

An experimental study of mass transfer of platinum-group elements, gold, nickel and copper in sulfur-dominated vapor at magmatic temperatures

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Abstract

We report results of an experimental study on platinum-group elements (PGE) and Au mass transfer by an S-vapor in the Fe–Ni–Cu sulfide system at magmatic temperatures. Using the tube-in-tube technique, we have examined the quantity of PGE, Au and base-metals (BM) transferred via the vapor from the PGE donor [S-rich (Fe,Ni,Cu)_{1-x}S doped with about 2000 ppm of each PGE and Au] to a S-poor PGE-free pyrrhotite (Po) used as the PGE receiver. At the end of the experiments, the receiver Po contained significant quantities of Ni, Cu, Au, Pt and Pd, but little Ir, Ru and Rh. The most important factors influencing the vapor mobility of Ni, Cu, Au and PGE are the phase assemblage present in the donor, which in turn is controlled by temperature, S, Ni and Cu content of the system, and the sulfur fugacity (f_{S_2}). In experiments containing only Au-alloy and monosulfide solid-solution (Mss) in the donor, Cu is transferred more than Ni. Gold is transferred 10 times more efficiently than Pd and Pt, and Pd and Pt are transferred 10 times more efficiently than Rh, Ru and Ir. At the lowest S contents, when Pt-alloys form in the donor system, Pt is transferred less than Pd. In experiments containing Mss and sulfide liquid, the amount of all PGE transferred is higher, although the order remains the same Pd–Pt > Rh–Ru–Ir. The amount of Ni transferred is higher than in the Mss-alloy system. In contrast, the amount of Au transferred is lower where the sulfide liquid is present.

The amount of S in the receiver Po may be used as a proxy for f_{S_2} . Within each phase assemblage the amount of Ni and PGE transferred increases with the amount of S in the receiver Po suggesting that these elements are transferred as sulfide complexes. In contrast, Cu and Au show no correlation with f_{S_2} suggesting that these elements are transferred as metals.

These results are not directly applicable to natural systems because the simplicity of the experiments. Nevertheless three geological systems where these results could be relevant are considered. Firstly, in the case of PGE deposits some are enriched in Pd, Cu and Au, while some are rich in Pt. According to our experiments this could occur if a magmatic sulfide underwent S devolatilization to form S-poor Mss plus Pt-alloy (to form the Pt-rich deposits) and the vapor transported Cu, Au and Pd to a lower pressure and temperature site and deposited these metals there to form the Pd-rich deposits. Secondly, in the case of magmatic Ni–Cu sulfide deposits, which in many cases are enriched in Cu and Pd; S, Cu and Pd could be transferred from the country rock as a vapor leaving Mss and Pt-alloy in the country rock. Finally, during S devolatilization of mantle nodules, Pd, Cu and Au could be removed by the vapor.

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1. Introduction

The possible mass transfer of platinum-group elements (PGE) in S-vapor could be important in a number of geological settings. For example, there is considerable debate as to how some PGE-dominated ores in mafic and ultramafic rocks form. Deposits such as the Roby Zone of the Lac-des-Iles Complex, Ontario, the Platinova reef, Skaergaard, Greenland and the JM reef Stillwater, Montana are significantly enriched in Cu, Au and Pd relative to most platinum-group elements (Os, Ir, Ru, Rh, Pt) (Naldrett, 2004). Some workers suggest that the enrichments of Cu, Au and Pd are due to redistribution of the metals by deuteric fluids using a model that suggests after magmatic sulfides have collected the PGE to form the proto-ore, sulfur was removed by deuteric fluids; and at the same time various metals, including the PGE and Au, could dissolve in this fluid and be redeposited to form the Cu–Pd deposits (Ballhaus and Stumpfl, 1986; Boudreau, 1988; Lavigne and Michaud, 2001). Another group of deposits where vapor mass transfer of sulfur and possibly other metals has been suggested are magmatic Ni–Cu deposits, e.g. Noril'sk, Siberia (Grinenko, 1985), Duluth, Minnesota (Ripley and Alawi, 1988; Theriault et al., 2000) and Pechenga, Russia (Barnes et al., 2001). In these cases it has been suggested that S and possibly Cu and Pd are transferred from the country rocks into the magma by vapor (Barnes et al., 1997). It has also been argued that the enrichment of Pd and Au in alkali Cu-porphyrines is in part due to volatile mass transfer (e.g. Economou-Eliopoulos, 2005). Thus many authors argue that Pd and Cu are mobile elements at magmatic temperatures in ore bearing systems, but there is little experimental evidence showing that Pd and Cu are more mobile than the other PGE. In addition to ore environments, the behavior of PGE in the mantle nodules may be influenced by vapor mass transfer. Lorand et al. (2003) suggest that S, Se, Cu, Pd and Os are removed from mantle nodules by volatilization during emplacement of the lavas that carry the nodules. To investigate whether a magmatic vapor or fluid phase could contribute to the PGE and Cu enrichment process, it is necessary to know if there is any difference in the distribution behavior of the PGE, especially Pt and Pd, in the presence of the vapor phase. In other words, can the vapor phase selectively transfer Cu and Pd compared to Pt at magmatic temperatures?

At magmatic temperatures metals may be transferred in the vapor phase as sulfides, oxides, chlorides, and fluorides, as well as native elements (e.g. Krauskopf, 1957; Candela, 1994; Williams-Jones and Heinrich, 2005). Based on the thermodynamic evaluation of the volatilities of the PGE in the metallic, oxide and chloride

form at magmatic temperatures (527–1327 °C), Wood (1987) reported that the vapor mass transfer of the PGE as chloride complexes may play an important role in concentrating the PGE in mafic igneous complexes such as the Stillwater or the Bushveld. Hanley et al. (2005a) confirmed the importance of Cl-rich fluids by showing that Au and Pt are high soluble in Cl-rich brines and Cl-vapor at 800 °C. Fleet and Wu (1995) studied vapor mass transfer of PGE in the system Fe–Ni–PGE–Au–S–FeCl₂–NaCl–C at 1000 °C. Interestingly, they found that the vapor mass transfer 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-bearing species may also be an important mass transfer agent for PGE, even when Cl is present in the vapor.

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 investigate the vapor mass transfer model by studying an S-dominated vapor as a potential carrier of PGE at magmatic temperatures. Thus, it is important to investigate experimentally whether sulfur vapor can transfer enough precious metals to form a deposit.

Baker et al. (2001) demonstrated the possibility of the mass transfer of sulfur and metals Cu, Ni, and Pt via a sulfurous fluid phase dominated by H₂S. Fleet and Wu (1993, 1995) studied the volatile mass transfer of PGE in sulfide–chloride assemblages and concluded that sulfur alone, in the absence of other ligands, does not appear to be an important mass transfer agent for PGE. Fleet and Stone (1991) found that PGE were present at less than the detection limit of the electron microprobe in vapor deposited troilite (FeS), in contrast to Ni that was present at the wt.% level. On these grounds, Fleet and Stone (1991) suggested that S-bearing vapor did not selectively transfer PGE over base–metals. However, the FeS in Fleet and Stone's experiments had a very low S content and such compositions accommodate very little PGE (Ballhaus and Ulmer, 1995; Makovicky and Karup-Moller, 1999; Majzlan et al., 2002; Peregoedova and Ohnenstetter, 2002). Therefore the potential capability of S-poor, low-temperature troilite in the Fleet and Stone (1991) experiments to host platinum-group elements is very low. Because the partitioning of metals such as Ir, Rh and Pt, Pd and Cu into pyrrhotite (Po) and monosulfide solid-solution (Mss) structures increases with the sulfur concentration in these minerals (Ballhaus and Ulmer, 1995; Li et al., 1996; Barnes et al., 2001), higher PGE concentrations could be expected in a case

Table 1
Starting compositions of the receivers and donors

Number	S (wt.%)	Fe (wt.%)	Ni (wt.%)	Cu (wt.%)	PGE (wt.%)	Au (wt.%)
<i>Receivers</i>						
po-1	36.7	63.2	<0.02	<0.02	<0.000002	<0.000002
po-2	40.01	59.9	<0.02	<0.02	<0.000002	<0.000002
<i>Donors</i>						
Series 5	38.46	60.06	0	0	0.2 of each	0.2
Series 6	38.3	56.18	2	2	0.2 of each	0.2
Series 7	38.04	48.44	6	6	0.2 of each	0.2
Series 9	37.64	36.87	12	12	0.2 of each	0.2

of a pyrrhotite richer in S than those in the experiments of Fleet and Stone (1991).

The vapor mass transfer of metals in the experiments of Fleet and Wu (1993, 1995) was accomplished by the process of sublimation. This process requires the concentration of Fe-bearing species in the vapor to be high enough to allow the vapor deposition of FeS at the cold end of the tube. The necessary high concentration was reached in PGE–Fe–Ni–Cu–S+NaCl and Fe–Ni–PGE–Au monosulfide±S±FeCl₂±NaCl±C experiments of Fleet and Wu (1993, 1995) by the formation of Fe-chloride complexes. In the absence of chloride, the concentration of metals in the vapor was not high enough for growth of crystals from the gaseous phase. Therefore, the PGE vapor mass transfer by S-bearing species cannot be observed directly during sublima-

tion experiments, but may exist during transfer of sulfur through the vapor from an S-rich to an S-poor PGE-bearing base–metal sulfide.

In the present paper, we report results of experiments on Ni, Cu, PGE and Au mass transfer via an S-dominated vapor during the process of S transfer from an S-rich PGE-bearing Fe–Ni–Cu sulfide to an S-poor pyrrhotite.

2. Experimental

2.1. Synthesis of starting material

To carry out the experiments the following phases were synthesized: S-poor PGE-free Po (Table 1, Po receiver 1); S-rich PGE-free Po (Po receiver 2); S-rich (Fe,Ni,Cu)_{1-x}S, doped with about 2000 ppm of each Pt, Pd, Rh, Ru, Ir, Os and Au (Table 1, PGE donors of the 5, 6, 7 and 9 series). Pure elements were used: iron wire 99.99%, nickel wire 99.995%, copper foil 99.99%, sulfur pieces 99.999%, platinum wire 99.99%, palladium tube 99.99%, rhodium powder 99.99%, ruthenium sponge, 20 mesh, 99.95%, iridium powder 99.995%, osmium powder, 20 mesh, 99.95% and gold foil 99.99% from Johnson-Matthey.

