



RAPPORT FINAL

2003-2004

Sous-projet SC4

Transport par vapeur des éléments du groupe du platine à des températures magmatiques

Par

Anna Peregoedova*, Sarah-Jane Barnes**, Don R. Baker*

*Earth & Planetary Sciences, McGill University, Montréal, Canada, H3A2A7
(aperegoe@eps.mcgill.ca, donb@eps.mcgill.ca)

**Sciences de la Terre, Université du Québec à Chicoutimi, Chicoutimi, Canada, G7H2B1
(sjbarnes@uqac.ca)

Soumis à l'administration de DIVEX
avril, 2004 – à Montréal

SUMMARY

Our project has investigated experimentally the role of S-dominated vapor in the formation of economically important platinum-group element (PGE) ores. The research has been conducted in two general directions: 1) experimental study of possibility of the PGE transport by a S vapor in the Fe-Ni-Cu sulfide system at magmatic temperatures; and 2) experimental study of the PGE enrichment mechanisms of a sulfide phase as a result of its desulfurization by the vapor phase and the formation of individual PGE alloys at low-S conditions.

Open-system, with respect to the gas-phase, conditions were set up using the tube-in-tube technique in both series of experiments. In the vapor transport experiments, a S-rich donor, $(\text{Fe,Ni,Cu})_{1-x}\text{S}$ of variable base-metal (BM) ratio, was doped with 2000 ppm of each PGE and Au. A S-poor pyrrhotite (Po) was used as the PGE receiver. The metal/S ratio of the system was varied by changing the donor/receiver ratio to assess whether the metals were transported as S-species or metals. In the system Fe-S-PGE the run products were receiver Po and donor PGE-bearing Po containing individual grains of Au. In the system Fe-Cu-Ni-S-PGE the run products were receiver Po and a donor association composed of monosulfide solid-solution $[\text{Mss}, (\text{Fe,Ni,Cu})_{1-x}\text{S}] \pm \text{Cu-Au rich sulfide melt} \pm \text{individual PGE phase (PGM)}$. The S-removal experiments were carried out at 1000-980°C in the system Fe-Ni-Cu-S doped with 0.2 wt.% of Pt, Ir and 0.5 wt.% of Pd and with sulfur fugacity ($f\text{S}_2$) buffered by S-poor pyrrhotite. The quantity of the Po buffer was 30-40 times larger than that of the S-rich sample composed of PGE-bearing $\text{Mss} \pm \text{Cu-rich sulfide melt}$. In the course of experiments, the S transfer from the PGE-bearing BM sulfide to the Po buffer has occurred via vapor phase thus simulating a natural desulfurization process. Final compositions of the run products from both series of experiments were determined by electron microprobe at McGill University (major PGE, BM and S), and by laser ablation ICP-MS at the University of Quebec in Chicoutimi (trace PGE with the detection limit for all PGE in the 10 to 30 ppb range).

In the vapor transport experiments, the receiver Po contained significant quantities of transported Pt and Pd (PPGE), Os and Au, but little Ir, Ru and Rh (IPGE). In addition, a much higher quantity of Ni was transported through the vapor-phase (700 ppm to 11300 ppm) compared to Cu (1000 ppm). There is a dependence of the amount of Ni and PPGE transported on the metal/S ratio of the system. This suggests that Ni and the PPGE were transported as base-metal sulfide species whereas Cu and the IPGE were transported as metals. The removal of sulfur from the PGE-bearing sulfide via a vapor phase in our desulfurization experiments resulted in: 1) exsolution of Pt and Ir from S-depleted base-metal sulfides in the form of PGE alloys leading to the enrichment of a sulfide residue in the heavy PGE; 2) partial or even complete melting of the sulfide leading to the formation of S-poor monosulfide solid solution $[(\text{Fe,Ni,Cu})_{1-x}\text{S}]$, Fe-Pt-Ir alloy and highly mobile Cu-Ni-Pd rich sulfide liquid. This could separate palladium from

platinum and iridium in natural ore systems resulting in a change from the initial Pd/Pt and Pd/Ir ratio.

In most natural examples where fluid mobilization of PGE has been suggested, the remobilized material is enriched in Cu, Pd and to a lesser extent Pt. Our experiments suggest that transport by S-vapor is not the mechanism for this remobilization, as Pd was not fractionated from Pt, and Cu was not significantly transported by the vapor compared to Ni. A more promising candidate for the remobilization of the Cu and Pd is the Cu-rich sulfide melts that formed in the desulfurization experiments.

1. INTRODUCTION

Platinum-group element (PGE) concentrations in PGE-bearing deposits (e.g. the Merensky and UG-2 reefs of the Bushveld Complex; the JM reef of the Stillwater, the Lac Des Iles Roby Zone) are fairly low (6-14 ppm). Thus the minerals containing PGE are not visible to the naked eye in most cases. The rocks containing platinum-group elements vary from chromitites to pyroxenites, gabbro-norites or anorthosites. Therefore, rock type cannot necessarily be used as a guide to which rocks host PGE deposits. In general there is little evidence in the field or hand specimen to guide exploration efforts. Models as to why some mafic and ultramafic rocks contain economic levels of PGE could help in exploration efforts.

There are three basic models in vogue for the formation of PGE-dominated deposits. The first suggests that PGE are collected by a sulfide liquid, that separated from a silicate magma. The second suggests that the PGE crystallize as platinum-group minerals directly from a silicate magma and the third suggests that the PGE partition into a vapor phase and precipitate when they encounter vapor-undersaturated magma. Much petrographic and geochemical evidence exists pointing to a role for vapor or fluids in the concentration of PGE to ore grade in mafic/ultramafic igneous complexes (Boudreau 1988, Ballhaus and Stumpfl 1986, Farrow and Watkinson 1987, Mathez 1989, Stone et al. 1994). Therefore, it is very important to investigate whether the magmatic vapor can contain enough precious metals to form a deposit.

As shown previously, at magmatic temperatures metals may be transferred to the vapor state as sulfides, oxides, chlorides, fluorides as well as native elements (Krauskopf 1957). Based on the thermodynamic evaluation of the volatilities of the platinum-group elements in the metallic, oxide and chloride form at magmatic temperatures (527 – 1327°C) Wood (1987) reported that the vapor transport of the PGE as chloride

