A Review of the Behaviour of Platinum Group Elements within Natural Magmatic Sulfide Ore Systems

The importance of semimetals in governing partitioning behaviour

By D. A. Holwell*

Department of Geology, University of Leicester, University Road, Leicester LE1 7RH, UK;
***E-mail: dah29@le.ac.uk**

and I. McDonald

School of Earth and Ocean Sciences, Cardiff University, Main Building, Park Place, Cardiff CF10 3YE, UK

The largest and most significant type of geological deposit of platinum group elements (PGEs) is that associated with magmatic base metal sulfide minerals in layered mafic or ultramafic igneous intrusions. The common association of PGEs with sulfide minerals is a result of processes of magmatic and sulfide liquid segregation and fractionation. The mineralogical nature of the ores is dependent on a number of factors during sulfide liquid fractionation. The most significant of these with regard to the mineralogy of the two most important metals, platinum and palladium, is the presence and concentration of semimetals such as bismuth and tellurium within the mineralising sulfide liquid. Whereas rhodium, iridium, osmium and ruthenium are almost always present in solid solution within the resultant base metal sulfide minerals; should sufficient semimetals be present, Pd and especially Pt will form discrete minerals (such as platinum bismuthides) around the margins of, and possibly away from, the sulfides.

Introduction

Economic deposits of platinum group elements (PGEs) in the Earth's crust are rare. Where they do occur, they are present in three main geological environments. By far the largest and most significant of these is together with magmatic base metal sulfide minerals within silicate or chromitite reefs in layered mafic or ultramafic igneous intrusions. These deposits are commonly platinum- and palladium-dominant, and can produce significant nickel and copper as byproducts or coproducts when mined. Less significant are PGE deposits in chromitites from ophiolite massifs, which are more dominant in iridium and ruthenium. Placer deposits of PGEs, usually sourced from Ural-Alaskan-type ultramafic intrusions, can include Pt-rich nuggets; however, they are a minor source of PGEs and are not exploited on a large scale.

The common association of PGEs with sulfide minerals is the result of processes of magmatic and sulfide liquid segregation. The behaviour of the individual PGEs during these processes is critical in determining the nature of the resulting ore deposits. Factors like the sulfide-to-PGE ratio and the presence of semimetals such as bismuth, tellurium and arsenic in the magma will all affect where the individual PGEs are likely to be present in the final, crystallised rock. Knowledge of the distribution of the PGEs is fundamentally important when evaluating the economic potential of a deposit and designing efficient metal recovery systems. For example, many platinum group metal ore processing plants use froth flotation, a concentration stage that depends on the PGEs being held within sulfide minerals. However, this may not be the case and a detailed investigation of the nature of each ore type is critical in assessing the fundamentals of an individual deposit. Recent developments in laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) (1) have allowed the behaviour of precious metals in sulfide minerals to be studied to an extent not previously possible with other microanalytical techniques. This paper reviews a number of recent LA-ICP-MS studies and draws on the findings of these to collate a generic model for the behaviour of the PGEs in natural sulfide systems.

Processes of PGE-Rich Magmatic Sulfide Ore Formation

Magmatic sulfide deposits form when a fractionating body of magma that has intruded into the crust reaches sulfide saturation, that is, the point where the magma can no longer hold sulfur in solution, and an immiscible sulfide liquid exsolves from the silicate magma. The sulfide droplets are denser than the silicate magma and will, in a relatively quiescent magma, naturally sink through it, although this may not be the case in particularly turbulent magma chambers or conduit systems. Chalcophile elements such as Cu, Ni, the PGEs, gold, silver and some semimetals such as Bi and Te, will be effectively collected by any sulfide liquid as they have high distribution coefficients between sulfide and silicate melts.

The falling sulfide droplets may accumulate in stratigraphic layers, or 'reefs', which can typically be on a scale of a few millimetres to a few metres in thickness, forming concentrations of PGEs that can potentially be mined economically. Depending on the timing of sulfide saturation, reefs may occur at any height within the magmatic stratigraphy in such intrusions. Examples of PGE-sulfide reefs include the Merensky Reef of the Bushveld Complex, South Africa, the Main Sulfide Zone of the Great Dyke of Zimbabwe and the J-M Reef in the Stillwater Complex, Montana, USA (Figure 1). An extensive review of the formation and nature of magmatic sulfide deposits can be found in Naldrett (2), and for PGE deposits in particular, in Maier (3).

There are a number of ways a magma may reach sulfide saturation. Mavrogenes and O'Neill (4) have shown that sulfide solubility increases strongly with decreasing pressure and basaltic magmas emplaced at shallow pressures will be undersaturated in sulfide; the role of externally-derived sulfur is therefore considered by many to be a critical factor in the development of large, economic magmatic Ni-Cu-PGE deposits. Assimilation of country rock-hosted sulfur is considered essential in producing sulfide saturation in high-degree mantle melts such as komatiites (see for example (5, 6)). In basaltic melts, such as those that formed the Bushveld and Stillwater Complexes, sulfide saturation can be attained during low-pressure fractional crystallisation. However, assimilation of country rock sulfur is considered by many researchers as the most reasonable mechanism for producing the large amounts of sulfide required for giant magmatic ore deposits (see for example (7, 8)).