The required amount of metals and S for each run were weighed out in silica tubes using a 6-figure balance. The PGE-free pyrrhotite receivers 1 and 2 were synthesized by melting a mixture of pure S and Fe in evacuated silica glass tubes in a 1 atm vertical furnace.

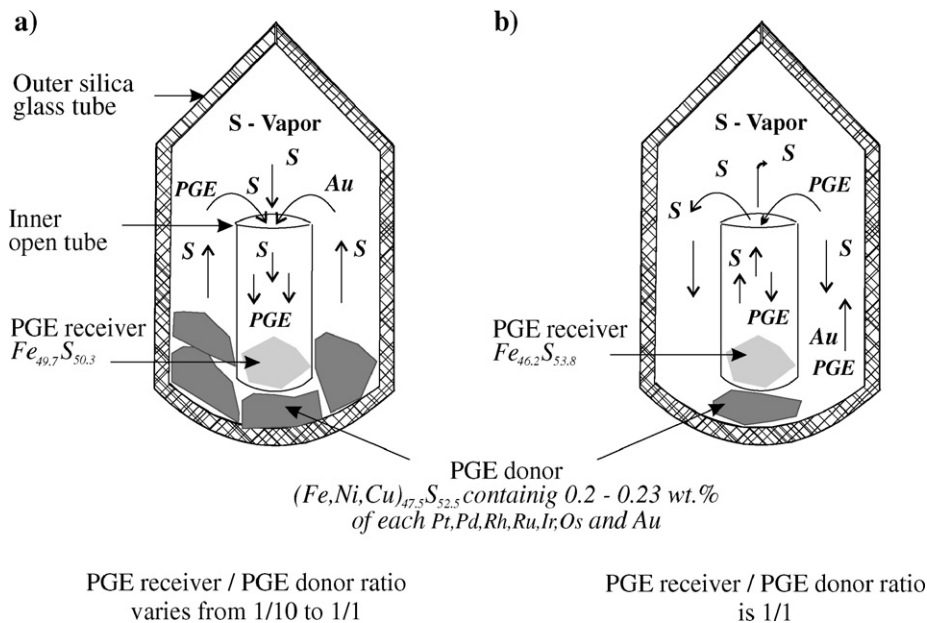


Fig. 1. Tube-in-tube vapor mass transfer experiments used in this study: (a) sulfur and metal transfer in the same direction; (b) sulfur and metal transfer in opposite directions (reverse experiments).

Double tubes were used to avoid oxidation of samples in the case of a leak in the outer tube. The samples were heated to 500 °C for approximately 7 days until complete visual disappearance of elementary sulfur. The temperature was then raised to 1230 °C for 30 min. The charges were then cooled to 1000 °C at a rate of 1 °C/min and quenched in cold water. The synthesized pyrrhotites were then checked for phase homogeneity under electronic microscope.

The PGE-bearing base–metal sulfides (PGE donors) were synthesized using a two-step procedure. First, we synthesized four PGE-free sulfide samples by melting a mixture of base–metals and sulfur following the same procedure as for the synthesis of the Po receivers. Then, we added PGE to the presynthesized powdered sulfides and heated to 1230 °C for 1 h. The charges were then quenched in cold water to obtain homogeneous distribution of PGE across the sample. The starting compositions of the PGE donors based on weighing are listed in Table 1.

2.2. Experimental procedure

The vapor mass transfer experiments were performed in evacuated silica-glass tubes using the tube-in-tube technique (Toulmin and Barton, 1964, Kullerud, 1971) (Fig. 1). An open silica-glass tube containing a piece of S-poor PGE-free pyrrhotite (Table 1, Po receiver) was placed inside a larger tube filled with an S-rich PGE-bearing base–metal sulfide (Table 1, PGE donor). Although both the PGE receiver and PGE donor were physically separated they coexisted with a common gas-phase (Fig. 1a). The double tube was evacuated and placed into the hot spot of the same 1 atm vertical furnace used to synthesize starting material. The length of the hot spot is 4–5 cm with a temperature gradient ± 2 °C while the PGE donor and the Po receiver occupied less than 1 cm of the tube space so that the entire tube was located in the zone of constant temperature during the experiments.

The samples were heated at 1000 °C or 1100 °C for 2 or 14 days and then quenched in cold water. In the course of the experiments the transfer of sulfur from the S-rich PGE donor to the S-poor Po receiver occurred. The run conditions and phases present are reported in Table 2.

The 2-day experiments were intended to investigate the kinetics of the vapor mass transfer process and the relative mobility of Ni, Cu and precious metals. Several experiments were performed for 14 days to see if the quantity of metals transferred via vapor phase increased with experimental duration. It is important to note that

the entire donor–receiver system in our vapor mass transfer experiments could not reach equilibrium for all the metals. In contrast, the chemical potential of sulfur equalizes very fast in the experiments of the kind (Naldrett, 1967). Thus, we assume that the PGE donors and the receiver Po in our experiments were in equilibrium for sulfur (as discussed later). Despite the lack of

Table 2
Run conditions and run products of vapor transport experiments

Run #	Run conditions				Donor phase association at the end of experiment
	T_r , °C	Duration (days)	PGE-receiver	R/D^a	
<i>Series 5</i>					
5–0	1000	2	no	–	PGE-Poss+Au alloy
5–1	1000	2	Fe49.7S50.3	1/8	PGE-Poss+Au alloy
5–2	1000	2	Fe49.7S50.3	1/5	PGE-Poss+Au alloy
5–3	1000	2	Fe49.7S50.3	1/1	PGE-Poss+Au alloy+Pt alloy
5–4–RV	1000	2	Fe46.2S53.8	1/1	PGE-Poss+Au alloy
5–5	1100	2	Fe49.7S50.3	1/10	PGE-Poss+Au alloy
<i>Series 6</i>					
6–0	1000	2	no	–	PGE-Mss+Au alloy
6–1	1000	2	Fe49.7S50.3	1/9	PGE-Mss+Au alloy
6–2	1000	2	Fe49.7S50.3	1/5	PGE-Mss+Au alloy
6–3	1000	2	Fe49.7S50.3	1/1	PGE-Mss+Au alloy+Pt alloy
6–4–RV	1000	2	Fe46.2S53.8	1/1	PGE-Mss+Au alloy
6–5	1100	2	Fe49.7S50.3	1/11	PGE-Mss+Liquid
6–6	1000	14	Fe49.7S50.3	1/10	PGE-Mss+Au alloy
<i>Series 7</i>					
7–0	1000	2	no	–	PGE-Mss+Liquid
7–1	1000	2	Fe49.7S50.3	1/8	PGE-Mss+Liquid
7–2	1000	2	Fe49.7S50.3	1/5	PGE-Mss+Liquid
7–3	1000	2	Fe49.7S50.3	1/1	PGE-Mss+Liquid
7–4–RV	1000	2	Fe46.2S53.8	1/1	PGE-Mss+Liquid
7–5	1100	2	Fe49.7S50.3	1/9.5	PGE-Mss+Liquid
7–6	1000	14	Fe49.7S50.3	1/10.5	PGE-Mss+Liquid
<i>Series 9</i>					
9–0	1000	2	no	–	PGE-Mss+Liquid
9–1	1000	2	Fe49.7S50.3	1/10	PGE-Mss+Liquid+(Ru,Os,Ir)S2
9–3	1000	2	Fe49.7S50.3	1/1	PGE-Mss+Liquid
9–4–RV	1000	2	Fe46.2S53.8	1/1	PGE-Mss+Liquid
9–5	1100	2	Fe49.7S50.3	1/10	Liquid+(Ru,Os,Ir)S2
9–6	1000	14	Fe49.7S50.3	1/9.5	PGE-Mss+liquid+(Ru,Os,Ir)S2

^a Receiver/donor ratio in the course of experiments.

equilibrium in metals donor/receiver distribution in our experiments we assume that donor phase associations were stable at run temperature. To prove it we carried out blank experiments (Table 2, runs X-0) that did not contain receiver Po in the tubes and we observed the homogeneous texture of the donor association, the homogeneous distribution of base–metals and the PGE throughout the donor samples as well as similarity in donor phase compositions in both blank experiments and vapor mass transfer experiments (Table 3).

To assess whether the vapor mass transfer of metals depends on the bulk S-content of the donor–receiver system, and on the quantity of S transferred from the S-rich donor to the S-poor receiver, we varied the metal/S ratio of the system by changing the donor/receiver ratio from about 10:1 through 5:1 to 1:1. It is important to note, however, that by changing the donor/receiver ratio we also change the quantity of the PGE potentially exposed to the vapor mass transfer process. To understand whether PGE vapor mass transfer correlates with the vapor mass transfer of S, and to differentiate its influence from the influence of the quantity of PGE available for transport in our experiments, we also performed experiments with the opposite direction of the S transfer (reverse experiments) where the PGE receiver was richer in S than the PGE donor and the donor/receiver ratio was close to 1 (Fig. 1b). Finally, the quantity of Ni and Cu in the PGE donor was varied from 0 to 12 wt.% in order to investigate whether PGE vapor mass transfer depends on the sulfide association coexisting with the vapor phase (Table 1).

2.3. Analytical methods

Both starting sulfides and products of vapor mass transfer experiments were studied by using the McGill University electron microprobe. The synthetic CuFeS_2 , $(\text{Fe,Ni})_9\text{S}_8$, FeS (507) sulfides and Au-bearing alloy provided by CANMET (Canada) as well as Ni, Pt, Ir, Pd, Rh, Ru and Os metals from Johnson-Matthey were used as standard. The analytical conditions were as follows: accelerating voltage 20 kV, beam current 30 nA, counting times up to 120 s on peaks and 60 s on backgrounds, spot diameter of about 2 μm . A defocused electron beam of 20–30 μm in diameter was used to determine the bulk compositions of quenched sulfide liquid and base–metal sulfides containing exsolved PGE phases. The detection limits were as follows: 370 ppm for Ni, 260 ppm for Cu, and 140–1500 ppm for PGE depending on counting time.