may play an important role in concentrating the PGE in mafic igneous complexes such as the Stillwater or the Bushveld. Fleet and Wu (1995) have confirmed this conclusion for Pt and Pd by experimentally studying vapor transport of PGE in the system Fe-Ni-PGE-Au-S-FeCl₂-NaCl-C at 1000°C. Interestingly, in they found that the vapor transport of PGE and Au in the presence of Cl depends on the sulfur activity and the composition of the base-metal sulfide matrix. Therefore, S-species could be an important transport agent for PGE even when Cl is present in the vapor. Moreover, the volatility of any metal depends not only on the predominant metal species in the vapor but also on the most stable solid or liquid phase with which the vapor is in equilibrium (Krauskopf 1957, 1964). Inasmuch as PGE occur mainly as sulfides or alloys in mafic/ultramafic igneous complexes, it seems reasonable to develop the vapor transport model by studying a S-dominated vapor first as a potential carrier of platinum-group elements at magmatic temperatures. In addition to, vapor transport of sulfur and possibly other metals is considered important for formation of some base-metal sulfide deposits (Grinenko, 1985; Ripley and Alawi, 1998; Theriault et al., 2000; Barnes et al., 2001). There are a number of examples of PGE ore deposits where it has been proposed that after sulfides have collected the PGE to form the proto-ore, sulfur was removed by fluids. On the one hand, various metals, including the PGE, could dissolve in this fluid and move away (Gain, 1985; Boudreau, 1988; Lavigne and Michaud, 2001), on the other hand the S-removal could lead to a PGE enrichment of a sulfide residue due to the formation of individual PGE alloys at low S conditions. Thus, it has been observed in high temperature experiments in the Fe-Ni-S and Fe-Cu-Ni-S systems doped with platinum-group elements that at low concentrations of sulfur Ir and Pt bearing metal alloys form (Fleet and Stone, 1991; Li et al., 1996; Makovicky and Karup-Moller, 2000; Makovicky, 2002; Peregoedova and Ohnenstetter, 2002). Therefore, both mechanisms of PGE concentration caused by the S removal through the vapor phase, e.g. vapor transport of PGE and formation of PGE rich residue, should be taken into consideration when investigating the role of S-vapor for formation of PGE deposits.

1.1 Objectives

The main aim of the present project is to investigate by means of experiments the role of a S-dominated vapor for formation of economically important PGE-bearing ores. The research had been conducted in two general directions:

1. Experimental study of the PGE transport by a S vapor in the Fe-Ni-Cu sulfide system at magmatic temperatures including the investigation of predominant PGE transport agents (native elements or S-species) responsible for the PGE mobility in a S-dominated vapor.

2. Experimental study of the process of PGE enrichment in a sulfide as a result of its desulfurization through the vapor phase leading to the formation of individual PGE minerals at low S conditions.

2. EXPERIMENTAL

Both series of experiments were performed by the method of evacuated silica-glass tubes using a “tube-in-tube” technique (Fig 1.).

In our vapor transport experiments, an open silica-glass tube containing a piece of S-poor, PGE-free pyrrhotite of a composition close to FeS (PGE receiver) was placed inside a larger tube filled with a S-rich PGE-bearing base-metal sulfide (PGE donor) in such a manner that both PGE receiver and PGE donor coexisted with a common vapor-phase but were not in physical contact with each other (Fig. 1A). The outer tube was evacuated, sealed and equilibrated at 1100°C or 1000°C in a 1 atmosphere vertical furnace for 2 days with subsequent quenching in ice water. In the course of the experiments the transfer of sulfur from S-rich PGE donor to S-poor PGE receiver occurred. At the same time the PGE were transported and we observed an enrichment of initially S-poor Po not only in sulfur but also in Ni, Cu, Au and some platinum-group elements. Vapor transport experiments were conducted for Pt, Ir, Pd, Rh, Ru and Au added to the donor base-metal sulfide (BMS) in the quantity of about 2000 ppm. In our short-duration (2 days) experiments we have investigated the kinetics of the vapor transport process and made conclusions about the relative ability of various precious metal to be mobilized and transferred. To assess whether the metals were transported as S-species or metals we varied the metal/S ratio of the system by changing the donor/receiver ratio from 10/1 through 5/1 to 1/1. To understand if the PGE vapor transport correlates with the vapor transport of S we have also carried out a series of experiments with the opposite direction of the S transfer where the PGE receiver was richer in S than the PGE donor. Finally,

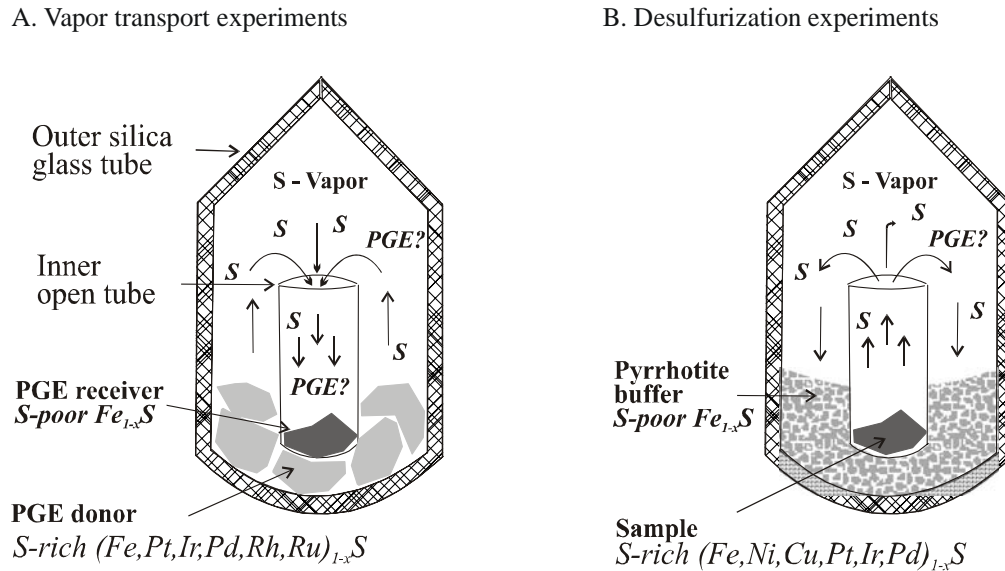


Figure 1. Schematic of the “tube-in-tube” assemblage: A. Vapor transport experiments; B. Desulfurization experiments.

the base-metal ratio in the PGE donor was varied in order to reveal if the PGE vapor transport depends on the sulfide association coexisting with the vapor phase (Table 1).

In the system Fe-S-PGE, the PGE donor consisted of PGE-bearing Po associated with Au alloy; the PGE exsolutions in the Po matrix are interpreted to have formed during quenching (Fig. 2A). In the system Fe-Cu-Ni-S-PGE, the donor assemblage was composed of the monosulfide solid-solution [Mss, $(Fe, Ni, Cu)_{1-x}S$] ± Cu-Au rich sulfide melt (Fig. 2B) or sulfide melt + $(Ru, Os, Ir)S_2$ in the richest in Cu and Ni experiments, respectively (Fig 2C).

Experiments of the second series were carried out in the system Fe-Ni-Cu-S doped with Pt, Ir and Pd and with fS_2 buffered by S-poor pyrrhotite to model a natural desulfurization process. The starting sulfide assemblages were synthesized in evacuated silica glass tubes by melting a mixture of pure elements at 1200°C. As Mss [$(Fe, Ni, Cu)_{1-x}S$] with a variable base-metal ratio is the dominant sulfide phase in the mantle (Allard et al., 2000), the starting compositions of the present experiments were chosen so that, the run products at 1000°C would be either [Po], [Mss] or [Mss + liquid] similar to our vapor transport experiments (Fig. 3).