Sulfide saturation and the generation of economic sulfide mineralisation can also be achieved through other types of contamination. Silica contamination due to the assimilation of felsic country rocks can decrease the solubility of sulfur in a mafic magma (9), which can trigger sulfide saturation. In addition, an increase in magma oxygen fugacity, for example in response to the assimilation of oxygen-bearing country rocks, can lower the iron(II) oxide content and thus the sulfur-carrying capacity of the magma (10). As a variety of contamination-related processes are capable of inducing sulfide saturation, sulfide mineralisation is common at the bases and margins of intrusions, where contamination is most prevalent. Examples include the Platreef of the Bushveld Complex; the Basal Series of the Stillwater Complex; the Penikat-Portimo Complex, Finland; the Muskox intrusion, Canada; the Fedorov-Pansky intrusion, Russia (11); and conduit systems such as Noril'sk, Russia (8) and the Uitkomst Complex, South Africa (7). These are shown in Figure 1.
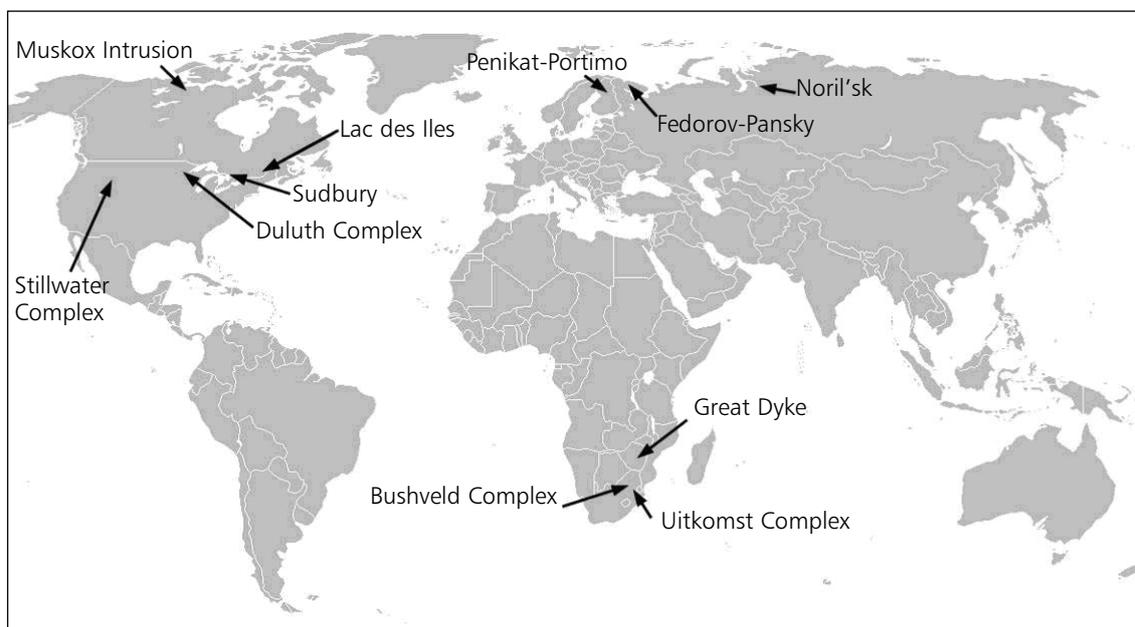
Fig. 1. Global distribution of major magmatic platinum group element sulfide deposits

Experimental Studies on Sulfide Liquid Fractionation

Following the separation of a sulfide liquid from a silicate magma at temperatures of around 1200ºC, typical of mafic magmas, the first phase to crystallise from the sulfide droplet is monosulfide solid solution (mss), at around 1000ºC. Ni is generally compatible with mss and will partition into it at this stage. This leaves a Cu-rich residual liquid, which crystallises to intermediate solid solution (iss) at around 900ºC, so at this point there is a Ni-rich mss portion and a Cu-rich iss portion. As the temperature cools to below 650ºC, the mss recrystallises to pyrrhotite (FeS) and pentlandite ((Fe, Ni)$_9$S$_8$) and the iss recrystallises to chalcopyrite (CuFeS$_2$). The precise temperature of these recrystallisations is dependent on how rich the mss is in sulfur (2). This results in the typical magmatic sulfide assemblage of pyrrhotite-pentlandite-chalcopyrite found in natural magmatic sulfide ores.

Experimental data in the Fe-Ni-Cu-S system have been used to explore the partitioning behaviour of PGEs during the crystallisation of mss from a sulfide liquid (see for example (12–16)). These studies have found that in sulfur-rich, alloy-poor systems (applicable to deposits such as the Platreef and Noril'sk), the iridium group PGEs (IPGEs) (Ir, Os and Ru) and rhodium partition into mss, which then cools and

recrystallises to pyrrhotite and pentlandite, with these elements remaining in solid solution in these phases.

According to the experiments, Pt, Pd, Au and Ag will partition into the Cu-rich residual liquid after mss crystallisation. However, Peregoedova (17) showed experimentally that Pt and Pd (and by implication, Au) are also incompatible with iss. Therefore, rather than these elements partitioning into iss when it crystallises, and then, with falling temperature, into chalcopyrite, it seems that they are concentrated in a late-stage, immiscible semimetal-rich melt (18), which may be predominantly enriched in Te, Bi, As or antimony. As a consequence, Pt and Pd combine with the semimetals to form discrete platinum group minerals (PGMs) and electrum (Au-Ag alloy) around the margins of sulfide grains. This phenomenon is, however, dependent on the presence and concentration of semimetals within the sulfide liquid, the absence of which may cause Pt and Pd to be present in solid solution within the sulfide phases. In addition, Helmy *et al.* (18) noted that Pt has a much greater tendency to enter this semimetal melt than Pd, raising the possibility that where there is a limited amount of this melt, only Pt may be present within it. The present paper reviews examples from natural sulfide ore systems to investigate these relationships, whether they are present in naturally-formed sulfides, and if so,

what the most important factors are in determining the resultant mineralogical characteristics of the ores.