The concentrations of PGE and Au in the Po receiver at the end of vapor mass transfer experiments were too low

to be determined by microprobe analysis, thus these were determined by laser ablation induced coupled plasma mass spectrometry (LA-ICP-MS) at the University of Quebec, Chicoutimi (UQAC). The laser employed was a New Wave Research Nd:YAG UV laser operating at 213 nm. The beam size was 100 μm , with a power of 0.8 mJ/pulse. Laser frequency was maintained at 20 Hz for all analyses, which resulted in cylindrical laser pits of 80–100 μm deep. A signal was collected for 140 s, 30 s of blank and 110 s with the beam switched on. Ablation was carried out using a helium carrier gas, which continually flushed the air-tight laser cell, and was mixed with argon before entering the ICP-MS. The ablated material was analyzed using a Thermo X7 quadrupole ICP-MS operating in time resolved mode using peak jumping using a dwell time of 10 ms/peak. All elements were measured in standard resolution mode with a peak width of ~ 0.70 amu. The Po receivers are essentially FeS, so no Ni or Cu interference corrections were necessary and a collision cell was not used.

There are no sulfide international reference materials (RM) available to calibrate for LA-ICP-MS. Therefore we made two in house reference materials. The first RM was Ni-sulfide bead made by fire assay doped with ~ 1.6 ppm of each of the PGE and Au using AA solutions. The second RM is FeS doped with ~ 10 ppm PGE and Au. The choice of FeS as a second RM was based on the fact that the receivers are essentially FeS, and we wished to matrix match our samples and RM. Po-52 was synthesized as follows. Two batches of FeS were prepared, one PGE free and one containing 0.1 wt.% PGE. Both the PGE-free and PGE-bearing FeS was prepared by weighing out reagent grade metals and S in the desired proportions (as described above). The mixtures of pure elements were then placed in double silica glass tubes and heated to 500 $^\circ\text{C}$ over 7 days. The tubes were then heated in a vertical 1 atm furnace at 1260 $^\circ\text{C}$ for 1 h to assure complete melting of the elements. The temperature was then reduced to 1000 $^\circ\text{C}$ at the rate of 1 $^\circ\text{C}/\text{min}$. The charges were annealed at 1000 $^\circ\text{C}$ for 4 days. They were then quenched by dropping the tubes into cold salt water. In order to obtain FeS with only 5–10 ppm PGE the FeS with 0.1 wt.% PGE was diluted with the PGE-free FeS. This was then heated for 1 h at 1260 $^\circ\text{C}$ and quenched in cold salt water. Pieces of the synthesized PGE-bearing FeS (Po-52) were then mounted and polished and examined by optical and electron microscopes for exsolutions of platinum-group minerals (PGM). No exsolutions were observed either optically or by back-scatter electron imaging. The Fe and S contents of Po-52 were determined by microprobe analysis at McGill University as 61.05 wt.% Fe and 38.62 wt.% S.

Table 3
Compositions of phases stable in the PGE donors at the end of the experiments, determined by microprobe analysis

Run #	Phase	N	Beam size, μm	Composition ^a , wt. %											
				Fe	Ni	Cu	S	Pt	Pd	Rh	Ru	Os	Ir	Au	Total
5–0	Poss	4	25	60.93 (0.2)	0	0	38.3 (0.14)	0.28 (0.05)	0.23 (0.06)	0.20 (0.04)	0.24 (0.02)	0.12 (0.02)	0.23 (0.03)	<0.05	100.63 (0.23)
5–1	Poss	5	20	60.88 (0.2)	0	0	38.40 (0.08)	0.27 (0.02)	0.23 (0.02)	0.21 (0.02)	0.23 (0.01)	0.20 (0.02)	0.21 (0.05)	<0.05	100.68 (0.24)
5–2	Poss	9	20–25	61.16 (0.25)	0	0	38.37 (0.11)	0.26 (0.05)	0.22 (0.03)	0.23 (0.02)	0.22 (0.01)	0.12 (0.01)	0.20 (0.04)	<0.05	100.86 (0.29)
5–3	Poss	7	2	62.22 (0.59)	0	0	37.66 (0.07)	<0.08	0.21 (0.04)	0.24 (0.02)	0.23 (0.01)	<0.03	0.16 (0.04)	<0.05	100.88 (0.58)
5–4	Poss	7	20	60.26 (0.25)	0	0	39.1 (0.23)	0.32 (0.02)	0.22 (0.04)	0.22 (0.04)	0.10 (0.01)	0.05 (0.02)	0.13 (0.02)	0.12 (0.02)	100.57 (0.43)
5–5	Poss	11	30	60.76 (0.86)	0	0	38.18 (0.15)	0.25 (0.05)	0.18 (0.04)	0.19 (0.03)	0.21 (0.01)	0.13 (0.04)	0.20 (0.03)	0.10 (0.07)	100.27 (1.03)
6–0	Mss	11	0–25	56.82 (0.41)	2.05 (0.06)	2.08 (0.02)	38.19 (0.18)	0.30 (0.04)	0.23 (0.06)	0.23 (0.04)	0.27 (0.02)	0.24 (0.02)	0.23 (0.06)	0.09 (0.05)	100.72 (0.61)
6–1	Mss	11	20–25	56.87 (0.36)	2.04 (0.06)	2.01 (0.03)	38.01 (0.20)	0.29 (0.04)	0.2 (0.03)	0.22 (0.01)	0.26 (0.02)	0.23 (0.02)	0.23 (0.02)	0.05 (0.03)	100.41 (0.60)
6–2	Mss	13	20–25	57.21 (0.41)	2.06 (0.05)	2.03 (0.04)	37.97 (0.13)	0.33 (0.05)	0.22 (0.04)	0.24 (0.02)	0.28 (0.01)	0.25 (0.02)	0.23 (0.04)	0.05 (0.03)	100.87 (0.51)
6–3	Mss	9	20–25	58.44 (0.51)	2.11 (0.04)	1.98 (0.02)	37.25 (0.08)	<0.08	0.24 (0.05)	0.23 (0.03)	0.29 (0.02)	<0.03	0.16 (0.02)	<0.05	100.8 (0.59)
	Pt alloy	1	2	13.25	0.38	0.5	0.1	74.62	1.19	0.37	0.03	0.17	2.17	6.79	99.57
6–4	Mss	9	20–25	56.51 (0.37)	1.96 (0.03)	1.99 (0.03)	38.64 (0.12)	0.29 (0.04)	0.22 (0.04)	0.27 (0.04)	0.34 (0.05)	0.32 (0.07)	0.26 (0.04)	0.11 (0.03)	100.93 (0.40)
6–5	Mss	4	30	56.31 (0.38)	1.98 (0.04)	1.79 (0.09)	37.88 (0.21)	0.21 (0.03)	0.14 (0.03)	0.24 (0.02)	0.25 (0.01)	0.24 (0.03)	0.21 (0.01)	<0.05	99.28 (0.54)
	Liquid	5	30	45.61 (1.01)	3.49 (0.18)	7.54 (0.85)	35.18 (0.26)	2.06 (0.52)	1.48 (0.25)	0.1 (0.02)	0.03 (0.01)	<0.03	<0.08	4.59 (0.67)	100.15 (0.39)
6–6	Mss	6	30	56.71 (0.16)	2.06 (0.01)	2.1 (0.03)	37.85 (0.07)	0.29 (0.04)	0.22 (0.06)	0.2 (0.02)	0.17 (0.02)	0.18 (0.02)	0.15 (0.06)	0.05 (0.02)	99.97 (0.17)
	Au alloy	3	0	0.87 (0.45)	0.04 (0.02)	0.6 (0.05)	0.21 (0.02)	<0.55	0.73 (0.05)	<0.09	<0.03	<0.08	<0.2	99.37 (0.23)	101.84 (0.56)
7–1	Mss	9	20–30	51.00 (0.72)	5.94 (0.09)	4.28 (0.10)	38.13 (0.11)	0.20 (0.02)	0.13 (0.05)	0.23 (0.03)	0.19 (0.01)	0.18 (0.02)	0.23 (0.04)	<0.05	100.54 (0.79)
	Liquid	5	30	35.24 (1.01)	6.87 (0.84)	20.99 (1.00)	33.52 (0.25)	0.39 (0.41)	0.87 (0.09)	<0.04	<0.01	<0.03	<0.08	2.03 (0.48)	99.95 (0.53)
7–2	Mss	7	2	50.75 (0.25)	5.87 (0.08)	4.04 (0.09)	37.81 (0.09)	0.15 (0.03)	0.13 (0.04)	0.24 (0.02)	0.23 (0.01)	0.2 (0.03)	0.23 (0.05)	<0.05	99.68 (0.24)
	Liquid	5	30	39.32 (0.99)	9.26 (0.70)	13.9 (1.53)	34.97 (0.42)	0.65 (0.27)	1.04 (0.17)	0.08 (0.01)	0.03 (0.01)	0.05 (0.01)	<0.08	0.79 (0.27)	100.13 (0.40)
7–3	Mss	7	0–2	53.27 (0.47)	5.09 (0.09)	3.06 (0.04)	37.33 (0.11)	0.11 (0.02)	<0.09	0.26 (0.02)	0.27 (0.02)	0.13 (0.02)	0.23 (0.03)	<0.05	99.82 (0.47)
	Liquid	8	25–30	41.25 (1.49)	9.77 (0.62)	13.18 (1.82)	33.96 (0.42)	0.54 (0.15)	0.62 (0.14)	0.15 (0.03)	0.04 (0.02)	<0.03	0.09 (0.02)	0.51 (0.17)	100.14 (0.23)
7–4	Mss	8	0–2	50.40 (0.49)	5.92 (0.08)	4.23 (0.04)	37.93 (0.10)	0.15 (0.03)	0.12 (0.04)	0.25 (0.03)	0.24 (0.01)	0.22 (0.02)	0.22 (0.04)	<0.05	99.7 (0.50)
	Liquid	5	25–30	38.10 (0.51)	7.0 (0.67)	17.79 (0.93)	34.88 (0.13)	0.51 (0.21)	0.69 (0.12)	0.06 (0.03)	0.02 (0.01)	<0.03	<0.08	0.75 (0.07)	99.85 (0.42)
7–5	Mss	3	2	55.89 (0.19)	1.98 (0.01)	1.74 (0.01)	37.74 (0.05)	0.17 (0.03)	0.14 (0.02)	0.25 (0.00)	0.29 (0.01)	0.28 (0.03)	0.27 (0.05)	<0.05	98.77 (0.15)
	Liquid	5	25–30	44.43 (1.78)	5.13 (1.10)	10.63 (3.16)	35.96 (0.26)	0.95 (0.63)	0.87 (0.72)	0.09 (0.03)	<0.01	<0.03	<0.08	1.31 (1.19)	99.52 (0.48)
7–6	Mss	4	2	50.44 (0.49)	5.75 (0.07)	4.55 (0.43)	37.79 (0.10)	0.18 (0.04)	0.13 (0.02)	0.23 (0.02)	0.19 (0.01)	0.17 (0.02)	0.17 (0.06)	<0.05	99.61 (0.26)
9–1	Mss	5	2	44.03 (0.52)	12.08 (0.23)	4.96 (0.44)	37.62 (0.12)	0.1 (0.03)	<0.09	0.42 (0.05)	0.24 (0.03)	0.24 (0.02)	0.41 (0.06)	<0.05	100.16 (0.42)
	Liquid	9	30	32.72 (0.79)	11.18 (1.55)	20.63 (1.93)	34.74 (0.24)	0.42 (0.10)	0.28 (0.08)	<0.04	<0.01	<0.03	<0.07	0.4 (0.13)	100.43 (0.28)
	(Ru,Os,Ir)S2	3	0	2.31 (0.09)	1.41 (0.05)	0.79 (0.14)	33.37 (0.60)	<0.2	<0.17	3.7 (0.12)	19.09 (0.46)	22.6 (0.54)	16.49 (0.53)	<0.12	99.83 (1.12)
9–3	Mss	5	2	47.34 (0.51)	9.95 (0.45)	3.69 (0.31)	36.98 (0.22)	<0.08	<0.09	0.45 (0.02)	0.44 (0.01)	0.45 (0.03)	0.51 (0.03)	<0.05	99.89 (0.34)
	Liquid	5	30	32.85 (1.16)	13.33 (1.15)	20.28 (1.09)	33.15 (0.44)	0.39 (0.12)	0.31 (0.07)	0.05 (0.03)	<0.01	<0.03	<0.07	0.35 (0.14)	100.74 (0.23)
9–4	Mss	5	2	45.99 (0.29)	10.84 (0.09)	3.66 (0.08)	37.73 (0.08)	<0.08	<0.09	0.42 (0.02)	0.31 (0.01)	0.31 (0.01)	0.44 (0.05)	<0.05	99.8 (0.44)
	Liquid	8	30	36.27 (0.67)	13.59 (0.60)	14.44 (1.23)	35.12 (0.16)	0.33 (0.05)	0.27 (0.05)	0.11 (0.02)	0.04 (0.02)	0.06 (0.03)	<0.07	0.18 (0.05)	100.46 (0.22)
9–5	Liquid	12	30	37.40 (0.39)	11.39 (0.66)	13.7 (1.23)	36.16 (0.17)	0.26 (0.04)	0.21 (0.05)	0.19 (0.02)	0.1 (0.01)	0.11 (0.03)	0.16 (0.04)	0.27 (0.08)	99.93 (0.22)
	(Ru,Os,Ir)S2	3	0	1.59 (0.27)	0.88 (0.08)	0.28 (0.02)	33.25 (0.45)	<0.22	<0.17	2.06 (0.40)	21.25 (0.52)	27.06 (1.89)	13.75 (1.40)	<0.12	100.17 (0.89)
9–6	Mss	5	2	45.31 (0.54)	11.15 (0.43)	4.03 (0.31)	37.8 (0.22)	0.09 (0.01)	<0.09	0.44 (0.02)	0.24 (0.01)	0.23 (0.02)	0.43 (0.03)	<0.05	99.78 (0.13)
	Liquid	9	30	35.49 (0.86)	11.22 (1.17)	17.2 (0.78)	35.4 (0.21)	0.27 (0.07)	0.26 (0.05)	0.09 (0.04)	0.02 (0.01)	0.04 (0.02)	<0.07	0.27 (0.06)	100.32 (0.25)
	(Ru,Os,Ir)S2	3	0	0.78 (0.12)	0.38 (0.07)	0.27 (0.07)	31.69 (0.73)	<0.2	<0.19	0.4 (0.08)	23.54 (0.65)	38.51 (1.13)	4.74 (0.21)	<0.12	100.43 (1.74)