The sulfur content of the starting samples was limited to approximately 53 at.%; Ni and Cu contents ranged from 0 to 4.5 at.%; sulfide samples were doped with

platinum-group elements of 0.2 wt.% (0.05 at.%) each for Pt and Ir, and 0.5 wt.% (0.2 at.%) for Pd. First we synthesized base-metal sulfides with platinum-group elements in solid solution and assured the complete dissolution of all added PGE into the structure of base-metal sulfides by annealing samples at 1000°C for 5-7 days. These PGE-bearing sulfides represented synthetic analogues of mantle sulfides and were further used to model changes occurring under conditions of S transport through the vapor phase. Sulfur fugacity was estimated by the pyrrhotite indicator according to the equation of Toulmin & Barton (1964). Then we performed “tube-in-tube” experiments with the use of a S-poor pyrrhotite buffer (63.5 wt.% Fe, 36.5 wt.% S) to model a sulfur removal from the PGE-sulfides synthesized previously. In these experiments an open silica-glass tube filled with a S-rich PGE-bearing sulfide sample (in pieces) was placed inside a larger tube filled with Po powder in such a manner that both the sample and the pyrrhotite coexisted with a common gas-phase but were not in physical contact with each other (Fig. 1B). The quantity of the Po buffer was 30-40 times larger than that of the sample. The “tube-in-tube” assemblage was annealed at 1000°C or 980°C for 7 days and quenched in salted ice water. In the course of the annealing, the sample was equilibrated with the pyrrhotite buffer and sulfur was exsolved from the sample into the vapor phase. Sulfur fugacity was estimated using the composition of Po buffer and was expected to be respectively -6.8 (in $\log f(S_2)$) at 1000°C and -7 at 980°C.

Table 1. Starting base-metal compositions of the PGE donors in the vapor transport experiments.

Run #	Starting composition, at.%				T°C	Sulfide assemblage
	Fe	Ni	Cu	S		
Vt5	47.1	0	0	52.5	1100	Po + Au alloy
					1000	Po + Au alloy
Vt6	44.2	1.5	1.4	52.5	1100	Mss + Au alloy
					1000	Mss + Au alloy
Vt7	38.4	4.5	4.2	52.5	1100	Mss + liquid
					1000	Mss + minor liquid
Vt9	29.5	9.1	8.4	52.5	1100	Liquid + (Ru,Os,Ir)S ₂
					1000	Liquid + minor Mss

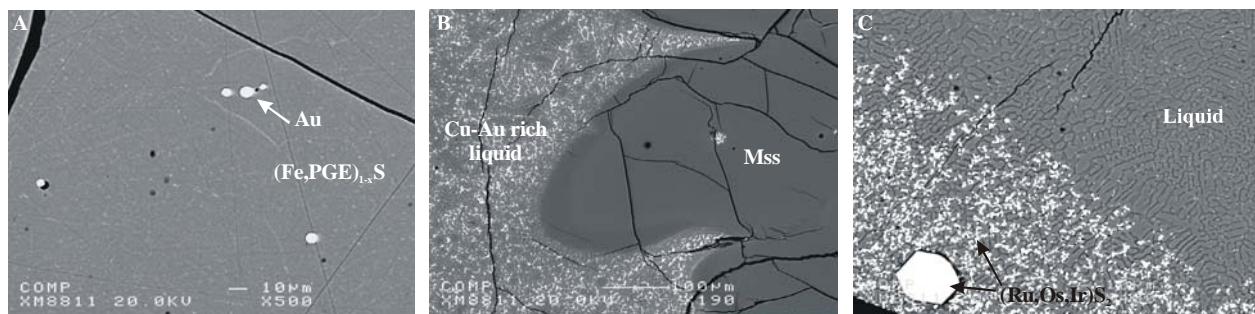


Figure 2. Back-scattered electron images of the donor BMS association in vapor transport experiments at 1100°C: A. Sample Vt5; B. Sample Vt7; sample Vt9.

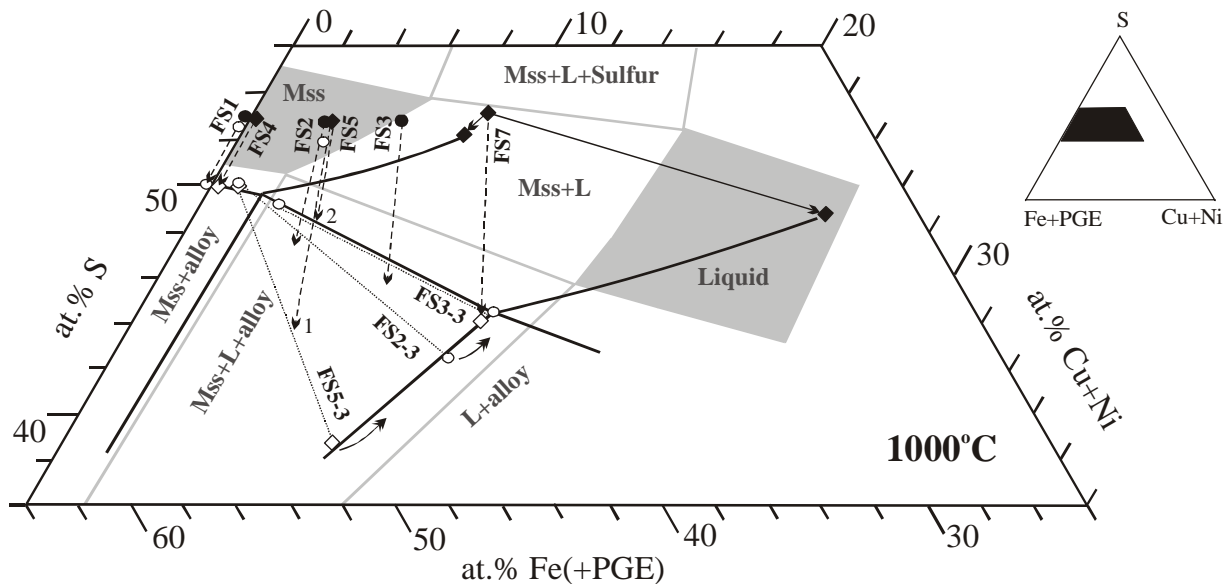


Figure 3. Diagram showing schematically the displacement of the bulk compositions of the experimental runs across the phase fields of the system Fe-Ni-Cu-S at 980-1000°C in the desulfurization experiments: solid circles and diamonds are the starting compositions with corresponding phase compositions for the experiments with Pt-Ir and Pd, respectively; open circles and diamonds are the compositions of the final products of the f/S_2 buffering experiments with Pt-Ir or Pd, respectively; solid lines are the boundary between the phase associations according to the present experiments; shadowed fields are the same boundaries in more PGE-enriched systems (Li et al., 1996); dashed lines with arrows show the approximate shift of the sulfide composition with lowering sulfur fugacity; dotted lines are the tie-lines between coexisting Mss and sulfide liquid.

Table 2. Quantity of Ni and Cu transported via vapor depending on the quantity of S transported at 1000°C.

Run#	Vt7-1	Vt7-2	Vt7-3	Vt7-4
Po receiver/Po donor ratio	1/10	1/5	1/1	Opposite S transfer
Ni transported	0.35 wt.%	0.29 wt.%	0.02 wt.%	0.08 wt.%
Cu transported	0.06±0.03 wt.%	0.08±0.04 wt.%	0.09±0.04 wt.%	0.04±0.04 wt.%

Table 3. Quantity of Ni and Cu transported via vapor depending on the initial Cu+Ni content and fraction of liquid in the donor at 1100°C.

