesis. Deposits studied include relatively low-temperature black shale-hosted Ni- and base metal deposits (e.g. Horan et al. 1994; Pasava et al., 2010), hydrothermal Au and related sulfide mineralization (e.g., Selby and Zhao 2012), higher-T porphyry Cu-Mo systems (e.g., Drobe et al. 2013; Barra et al. 2003) and magmatic Ni-Cu-PGE deposits (see reviews by Lambert et al., 1998a, b; 1999a). We will briefly review the application of the Re-Os system to magmatic Ni-Cu-PGE deposits, but stress that the system has applicability far beyond the high-T realm covered here.

All aspects of the Re-Os system that are of importance for geochronology have been covered in other chapters of this book and will not be repeated here (Day and Harvey, 2015; Harvey et al. 2015). The direct dating of molybdenite using the Re-Os system is reviewed by Stein et al. (2001). We will review geochronological applications for several deposits, as appropriate, below. Our emphasis will be on the application of Re-Os isotope measurements as indicators of the source of Os in magmatic ore deposits and the degree of crustal contamination that source magmas have undergone. To this end it is important to review the partitioning behavior of Re and Os into sulfide and silicate melts, silicate and oxide minerals and metallic alloys. One of the basic tenets of the Re-Os system is that during partial melting of the mantle Re is strongly partitioned into the melt, whereas Os is retained in the mantle (e.g., Morgan et al. 1981; Hauri 2002). The high Re/Os ratios developed in the partial melts lead to the production of radiogenic Os in the crust, and much higher $^{187}$Os/$^{188}$Os ratios than in the residual mantle. Mantle-derived magmas that then interact with crust during or after emplacement may be characterized by elevated $^{187}$Os/$^{188}$Os ratios. Although the distribution of Re and Os appears to be well-constrained, the carriers of Re and Os in the mantle remain controversial. Within the mantle both Re and Os appear to be largely controlled by chalcophile tendencies. Studies by Mallmann and O’Neill (2007), Brenan et al. (2003), and Righter and Hauri (1998), indicate that Re may be partitioned into silicate and oxide minerals, but is much more strongly partitioned into sulfide. Experimental studies by Brenan (2008) and Fonseca et al. (2011) indicate that $D_{Os}$(sulfide melt- silicate melt) is on the order of $10^4$ - $10^5$, and $D_{Re}$ (sulfide melt-silicate melt)
for basaltic systems is between ~ 400 and 800 (see also Brenan et al. 2015). If sulfide minerals in the mantle are exhausted during partial melting the high Re/Os values of partial melts can only be explained if Os is retained in the mantle in residual phases such as Os-Ir alloys (e.g., Fonseca et al. 2011). If sulfide minerals are retained, then the results of Brenan (2008) suggest that Os may be considerably more compatible than Re in residual sulfide, and observed Re/Os ratios in basaltic partial melts can be produced. Additional studies are needed to better constrain the sites of Re and Os in the mantle, and particularly the partitioning of Os into residual phases such as alloys during high degree partial melting of the mantle where sulfide minerals are completely dissolved in the partial melt. Many studies of magmatic Ni-Cu-PGE deposits are consistent with Re-enrichment in the crust. Whether this is completely a function of melting where sulfide is retained in the mantle, the retention of Os in alloys, or local interaction between mantle magmas and crustal sedimentary rocks where Re may be strongly enriched over Os (e.g. organic – rich shales) must be determined on a deposit to deposit basis.

Examples of the application of the Re-Os isotope system to several Ni-Cu-PGE deposits are presented below. However, we first review the basic tenets of how the system has been applied in the evaluation of contamination of mafic and ultramafic magmas. The $\gamma_{\text{Os}}$ terminology has been defined in other chapters (Harvey et al. 2015), but in brief is the deviation in $^{187}$Os/$^{188}$Os from Bulk Silicate Earth (BSE), taken as either Primitive Mantle or Chondrite, at the time of interest; $\gamma_{\text{Os}} = (\frac{^{187}\text{Os}^{188}\text{Os}(\text{sample}) - ^{187}\text{Os}^{188}\text{Os}(\text{PM or CH})}{^{187}\text{Os}^{188}\text{Os}(\text{PM or CH})}) \times 100$ (see Shirey and Walker 1998 and Carlson 2005). When isochronous behavior is demonstrated the initial $^{187}$Os/$^{188}$Os value is utilized in the $\gamma_{\text{Os}}$ calculation. Gamma Os values that show significant deviation from 0 typically result from either crustal contamination or hydrothermal processes involving the transport of Re, Os or both. Derivation of magma from recycled crust in the mantle or metasomatically enriched lithosphere may also produce negative or positive deviation from 0, although the number of intrusions with $\gamma_{\text{Os}}$ values near those of BSE suggests that processes occurring in the crust are of more significance in controlling $\gamma_{\text{Os}}$. An isochron diagram is useful for illustrating the effects of these processes. Figure 22 shows a mantle-derived magma with a low $^{187}$Re/$^{188}$Os ratio ( mafic magmas may have a wide range of Re/Os ratios but here we take a value less than 150 as being representative of basaltic magmas), which interacts with a crustal sedimentary rock with an elevated $^{187}$Re/$^{188}$Os ratio. We utilize a sedimentary contaminant with an age of 1.85 Ga, and mixing between the mantle magma and the sedimentary contaminant at 1.1 Ga. The choice of initial $^{187}$Os/$^{188}$Os ratio is arbitrary, but we use a chondritic initial for both the mantle-derived magma and the sedimentary contaminant (e.g. mantle-derived detritus, or seawater controlled by leaching of chondritic oceanic crust). The isochron which represents growth of the sedimentary rock from 1.85 Ga until 1.1 Ga is shown for reference, as is the isochron for uncontaminated mantle. At 1.1 Ga a mantle-derived magma is emplaced and is contaminated with Os derived from the sedimentary rock (point M). Crystallization of the contaminated magma and decay from the time of mixing (1.1 Ga) until the present will produce an isochron yielding the age of the mixing event with an elevated initial Os/$^{188}$Os, and an elevated $\gamma_{\text{Os}}$ value. If multiple pulses of magma are involved that may have interacted to different degrees with the sedimentary country rocks (different $f$ values), then a knowledge of the age of the intrusion (e.g. from U-Pb isotope measurements) is required to assess the range of $\gamma_{\text{Os}}$ values. The two-component isotopic mixing equation has the form:
\[
(187\text{Os}/188\text{Os})_{\text{mix,o}} = \left(\frac{(C_{\text{Os}}^s)(f)}{(C_{\text{Os}}^c)(1-f)} + (C_{\text{Os}}^c)(1-f)\right)\left((187\text{Os}/188\text{Os})_{s,o} + (187\text{Re}/188\text{Os})_{s,t2}(e^{2t_1} - e^{2t_2})\right) \\
+ \left(\frac{(C_{\text{Os}}^c)(1-f)}{(C_{\text{Os}})(f)} + (C_{\text{Os}}^c)(1-f)\right)\left((187\text{Os}/188\text{Os})_{c,o} + (187\text{Re}/188\text{Os})_{c,t2}(e^{2t_1} - e^{2t_2})\right)
\]