^a Number of analyses to calculate the average composition; numbers in parentheses are standard deviations.

The PGE and Au concentrations in both NiS 1.6 and Po-52 were determined by dissolving small (~10 mg) pieces of the sulfides and then carrying out standard addition analyses on the solutions (Table 4). The values obtained from the solution analyses of NiS 1.6 were then used for in situ analyses of the bead to calibrate the machine during LA-ICP-MS. The homogeneity of the bead was assessed by carrying out 16 spot analyses on the bead and the relative standard deviation varies from 6% to 12% for the PGE and 20% for Au (Table 4). The NiS 1.6 was then used in determining PGE and Au in situ Po-52. The in situ values for Po-52 using NiS 1.6 are within error of those determined for Po-52 by standard addition analyses (Table 4). The data from the LA-ICP-MS were reduced using PlasmaLab software, with ^{33}S as the internal standard which follows the general method (Jackson et al., 1992). The count rate on ^{33}S was 325 000–400 000 counts per second with a gas blank of <1000 counts per second. The relative standard deviation on the ^{33}S count rate was <3%. The homogeneity of Po-52 was tested by determining the PGE and Au contents by LA-ICP-MS in 6 different spots. The relative standard deviation is between spots 6% and 16% depending on the element (Table 4). The standard was run twice every 10–15 analyses. All data was collected in 2 consecutive days. The detection limits as defined by 3 sigma times twice background counts were approximately 20 ppb. As a test of accuracy PGE and Au contents in the reference material (PGE-A) were determined and our results agree with recommended results within analytical error (Table 4).

The PGE composition of the pyrrhotite receivers were determined by LA ICP-MS before and after the vapor mass transfer experiments to be sure that they did not initially contain any PGE (Table 1). In general, two analyses were made on each pyrrhotite receiver at the end of experiments, one point in the center of a grain and second one close to the border to investigate whether the transferred metals were distributed homogeneously within the receiver.

3. Results

3.1. Phase assemblages of the PGE donors at 1000°C and 1100 °C

In the Ni- and-Cu free experiments (the 5-* series) and in the Ni- and Cu-poor experiments (the 6-* series), the phases observed in the donor assemblage at the end of the 1000 and 1100 °C runs are Po+ Au alloy or Mss+ Au alloy (Table 2); one exception to this is 1100 °C experiment 6–5 in which liquid was found instead of the Au alloy. The tiny PGE exsolutions observed in the Po matrix are interpreted to have formed during quenching and are not considered stable phases (Fig. 2a). On the other hand, the Au alloy occurs as rare rounded grains of 5–10 μm in diameter and because of its morphology is considered to be a stable phase (Fig. 2a). The PGE, Ni and Cu concentrations in the donor Po or Mss are very similar at the beginning and the end of the experiments, with approximately 2000 ppm of each PGE (Table 3). This lack of significant compositional change during the experiments suggests that the PGE, Ni and Cu do not readily partition from the donor to the vapor phase, but prefer the Po or Mss structure. The two exceptions are the low concentrations of Pt and Os in runs 5–3 and 6–3. The Po and Mss in these runs have low S concentrations and S-poor Po and Mss are known to accommodate less PGE than S-rich Po and Mss (Ballhaus and Ulmer, 1995; Li et al., 1996; Barnes et al., 2001; Mungall et al., 2005). Thus Pt formed rare grains of Pt–Fe alloy in these experiments, so small that it could be analysed only in one grain (Table 3, run 6–3). According to the Fe–Os–S diagram Os alloy could be stable in these samples at run temperatures (Karup-Møller and Makovicky, 2002), or Os may have been removed in the vapor. The LA-ICP-MS system at UQAC was not calibrated for Os at the time these charges were analysed. Gold does not appear to have been accommodated in the Po or Mss structure, probably because Au does not readily form the d_{2sp^3} orbitals necessary to fit into the Mss structure and it

Table 4
Estimation of accuracy and precision for PGE and Au analyses using LA-ICP-MS

Sample	Method	Laboratory		101 Ru (ppm)	103 Rh (ppm)	105 Pd (ppm)	193 Ir (ppm)	195 Pt (ppm)	197 Au (ppm)
NiS 1.6	Standard addition	UQAC	$n=4$	2.02	1.77	3.01	1.97	2.46	1.37
			± 1 sigma	0.23	0.09	0.29	0.09	0.14	0.17
NiS 1.6	LA-ICP-MS	UQAC	$n=15$	1.81	1.65	2.91	1.99	2.43	1.52
			± 1 sigma	0.07	0.08	0.13	0.12	0.07	0.15
PO-52	Standard addition	UQAC	$n=6$	9.94	7.50	10.21	10.80	8.28	9.30
			± 1 sigma	1.20	0.42	0.96	0.92	0.43	1.38
PO-52	LA-ICP-MS	UQAC	$n=6$	6.61	7.04	9.34	9.49	9.79	8.87
			± 1 sigma	1.06	0.48	0.75	0.84	0.87	0.81

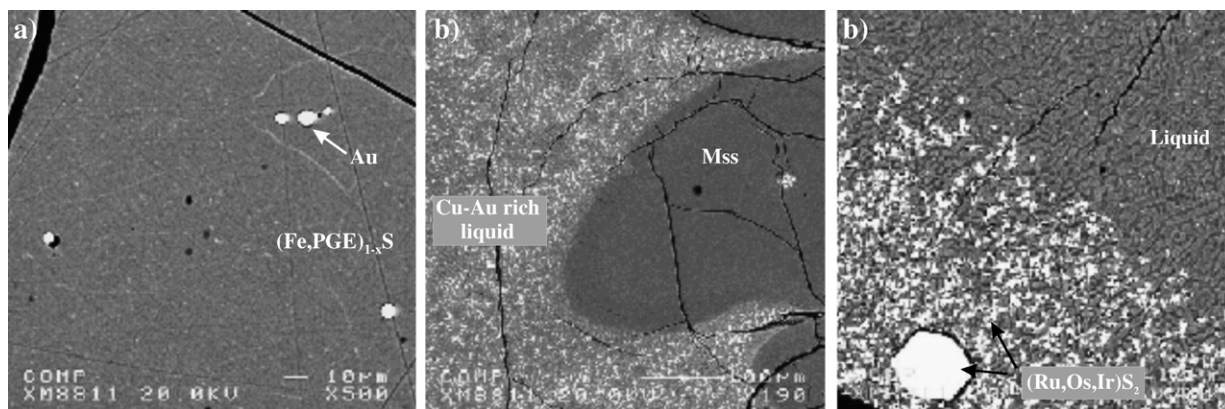


Fig. 2. Back-scattered electron images of base–metal sulfide associations of the PGE donor in the vapor mass transfer experiments at 1100 °C: (a) donor assemblage composed of Mss and Au alloy (run 5–5); (b) donor assemblage composed of Mss and sulfide liquid (run 7–5); (c) donor assemblage composed of the sulfide liquid and (Ru, Os, Ir)₂S₂ (run 9–5).

has a covalent radius considerably larger than that of Fe (Barnes et al., 2001).