Run#	Vt6-5	Vt7-5	Vt9-5
Ni and Cu in Po donor (each)	2 wt.%	4 wt.%	12 wt.%
BMS association	Mss+Au alloy	Mss+Liquid	Liquid+(Ru,Os,Is)S ₂
Ni transported	0.07 wt.%	0.34 wt.%	1.13 wt.%
Cu transported	0.06±0.01 wt.%	0.06±0.01 wt.%	0.09±0.02 wt.%

2.1 Analytical techniques

The products of experiments were studied mainly by electron microprobe. The sulfides CuFeS₂, FeS and (Fe,Ni)₉S₈ as well as Ni, Pt, Ir and Pd metals were used as standards. The analytical conditions were as follows: accelerating voltage 20 kV, beam current 30 nA, counting times up to 60s, spot diameter of 3 μm. A defocused electron beam of 30 μm in diameter was used to determine the bulk compositions of sulfide liquid and base-metal sulfides containing exsolution-induced PGM when the size of PGM was too small to analyze individually. The detection limits for platinum-group elements were 600–1500 ppm depending on counting time. The laser ablation microprobe - inductively coupled plasma mass spectrometer or LAM-ICPMS at the University of Quebec in Chicoutimi was used to determine the PGE concentration at ppm level in the vapor transport experiments. The detection limit for all PGE is in the 10 to 30 ppb range.

3. RESULTS

3.1 Vapor transport experiments

By the end of the vapor transport experiments, significant concentrations of Ni, Cu, Au and Os, some Pt, Pd and extremely low amounts of Rh, Ru and Ir were detected in the initially Ni-Cu-PGE-free Po receiver. The quantity of Ni transported increases with increasing quantity of S transported as well as with increasing Ni-content of the donor and amount of liquid in the donor BMS association (Tables 2 and 3). The highest quantity of Ni transported to the Po receiver via vapor phase was observed in the 1100°C experiment in the richest in Cu and Ni sample Vt9, 1.13 wt.% Ni. Almost no Ni was detected in the Po receiver in experiments with the opposite direction of the S transfer. Therefore in the S-dominated vapor, Ni is probably transported by S-species.

In contrast to Ni, the quantity of Cu transported does not depend on the quantity of S transported, the Cu-content of the donor and the amount of liquid in the BMS association (Tables 2 and 3). In all samples, the quantity of Cu found in the Po receiver by the end of experiments is much lower than that of Ni, about 0.1 wt.% or less. The same low quantity of Cu was transported in the experiments with the opposite direction of the S transfer. Therefore, Cu in our experiments is probably transported by metal species. According to the calculation by Krauskopf (1957), the vapor pressure of metallic Cu is much higher in magmatic vapor than that of metallic Ni. In our experiments Ni is much better transported in vapor if compared with Cu. Therefore, the suggestion about the Ni transport by S-species in our experiments seems to be reasonable.

Among the precious metals considered in this project, Au and Os were the most mobile elements in the S vapor (Fig. 4). The concentration of Au and Os detected in the Po receiver reaches 1000 ppm but varies in dependence on the Cu and Ni content of the donor, i.e. the base-metal sulfide association coexisting with the vapor.

250-300 ppm of Au were detected in the Po receivers that coexisted with the Fe-rich donors (0 - 4 at.% Cu and Ni) containing Au alloy in the sulfide association (Fig. 2A). With increasing Cu and Ni to 8 - 24 at.%, the quantity of Au transported decreases to 50 ppm or less (Fig. 5) because Au is captured by sulfide liquid that dominates the Cu- and Ni-rich sulfide associations (up to 6 wt.% Au in the liquid). Inasmuch as the transport of Au by vapor does not correlate with sulfur transfer in our experiments and increases in Au alloy-bearing assemblages, we suggest that Au was transported

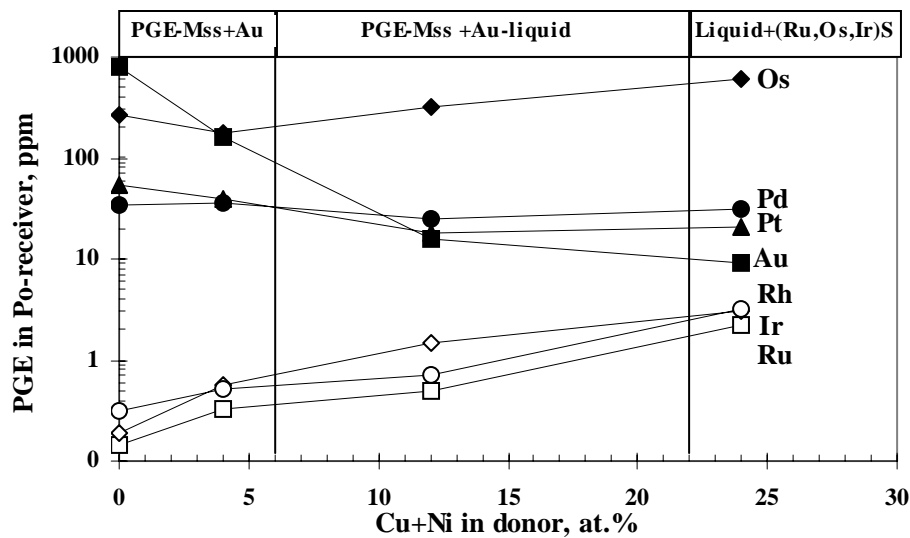


Figure 4. PGE vapor transport depending on bulk Cu+Ni content in the donor at 1100°C.

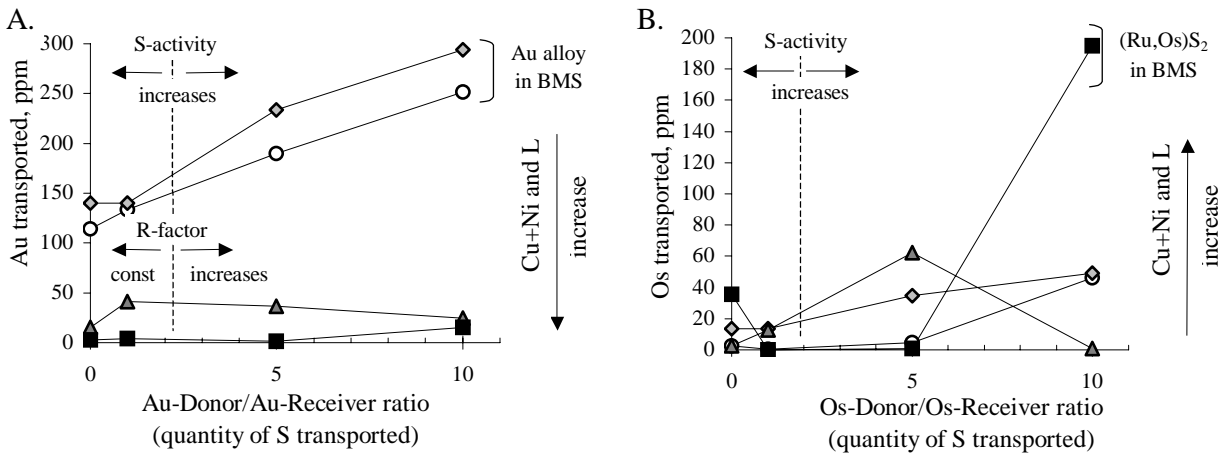


Figure 5. Dependence of Au and Os transported on mineral associations coexisted with a vapor phase at 1000°C.

mainly as metal species. On the contrary, the transport of Os was largest (200 ppm) in Cu- and Ni-rich experiment where Os-rich sulfide, $(\text{Ru,Os,Ir})\text{S}_2$, was stable together with the sulfide liquid (Fig. 2C). Whereas the Os transport was low (< 60 ppm) in Fe-rich experiments (Fig. 5).