Where \(f\) = mass fraction of the mantle-derived source magma, \(C_{\text{Os}}^s\) and \(C_{\text{Os}}^c\) = concentration of Os in the source magma and contaminant, respectively, subscripts \((\text{mix,o})\), \((s,o)\), and \((c,o)\) refer to the initial \(187\text{Os}/188\text{Os}\) ratio of the mixture, source magma, and contaminant, subscripts \((c,t2)\) and \((s,t2)\) refer to the \(187\text{Re}/188\text{Os}\) ratios of contaminant and source magma at the time of mixing, \(T = 4.557 \times 10^9\), \(t_1\) = age of the contaminant, and \(t_2\) = time of mixing.

We illustrate in Figure 23 that in addition to multiple magma pulses and variable degrees of contamination, a suite of non-linear \(187\text{Os}/188\text{Os}\) values may also indicate either Re loss/gain or Os gain/loss via lower-temperature interaction with fluids. Xiong and Wood (2001) have shown that Re may be soluble as a hydroxyl species in low-\(T\) fluids, and recent studies by Foustoukos et al. (2014) further quantify the extent to which Re and Os may be transported via hydrothermal fluids. Figure 23 illustrates a case of crystallization from 1.1 Ga until 0.5 Ga, when hydrothermal alteration changed the Re/Os ratio of the system. In the case of Re loss or Os gain the resultant \(187\text{Os}/188\text{Os}\) values will plot above the isochron for the uncontaminated system and these points may be difficult to distinguish from those produced by variable degrees of crustal contamination of multiple pulses of magma. Sampling at small spatial intervals may be required to resolve the interpretation; evidence of high degrees of hydrothermal alteration would be expected. In the case of Re gain or Os loss the resultant \(187\text{Os}/188\text{Os}\) values will fall below the expected isochron for uncontaminated mantle and will produce negative \(\gamma_{\text{Os}}\) values. Scatter in \(187\text{Os}/188\text{Os}\) values must be carefully evaluated as it may not be indicative of contamination of mantle-derived magma, but perturbation of the Re-Os system by interaction between igneous rock and low-temperature fluids.

The “R-factor” and its application to Re-Os isotopes

The “R-Factor” (ratio of sulfide liquid to silicate magma) has been discussed above, and is often mentioned in conjunction with Re-Os isotope studies (e.g., Lambert et al. 1998a, b, 1999a). If S in the ore-forming system has been primarily derived from country rocks, and contamination has involved only S, then the R-factor directly relates to f values where f(silicate) = R/(1+R). In the more general case where a sulfide-undersaturated magma assimilates country rock, including S, utilization of the “R-factor” is appropriate after the separation of immiscible sulfide liquid. Although both Re and Os may be strongly partitioned into the sulfide liquid (see above), no isotopic fractionation accompanies this process. If Os is more strongly partitioned into the sulfide liquid than is Re, then the Re/Os ratio of the sulfide liquid may be lower than that of the coexisting silicate magma, but crystallization products of both liquids should lie along the same isochron provided closed system conditions have prevailed. This is an important point in the evaluation of massive sulfides that are suspected of separating from a parent liquid that is now represented by a silicate assemblage that contains only disseminated sulfides. If the systems share a common origin then they should fall along the same isochron.
Examples of the application of the Re-Os isotope system to magmatic ore deposits

The Sudbury Igneous Complex. The Sudbury Igneous Complex (SIC) was the world’s largest producer of Ni, with significant production of PGEs as by-products. Walker et al. (1991) presented results of one of the earliest applications of the Re-Os system to magmatic ore deposits, in this case the Ni-Cu ores of the SIC. The work by Walker et al. (1991) was followed by studies by Dickin et al. (1992) and Morgan et al. (2002) who obtained greater precision in measurements using negative thermal ionization mass spectrometry. All of these studies confirmed the presence of crustal Os in the ores. Samples collected from the McCreedy West and Falconbridge mines produced isochrons of 1835 ± 70 Ma and 1825 ± 340 Ma, respectively (Morgan et al. 2002; Fig. 24). The ages agreed within uncertainty with that of 1850 ± 1 Ma determined using U-Pb methods by Krogh et al. (1984). Gamma Os values for the McCreedy West data averaged 346 ± 10 and that from Falconbridge was 375 ± 12. The $^{187}$Os/$^{188}$Os values could be modelled as resulting from mixtures of Proterozoic and Archean country rocks, However, Morgan et al. (2002) also used $^{186}$Os/$^{188}$Os ratios to indicate that in addition to metasedimentary rocks a third component was necessary to explain the Re-Os systematics of the Falconbridge and McCreedy West samples. The third component was thought to be either mafic rocks of Archean or Proterozoic age. It is now thought that the Sudbury melt sheet included Ni-Cu and PGE-bearing sulfides from Proterozoic mafic rocks in the target area (Keays and Lightfoot 2004). Of particular significance is the conclusion that the Re-Os isotope systematics of the Sudbury ores can only be explained if a significant portion of Os was derived from crustal metasedimentary rocks, in agreement with the origin of the SIC as an impact melt sheet.