LA-ICP-MS Studies from Natural Magmatic PGE-Sulfide Deposits

LA-ICP-MS is increasingly being used in geometallurgy for a wide range of applications. One of the most successful of these is the investigation of trace amounts of precious metals in rock-forming minerals, (1) especially base metal sulfides. Ore microscopy studies and scanning electron microscopy (SEM)-based analyses are not sufficient for detecting trace levels of precious metals within sulfide minerals. LA-ICP-MS techniques are the most precise way of achieving detection to levels as low as tens of parts per billion, which is more sensitive than other *in situ* techniques. For example, it is around one order of magnitude greater than that which can be achieved by secondary ion mass spectrometry (SIMS) and around three orders of magnitude more sensitive than micro proton induced X-ray emission (micro-PIXE).

LA-ICP-MS involves the ablation of a sample, usually a polished block, using a laser in an inert atmosphere. The laser beam diameter may be varied but is typically set to somewhere in the range of 10 μm to 100 μm. The sample position can be adjusted so the laser can be targeted at areas with an accuracy of micrometres. The laser ablates a pit in the sample, and the vaporised material is passed through a conventional ICP-MS for analysis. It is possible to move the sample during the ablation, allowing line analysis to be performed on a trench ablated along the sample, which gives the advantage of being able to pass over one or more mineral phases to assess any lateral variations in element concentration through the crystals. Typical analyses take around 60 to 120 seconds and data is collected three or four times per second for all the elements of interest. The data is displayed visually as a time-resolved analysis (TRA) spectrum, which shows relative abundance (in counts per second) of the detected isotopes *versus* time. Further details of the technique can be found in McDonald (19).

This technique has the ability to reveal fine-scale mineralogical characteristics, including where certain elements are held in a physicochemical sense. For example, certain precious metals may be present in solid solution within a sulfide mineral (evenly or unevenly distributed throughout the crystal lattice), or as discrete minerals (microinclusions) often too small to detect by other methods. The use of line analysis is particularly useful in determining this fundamental difference, with elements in solid solution being detected in constant amounts with time, and any discrete minerals showing up as short peaks within the analysis. The ability to identify such fundamental mineralogical differences is one of the biggest advantages of the LA-ICP-MS technique.

The Platreef, Bushveld Complex

The Bushveld Complex in South Africa is the world's largest layered igneous intrusion, and is the single largest repository of PGE deposits on Earth. The PGE deposits are hosted within the layered mafic-ultramafic sequence of the Rustenburg Layered Suite. The Complex is made up of five limbs: large, roughly symmetrical eastern and western limbs; a smaller northern limb; a southern limb, covered by younger sediments; and an extension of the western limb, called the far western limb. The eastern and western limbs of the Complex host the Upper Group 2 (UG2) chromitite layer and the pyroxenite-hosted Merensky Reef, and the Platreef is located in the smaller northern limb. Unlike the deposits in the eastern and western limbs, the Platreef rests directly on country rock sediments and Archaean basement.

The Platreef is a 10 m to 400 m thick sequence of pyroxenitic rocks at the base of the igneous succession in the northern limb (20–23), Figure 2 (24). It is considered to be, in genetic terms, an orthomagmatic sulfide deposit, with the least contaminated sections containing disseminated, fractionated, polyphase blebs of pyrrhotite, pentlandite and chalcopyrite with associated PGMs (Figure 3) within the interstitial regions of feldspathic pyroxenites (23, 25). There is also, however, a great deal of hydrothermal alteration and contamination from footwall rocks along strike, which varies greatly in volume and nature according to local footwall lithology. Two recent studies on the Platreef (25, 26), from sections with radically different floor rocks, have utilised the LA-ICP-MS analytical technique together with conventional SEM studies to investigate the nature and distribution of the PGEs in base metal sulfide phases and PGM phases, respectively, and have revealed fundamental differences between the two areas.

Holwell and McDonald (23) identified that the anhydrous nature of the floor rocks in the northern part of the Platreef prevented significant amounts of contamination and hydrothermal activity and led to the most 'primary' style of Platreef mineralisation

Fig. 2. Geological map of the Platreef, Bushveld Complex, South Africa (24)
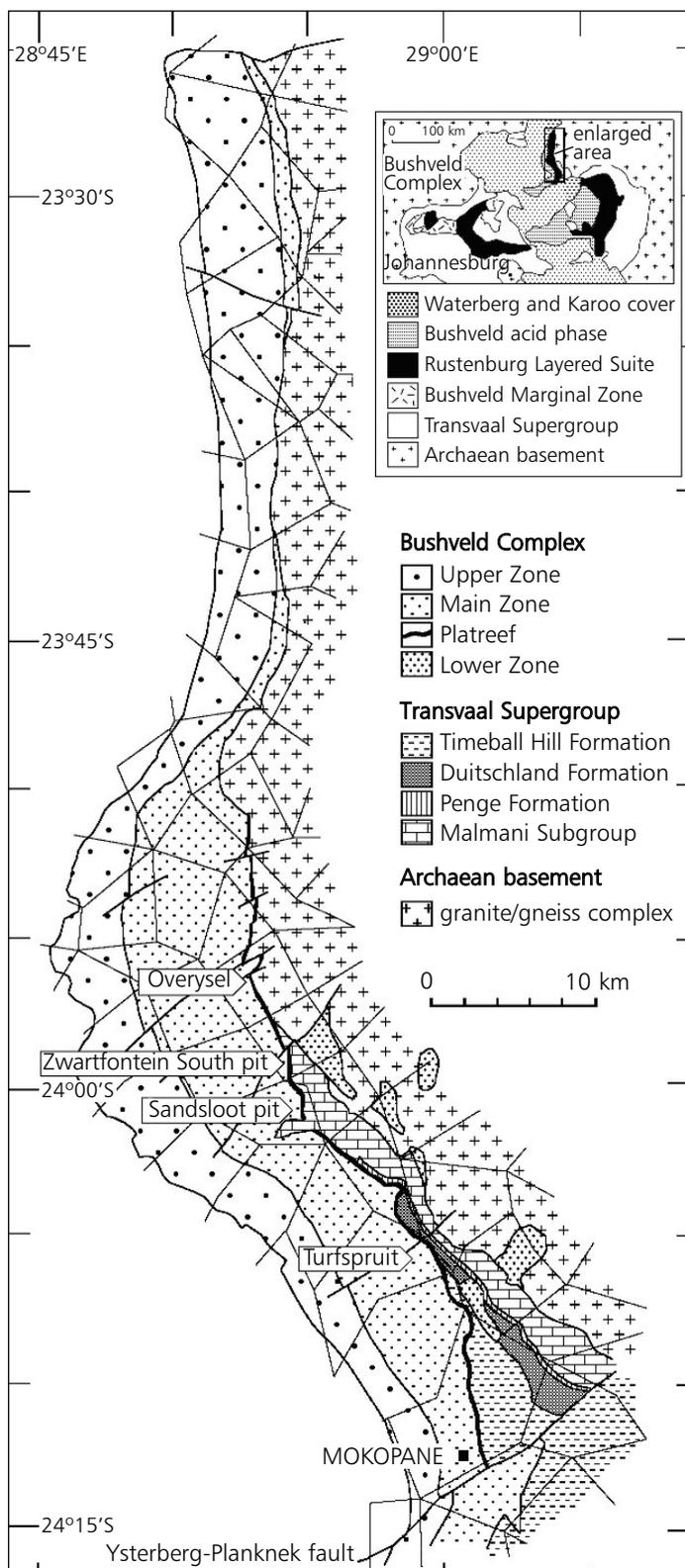
preserved along strike. They subsequently undertook a LA-ICP-MS investigation of these 'primary' sulfides, such as those shown in **Figure 3** (25). Some of the LA-ICP-MS results of pyrrhotite, pentlandite and chalcopyrite from this study are shown as TRA spectra in **Figure 4**.