Pt and Pd demonstrated similar behavior regarding the transport through the S-dominated vapor (Figs. 4 and 6). Up to 50-60 ppm of Pt and Pd were detected in Po receivers by the end of experiments. The strong positive correlation between Pt and Pd vapor transport and the

quantity of S transferred was observed, therefore the mobilization in the form of S-species is implied. Finally, only 2 ppm or lower of Ru, Rh and Ir were transported to Po receivers in our vapor transport experiments.

3.2 Desulfurization experiments.

The main results of S-buffered experiments are summarized in the Table 4.

With the use of a pyrrhotite buffer, the sulfur fugacity

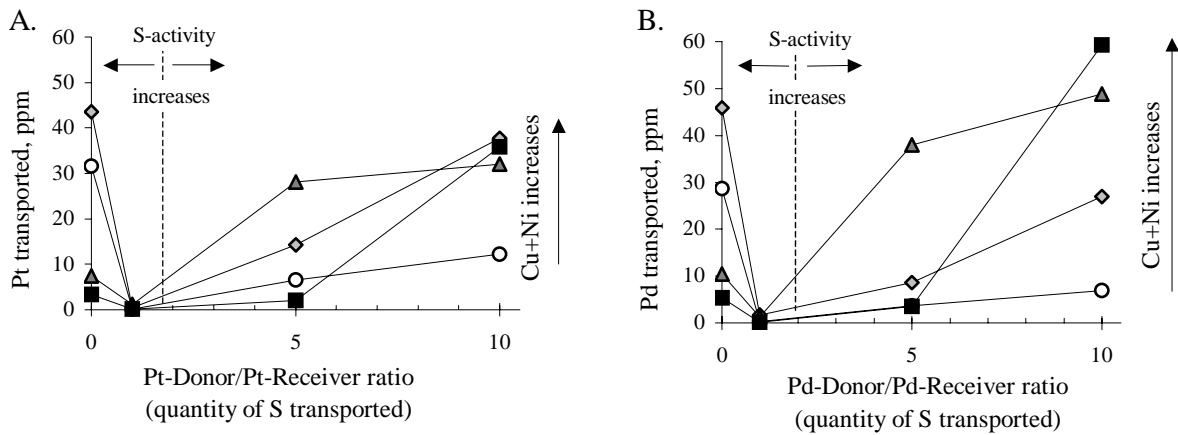


Figure 6. Dependence of Pt and Pd transported on the S-activity in the system at 1000°C.

 Table 4. Summary of experiments with the use of pyrrhotite as $f(S_2)$ indicator or buffer.

Run#	Starting composition, at.%							T°C	Pyrrhotite	log $f(S_2)$, atm.	Run Products
	Fe	Ni	Cu	Ir	Pt	Pd	S				
FS1-1	47.10			0.05	0.04		52.81	1000°C	indicator	-0.9	(Fe,Pt,Ir) _{1-x} S
FS1-3								1000°C	buffer 2	"< -6.9"	Fe _{1-x} S + Fe-Ir-Pt alloy
FS2-1	44.24	1.48	1.39	0.04	0.04		52.81	980°C	indicator	">-0.9"	Mss
FS2-3								980°C	buffer 2	< -7.1	Mss + Liquid + Fe-Ir-Pt alloy
FS3-1	41.34	3.00	2.77	0.05	0.04		52.80	1000°C	indicator	">>-0.9"	Mss
FS3-3								1000°C	buffer 2	-6.7	Mss + Liquid + Fe-Ir-Pt alloy
FS4-1	46.90					0.21	52.89	1000°C	indicator	"-0.9"	(Fe,Pd) _{1-x} S
FS4-3								1000°C	buffer 2	< -6.9	Fe _{1-x} S + Fe-Pd alloy
FS5-1	44.09	1.48	1.37			0.20	52.86	1000°C	indicator	">-0.9"	Mss
FS5-3								1000°C	buffer 2	-6.6	Mss + liquid
FS7-1	37.85	4.50	4.23			0.21	53.22	1000°C	indicator	">>-0.9"	Mss + liquid
FS7-3								1000°C	buffer 2	-6.5	Liquid + Mss(?)

Note: $f(S_2)$ values given in commas were estimated by comparison with $f(S_2)$ values determined by X-ray diffraction; SC - slow cooling; Buffer 1 - Fe (61.2 wt.%), S (38.8 wt.%); Buffer 2 - Fe (63.5 wt.%), S (36.5 wt.%)

was reduced in these experiments by $\sim 4.5 - 5.6 \log f(S_2)$ reducing the absolute value to -6.5 and -7.1 . The decrease in sulfur fugacity resulted in a partial transfer of sulfur from the sulfide to the vapor. Consequently the metal/sulfur ratio of the initial sulfides increased causing two important events: formation of PGE-bearing alloys and partial melting of the sulfides. In the Cu-Ni free S-buffered experiments the run products were pyrrhotite and PGE-bearing alloys. In the Pt-Ir doped experiments the alloy composition was not analyzed due to its small size. Based on the data of Makovicky and Karup-Moller (2000), this alloy apparently represents $\gamma(\text{Fe, Ir, Pt})$ solid solution, with a composition dominated by Fe. The composition of alloy formed in experiments doped with Pd is very close to PdFe (Pd analogue of tetraferroplatinum PtFe). The Fe-Ir-Pt alloys occur as oriented lamellae in the pyrrhotite matrix (Fig. 7A). In contrast, the grains of the Pd-Fe alloy are mainly concentrated close to the boundaries with vapor phase as rounded relatively big blebs (Fig. 7B). The difference in texture is interpreted to indicate of the higher mobility of palladium compared to platinum and iridium. No detectable amounts of Pt, Ir or Pd were found in the pyrrhotite matrix hosting the PGE-bearing alloys suggesting preferential distribution of the PGE to the metal phase. In the Ni-Cu bearing experiments the run products were Mss, liquid and Fe-Ir-Pt alloy (Fig. 7C) in the Pt-Ir doped experiments and Mss and liquid in the Pd doped experiments. The Mss is depleted in Cu, Ni and Pd relative to the liquid. The composition of Fe-Ir-Pt alloy corresponds to the Fe-rich $\gamma(\text{Fe, Ir, Pt})$ solid solution.