Ni-Cu-PGE deposits of the Noril’sk region, Siberia. Walker et al. (1994) and Malitch and Latypov (2011) have presented Re-Os isotopic data from the Noril’sk, Talnakh, and Kharaelakh ore-bearing intrusions. Data from both studies provide isochrons that are consistent with the U-Pb ages of the intrusions (~ 247 Ma) and $\gamma_{Os}$ values that show slight differences between intrusions but range from only 0.4 to 12.9 (Figure 25). Both Walker et al. (1994) and Malitch and Latypov (2011) suggested that the Re-Os isotopic values may be indicative of their mantle source and in particular deep mantle that had incorporated ancient Re-enriched crust. Alternatively, the $\gamma_{Os}$ values could be indicative of very minor amounts of crustal contamination in the lithosphere. The very low $\gamma_{Os}$ values do not indicate the extensive interaction with crustal material that is suggested by the elevated sulfur isotope compositions of the ores (e.g. Grinenko 1966; Ripley et al. 2003; Malitch et al. 2014) and the anomalous Sr isotope compositions reported by Arndt et al. (2003). This may reflect the derivation of S and Sr from evaporates which would tend to have low concentrations of Re and Os. Alternatively, Lesher and Burnham (2001) suggested that due to mass action constraints, Re-Os isotopic values may be “re-set” to near chondritic values and S isotope values little affected as uncontaminated mantle-derived magmas exchanged with sulfides in a conduit environment. A similar process has been proposed to explain the Re-Os isotopic systematics of the Eagle deposit (see below).

The Voisey’s Bay Ni-Cu-Co deposit, Labrador. Lambert et al. (1999b 2000) have utilized the Re-Os isotope system in the interpretation of the genesis of the Voisey’s Bay Ni-Cu-Co deposit. The deposit is known as a “conduit-type” because of the clear occurrence of sulfide
Mineralization in dike-like bodies that connect larger intrusions (e.g., Naldrett and Li 2007; Lightfoot et al. 2012). Massive sulfide mineralization occurs in a widened portion of the dike that connects the western deeps intrusion and the upper Eastern deeps intrusion. Mining of the massive sulfide, or “Ovoid”, is currently in progress. Lambert et al. (1999b 2000) identified two scales of Re-Os isotope development, and a multi-stage process of mineralization. Whole rock samples of the massive sulfide assemblage remained closed over a large spatial interval, and an imprecise 1323 ± 135 Ma isochron was generated; this age was within error of the 1332.7 ±1 Ma badelleyite U-Pb age for the Voisey’s Bay intrusion of Amelin et al. (1999). Of particular significance is the initial $^{187}\text{Os}/^{188}\text{Os}$ value determined from the isochron plot (Figure 26). This initial ratio yielded a $\gamma_{\text{Os}}$ value of 1040 ± 200, signifying extensive contamination with old crustal material. The Proterozoic Tasiuyak Gneiss was taken to be a likely source, as other petrogenetic indicators also suggested that assimilation of the Tasiuyak Gneiss had been extensive (e.g., Li and Naldrett 2000). Archean rocks of the Nain Province could not be entirely eliminated, and Lambert et al. (2000) suggested that a two-stage process of magma contamination had occurred, with high-MgO basaltic magmas first contaminated in the lower crust. The results from the study of the whole rock massive sulfides provide an excellent example of how the Re-Os system may provide both geochronologic data and information on magma-country rock interaction. In this case the Re-Os system of the sulfides was homogenized prior to crystallization of the sulfide assemblage. Lambert et al. (2000) also showed that disseminated sulfide-bearing intrusive rocks showed a great deal of scatter on an isochron plot, and suggested that variable degrees of mixing with country rocks were responsible. In addition, sulfide mineral separates from the massive sulfides defined an isochron with an age of 1004 ±20 Ma, consistent with re-setting of the sulfide system on the mineral scale as a result of hydrothermal alteration associated with the Grenville orogeny.

**The Eagle Deposit, Midcontinent Rift System, Michigan.** The Eagle deposit is a newly discovered Ni-Cu-PGE sulfide deposit in mafic rocks associated with the 1.1 Ga Midcontinent Rift System of Minnesota, Michigan and Canada. Mineralization occurs within irregularities in a dike-like body which is part of the Marquette-Baraga Dike Swarm (Ding et al. 2010). It bears similarities to the Voisey’s Bay deposit in terms of its conduit environment. Ding et al. (2012) present Re-Os isotopic data from disseminated, net-textured and massive sulfides. Results produced an isochron of 1106 ±34 Ma (Figure 27), in good agreement with the U-Pb age of the intrusion of 1107 ±2 Ma reported by Ding et al. (2010). The $\gamma_{\text{Os}}$ value corresponding to the initial $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.1607 was 34, and could be explained by less than 3% bulk contamination of a mantle-derived picritic magma with Proterozoic country rocks. The apparent low degree of contamination is contrary to models for ore genesis that favor extensive crustal contamination. Ripley and Li (2003) and Ding et al. (2012) showed how exchange reactions in magma conduits involving early-formed sulfide and uncontaminated magmas could produce isotopic values approaching those of the uncontaminated magma and mask evidence for earlier high degrees of contamination (Figure 28).