Figure 4(a) shows a TRA spectrum for a pyrrhotite grain from the Platreef pyroxenites, with smooth, parallel patterns of Ir, Os and Ru with sulfur, indicating that the IPGEs are present in solid solution in the pyrrhotite. Pentlandite was also found to contain concentrations of the IPGEs. In contrast though, pentlandite is the major carrier of Pd and Rh. Concentrations of Pd and Rh within individual pentlandite crystals are quite variable and high Rh contents do not necessarily correlate with high Pd contents. Some minor Pt (<0.2 ppm) is apparently present in solid solution in a few pentlandite analyses, one example of which is shown in **Figure 4(b)**. This demonstrates smooth profiles for all PGEs, with particularly high abundances of Pd and Rh mirroring Ni and S, thus confirming their presence in solid solution. No PGEs were present in solid solution within chalcopyrite; however, some Pt (with correspondingly high Bi and occasionally high Te concentrations) was detected that did not mirror base metal concentrations. The TRA spectrum for one of these examples is shown in **Figure 4(c)** where Pt and some trace Pd, rather than mirroring the sulfur and base metal contents, show distinct peaks along with Bi. In these relationships, Pt appears to be present as discrete, micrometre to sub-micrometre-sized PGM microinclusions, rather than in solid solution in the sulfide. A further example is also present in the TRA spectra for a pentlandite shown in **Figure 4(d)**. Such microinclusions are present in all of the major sulfide phases.

Hutchinson and McDonald (26) investigated the nature of the Platreef ores in the Turfspruit area where the floor rocks are particularly volatile-rich sediments and contamination from these country rocks has been particularly prevalent (22). Their LA-ICP-MS data showed virtually no Pd held within solid solution in any pentlandite, but a vast increase in the number of Pd-bearing PGMs, particularly Pd arsenides and antimonides, which are not observed further north (26). This key difference in platinum group mineralogy is likely to be due to localised contamination *via* the assimilation of Sb- and As-bearing sediments in the Turfspruit area, with Sb and As scavenged by the sulfide liquid. This produced a relatively high proportion of immiscible semimetal melt when iss crystallised, into which virtually all the Pt and, unlike further north, all the Pd partitioned. On further cooling this produced the large amount of Pt and Pd antimonide and arsenide minerals found in the area.

The Merensky Reef, Bushveld Complex
The Merensky Reef is a thin (typically <2 m), stratiform PGE deposit located at the top of the Critical Zone in the eastern and western limbs of the Bushveld Complex, and is hosted by pyroxenitic cumulate rocks. The PGEs are associated with base metal sulfides in a similar manner to those in the Platreef. In addition, there are also some thin (~1 cm) chromitites which have PGEs associated with them. It is widely believed that the reef is orthomagmatic in origin and formed from the separation of a sulfide liquid from a silicate magma (see for example (27)).

Ballhaus and Sylvester (28) conducted a LA-ICP-MS study of sulfide minerals within the Merensky Reef deposit of the Bushveld Complex. They found Ir, Os and Ru to be present in solid solution in pentlandite and pyrrhotite, Rh and some Pd in pentlandite and Pt, Au and the remainder of the Pd present as discrete PGM phases, identical to the observations made by Holwell and McDonald (25) for the Platreef. A number of microinclusions or micronuggets were also identified, including Os-Ir-Pt alloys and Pt-Bi-Te minerals.

Godel *et al.* (29) conducted a similar multi-disciplinary study, using both LA-ICP-MS of sulfides and PGM studies to investigate the behaviour of the PGEs within the Merensky Reef. They found that pentlandite was the main host of Pd and Rh; pyrrhotite hosted Ir, Os, Ru and some Rh; and chalcopyrite hosted no PGEs in solid solution. Pt and Au were not found in solid solution in any base metal sulfide phases and occurred exclusively as PGMs and electrum, respectively. The same patterns were found in sulfides within the chromitites.