The present experiments confirm that base-metal sulfides can concentrate significant amounts of platinum, iridium and palladium in solid solution at high temperatures (at least 0.2 wt.%). We also found that S loss from base-metal sulfides could produce: 1) the exsolution of Pt and Ir from base-metal sulfide solid solution in the form of PGE-bearing alloys, 2) partial or even complete melting of the Cu-Ni bearing sulfides to form Mss, Cu-Pd rich liquid and Fe-Ir-Pt alloys. Both these events are geologically extremely important and may explain the presence of the two types of sulfide found in the mantle (Mss-dominated sulfides and S-poor sulfides consisting mainly of pentlandite and chalcopyrite), the alloy-enriched reefs in layered intrusions, and possibly the crystallization of PGM from silicate magmas. Thus, PGE alloys exsolved from Mss after S reduction are possibly responsible for the Pt anomalies seen in some xenoliths and for the enrichment of chromitites in Pt. We also suggest that the Cu-Pd rich liquid formed by partial melting of

sulfides could migrate away from Mss and alloys, thus spatially decoupling Ir-Pt and Cu-Pd as observed in reefs and mantle nodules.

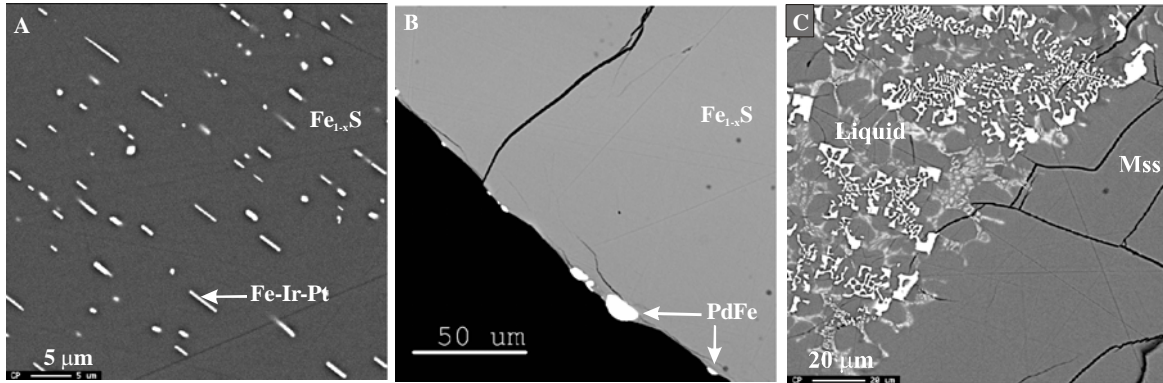
3.3 Discussion

The present experiments show that in sulfide systems where a vapor phase is dominated by sulfur, the vapor transport of metals at magmatic temperatures occurs in the following order: $\text{Ni} > \text{Cu} > \text{Au}$, $\text{Os} \gg \text{Pt}$, $\text{Pd} \gg \text{Ru}$, Rh , Ir . According to literature data, this order varies depending on the vapor composition. If Cl is present in the system, Cu mobilizes faster than Ni in contrast to the S-dominated systems (Fleet and Wu, 1995). Moreover, Ni transport is very low in case of the $\text{SiO}_2\text{-NaCl}$ saturated aqueous fluids in the system Fe-Ni-Cu-S (Ballhaus et al. 1994). The results of our experiments regarding significant vapor transport of Ni are in a good agreement with the data obtained by Baker et al. (2001) for high-pressure H_2S -containing sulfurous fluid. This demonstrates the significance of vapor/fluid composition on the mobilization of ore metals and their transport at magmatic temperatures.

In most of the natural examples where fluid mobilization of PGE has been suggested, the remobilized material is enriched in Cu, Pd and to a lesser extent in Pt. Our experiments suggest that transport by S-vapor is not the mechanism for this remobilization, as Pd was not fractionated from Pt, and Cu was not significantly transported by the vapor compared to Ni. A more promising candidate for the remobilization of the Cu and Pd is the Cu-rich sulfide melts that formed in the desulfurization experiments. Mantle sulfides generally consist of monosulfide solid solution enriched in Ni and to a lesser extent in Cu. It is difficult to reduce the sulfur fugacity in natural conditions sufficiently enough to exsolve trace quantities of PGE from Mss structure, but it is possible to promote partial melting of the sulfide as compositions of many mantle sulfides are very close to the [Mss+Liquid] boundary (Alard et al., 2000). A small decrease in bulk S content is sufficient to reach this boundary and start melting as in our desulfurization experiments.

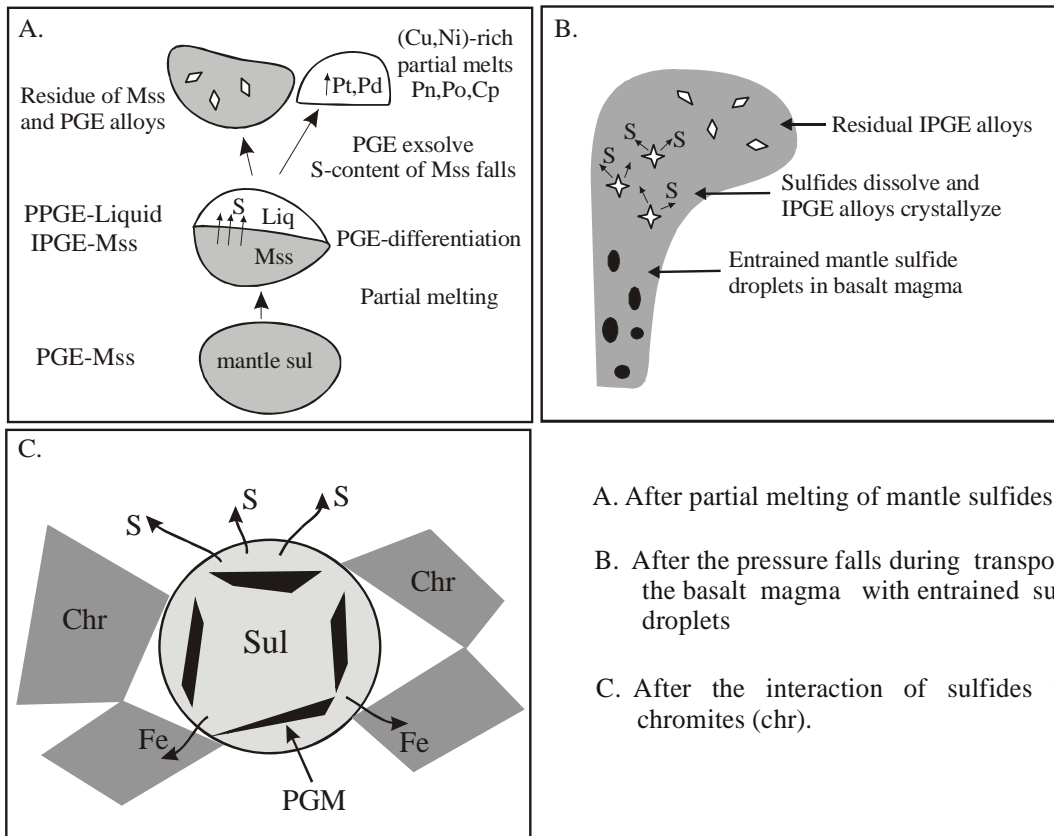
This behavior could be important in a number of geological situations. The first situation is during partial melting of the mantle where the monosulfide solid solution hosts most of the mantle's PGE (e.g. Bulanova et al., 1996; Pattou et al., 1996). In the course of the partial melting the sulfides may be partly dissolved

Figure 7. Back-scattered electron images



- A. Exsolution-induced lamellae of the Fe-Pt-Ir alloy in the matrix of pyrrhotite appearing after reduction of fS_2 (run FS1-3, 1000°C)
- B. Grains of the Pd-Fe alloy formed by exsolution from pyrrhotite after reduction of fS_2 (run FS4-3, 1000°C)
- C. Partial melting of the Pt-Ir bearing Mss caused by sulfur reduction and resulted in the formation of a Cu-Ni rich sulfide liquid (multiphase quench mixture) and PGE alloys (bright crystals associated with the liquid) (run FS2-3, 980°C).