**The Stillwater Complex, Montana.** As described above, the 2700 Ma Stillwater Complex hosts one of the world’s major PGE reef-style deposits. The J-M Reef and host rocks, as well as PGE-bearing chromitites in the Ultramafic Series, have been studied using the Re-Os isotope system by a number of researchers (e.g., Lambert et al. 1989, 1994; Martin 1989, Marcantonio et al. 1993; Horan et al 2001). Lambert et al. (1989, 1994), Martin (1989), and Horan et al (2001) have all concluded that two sources of Os were involved in the generation of the Complex. Lambert et
al. (1994) reported that PGE-enriched units of the Complex (B chromitite seam and the J-M Reef) were isochronous and characterized by elevated $\gamma_{\text{Os}}$ values of 12 to 34. PGE-poor chromitites (G and H) were found to be near-chondritic with $\gamma_{\text{Os}}$ values of -2 to +4. The Re-Os data were consistent with other petrogenetic data that indicated that two magma types were involved—one an ultramafic magma with little sign of crustal contamination but possible derivation from the subcontinental lithospheric mantle, and the other a more mafic to anorthositic magma that had been contaminated with Archean crust prior to emplacement. The mixing of these two magma types was proposed to account for the elevated $\gamma_{\text{Os}}$ values and was thought to be instrumental in the formation of the J-M Reef. Horan et al. (2001) separated chromite from chromite seams and silicate–rich layers of the Ultramafic Series. They found variable $\gamma_{\text{Os}}$ values ranging from 2 to 16.4, and also suggested that two magmas were involved in the formation of the Ultramafic Series, one which was near-chondritic and the other which was characterized by elevated $\gamma_{\text{Os}}$ values and had been contaminated by sedimentary rocks beneath the Complex. Martin (1989) concluded that a chondritic mantle melt was contaminated with mafic to intermediate crust at the time of the Ultramafic-Banded Series transition and at the time of J-M Reef formation. Marcantonio et al. (1993) indicated that chromitites from the Ultramafic Series were derived from a mantle magma that had been affected by little or no interaction with continental crust. The minor scatter in the chromitite Os isotope values was attributed to hydrothermal processes. Molybdenite (Re-rich and Os-poor) was separated from the G-chromitite and yielded an age of 2740, in agreement with the accepted age of the Complex. Marcantonio et al. (1993) suggested that all elevated $\gamma_{\text{Os}}$ values found in the Complex could have resulted from interaction with hydrothermal fluids of the type which produced the molybdenite.

The Great Dyke, Zimbabwe. Schoenberg et al. (2003) have studied chromite separates from chromitites of the 2576 Ma Great Dyke. Results from their study show that most chromitites form an imprecise isochron of 2580 ± 500 Ma (Fig. 29). Mixing calculations involving Archean country rocks suggest that from 0 to 33% of the Os in the chromitites may have been of crustal origin. When combined with other isotopic and petrologic data the authors concluded that the source magmas underwent no interaction with subcontinental lithospheric mantle, and that the parent magma of the Great Dyke was plume-derived with a heterogeneous Os isotope signature, not unlike some oceanic basalts where the incorporation of recycled oceanic crust has been proposed. Significant contamination by Archean granitoid crust was ruled out based on the low Os concentrations and unradiogenic Os isotope ratios of representative country rock samples.

The Bushveld Complex, South Africa. Re-Os isotope studies of chromitites, pyroxenites, sulfides and alloys have been conducted as an aid in evaluating the genesis of PGE enrichment in the UG2 chromitite (McCandless and Ruiz 1991; Schoenberg et al. 1999), the Merensky Reef (Hart and Kinloch 1989; McCandless and Ruiz 1991; Schoenberg et al. 1999), and the Platreef (Reisberg et al. 2011). Results of these studies have been summarized by Reisberg et al. (2011), and are shown here in Figure 30. The results from all of these studies indicate that the Bushveld parent magmas underwent variable degrees of contamination by crust, in agreement with other isotopic indicators of crustal contamination. Schoenberg et al. (1999) note that chromitites show increasing $^{187}\text{Os}/^{188}\text{Os}$ values upward, from near chondritic values in the lower chromitites to strongly enriched values in the upper chromitites. The enrichment was thought to be a result of enhanced degrees of crustal contamination. Hart and Kinloch (1989) analyzed erlichmanite and laurite grains from the Merensky Reef, and found that erlichmanite was near chondritic, with $^{187}\text{Os}/^{188}\text{Os}$ values similar to those of the lower chromitites. Laurite grains were strongly
radiogenic, with $^{187}$Os/$^{188}$Os values similar to those of sulfides and whole rocks from the Reef reported by both McCandless and Ruiz (1991) and Schoenberg et al. (1999). McCandless and Ruiz (1991) suggested that the contaminant was Re-rich black shales that occur below the Complex. Schoenberg et al. (1999) proposed that primitive mantle-derived magma mixed with highly contaminated granophytic roof melt near the top of the chamber. In both scenarios the Merensky Reef records a substantial contribution of crustally derived Os. The chondritic erlichmanite grains found in the Reef by Hart and Kinloch (1989) suggest that uncontaminated mantle-derived magma was first emplaced at the level of the Reef, but that highly crustally contaminated magma followed. It is also possible that the erlichmanite grains represent mantle xenocrysts and that crustally contaminated magmas from chambers at depth entrained them. The radiogenic signals from pyroxenites of the Platreef also led Reisberg et al. (2011) to propose that the Platreef parental magma was crustally contaminated by black shales, and well-mixed prior to emplacement. They note that the rapid return to less radiogenic Os isotope compositions above the Merensky Reef cannot mark a change from one magma type to another, but must represent the input of a large quantity of radiogenic Os at the level of the reef. The spike in $^{187}$Os/$^{188}$Os values at the level of the Merensky Reef and the Platreef was thought to indicate the contamination of magma by a crustal lithology unusually rich in radiogenic Os – most likely black shales. The Reisberg et al. (2011) model differs somewhat from the McCandless and Ruiz (1991) model in that Reisberg et al. (2011) propose contamination in magma chambers at intermediate crustal depths, rather than immediately below the current base of the Complex. Using representative concentrations and $^{187}$Os/$^{188}$Os ratios Reisberg et al. (2011) determined that less than 1% bulk assimilation of black shale was necessary to account for the enriched signals in the Platreef. They also suggested that minor additional crustal contamination may have occurred at the level of emplacement of the Platreef.