The runs with intermediate and high Ni and Cu contents (7-* and 9-* series), and the only low Ni and Cu run done at 1100 °C, contain Mss plus base–metal sulfide liquid; no Au alloy is present (Fig. 2b). This result indicates that Au is strongly partitioned into the sulfide liquid (Table 3) and thus, no separate phase is required to accommodate it at the concentrations present in these experiments.

In the S-, Ni-, and Cu-rich experiments 9–1, 9–5 and 9–6, the sulfur fugacity was so high that synthetic laurite [(Ru, Os, Ir)S₂] formed in association with the sulfide liquid (Fig. 2c). Additionally, the high temperature run 9–5 contained no Mss (Table 2).

A number of previous studies have shown that Os, Ir, Ru and Rh preferentially partition into Mss, while Cu, Pd, Pt and Au preferentially partition into base–metal sulfide liquid (Fleet et al., 1993; Li et al., 1996, Barnes et al., 2001; Peregoedova et al., 2004; Mungall et al., 2005). The behavior of Ni depends on the temperature and the S-content of the Mss. At high temperatures (1000–1180 °C) Ni is moderately incompatible in Mss, but at lower temperatures Ni becomes moderately compatible in Mss (Li et al., 1996; Barnes et al., 2001). In our experiments elements partitioned themselves in the same manner. Thus, the base–metal sulfide liquid is rich in Cu, Au, Pd, Pt and poor in Os, Ir, Ru and Rh.

3.2. Vapor mass transfer of Ni, Cu, Au and PGE

We observed significant concentrations of Ni, Cu, Au, Pd and Pt in the receiver Po at the end of the vapor mass transfer experiments and an increase in the concentration of S in the receiver Po. In contrast, very little

Ir, Ru or Rh was present in the receiver Po. All metals were distributed homogeneously within the grains of the Po receivers (Table 5). We observed that the quantity of metals transferred via the vapor phase varies depending on the following parameters of the system: temperature, duration of experiments, base–metal ratio and phase association of the donor, and S-content of the receiver Po which may be used as proxy of sulfur fugacity in the system (Toulmin and Barton, 1964). Each of these parameters is discussed below.

3.2.1. Vapor mass transfer dependence on the temperature

To demonstrate the temperature dependence the concentration of the metals in the receiver at 1000 and 1100 °C can be compared for experiments of the same duration and donor-to-receiver ratio (e.g., runs 5–1 and 5–5; runs 6–1 and 6–5, etc.). After 2 days at 1100 °C, the Po receiver was found to contain: 0.07–1.13 wt.% Ni, 0.06–0.09 wt.% Cu, 9–970 ppm Au, 20–60 ppm Pt, 20–40 ppm Pd, 0.1–3.6 ppm Ru and Rh, and 0.4–5.6 ppm Ir, depending on the base–metal ratio of the donor (Tables 2 and 5). At 1000 °C, the mass transfer of some metals in the vapor phase increased, but decreased for others (Fig. 3). If temperature has no effect on mass transfer of the element, the experimental results should plot on a line with a slope of 1. This is the case for Cu (Fig. 3). Elements which are better transferred at high temperatures lie above the line with a slope of 1; this is the case for Ru, Rh and Ir.

The elements, Pt, Pd and Au show greater mass transfer at higher temperature in the Ni- and Cu-free run, but in runs containing Ni and Cu they show greater mass transfer at low temperatures. (Fig. 3). This is due to the presence of a base–metal sulfide liquid (Table 3) in

Table 5
Composition of the Po receivers at the end of the experiments

Run #	Major elements by electron microprobe					PGE and Au by LA-ICP-MS						
	Fe (wt.%)	Ni (wt.%)	Cu (wt.%)	S (wt.%)	Total (wt.%)	Area	Ru (ppm)	Rh (ppm)	Pd (ppm)	Ir (ppm)	Pt (ppm)	Au (ppm)
5-1	61.51 (0.26)	0	0	38.37 (0.10)	99.89 (0.34)	center	<0.02	<0.02	7 (1)	0.03 (0.02)	12 (2)	253 (54)
						border	<0.02	<0.02	7 (1)	0.06 (0.03)	13 (3)	257 (55)
5-2	61.70 (0.33)	0	0	38.35 (0.10)	100.05 (0.27)	center	<0.02	<0.02	3.6 (1)	<0.02	6.6 (2)	185 (55)
						border	<0.02	<0.02	3.6 (1)	<0.02	6.4 (2)	194 (56)
5-3	61.94 (0.42)	0	0	38.09 (0.12)	100.02 (0.51)	center	<0.02	<0.02	0.24 (0.13)	<0.02	0.08 (0.06)	132 (35)
						border	<0.02	<0.02	0.23 (0.12)	<0.02	0.07 (0.05)	140 (32)
5-4	61.23 (0.29)	0	0	38.81 (0.14)	100.05 (0.20)	center	<0.02	0.03 (0.02)	29 (4)	<0.02	31.5 (5.5)	114 (18)
						border	<0.02	<0.02	31 (6)	<0.02	33.4 (7)	135 (27)
5-5	61.58 (0.38)	0	0	38.62 (0.07)	100.19 (0.38)	center	0.15 (0.13)	0.22 (0.06)	39 (5)	0.37 (0.10)	61 (10)	970 (149)
						border	0.1 (0.1)	0.19 (0.06)	35 (6)	0.23 (0.08)	53 (11)	779 (171)
6-1	61.30 (0.25)	<0.037	0.09 (0.03)	38.66 (0.09)	100.07 (0.33)	border	0.16 (0.12)	0.19 (0.07)	27 (6)	0.20 (0.07)	38 (9)	294 (74)
6-2	60.92 (0.39)	<0.037	0.11 (0.03)	38.61 (0.14)	99.68 (0.52)	center	<0.02	0.07 (0.03)	16 (3)	<0.02	25 (6)	295 (68)
						border	0.13 (0.11)	0.15 (0.06)	16 (3)	0.25 (0.09)	26 (6)	304 (75)
6-3	62.12 (0.42)	<0.037	0.15 (0.02)	37.74 (0.08)	100.01 (0.43)	border	<0.02	<0.02	1.8 (0.4)	0.07 (0.04)	0.46 (0.15)	140 (33)
6-4	60.65 (0.17)	0.05 (0.02)	0.1 (0.04)	38.90 (0.33)	99.71 (0.28)	border	<0.02	<0.02	46 (8)	<0.02	44 (9)	140 (28)
6-5	61.08 (0.29)	0.07 (0.01)	0.06 (0.01)	38.70 (0.12)	99.91 (0.36)	center	0.29 (0.15)	0.53 (0.14)	36.5 (8)	0.45 (0.13)	40 (10)	166 (41)
						border	0.36 (0.17)	0.58 (0.17)	36.8 (9)	0.59 (0.18)	40 (11)	160 (48)
6-6	60.53 (0.16)	0.25 (0.02)	0.21 (0.01)	38.67 (0.06)	99.66 (0.13)	center	0.1 (0.08)	0.30 (0.07)	134 (24)	0.13 (0.05)	172 (37)	224 (49)
						border	0.20 (0.11)	0.44 (0.10)	158 (28)	0.20 (0.06)	205 (41)	279 (62)
7-1	60.13 (0.36)	0.35 (0.02)	0.06 (0.03)	39.20 (0.13)	99.74 (0.37)	center	<0.02	0.34 (0.08)	50 (9)	<0.02	33 (6)	27 (6)
						border	0.11 (0.07)	0.34 (0.07)	48 (7)	0.08 (0.03)	31 (5)	23 (4)
7-2	60.34 (0.25)	0.29 (0.02)	0.08 (0.04)	39.08 (0.18)	99.79 (0.26)	center	0.04 (0.05)	0.14 (0.04)	38 (5)	0.04 (0.02)	28 (4)	37 (7)
						border	0.17 (0.10)	0.28 (0.07)	38 (7)	0.22 (0.06)	28 (5.5)	36 (8)
7-3	61.42 (0.22)	0.05 (0.0)	0.09 (0.04)	38.23 (0.26)	99.79 (0.44)	center	<0.02	<0.02	1.2 (0.3)	<0.02	1.2 (0.3)	40 (10)
						border	<0.02	<0.02	1.3 (0.3)	<0.02	1.2 (0.3)	42 (9)
7-4	60.55 (0.31)	0.08 (0.01)	0.04 (0.04)	39.36 (0.19)	100.03 (0.31)	center	<0.02	<0.02	10.3 (2)	<0.02	7.2 (1.6)	15 (4)
						border	<0.02	0.09 (0.03)	10.7 (2)	<0.02	7.8 (1.6)	15 (3)
7-5	60.48 (0.46)	0.34 (0.02)	0.06 (0.01)	39.19 (0.19)	100.07 (0.43)	center	0.35 (0.18)	1.46 (0.38)	23 (6)	0.51 (0.14)	16 (4)	13 (4)
						border	0.59 (0.25)	1.49 (0.39)	23 (6)	0.89 (0.27)	16 (4)	13 (4)
7-6	58.50 (0.31)	2.07 (0.06)	0.29 (0.01)	39.05 (0.11)	99.90 (0.33)	border	0.99 (0.26)	1.39 (0.28)	296 (57)	1.11 (0.22)	184 (42)	97 (23)
9-1	60.10 (0.41)	0.14 (0.01)	0.10 (0.03)	39.53 (0.08)	99.87 (0.36)	center	0.16 (0.09)	0.76 (0.12)	69 (12)	0.09 (0.04)	41 (7)	18 (4)
						border	1.11 (0.30)	1.90 (0.36)	60 (12)	1.07 (0.20)	37 (8)	14 (4)
9-3	61.02 (0.19)	<0.037	0.08 (0.02)	38.77 (0.04)	99.88 (0.23)	center	<0.02	<0.02	0.12 (0.08)	<0.02	0.13 (0.07)	3.7 (1.2)
						border	<0.02	<0.02	0.13 (0.08)	<0.02	0.12 (0.07)	3.9 (1.1)
9-4	60.48 (0.48)	0.24 (0.03)	0.10 (0.00)	39.20 (0.17)	100.02 (0.36)	center	<0.02	<0.02	5 (1)	<0.02	3.3 (1)	2.3 (0.9)
						border	<0.02	<0.02	5.6 (1)	<0.02	3.6 (1)	2.8 (0.9)
9-5	59.20 (0.23)	1.13 (0.03)	0.09 (0.02)	39.44 (0.12)	99.86 (0.28)	center	0.77 (0.28)	2.98 (0.59)	32 (6)	0.95 (0.22)	21 (5)	9 (2)
						border	3.72 (0.89)	3.23 (0.65)	30 (6)	5.60 (1.25)	20 (5)	9 (2)
9-6	53.40 (0.19)	7.18 (0.14)	0.49 (0.02)	38.88 (0.26)	99.96 (0.19)	center	1.37 (0.38)	4.65 (0.94)	209 (45)	1.68 (0.35)	130 (31)	22 (6)
						border	1.28 (0.33)	4.27 (0.81)	188 (37)	1.56 (0.32)	117 (25)	19 (4)