Figure 8. Models of geological situations in which the base-metal sulfides can lose S resulting in the crystallization of PGE alloys.



A. After partial melting of mantle sulfides (sul).

B. After the pressure falls during transport of the basalt magma with entrained sulfide droplets

C. After the interaction of sulfides with chromites (chr).

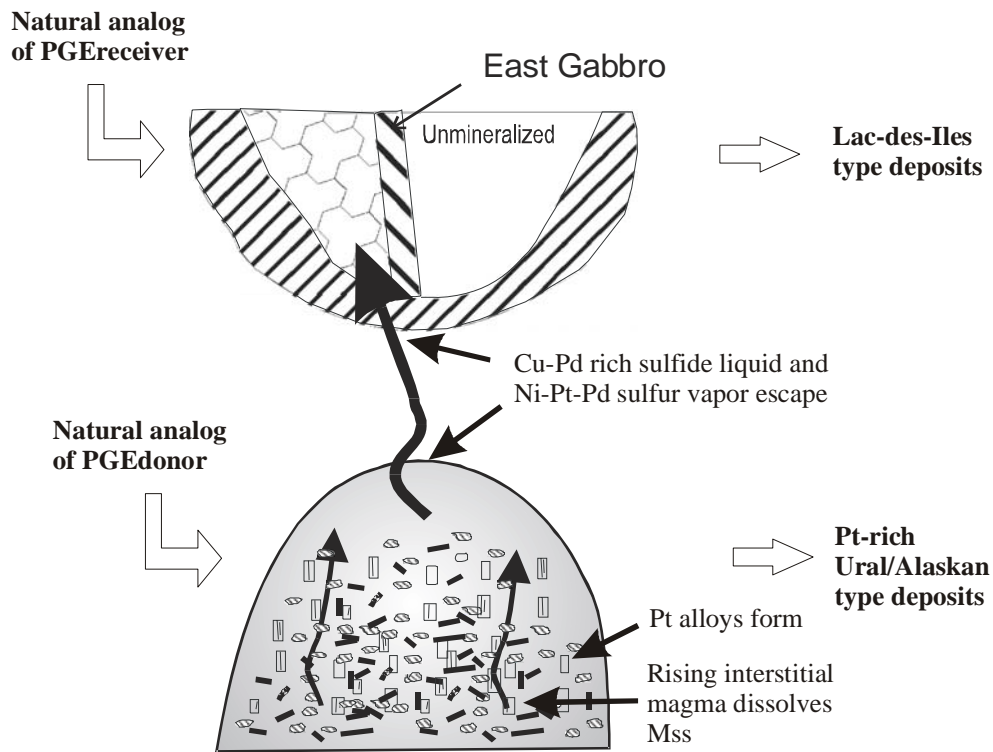


Figure 9. A model of PGE receivers and donors in natural conditions.

producing a sulfide liquid enriched in Cu and Pd and Mss residue with high concentrations of IPGE (Ir, Os, Ru and Rh) (Alard et al., 2000; Barnes et al., 2001; and our results). During dissolution of the Mss its sulfur content could fall leading to the exsolution of PGE from the structure of Mss with the formation of PGE-bearing alloys (Fig. 8A). A second situation where metal alloys could form from base-metal sulfides is during magma transport (Fig. 8B). It is possible that mantle derived melts entrain some sulfide droplets with them (Barnes et al., 2001; Bockrath and Ballhaus, 2002). The solubility of sulfide in basaltic melt increases with decreasing pressure (Mavrogenes and O'Neil, 1999). Thus, during magma ascent the sulfide droplets could be partly resorbed and the S-content of the sulfide liquid could fall sufficiently for alloys to form. Thirdly (Fig. 8C), it has been suggested that in chromite-rich portions of the Bushveld reefs sulfides trapped between the chromite grains could lose Fe to the chromite and S to the vapor leaving behind platinum-group minerals crystallized under conditions of low sulfur fugacity (von Gruenewaldt et al., 1986; Naldrett and Lehmann, 1988; Merkle, 1992; Mathez, 1999; Barnes and Maier, 2002).

Additionally, the results of the present experiments can be directly used to develop the genetic models for

various types of natural ore deposits. The Pt-rich deposits of the Ural or Alaskan type are considered as natural analogues of the PGE donor employed in our experiments. Pt alloys present in these deposits could have formed as a result of the desulfurization of the original PGE-bearing Mss due to the reaction with percolating S-undersaturated magma. On the other hand, the S vapor containing Ni, Pt and Pd and the Cu-Pd rich sulfide liquid released in the course of the desulfurization process can play a role in the formation of deposits such as Lac-des-Iles (Fig. 9).

4. CONCLUSIONS

In most natural examples where fluid mobilization of PGE has been suggested, the remobilized material is enriched in Cu, Pd and to a lesser extent Pt. Our experiments suggest that transport by S-vapor is not the mechanism for this remobilization, as Pd was not fractionated from Pt, and Cu was not significantly transported by the vapor compared to Ni. A more promising candidate for the remobilization of the Cu and Pd is the Cu-rich sulfide melts that formed in the desulfurization experiments. However, the

desulfurization by removal of the S-dominated vapor at magmatic temperatures could play an extremely important role in formation of economically important PGE-concentrations, and has the following consequences:

1. The transport of Au, Pt and Pd through the S-dominated vapor phase together with Ni and Cu.
2. The exsolution of Pt and Ir from S-depleted base-metal sulfides in the form of PGE alloys leading to the enrichment of a sulfide residue in these heavy platinum-group elements.
3. Partial or even complete melting of the sulfide leading to the formation of S-poor monosulfide solid solution, Fe-Pt-Ir alloy and highly mobile Cu-Ni-Pd rich sulfide liquid. This could separate palladium from platinum and iridium in natural ore systems resulting in changes of the initial Pd/Pt and Pd/Ir ratios.