The J-M Reef, Stillwater Complex
The Stillwater Complex in Montana, USA, is another layered ultramafic to mafic intrusion, which contains several PGE-rich layers including the J-M Reef, which has the highest Pt + Pd grade of all known PGE reefs (~18 ppm, with a Pt:Pd ratio of around 1:3.3), with the PGEs associated with base metal sulfides in olivine gabbronorites. Godel and Barnes (30) presented the results of a LA-ICP-MS study of sulfides in the J-M Reef of the Stillwater Complex. In this study, pentlandite
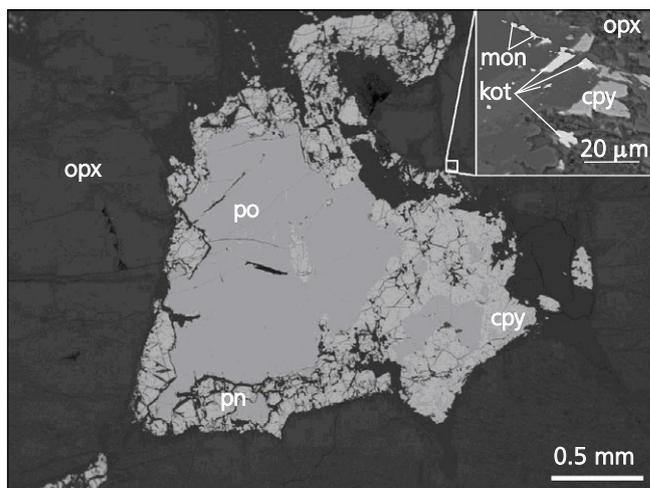

Fig. 3. Typical nature of interstitial magmatic base metal sulfide grains within the Platreef, consisting of pyrrhotite (po) rimmed by pentlandite (pn) and chalcopyrite (cpy) with platinum group minerals (in this case moncheite (mon) and kotulskite (kot)) around the margins. Cumulus silicate phases are orthopyroxene (opx) (24)
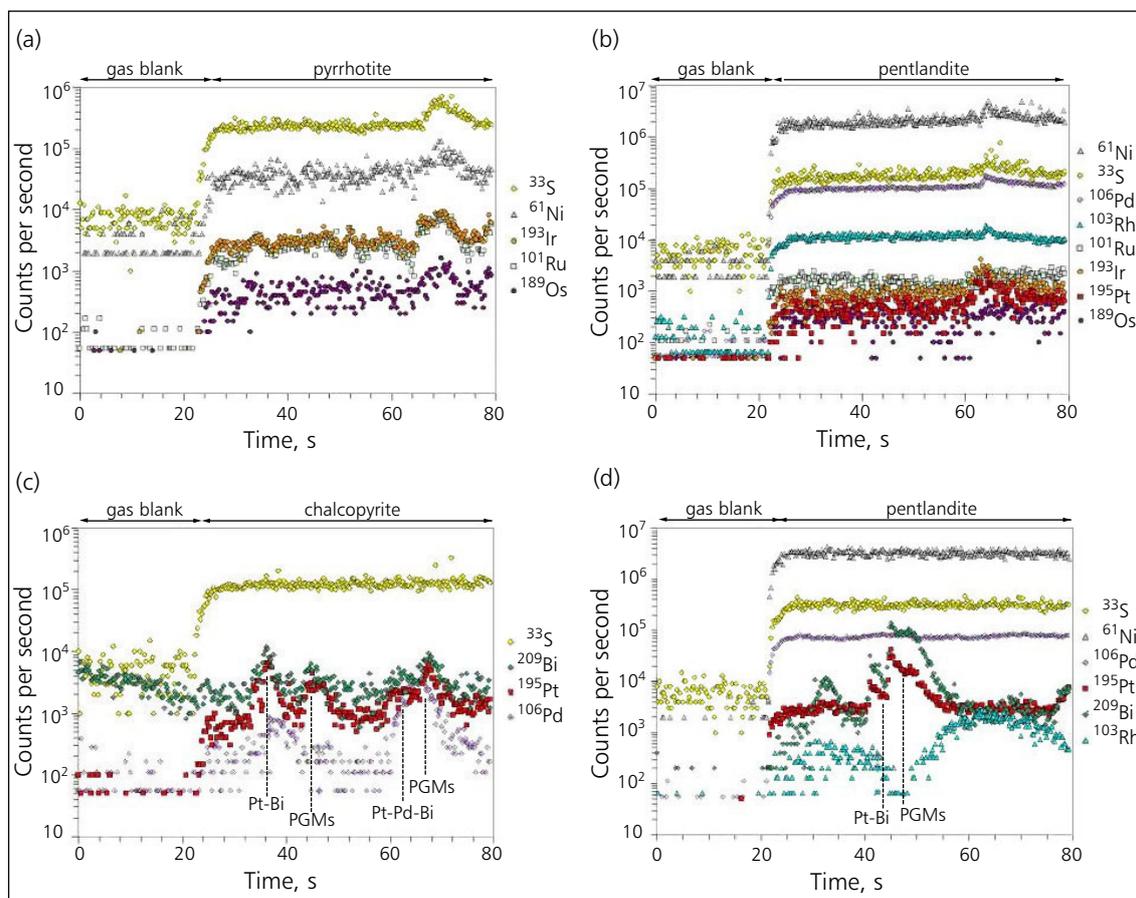
31

Fig. 4. Time-resolved analysis (TRA) spectra from line analysis of sulfides from the Platreef (25): (a) pyrrhotite; (b) pentlandite; (c) chalcopyrite showing microinclusions; and (d) pentlandite showing microinclusions (25)

was found to carry the most PGEs in solid solution, primarily Pd, with some IPGEs. No Pt was found in solid solution, with all Pt being present as discrete minerals. However, it is pertinent to note that the J-M Reef is highly altered, so the final host minerals of the PGEs, particularly the more hydrothermally-mobile Pd, may not represent the products of a fractionated sulfide liquid.