Numbers in parentheses are standard deviations.

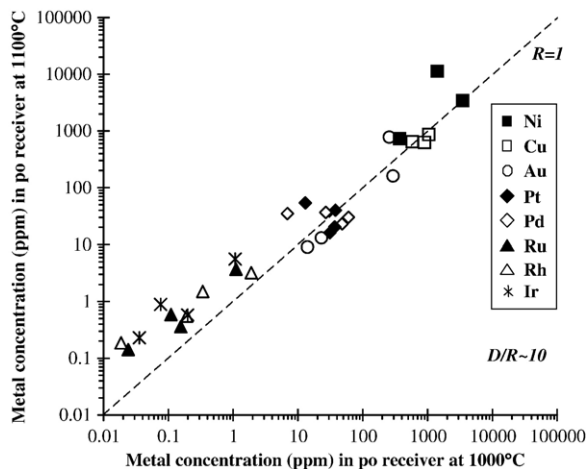


Fig. 3. Metal concentrations in receiver Po in receiver at 1000 vs. Po receiver at 1100 °C. The ratio of donor to receiver is similar ($\sim 1/10$) for all the runs shown and thus the fS_2 should be similar. The dashed line corresponds to equal metal concentrations at both temperatures; points above the line indicate preferential enrichment at 1100 °C. Ir, Ru and Rh appear to be enriched at higher temperature, while most of the other elements do not show enrichment. Error bars smaller than the symbols.

the donor assemblage of the Ni–Cu bearing runs, into which Au, Pt, and Pd partition. At 1100 °C there is more of this liquid present and the vapor mobility of Au, Pt and Pd decreases as they are preferentially partitioned into the sulfide liquid (Table 3). Thus the mass transfer of elements through the vapor phase is affected by both the kinetics of the mass transfer in the various phases (solid, liquid, vapor) and the stable phase assemblage that controls the partitioning of elements between the phases.

3.2.2. Vapor mass transfer dependence on the duration of experiments

The influence of experimental duration on the quantity of S and metals transferred through the vapor phase can be considered by the comparison of results for runs completed at the same temperature (1000 °C) and donor to receiver ratio ($D/R \sim 10$), but with a duration of 2 versus 14 days (runs 6–1 vs. 6–6, 7–1 vs. 7–6, 9–1 vs. 9–6) (Tables 2 and 5). The S-content in the receiver Po is the same (within error) in the 2-day and 14-day runs. This observation plus the fact that the atomic % of S in the donor Mss and the receiver Po are identical within error suggest that S reached equilibrium in less than 2 days. In contrast, the amount of Ni, Cu, Pt, Pd and Rh present in the receiver Po increased significantly with increasing experimental duration (Fig. 4). For Au, Ru and Ir, a time dependence of vapor mass transfer seems to exist as well. For example, in the 2-day run, 9–1, the

central part of the Po grain contains only 0.16 ppm Ru but the border contains 1.11 ppm Ru (Table 5). In the 14-day experiment, 9–6, the center and the border of the Po grain show almost equal concentrations of Ru, 1.37 and 1.28 ppm. Thus, the longer-duration experiment led to the homogenisation of the Ru concentration through the grain of the Po receiver, which required more Ru mass transfer. Additionally, the quantity of Au, Ru, and Ir transferred via the vapor phase increases with increasing duration of experiments of series 7 (Table 5).

3.2.3. Vapor mass transfer dependence on the base-metal ratio and phase association of the donor

The amount of Cu present in the Po receiver is similar (~ 0.09 wt.%) for all phase assemblages and run compositions in the 2 day runs (Table 5, Figs. 5 and 6), suggesting that mass transfer of Cu is not influenced by the phases present or their composition. Similarly, the amount of Pt and Pd in the Po receiver (30–60 ppm, Figs. 5 and 6) is approximately the same for both elements for all runs with $D/R \sim 10$, suggesting that the mass transfer of these elements is also not affected by the change in the assemblages from Mss+Au alloy to Mss+Liquid or Mss+Liquid+(Ru,Os,Ir) S_2 . However, in the two low S runs, 5–3 and 6–3, in addition to the Au alloy, Pt alloys formed in the donor phase and the receiver contains significantly less Pt than Pd (Tables 2 and 5, Fig. 7) indicating that the presence of the Pt alloy influenced the behavior of Pt.

The Au content of the receiver changed markedly from a high of ~ 900 ppm at 1100 °C in the Ni-

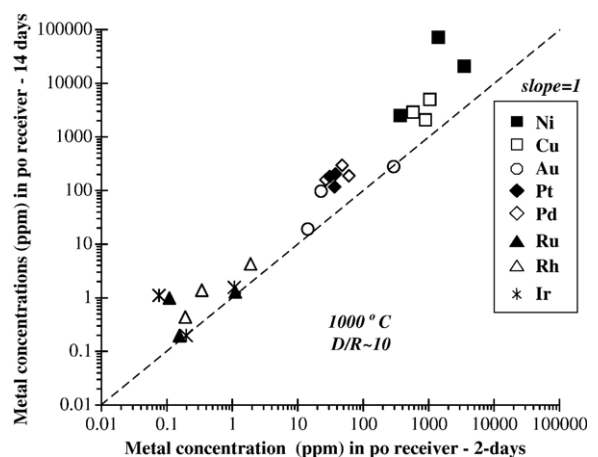


Fig. 4. Metal concentrations in receiver Po in receiver after 2 days vs. Po in receiver after 14 days $T=1000$ °C. The ratio of donor to receiver is similar ($\sim 1/10$) for all the runs shown and thus the fS_2 should be similar. The dashed line corresponds to equal metal concentrations for both 2 and 14 days. All elements are more enriched in the longer runs. Error bars smaller than the symbols.

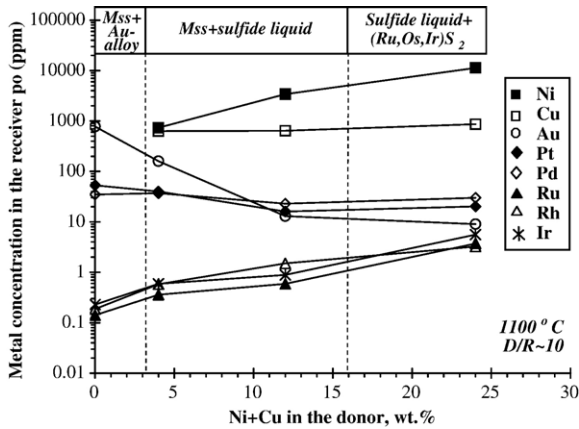


Fig. 5. Variations in the vapor mass transfer of metals depending on the bulk Ni+Cu content and base–metal sulfide assemblages of the donor at 1100 °C (D/R is the donor/receiver ratio). Error bars smaller than the symbols.

and Cu-free system to a low of ~ 9 ppm in the Cu- and Ni-rich runs (Figs. 5 and 6). The change in the Au content of the receiver coincides with the appearance of a base metal sulfide liquid in the donor assemblage and the disappearance of Au alloy. It appears that the Au is accommodated in the liquid and is not as readily available for vapor mass transfer when a base metal liquid is present.

Ni, Rh, Ru and Ir all show similar behavior. The concentration of these elements in the receiver changes by one and one-half orders of magnitude. The concentrations are lowest in the Ni- and Cu-free runs and highest in the Ni- and Cu-rich runs (Figs. 5 and 6). This suggests that vapor mass transfers of these metals from Po and Mss is less efficient than vapor mass transfers from the base–metal sulfide liquid, because the Ni- and Cu-free runs contain no liquid and the Ni- and Cu-rich runs consist largely of liquid.