Summary. The Re-Os isotope system has obvious utility in the age-dating of magmatic ore deposits. In addition, the system may be a sensitive indicator of the importance of crustal contamination in ore formation. Results range from those where there is very little Os isotope indication of crustal contamination being involved in ore genesis (e.g. Noril’sk, Great Dyke) to those where the addition of crustal Os is strongly indicated (e.g., Sudbury, Voisey’s Bay, Bushveld). In conduit deposits such as Noril’sk and Eagle where other isotopic systems (e.g., S, Rb-Sr) support a strong role for crustal contamination, a process such as isotopic exchange and mixing involving sulfide-rich magma in the conduit and uncontaminated magmatic pulses may explain the decoupling between the isotopic systems. Another end-member interpretation is that in some environments country rock contaminants may contain insufficient Re and Os to perturb the mantle characteristics of the source magma, whereas concentrations and isotopic values are sufficient to readily perturb other isotopic systems such as S. A third interpretation would be that in systems where no Os isotope evidence for contamination exists, the magma was derived from a mantle source that had been modified by the addition of crustal components such a S (e.g., addition of altered crust via subduction) and as a result was characterized by anomalous S isotopic ratios, but the amount of radiogenic Os added was too small to perturb the mantle Os signal. Subcontinental lithospheric mantle is thought to be Re-depleted and hence melts derived from that source should be expected to have negative $\gamma_{Os}$ values. The Re-Os isotopic system will no doubt continue to be a major tool for the evaluation of the source of Os and the significance of crustal contamination in magmatic Ni-Cu-PGE deposits. Care must be taken to ensure that isotope perturbations have not been caused by hydrothermal activity and the mobility of Re and Os in relatively low-temperature fluids.
Conclusions

Most PGE ore deposits are found within or at the contact with mafic-ultramafic intrusions and are associated with base metal sulfide minerals, pyrrhotite, pentlandite and chalcopyrite. The PGE are present in pyrrhotite, pentlandite and in PGM found among the BMS and at the contact between BMS and chromite or silicates. The standard model for the formation of the deposits is that a mafic to ultramafic magma became saturated in a base metal sulfide liquid and the PGE partitioned into this sulfide liquid. The PGE content of the liquid is dependent on the composition of the silicate magma but also on the amount of magma with which it interacted. In order to form a PGE ore deposit the sulfide liquid must interact with a very large amount of silicate magma. Some deposits such as the droplet ore of Noril’sk 1 or Merensky reef and Main sulfide zone may have formed in this manner. Other deposits require additional processes to explain the variations in PGE content of the ores. Fractional crystallization of the sulfide liquid is an important process that leads to the formation of an MSS cumulate depleted in Cu but enriched in Re, Os, Ir, Ru and Rh. The fractionated liquid is enriched in Cu, Pt, Pd, Au and TABS. Intermediate solid solution sulfide crystallizes from the fractionated liquid but Pt, Pd, Au and TABS do not partition into ISS and they concentrate into the very last liquid. In most cases this liquid is trapped with ISS cumulate and as a result the Cu-rich ore is also Pt, Pd and Au and TABS rich. The variations in PGE contents in some ores such as the McCreedy East deposit of Sudbury or the Talnakh and Kharaelakh deposits of the Noril’sk area are the result of this crystal fractionation. The Pt-Pd-,Au-TABS rich liquid would not crystallize until relatively low temperatures (500-600 °C). Therefore, it is possible that the liquid could be injected into the fractures around or within the intrusion during some structural disturbance. Also even once crystallized it could melt at lower amphibolite faces conditions and migrate during metamorphism. Possibly the low-S-high-Pt-Pd deposits such as the High Grade ore of Lac des Iles or Broken Hammer of Sudbury formed by mobilization of Pd-Pt-TABS liquid.

Because of the chalcophile nature of both Re and Os the Re-Os isotopic system is widely applied in the evaluation of ore genesis. The system has wide applicability in the geochronology of magmatic ore systems. In addition, the long-term enrichment of Re in the crust has made the system a very sensitive one in the evaluation of the degree of interaction between mantle-derived magmas and continental crust. Osmium isotope ratios may provide an indication of the source of Os in an ore deposit, as well as the extent of country rock contamination that may have been important in the ore-forming process.

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community who organized and participated in conferences and field trips to the world’s Ni and PGE deposits; seeing these deposits and discussions with colleagues on these occasions greatly helped to clarify our ideas. We thank the editors Dr. Havey and Day for the invitation to write this chapter and the reviewers Dr. D. Holwell and ? for their time and effort in helping to improve the manuscript.
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Figure captions

Figure 1 Main producers of Pt and Pd in 2013, calculated from Cowley (2013)

Figure 2 Geology of the Bushveld Complex showing the location of the 3 main deposits, Platreef, Merensky reef and UG2 reef. (modified after Barnes and Maier 2002a)

Figure 3 Geology of the Noril’sk-Talnakh area showing the location of the Noril’sk 1, Talnakh and Kharaelakh i3ntrusions. Modified after Zientek et al. (1994)
**Figure 4** Simplified geology of Zimbabwe showing the location of the Great Dyke. Modified after Prendergast and Wilson (1989).

**Figure 5** Geology of the Stillwater Complex showing the position of the JM reef. Modified after Godel and Barnes (2008).

**Figure 6** Geology of the Lac des Iles Complex modified after Djon and Barnes (2012).

**Figure 7** Geology of Sudbury Igneous Complex showing location of the McCreedy East deposit, modified after Dare et al. (2014).