The Noril'sk Deposit

The Noril'sk-Talnakh area of Siberia, Russia, hosts the largest Ni-Cu-Pd deposits in the world. The deposits are magmatic in origin and formed within a conduit system which fed the Siberian Traps large igneous province. Barnes *et al.* (31) presented results of a LA-ICP-MS study of precious metal concentrations in magmatic sulfides from the Medvezky Creek Mine, Noril'sk. They found Rh, Ir, Os and Ru to be present in solid solution within pyrrhotite and pentlandite, Pd

to be present in pentlandite and Pt and Au not to have any affinity with any sulfide phase and to occur instead as discrete PGMs and electrum around the margins of the sulfide grains.

Other Deposits

Similar LA-ICP-MS analyses for other PGE-sulfide deposits, including the Great Dyke, Zimbabwe, and the Penikat-Portimo Complex, Finland, were reviewed by Barnes *et al.* (32). The findings from these studies also showed that Pd was present within pentlandite in the PV Reef of the Penikat-Portimo Complex and the Main Sulfide Zone of the Great Dyke, and that no PGEs were present within chalcopyrite in either deposit. Pd contents within the sulfide minerals were noted to vary greatly from one deposit to the next. The IPGEs and Rh were also found to be present in solid solution within pyrrhotite and pentlandite in both deposits.

Discussion

According to the experimental data in the Fe-Ni-Cu-S system that have been used to explore the partitioning behaviour of PGEs during the crystallisation of mss from a sulfide liquid, mss in natural sulfur-rich magmatic systems would be expected to be enriched in the IPGEs and Rh. These elements would then be present in solid solution within the cooling products of mss: pyrrhotite and pentlandite. The available LA-ICP-MS data from the various PGE-rich magmatic sulfide deposits mentioned above show precisely this pattern, with pyrrhotite and pentlandite both enriched in Ir, Os and Ru, with all three elements present in solid solution rather than as discrete PGMs. It is, however, the semimetals that have profound effects on the behaviour of Pt, Au and, in particular, Pd.

Figure 5 shows schematically the behaviour of the PGEs during fractionation of a sulfide droplet from magmatic temperatures, as implied from the data reviewed in this paper. At magmatic temperatures of around 1200ºC, the sulfide liquid contains dissolved PGEs, Au and semimetals, plus Fe, Ni and Cu (Figure 5(a)). On cooling to around 1000ºC, the IPGEs, Rh and Ni are concentrated in mss and Pt, Pd and Au and the semimetals will partition into the Cu-rich residual liquid after mss crystallisation (Figure 5(b)).

On further cooling to around 900ºC, iss crystallises out of the residual liquid. However, the Pt, Pd and Au, rather than partitioning into iss, are concentrated in an immiscible semimetal rich melt as they are incompatible in iss (Figure 5(c)). Work by Helmy *et al.* (18) suggests that this melt remains liquid after iss has crystallised. They also noted that Pt and Pd are more strongly complexed with Te and Bi than S, and Pd will only enter mss when the Pd:semimetal ratio is sufficiently high to have an excess of Pd that cannot be accommodated by the semimetal melt. Therefore some Pd may at this point partition into mss (Figure 5(c)), although the mechanism and temperature conditions for this are as yet unknown. A high Pd:semimetal ratio can thus explain the presence of Pd in pentlandite in some ores and *vice versa*. This control by semimetals appears to be the most fundamental factor affecting the mineralogical characteristics of magmatic sulfide-hosted Pt and Pd ores.

Finally, at low temperatures (200ºC to 650ºC) the mss recrystallises to pentlandite and pyrrhotite, respectively, with the IPGEs remaining in solid solution in both, and Rh and some Pd in solid solution in pentlandite. In all the LA-ICP-MS studies reviewed here, pentlandite is the major carrier of Rh, although Cabri *et al.* (33) found Rh to also be present in pyrrhotite in a micro-PIXE study of ores from Noril'sk. This relationship, whereby virtually all the IPGEs and Rh are present in pyrrhotite and pentlandite,
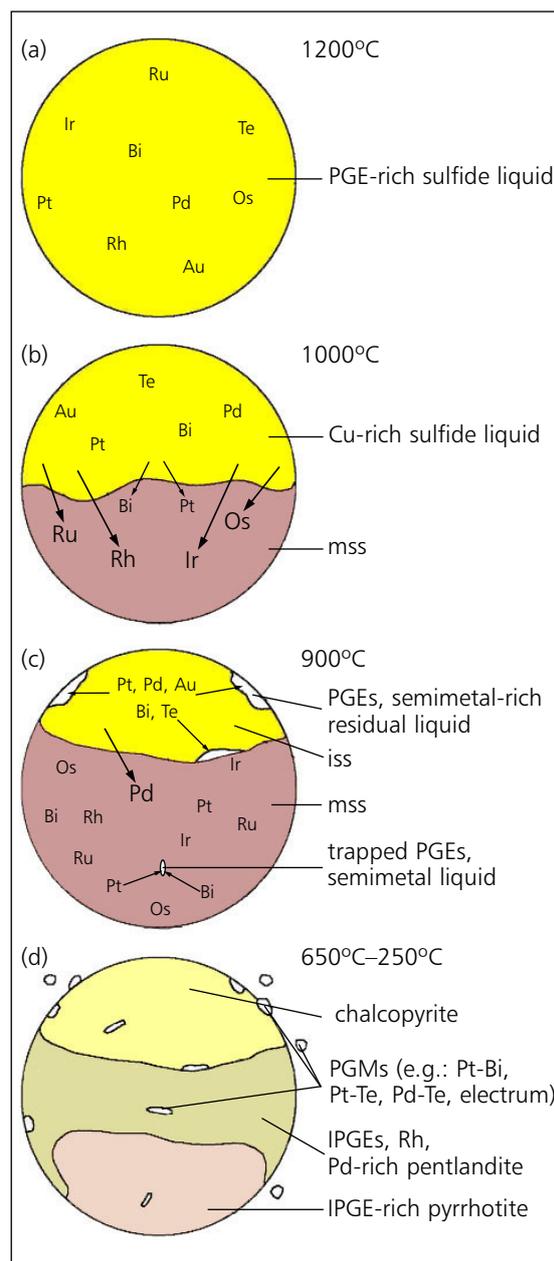

Fig. 5. Schematic representation of a fractionating, platinum group element-rich sulfide droplet (see text for explanation). Major partitioning behaviour at each stage is highlighted by larger text

appears to be almost universal in the magmatic sulfide deposits reviewed here. The iss recrystallises to chalcopyrite with no PGEs in solid solution, which is also a universal feature of the natural sulfides.