3.2.4. Vapor mass transfer dependence on the S-content of the system and the mechanism of mass transfer

Only metals and S were present in our samples. Thus there would appear to be only two possible species for the mass transfer of the metals, either as native metals or as sulfide complexes. In order to investigate these two possibilities, two approaches to the problem were taken. Firstly, the effect of changing the amount of S in the system was investigated using 3 different D/R values for the 2 day runs at 1000 °C (Runs labeled X-1 to 3). Inasmuch as the initial S-content of the Po receiver was the same for these experiments, while the donor/receiver ratio, i.e. the amount of S available for transfer, varied, one should expect a positive correlation between the final S content of the receiver Po in the experiment and

the amount of metal transferred, if the metal is being transferred as an S-species. In Ni and Cu free runs the Fe and S content of the receiver and donor at the end of the runs are the same within analytical error, therefore we assume that S has attained equilibrium. Toulmin and Barton (1964) showed that the Fe/S ratio of pyrrhotite may be used to estimate the sulfur fugacity of the system. Furthermore, it is standard practice to use the Fe/S ratio of pyrrhotite to monitor fS_2 in experimental work in sulfide systems (Naldrett, 1967; Kullerud, 1971; Sinyakova et al., 2001; Peregoedova and Ohnenstetter, 2002). In the papers above the authors use the method of X-ray diffraction (XRD) to determine the composition of pyrrhotite from its d_{102} value. In the present paper we use the microprobe analyses of the receiver Po to estimate the fS_2 according to the equation of Toulmin and Barton (1964). It should be noted however that the uncertainty in the determination of Po composition by the electron microprobe is enough to significantly affect the fS_2 determination (Peregoedova et al., 2004). In addition, the equation of Toulmin and Barton (1964) was deduced to correlate temperature, fugacity of sulfur and the composition of pure $Fe_{1-x}S$. In the present study Po receivers contain minor amounts of transferred Ni and Cu at the end of vapor mass transfer experiments except for Ni- and Cu-free runs of the series 5-* (Table 1). Therefore the values of fS_2 are only approximate and serve to estimate the order of magnitude only. Thus in the present experiments $\log fS_2$ varies from 0.4 in runs with a high D/R ratio to -2.4 in runs with a low D/R ratio (Table 6). We consider this range of fS_2 to be geologically reasonable, because it is similar to the range found in MORBs (Wallace and Carmichael, 1992) for a mafic

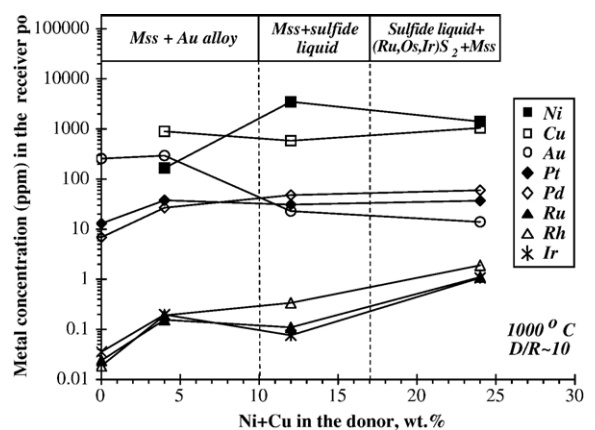


Fig. 6. Variations in the vapor mass transfer of metals depending on the bulk Ni+Cu content and base–metal sulfide assemblages of the donor at 1000 °C (D/R is the donor/receiver ratio). Error bars smaller than the symbols.

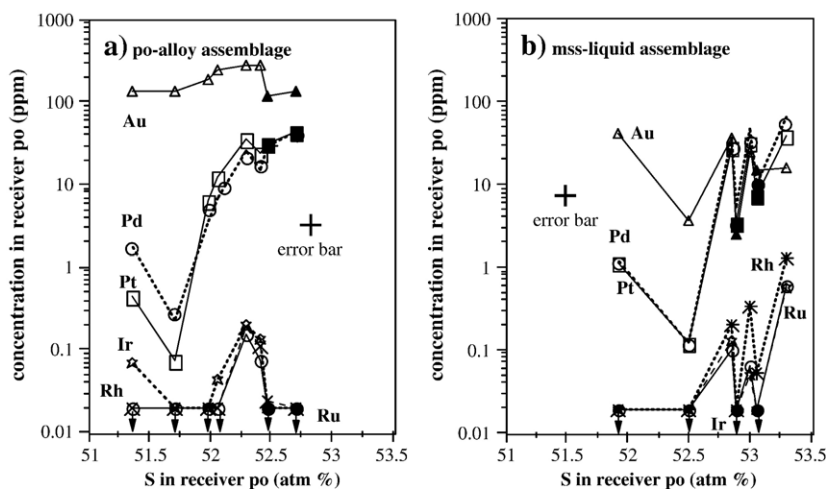


Fig. 7. Concentrations of Au, Pd, Pt, Rh, Ru, and Ir vs. S content in the receiver pyrrhotite at 1000 °C for (a) a donor assemblage of Po or Mss plus alloys and (b) a donor assemblage of Mss plus sulfide liquid. Note the order of mobility is Au>Pd>or=Pt>Rh~Ir~Ru. Note that concentration of the PGE increase with the amount of S in the pyrrhotite for normal runs (open symbols) suggesting that the PGE are transferred as S-species. Solid symbols for reversed runs, downward arrows indicate values less than detection level.

magma. In considering how the metals were transported we have used S-content in the receiver Po as a proxy for fS_2 . In order to separate the affects of different phase assemblages from the affects of fS_2 , the data for the Mss-alloy assemblage and for the Mss-liquid assemblage are presented on different diagrams (Figs. 7 and 8). The amount of metal transferred can be estimated by the concentration of the metal in the receiver Po at the end of experiment. Second, we carried out experiments where the receiver Po was initially richer in S than the donor Po or Mss. The rationale of this procedure is that the equilibration of the chemical potential for metals and for sulfur between the donor and the receiver would occur in opposite directions.

In the normal runs with the assemblages consisting of Mss plus alloys the concentrations of PGE and to a lesser extent Au increased as the amount of S increased in the receiver, i.e. as fS_2 increased (Fig. 7a, open symbols). The increase is particularly evident for Pd and Pt both of which change by 2 orders of magnitude. In the reversed runs (Fig. 7a, solid symbols) Au, Ir, Ru and Rh concentrations were lower than in normal runs. Similarly in the normal runs containing the assemblages of Mss and liquid ($\pm(Ru,Os,Ir)S_2$) the concentration of all PGE in the receiver increased as the S content of the receiver increased (Fig. 7b, open symbols). In contrast Au shows no correlation with the S-content of the receiver. As was mentioned above the Au behavior is probably controlled by the sulfide liquid in these runs. In the reversed runs (Fig. 7b, solid symbols) PGE and Au concentrations are lower than in normal runs.

Copper concentrations are similar in the receiver for all S-contents and in both assemblages (Fig. 8a and b). In most runs from the Mss-alloy assemblage Ni was present at less than the detection level, thus results from these runs cannot be used to study the influence of S on Ni mass transfer. In the assemblages containing Mss plus liquid the concentration of Ni in the receiver correlates with S-content of the receiver except in the reversed runs (solid symbols, Fig. 8b). The positive correlations between PGE and S-content in the receiver and Ni and S-content in the receiver in the Mss-liquid assemblage suggests that these elements were transferred as S-species. In contrast, the lack of correlation between Cu concentrations with S-content of receiver suggests that Cu is transferred as a metal. Gold shows no

Table 6
Calculated fS_2 based on S content of the receiver Po at 1000 °C

Run #	S in Po receiver, at. %	NFe (+Ni, Cu)S	$\log fS_2$
5-1	52.07	0.9585	-1.2
5-2	51.98	0.9604	-1.3
5-3	51.71	0.9657	-1.7
5-4 RV	52.47	0.9506	-0.6
6-1	52.30	0.9539	-0.8
6-2	52.41	0.9518	-0.7
6-3	51.35	0.9729	-2.4
6-4 RV	52.71	0.9458	-0.3
7-1	53.01	0.9398	0.1
7-2	52.86	0.9427	-0.1
7-3	51.93	0.9614	-1.4
7-4 RV	53.06	0.9389	0.2
9-1	53.30	0.9341	0.4
9-3	52.49	0.9501	-0.6
9-4 Rv	52.89	0.9422	0.0

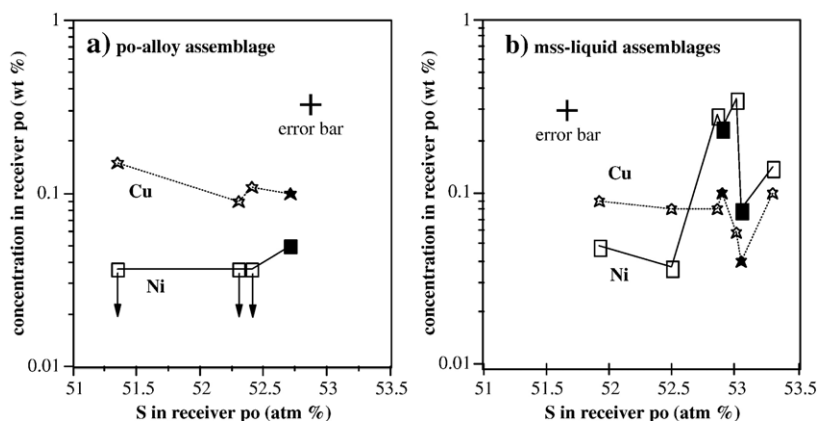


Fig. 8. Concentrations of Ni and Cu vs. S content in the receiver pyrrhotite at 1000 °C for (a) a donor assemblage of Po or Mss plus alloys and (b) a donor assemblage of Mss plus sulfide liquid. Note that the concentration of Cu does not change with the amount of S in the pyrrhotite indicating Cu was transferred as a metal. In the assemblage Mss plus sulfide liquid the Ni concentrations for normal runs (open symbols) increase with the amount of S in the receiver pyrrhotite suggesting that Ni is transferred as a S-species.

correlation in the Mss-liquid assemblage suggesting also that it is transferred as metal. However, in the Mss-alloy assemblage there is a weak correlation suggesting some possible mass transfer in the form of an S species.

The suggestion that some of the metals were transferred as S species is compromised by the observation that the metal content of the receiver in the reversed runs is low, despite the fact they have high S contents (Figs. 7 and 8, solid symbols). The low metal content of the Po in the reversed runs could be a kinetic effect. The similarity in the S-content of the receiver Po and donor Po or Mss at the end of the 2-day experiments suggests that S equilibrates between the donor and receiver very fast. In contrast, even after 14 days, the concentration of all of the metals in the receiver Po is much lower than that of the donor Po or Mss. The metals equilibrate between the donor and receiver very slowly. Therefore, the metals must leave the donor Po or Mss after the S has been removed from the donor in normal runs and after S has been added to the donor in reversed runs. In the normal runs the removal of S from the donor, could enhance the removal of metals from the donor because it will lead to a breakdown in the donor structure. In contrast, in reversed runs the S-addition to the donor could hamper the metal removal since it will coat the donor surface. This may not be as important for labile elements (those that reach equilibrium quickly) such as Au, Cu, Pd and Pt, but Ir is notoriously non-labile (inert). By analogy, we would argue that Ru and Rh also behave in a non-labile manner.