**Figure 8** Stratigraphic columns of Bushveld, Great Dyke and Stillwater showing the positions of the reefs. MR = Merensky, MSZ = Main sulphide zone, modified from figures of Barnes and Maier (2002a) Prendergast and Wilson (1989); Zientek et al. (2002).

**Figure 9** Cross sections of the a) Noril’sk 1 and b) Oktrabr’sky deposits redrawn and simplified from figures in Torgashin (1994) and Sluzhenikin et al. (2014).

**Figure 10** Zoned sulfide droplet from Noril’sk 1 (this work). Distribution of Fe, Cu, Ni determined by micro-XRF. Distribution of PGE determined by laser ablation ICP-MS. $^{108}\text{Pd}$ has been corrected for Cd and Zn interferences. $^{103}\text{Rh}$ has been corrected for Cu interference. $^{101}\text{Ru}$ has been corrected to Ni interference. Cb = Cubanite, Cp = Chalcopyrite. Pn = Pentlandite, Po = pyrrhotite.

**Figure 11** Mantle normalized concentrations in pentlandite, pyrrhotite, chalcopyrite and pyrite data sources listed in Table 3.

**Figure 12** Mantle normalized whole rock metal patterns for Noril’sk and Sudbury data sources listed in Table 4.

**Figure 13** Results of mass balance calculations showing that pentlandite hosts Re and all the PGE except Pt, pyrrhotite hosts Re and all the PGE except Pd and Pt, pyrite also hosts Re and most PGE except Pd and Pt. Chalcopyrite is not a significant host of any of the PGE. Data from: Barnes et al. (2006); Godel et al. (2007); Barnes et al. (2008); Godel and Barnes (2008); Dare et al. (2011); Djon and Barnes (2012).

**Figure 14** Mantle normalized whole rock metal patterns for PGE-dominated deposits. Data sources shown in Table 4.

**Figure 15** Concentrations of Sn, Sb, As, Bi, Te normalized to mantle values and plotted in order of compatibility with sulfide liquid. a) MORB, Upper Continental Crust and Black Shale; b) PGE dominated deposits; c) Cu-rich massive sulfides; d) Cu-poor massive sulfides. The mantle normalized concentrations of the elements in the ores increases from Sn to Te. The PGE-dominated deposits have low concentrations of these elements. The Ni-sulfide deposits are systematically richer in all the elements and the Cu-rich sulfides are richer than the Fe-rich sulfides. Data sources in Table 5.
Figure 16 a,b,c Plot of Pd vs Pt concentrations for basalts and komatiites from the literature (grey circles, rocks with >30 wt % MgO or >1500 ppm S), compared with; a) the compositions of the Noril’sk basalts (Lightfoot and Keays 2005), b) Bushveld chills (Barnes et al. 2010), c) Stillwater chills, cross (Zientek et al. 1986), d) Plot of Ir vs MgO for basalts and komatiites from the literature. Note that the Noril’sk basalts and Stillwater chills have similar Pt and Pd contents to unmineralized basalts and komatiites. The Bushveld chills have similar Pd values to unmineralized basalts and komatiites, but appear slightly richer in Pt than most of the basalts from the literature. Literature data from Maier et al. (2009)

Figure 17 Plot of enrichment factors (Cs/Cl) vs R-factor for elements with partition coefficients between 10 and 100 000. The enrichment factors of Pd for Talnakh and Kharaelakh (T&K) indicate lower R-factors ~3 000 than those of Noril’sk 1 ~ 20 000.

Figure 18 Plot of Cu/Pd vs Pd for PGE-dominated deposits. Solid lines show the mixing lines between sulfides formed at R-factors of 100, 1000 and 10 000 100 000 with cumulate consisting of 90% cumulate and 10 % trapped liquid fraction. Solid dots indicated 100 %, 10 %, 1 % and 0.1 % sulfides present in the rocks. Data from sources in Table 4

Figure 19 PGE Plot of Cu/Pd vs Pd for the Noril’sk basalts, the deposits in the Kharaelakh, Talnakh and Noril’sk 1 intrusions The dashed line shows the modelled composition of the basalt if a sulfide liquid is removed in co-tectic proportions, dots represent 0.1, 0.2 and 0.3 % crystallization. Note that many of the basalts plot along this line which suggests they have segregated a sulfide liquid. Also the sulfides found in the Noril’sk 1 intrusion require higher R-factors (~10 000) than the sulfides found in the Kharaelakh and Talnakh intrusions (~1 000) data from Zientek et al. (1994) and Lightfoot and Keays (2005).

Figure 20 Photomicrographs of sulfide droplets found in MORB glass (modified after Patten et al. 2012) a) Droplet that crystallized rapidly showing MSS and ISS intergrowth with Ni-rich phase between the two phases. b) A droplet that crystallized slightly more slowly resulting in solid MSS at the base and quenched textured ISS in the top left hand corner. c) A droplet that crystalized slowly with MSS at the margins and solid ISS in the center.