Crystallisation of the semimetal rich liquid on cooling forms discrete PGMs around the margins of the sulfide blebs and in small veinlets injected into the surrounding silicates, which explains the tendency for PGMs to be present around the margins of sulfide blebs (Figure 5(d)). Later alteration of the sulfide blebs, with replacement by secondary amphiboles around the margins of base metal sulfide blebs, appears not to affect the early formed PGMs, which are then isolated as satellite grains within secondary silicates around the base metal sulfide blebs, and are therefore no longer spatially associated with sulfides. This relationship of Pt- and Pd-bearing PGMs occurring as satellite grains around the margins of sulfide blebs has long been recognised in natural ores (34, 35).

The presence of trapped microinclusions of Pt-Bi-Te minerals in all sulfide phases implies that Bi and Te were present within the initial sulfide liquid at high temperature. In this sense, the differences between the Platreef studies by Holwell and McDonald (25) and Hutchinson and McDonald (26) show a fundamental difference in the sources of certain semimetals (primary magma *versus* external country rocks) and the profound influence that has had on the resultant mineralogy. The key factor in the mineralogical differences in Platreef ores from Turfspruit and Overysel in the northern Bushveld Complex is the proportion of semimetals within the mineralising sulfide liquid. Where there was a limited amount, Pt partitioned into the semimetal-rich melt with a little Pd, and most Pd was accommodated with-

---

Glossary

Term	Definition
amphibole	A group of hydrated double silicate minerals containing calcium, iron, magnesium, sodium and aluminium
bleb	A irregular bubble-like mass of one or more minerals
chalcophile	An element that has a high affinity for sulfur and thus readily forms sulfide minerals
chalcopyrite	$CuFeS_2$, a sulfide ore of copper
chromitite	A rock with high concentrations of chromite $((Fe, Mg)Cr_2O_4)$
feldspathic	Containing feldspar (aluminium silicates with potassium, sodium, calcium or barium)
felsic	Rock rich in silicate minerals such as feldspar and quartz
footwall	The layer of rock beneath a vein or expanse of ore
fugacity	Tendency of a compound in a mixture to vaporise or escape from the liquid phase
komatiites	Ultramafic rocks low in silica, potassium oxide and alumina and high in magnesium oxide
mafic/ultramafic	Rock rich in silicate minerals containing iron and magnesium, such as olivine and pyroxene
ophiolite	Oceanic crust rocks that have been moved onto a continental crust
orthomagmatic	Referring to the stage where silicates crystallise from magma
pentlandite	$(Fe, Ni)_9S_8$, a sulfide mineral of nickel
pyroxenite	Rock with high concentrations of pyroxenes (silicates of iron, magnesium and calcium)
pyrrhotite	$Fe_{(1-x)}S$, a sulfide mineral of iron $(0 \leq x \leq 0.2)$

in pentlandite. However, where there was an abundance of semimetals (as a result of contamination at high temperature), virtually all the Pt and Pd could be accommodated in the semimetal-rich melt, forming PGMs around the margins of the sulfide grains, and very little Pd in pentlandite. This is a direct result of the introduction of semimetals, particularly As and Sb, from the contaminant rock. Therefore, localised contamination of the ore-forming sulfide is fundamentally important in determining the metallurgical nature of the resultant ores.

Conclusions

In natural magmatic sulfide ore systems, PGEs are collected by immiscible sulfide droplets that segregate from a silicate magma. The studies reviewed here suggest that, during fractionation and cooling of the sulfide liquid, Rh, Ir, Os, Ru and Ni may partition effectively into the earliest crystallising phase, monosulfide solid solution, which on further cooling recrystallises to pentlandite and pyrrhotite, with these elements remaining in solid solution within the sulfide phases. The critical factor in determining the behaviour of Pt, Pd and Au appears to be the amount of semimetals available in the sulfide liquid, as Pd and especially Pt and Au will partition into an immiscible semimetal-rich liquid when all the sulfide has crystallised. If the amount of semimetals is limited, much of the Pd and perhaps some of the Pt will be present in solid solution within sulfides like pentlandite. If there is a relatively high concentration of semimetals, primarily due to localised contamination of the magma, the majority of the Pt and Pd will be present as discrete minerals, potentially not spatially associated with sulfides.