REFERENCES

- Alard, O., Griffin, W.L., Lorand, J.P. (2000). Non-chondritic distribution of the highly siderophile elements in mantle sulphides. *Nature* 407, 891-894.
- Baker, D.R., Barnes, S.-J., Simon, G., Bernier, F. (2001). Fluid transport of sulfur and metals between sulfide melt and basaltic melt. *Can. Mineral.* 39, 537-546.
- Ballhaus, C.G., Stumpfl, E.F. (1986). Sulfide and platinum mineralization in the Merensky Reef: evidence from hydrous silicates and fluid inclusions. *Contrib. Mineral. Petrol.* 94, 193-204.
- Barnes, S.-J., Maier, W.D. (2002). The distribution of platinum-group elements in the Merensky Reef, Impala Mines, Western Bushveld Complex. *J. Petrol.* 43, 103-128.
- Barnes, S.-J., van Achterbergh, E., Makovicky, E., Li, C. (2001). Proton microprobe results for the partitioning of platinum-group elements between monosulphide solid solution and sulphide liquid. In: W. D. Maier (Editor), *Platinum group elements and minerals in Southern African rocks*. *South African Journal of Geology* 104, pp.275-286.
- Bockrath, C., Ballhaus, C. (2002). PGE fractionation between sulfide-bearing mantle and basaltic melt during partial melting and melt segregation. 9th International Platinum Conference, Billings, Abstracts with Program, Billings, pp. 41-43.
- Boudreau, A.E. (1988). Investigations of the Stillwater Complex, VI. The role of volatiles in the petrogenesis of the J-M reef, Minneapolis section. *Can. Mineral.* 26, 193-208.
- Bulanova, G.P., Griffin, W.L., Ryan, C.G., Shestakova, Ye.O., Barnes, S.-J. (1996). Trace elements in sulfide inclusions from Yakutian diamonds. *Contrib. Mineral. Petrol.* 124, 111-125.
- Farrow, C.E.G., Watkinson, D.H. (1992). Alteration and the role of fluids in Ni, Cu, and platinum-group element deposition, Sudbury Igneous Complex contact, Onaping-Levack area, Ontario. *Mineral. Petrol.* 46, 67-83.
- Fleet, M.E., Stone, W. (1991). Partitioning of platinum-group elements in the Fe-Ni-S system and their fractionation in nature. *Geochim. Cosmochim. Acta* 55, 245-253.
- Fleet, M.E., Wu, T.W. (1993). Volatile transport of platinum-group elements in sulfide-chloride assemblages at 1000°C. *Geochim. Cosmochim. Acta* 57, 3519-3531.
- Fleet, M.E., Wu, T.W. (1995). Volatile transport of precious metals at 1000°C: Speciation, fractionation and effect of base-metal sulfide. *Geochim. Cosmochim. Acta* 59, No. 3, 487-495.
- Gain, S.B. (1985). The geologic setting of the platiniferous UG-2 chromitite layer on the Farm Maandagshoek, Eastern Bushveld Complex. *Econ. Geol.* 80, 925-943.
- Grinenko, L.N. (1985). Sources of sulfur of the nickeliferous and barren gabbro dolerite intrusion of the northwest Siberian platform. *Intern. Geol. Review* 27, 695-708.
- Krauskopf, K.B. (1957). The heavy metal content of magmatic vapor at 600°C. *Econ. Geol.* 52, 786-807.
- Krauskopf, K.B. (1964). The possible role of volatile metal compounds in ore genesis. *Econ. Geol.* 59, 22-45.
- Lavigne, M.J., Michaud, M.J. (2001). Geology of North American Palladium Ltd.'s Roby Zone Deposit, Lac des Iles. *Explor. Mining Geol.* 10, Nos 1 and 2.
- Li, C., Barnes, S.-J., Makovicky, E., Rose-Hansen, J., Makovicky, M. (1996). Partitioning of nickel, copper, iridium, rhenium, platinum, and palladium between monosulfide solid solution and sulfide liquid: effects of composition and temperature. *Geochim. Cosmochim. Acta* 60, 1231-1238.
- Mavrogenes, J.A., O'Neill, H.St.C. (1999). The relative effects of pressure, temperature and oxygen fugacity on the solubility of sulfide in mafic magmas. *Geochim. Cosmochim. Acta* 63, 1173-1180.
- Makovicky, E. (2002). Ternary and quaternary phase systems with PGE. In: L.J. Cabri (Editor), *The geology, geochemistry, mineralogy and mineral beneficiation of platinum-group elements*. Canadian Institute of Mining, Metallurgy and Petroleum, Special Vol. 54, pp. 131-175.
- Makovicky, E., Karup-Moller, S. (2000). Phase relations in the metal-rich portions of the phase system Pt-Ir-Fe-S at 1000°C and 1100°C. *Mineral. Mag.* 64, 1047-1056.
- Makovicky, E., Karup-Moller, S. (1999). The phase system Fe-Ir-S at 1100, 1000 and 800°C. *Mineral. Mag.* 63, 379-385.
- Majzlan, J., Makovicky, M., Makovicky, E., Rose-Hansen, J. (2002). The system Fe-Pt-S at 1100°C. *Can. Mineral.* 40, 509-517.
- Mathez, E.A. (1989). Vapor associated with mafic magma and control on its composition. In *Ore Deposition Associated with Magmas* (ed. J.A. Whitney and A.J. Naldrett). *Rev. Econ. Geol.* 4, 21-31.

- Mathez, E.A. (1999). On factors controlling the concentrations of platinum group elements in layered intrusions and chromitites. In: R.R. Keays, C.M. Lesher, P.C. Lightfoot, C.E.G. Farrow (Editors), *Dynamic processes in magmatic ore deposits and their application to mineral exploration. Short Course Notes - Geological Association of Canada 13*, pp.251-285.
- Merkle, R.K.W. (1992). Platinum-group minerals in the middle group of chromitite layers at Marikana, Western Bushveld Complex: indications for collection mechanisms and postmagmatic modification. *Can. J. of Earth Sc.* 29, 209-221.
- Naldrett, A.J., Lehmann, J. (1988). Spinel non-stoichiometry as the explanation for Ni-, Cu-, and PGE-enriched sulfides in chromitites. In: H.M. Prichard, P.J. Potts, J.F.W Bowles, and S.J. Cribb (Editors), *Geo-Platinum 87*, Elsevier, pp. 113-143.
- Pattou, L., Lorand, J.P., Gros, M. (1996). Non-chondritic platinum-group element ratios in the Earth's mantle. *Nature* 379, 712-715.
- Peregoedova, A.V., Ohnenstetter, M. (2002). Collectors of Pt, Pd and Rh in a S-poor Fe-Ni-Cu-sulfide system at 760°C: experimental data and application to ore deposits. *Can. Mineral.* 40, 527-561.
- Ripley, E.M., Alawi, J.A. (1988). Petrogenesis of pelitic xenoliths at the Babbitt Cu-Ni deposit, Duluth Complex, Minnesota, U.S.A. *Lithos* 21, 143-159.
- Stone, W.E., Crocket, J.H., Fleet, M.E. (1994). Platinum-group mineral-bearing amygdale sulfide in the flow top of Fred's Flow komatiite, Munro Township: Evidence for vapour transport and concentration of platinum-group elements. *Mineral. Petrol.*
- Theriault, R.D., Barnes, S.-J., Severson, M.J. (2000). Origin of Cu-Ni-PGE sulfide mineralization in the Partridge River Intrusion, Duluth Complex, Minnesota. *Econom. Geol.* 95, 929-943.
- Toulmin, P. III., Barton, P.B.Jr. (1964). A thermodynamic study of pyrite and pyrrhotite. *Geochim. Cosmochim. Acta* 28, 641-671.
- Von Gruenewaldt, G., Hatton, C.J., Merkle, R.K.W., Gain, S.B. (1986). Platinum-group element – chromitite associations in cumulates of the Bushveld Complex. *Econom. Geol.* 81, 1067-1079.
- Wood, S.A., 1987. Thermodynamic calculations of the volatility of the platinum group elements (PGE): The PGE content of fluids at magmatic temperatures. *Geochim. Cosmochim. Acta* 51, 3041-305