Figure 21 Back scatter electron images of PGM: a) and b) PGM that have crystallized from the fractionated interstitial liquid (modified from Dare et al. 2014); c) CuPtRhS exsolution in pyrrhotite and pentlandite from the Merensky reef (modified from Prichard et al. 2004); c) Residual PGM after the replacement of pentlandite, Lac des Iles (modified from Djon and Barnes 2012); e) Remobilized Pd bismuthotelluride, (modified from Dare et al. 2010)

Figure 22. $^{187}\text{Os}/^{188}\text{Os}$ versus $^{187}\text{Re}/^{188}\text{Os}$ isochron diagram illustrating mixing at 1.1 Ga between an uncontaminated mantle magma and a Re-rich sedimentary rock that had evolved between 1.85 Ga and 1.1 Ga. The contaminated magma (M) crystallizes at ~ 1.1 Ga and evolves to the position of the contaminated bulk rock, far above the $^{187}\text{Os}/^{188}\text{Os}$ value that the uncontaminated rock would have attained. Minerals A and B may crystallize from the contaminated magma, and together with the bulk rock value define an isochron with an elevated $\gamma_{\text{Os}}$ (i) value.
Figure 23. Isochron diagram illustrating the potential effects of Re loss/gain and Os loss/gain on today’s isotope ratios. In this example a rock derived from a mantle-derived magma at 1.1 Ga evolves to 0.5 Ga and then the system is opened via interaction with a fluid. In the case of Re loss/Os gain, the $^{187}$Re/$^{188}$Os values are reduced and the resultant values may evolve to $^{187}$Os/$^{188}$ Os values that lie above the expected isochron for unperturbed samples, and may be difficult to distinguish from samples with elevated $\gamma_{Os}$ values due to crustal contamination. In the case of relative Re gain/Os loss the resultant values are below those produced from uncontaminated magma and are characterized by negative $\gamma_{Os}$ values.

Figure 24. Isochron diagram for samples from the McCreedy West mine, Sudbury (modified from Morgan et al., 2002).

Figure 25. Isochron diagram for samples from the Noril’sk 1 and Talnakh intrusions (modified from Walker et al. 1994).

Figure 26. Isochron diagram for samples from the Voisey’s Bay deposit (modified from Lambert et al...1999b).

Figure 27. Isochron diagram for samples from the Eagle deposit (modified from Ding et al. Figure captions 2012).

Figure 28. Plot showing the decrease in Os and S isotope ratios due to exchange between sulfide in a conduit system and batches of uncontaminated, mantle derived magma. The equation of Ripley and Li (2003) was used to calculate the trends: $\delta^{34}$S$_{sul,exchanged} = (\delta^{34}$S$_{sul,initial} + R* (\delta^{34}$S$_{sil,initial} + \Delta))/1+ R*$. For Os the $^{187}$Os/$^{188}$Os ratio is used rather than the $\delta^{34}$S value. In this example the initial $^{187}$Os/$^{188}$Os ratio of the sulfide was set at 1, the $^{187}$Os/$^{188}$Os ratio of the mantle-derived magma was 0.15, the concentration of Os in the silicate magma was set at 1 ppb, the $\delta^{34}$S values of the magma and sulfide were 0 and 12 ‰, and the concentrations of S in the sulfide and magma were 30 wt. % and 1000 ppm, respectively. R* is $(C_{sil}/C_{sulf})*R$, where concentrations are S or Os and R is the silicate liquid/sulfide liquid mass ratio. N is the integrated silicate/sulfide mass ratio where in this example each pass of uncontaminated magma interacted with an equal mass of sulfide (R=1). $\Delta$ is the isotopic difference between sulfur or osmium in the sulfide mass and that in the silicate melt (at magmatic temperatures this value is ~ 0). If the R value for each increment of exchange is larger, then the rate of S or Os isotope decline is greater.

Figure 29. Isochron diagram for samples from the Great Dyke (modified from Schoenberg et al. 2003).

Figure 30. $^{187}$Os/$^{188}$ Os values from the Bushveld Complex (modified from Reisberg et al., 2011). The Sandsloot pyroxenites are from the Platreef and have values very similar to those of the Merensky Reef (Reisberg et al. 2011).
Fig. 1
Flood basalts (Triassic-Permian)
Clastics (Permian-Carboniferous)
Carbonates + Evaporites (Paleozoic)
Ontario
Quebec
U.S.A.
350 km

Archean and Proterozoic
Whitewater Group
Onaping Formation

Sedimentary rocks
Fallback Breccia

Sudbury Igneous Complex
Granophyre
Norite
Sublayer Norite
Diorite ‘offset’ dykes

Ni-Cu-PGE deposit

Palaeoproterozoic
Metavolcanic and Metasedimentary rocks
Granite plutons

Archean and Proterozoic

Gneiss and granite
Fault

North Range
McCreedy East
SRSZ
McCready West
Strathcona

Frood
Gertrude
Kelly Lake
Creighton
Copper Cliff South
Creighton Fault
SRSZ
Broken Hammer

South Range

Totten
Copper Cliff South
Kelly Lake
Creighton Fault

81°00’ 10 km

Ontario
Quebec
U.S.A.
350 km
Fig. 8

**Bushveld**

- W&E limb
- N limb
- Plat reef
- Great Dyke
- Stillwater

- MR
- UG2
- MSZ
- JM

**Key**

- Diorite, gabbronorite, magnetitite
- Gabbronorite, anorthosite, troctolite
- Norite, orthopyroxenite, chromitite
- Dolomite
- Orthopyroxenite
- Orthopyroxenite, chromitite, harzburgite, dunite
- Marginal zone
- Norite, pyroxentite
- Granite

7 km
0 km
Cross-section of Noril'sk 1 intrusion

Oktryabr'syk N-S Section

Fig. 10
Fig. 11 Sulfide droplet from Noril’sk 1.
Distribution of Fe, Cu, Ni determined by micro-XRF; Distribution of PGE determined by laser ablation ICP-MS. 108 Pd has been corrected for Cd and Zn interferences. Rh has been corrected for Cu interference. Ru has been corrected to Ni interference.
Fig. 12
Fig. 13
Fig. 14