References

1 L. J. Cabri, P. J. Sylvester, M. N. Tubrett, A. Peregoedova and J. H. G. Laflamme, *Can. Mineral.*, 2003, **41**, (2), 321

2 A. J. Naldrett, "Magmatic Sulfide Deposits: Geology, Geochemistry and Exploration", Springer-Verlag, Berlin and Heidelberg, Germany, 2004, 728 pp

3 W. D. Maier, *J. Afr. Earth Sci.*, 2005, **41**, (3), 165

4 J. A. Mavrogenes and H. St. C. O'Neill, *Geochim. Cosmochim. Acta*, 1999, **63**, (7–8), 1173

5 R. R. Keays, *Lithos*, 1995, **34**, (1–3), 1

6 D. D. Lambert, J. G. Foster, L. R. Frick, E. M. Ripley and M. L. Zientek, *Econ. Geol.*, 1998, **93**, (2), 121

7 C. Li, E. M. Ripley, W. D. Maier and T. E. S. Gomwe, *Chem. Geol.*, 2002, **188**, (3–4), 149

8 E. M. Ripley, P. C. Lightfoot, C. Li and E. R. Elswick, *Geochim. Cosmochim. Acta*, 2003, **67**, (15), 2805

9 C. Li and A. J. Naldrett, *Econ. Geol.*, 1993, **88**, (5), 1253

10 D. L. Buchanan and J. Nolan, *Can. Mineral.*, 1979, **17**, (2), 483

11 C. A. Lee, 'A Review of Mineralization in the Bushveld Complex and Some Other Layered Mafic Intrusions', in "Layered Intrusions", ed. R. G. Cawthorn, Developments in Petrology, Vol. 15, Elsevier Science BV, Amsterdam, The Netherlands, 1996, pp. 103–146

12 M. E. Fleet, S. L. Chryssoulis, W. E. Stone and C. G. Weisener, *Contributions Mineral. Petrol.*, 1993, **115**, (1), 36

13 C. Li, S.-J. Barnes, E. Makovicky, J. Rose-Hansen and M. Makovicky, *Geochim. Cosmochim. Acta*, 1996, **60**, (7), 1231

14 S.-J. Barnes, E. Makovicky, M. Makovicky, J. Rose-Hansen and S. Karup-Moller, *Can. J. Earth Sci.*, 1997, **34**, (4), 366

15 C. Ballhaus, M. Tredoux and A. Späth, *J. Petrol.*, 2001, **42**, (10), 1911

16 J. E. Mungall, D. R. A. Andrews, L. J. Cabri, P. J. Sylvester and M. Tubrett, *Geochim. Cosmochim. Acta*, 2005, **69**, (17), 4349

17 A. V. Peregoedova, 'The Experimental Study of the Pt-Pd-Partitioning between Monosulfide Solid Solution and Cu-Ni-Sulfide Melt at 900–840ºC', in "The 8th International Platinum Symposium (1998)", Rustenburg, South Africa, 28th June–3rd July, 1998, Symposium Series S18, The Southern African Institute of Mining and Metallurgy, Johannesburg, South Africa, 1998, pp. 325–373

18 H. M. Helmy, C. Ballhaus, J. Berndt, C. Bockrath and C. Wohlgemuth-Ueberwasser, *Contributions Mineral. Petrol.*, 2007, **153**, (5), 577

19 I. McDonald, 'Development of Sulphide Standards for the In-Situ Analysis of Platinum-Group Elements by Laser Ablation Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS)', in "10th International Platinum Symposium, Extended Abstracts", eds T. O. Törmänen and T. T. Alapieti, Proceedings of the 10th International Platinum Symposium, 8th–11th August, 2005, Oulu, Finland, Geological Survey of Finland, Espoo, Finland, pp. 468–471

20 P. E. B. Armitage, I. McDonald, S. J. Edwards and G. M. Manby, *Appl. Earth Sci. (Trans. IMM B)*, 2002, **111**, (1), 36

21 D. Hutchinson and J. A. Kinnaird, *Appl. Earth Sci. (Trans. IMM B)*, 2005, **114**, (4), 208

22 E. R. Sharman-Harris, J. A. Kinnaird, C. Harris and U. E. Horstmann, *Appl. Earth Sci. (Trans. IMM B)*, 2005, **114**, (4), 252

23 D. A. Holwell and I. McDonald, *Miner. Deposita*, 2006, **41**, (6), 575

24 D. A. Holwell, A. J. Boyce and I. McDonald, *Econ. Geol.*, 2007, **102**, (6), 1091

25 D. A. Holwell and I. McDonald, *Contributions Mineral. Petrol.*, 2007, **154**, (2), 171

26 D. Hutchinson and I. McDonald, *Miner. Deposita*, 2008, **43**, (6), 695

27 I. H. Campbell, A. J. Naldrett and S.-J. Barnes, *J. Petrol.*, 1983, **24**, (2), 133

28 C. Ballhaus and P. Sylvester, *J. Petrol.*, 2000, **41**, (4), 545

29 B. Godel, S.-J. Barnes and W. D. Maier, *J. Petrol.*, 2007, **48**, (8), 1569

30 B. Godel and S.-J. Barnes, *Chem. Geol.*, 2008, **248**, (3–4), 272

31 S.-J. Barnes, R. A. Cox and M. L. Zientek, *Contributions Mineral. Petrol.*, 2006, **152**, (2), 187

32 S.-J. Barnes, H. M. Prichard, R. A. Cox, P. C. Fisher and B. Godel, *Chem. Geol.*, 2008, **248**, (3–4), 295

33 L. J. Cabri, J. M. D. Wilson, V. V. Distler, D. Kingston, Z. Nejedlý and S. F. Sluzheniken, *Appl. Earth Sci. (Trans. IMM B)*, 2002, **111**, (1), 15

34 L. J. Cabri and J. H. G. Laflamme, *Econ. Geol.*, 1976, **71**, (7), 1159

35 H. M. Prichard, D. Hutchinson and P. C. Fisher, *Econ. Geol.*, 2004, **99**, (2), 365

The Authors

Dr David Holwell is currently a Lecturer in Applied and Environmental Geology at the University of Leicester, UK, where he is involved in research into magmatic PGE deposits in east Greenland and South Africa. He has also recently worked as an Exploration Geologist for SRK Exploration Services.

Dr Iain McDonald is currently manager of the ICP laboratories at the School of Earth and Ocean Sciences at Cardiff University, UK, where he leads an active research group working on the northern limb of the Bushveld Complex, South Africa. His main interests are geochemistry, mineral deposits and research into the formation of impact craters.