Percentage of each element in each mineral

Po Pn Cp PGM Py Mil

Noril'sk-1

Merensky

MSZ

JM

McCreedy

Roby

McCreedy altered

Roby altered
Fig. 15

a) Great Dyke and Bushveld
b) Bushveld Chromite-rich

Main sul zone Merensky Plat reef

1E+4 1E+3 1E+2 1E+1 1E+0 1E-1
Ni Os Ir Ru Rh Pt Pd Au Cu

1E+4 1E+3 1E+2 1E+1 1E+0 1E-1
Ni Os Ir Ru Rh Pt Pd Au Cu

1E+4 1E+3 1E+2 1E+1 1E+0 1E-1
Ni Os Ir Ru Rh Pt Pd Au Cu

Roby JM

Stillwater and Lac des Iles

c) Stillwater and Lac des Iles
Fig. 16 Concentrations of the metalloids commonly found in platinum-group minerals normalized to mantle values and plotted in order of compatibility. The PGE-dominated deposits have very low concentrations of these elements. The Ni-sulfide deposits are systematically richer in all the elements and the Cu-rich sulfides are richer than the Fe-rich sulfides.
Fig. 17
Fig. 19 Plot of Cu/Pd vs Pd for the PGE-dominated deposits, open stars, JM reef, Y UG-2, + Merensky, close stars Main Sulfide Zone, open crosses Roby Zone, asterix Platreef. Solid lines show the mixing lines between sulfides formed at different R-factors and a silicate or oxide cumulate with 10% trapped liquid of Bushveld chill composition. Solid squares indicated 100 %, 10 %, 1 %, 0.1 % and 0.01 % sulfides present in the rocks.
Liquid after 0.3 % fractionation and sulfide segregation in co-tectic proportions

Fig. 20 Plot of Cu/Pd vs Pd for the Noril'sk basalts, squares, the deposits in the Khaeralak (triangles), Talkalh (circles) and Noril'sk-I(diamonds) intrusions. Open symbols disseminated sulfides, closed symbols massive sulfides. Solid lines show the mixing lines between sulfides formed at R-factors of 100, 1000 and 10 000 with basalt. Solid dots indicated 100 %, 10 %, 1 % and 0.1 % sulfides present in the rocks. The dashed line shows the modelled composition of the basalt if a sulfide liquid is removed in co-tectic proportions, dots represent 0.1, 0.2 and 0.3 % crystallization. Note that many of the basalts plot along this line which suggests they have segregated a sulfide liquid. Also the sulfides found in the Noril'sk 1 intrusion require R-factors 10 000 than the sulfides found in the Kharaelakh and Talkalh intrusions (1 000).
Fig. 21 Photomicrographs of sulfide droplets found in MORB glass (Patten et al. 2012). a) A droplet that crystallized rapidly showing mss and iss intergrowth with Ni-rich phase between the two phases. b) A droplet that crystallized slightly more slowly resulting in solid mss at the base and quenched textured iss in the top left hand corner. c) A droplet that crystallized slowly with mss at the margins and solid iss in the center.
Fig. 22. Back scatter electron images of PGM. a) and a) PGM that have crystallized from the final interstitial liquid. (Dare et al. 2014). c) Malanite exsolution in pyrrhotite and pentlandite from the Merensky reef (Prichard et al. 2004). d) Residual PGM after the replacement of pentlandite, Lac des Iles Djon and Barnes (2011) e) Remobilized Pd bismuthotelluride, (Dare et al. 2010)
Re loss – Os gain; decay from 0.5 Ga until today

Re gain - Os loss; decay from 0.5 Ga until today

Decay from 1.1 Ga To 0.5 Ga

Initial ratio 1.1 Ga

Today unperturbed

$^{187}\text{Re}/^{188}\text{Os}$

$^{187}\text{Os}/^{188}\text{Os}$
Great Dyke

$^{187}\text{Os} / ^{188}\text{Os}$ vs $^{187}\text{Re} / ^{188}\text{Os}$

Age = $2.58 \pm 0.5 \text{ Ga}$

$Y_{\text{Os}(i)} = 0.8$

PUM at 2.58 Ga
Noril’sk I and Talnakh

\[
\frac{^{187}\text{Os}}{^{188}\text{Os}} \quad \frac{^{187}\text{Re}}{^{187}\text{Os}}
\]

Age = 245.7 ± 0.6 Ma

\[Y_{\text{Os(i)}} = 3.6\]
Sudbury, McCreedy West

\[ \frac{^{187}\text{Os}}{^{188}\text{Os}} \]

\[ \frac{^{187}\text{Re}}{^{188}\text{Os}} \]

Age = 1835 ± 70 Ma

\[ Y_{\text{os}}(i) = 346 \]
Age = 1106 ± 21 ma
$\gamma_{\text{Os}(i)} = 34$
The diagram shows a plot of $^{187}\text{Os}/^{187}\text{Os}$ versus $^{187}\text{Re}/^{187}\text{Os}$ for samples from Voisey’s Bay.

- **Massive sulfide - Ovoid**: represented by diamond symbols.
- **Massive sulfide - Discovery Hill**: represented by square symbols.
- **Massive sulfide - Eastern Deeps**: represented by triangle symbols.
- **Semi-massive - Eastern Deeps**: represented by cross symbols.
- **Disseminated sulfide - Eastern deeps**: represented by star symbols.

The graph indicates an age of $1323 \pm 135 \text{ Ma}$ and a $\nu_{\text{Os(i)}}$ value of $1040 \pm 200$. The linear trend is evident, suggesting a consistent isotope ratio over the plotted range.
Table 1. Partition Coefficients

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<th>Element</th>
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<th>max</th>
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<th>max</th>
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<th>max</th>
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### Table 2. The World's Major Platinum-group Element Resources

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<th>Cu %</th>
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<th>Pd ppm</th>
<th>Rh ppm</th>
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1. Godel et al. (2007); 2. Holwell and McDonald (2007); 3. Godel and Barnes (2008); 4. Barnes et al. (2008); 5. Djon and Barnes (2012); 6. This work; 7. Dare et al. (2011)
MSZ = Main sulfide zone
Table 4. Metal Concentrations in Platinum-group Element Deposits

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<th>Cu %</th>
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<th>Ir ppb</th>
<th>Ru ppb</th>
<th>Rh ppb</th>
<th>Pt ppb</th>
<th>Pd ppb</th>
<th>Au ppb</th>
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Reference