Although we interpret the correlation between increased S and metal contents in the receiver to indicate that the PGE and Ni are transferred as S-species, it could

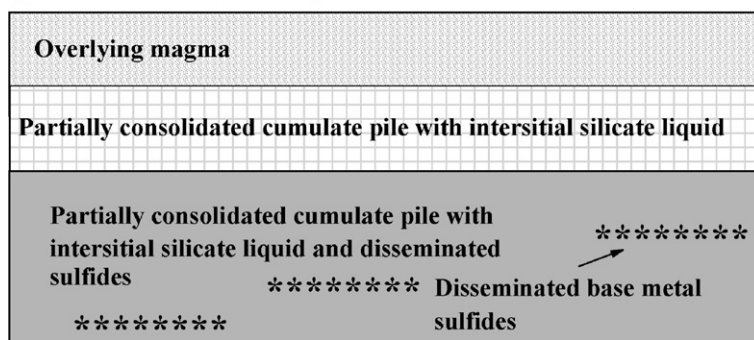
be argued that the higher metal content in the S-enriched Po receiver is an artifact of the experimental method. Thus in the S-rich runs, the donor Po exceeded the receiver Po by a factor of 10 while in the S-poor runs the ratio was 1:1. Therefore, in the S-rich runs more metals are available for mass transfer. This idea may be tested by considering the Pd, Pt and Au in the reversal Mss-alloy runs (Fig. 7a, solid symbols). These runs are S-rich, but with a donor to receiver Po ratio of 1. At the end of the experiments the Pd, Pt and Au contents in the receivers are similar to, or only slightly less than, those found in runs with a donor to receiver ratio of 10 despite the larger quantity of metals available for mass transfer in the normal runs. Thus, the results do not appear to be an artifact of the experimental technique.

4. Discussion

The present experiments show that in sulfide systems where the vapor is dominated by sulfur the order of metals transferred via the vapor phase depends in large part on the assemblage. In Ni- and Cu-poor systems where the assemblage is Mss plus Au and Pt alloys the order of transport is $Au > Pt > Pd > Rh = Ir = Ru$ and $Cu > Ni$. In Ni- and Cu-rich systems where the assemblage is Mss plus base-metal sulfide liquid the order is $Au - Pt - Pd > Rh = Ir = Ru$. The behavior of Ni depends on fS_2 ; at low fS_2 Cu is more mobile than Ni and at high fS_2 Ni is more mobile than Cu.

Literature data suggests that this order may be modified when other elements added to the system. In particular if Cl is present in the system, Cu is transferred faster than Ni (Fleet and Wu, 1995). Although Ni

a) Formation of cumulate pile with disseminated sulfides



b) Transfer of Cu, Pd and Au by fluid to form Pd-reef

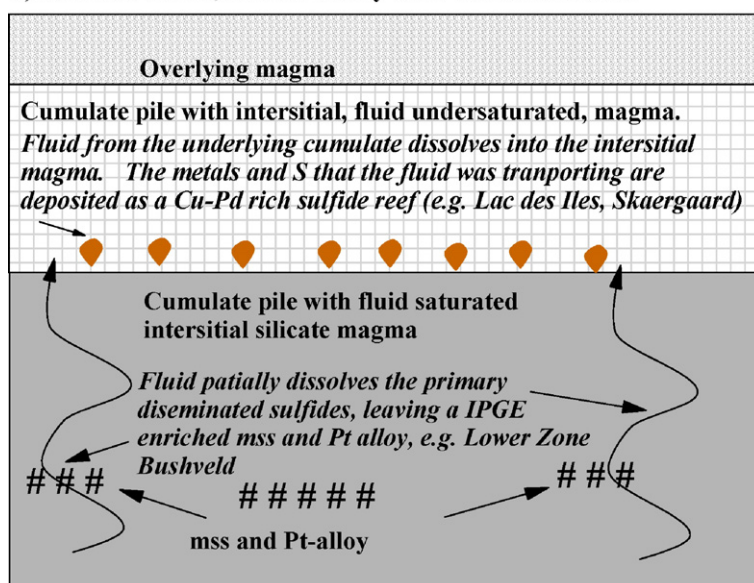


Fig. 9. Application of the results to the formation of PGE deposits. (a) Step 1 formation of a cumulate with base metal disseminated sulfides. (b) Step 2. In the lower part of the cumulate pile saturation of the interstitial silicate liquid with a fluid, this fluid partially dissolves the disseminated sulfides leaving Mss and Pt-alloy. The fluid rises into part of the cumulate pile containing silicate liquid that is not saturated in fluid and dissolves in this silicate liquid. The S, Pd and Au that the fluid was transferring are deposited to form a Pd deposit. Pt-alloy±Mss remains behind and could form a Pt deposit.

mass transfer was shown to be very low in the presence of $\text{SiO}_2\text{--NaCl}$ saturated aqueous fluids in the system Fe–Ni–Cu–S (Ballhaus et al., 1994), our experiments demonstrate significant vapor mass transfer of Ni in Cl-free fluids and are in a good agreement with the data obtained by Baker et al. (2001) for high-pressure, H_2S -containing sulfurous fluid.

In general, the discrepancy in the vapor mobility of metals in different experimental studies demonstrates the significance of vapor/fluid composition on the mobilization of ore metals and their mass transfer at magmatic temperatures. The vapor composition, as well as the mineral composition of ores, affects directly the mobility of

individual metals because they determine the dominant mass transfer species. In our experiments the vapor mass transfer of PGE and Ni correlates with the vapor mass transfer of S; Cu did not demonstrate such a correlation. Therefore, at magmatic temperatures in an S-dominated vapor, PGE and Ni might be transferred by S-species in contrast to Cu, which is most probably transferred as a metal species. In the present experiments Ni was much more efficiently transferred in vapor compared to Cu in the presence of the sulfide liquid. According to the calculation by Krauskopf (1957), the vapor pressure of metallic Cu is much higher in magmatic vapor than that of metallic Ni. Therefore, this calculation supports our suggestion

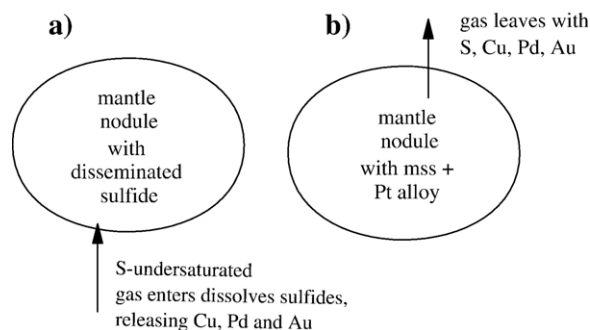


Fig. 10. Application of the results to the devolatilization of mantle nodules. (a) S-undersaturated gas from the alkali basalt or kimberlite infiltrates the nodule, (b) the gas partially dissolves the sulfides, leaving Mss and Pt alloy and removing S, Cu, Pd and Au.

that Ni is transferred as an S-species, at least in liquid bearing experiments.

One of the most important variables influencing the vapor mass transfer of precious metals is the S-content, or the sulfur fugacity, of the system. The S affect on the mobility of metals is particularly strong for Pt and Pd. These PGE are most probably transferred as the S-species, especially in case of the vaporization of the sulfide liquid. Another extremely important factor influencing the vapor mobility of metals in our experiments is the presence or absence of the sulfide liquid in the assemblages; the presence of the sulfide liquid favors the vapor mobility of Ni but significantly reduces the vapor mass transfer of Au.

Direct application of our results to natural systems is not possible because our experiments considered only S vapor, and in natural systems other species, especially Cl, CO₂ and H₂O are present. Nonetheless we suggest three geological settings where our experiments may be relevant. Firstly, in the case of Ni–Cu magmatic sulfide deposits, such as Duluth, our experiments may be used to explain the general observation that the Cu/Ni, Pd/Ir and Pd/Pt ratios of the ores are higher than in basaltic liquid from which the sulfides segregated (Barnes et al., 1997). The country rock sediments contain pyrite and chalcopyrite. Possibly S, Cu and Pd were transferred into the magma by vapor from the country rock and thus leading to the formation of an immiscible sulfide liquid in the magma and increase the Cu and Pd content of the magma.

Another ore environment where these experiments may be relevant is in the formation of PGE-deposits. Some of these are enriched in Cu, Pd and Au such as the Roby Zone, Lac des Iles, the Platinova reef, Skaergaard and the JM-reef, Stillwater and others are enriched in Pt, e.g. the Merensky reef, Bushveld and Tulameen. Pd-rich deposits of the Stillwater-type could have formed as

follows (Fig. 9). Initially the rocks contained a small quantity of magmatic sulfides. During cooling and compaction these sulfides were partially desulfurized to form Mss plus Fe–Pt-alloy plus a Cu–Pd–Au bearing fluid/vapor which rose into the overlying cumulate pile. As pointed out by Willmore et al. (2000), when the fluid encounters fluid-undersaturated interstitial silicate liquid it will dissolve in the silicate liquid. At this point the S and metals that were dissolved in the fluid will be deposited and possibly the rocks will be sufficiently enriched in metals to form a PGE deposit. Support for this model is also provided by Hanley et al. (2005b), who found that volatiles stripped S, Cu, Pd and some Pt from the cumulates below the JM-reef. The partial dissolution of disseminated sulfides by the volatiles could leave behind a cumulate enriched in IPGE and in some cases Pt, and we speculate that in general IPGE enrichment found in the Lower and Critical Zones of the Bushveld Complex (Barnes and Maier, 2002) could have been formed in this manner. In extreme cases one could imagine that all of the S is removed and only Pt alloy is left, leading to the formation of a Tulameen type deposit.

Finally for mantle nodules where S, Pd and Os loss by devolatilization has been suggested (Lorand et al., 2003), our experiments would suggest that S and Pd could be preferentially removed while leaving Ir, Rh, Ru and Pt behind (Fig. 10). Furthermore, our experiments predict that Au would also be removed along with S and Pd.

The behavior of Au, Ni, Rh, Ru, Ir change with the phase assemblage of the donor and its Ni/Cu ratio. The change in the behavior of Au, Ni, Rh, Ru and Ir affects in turn the Au to PGE ratios and PPGE (Pt, Pd) to IPGE (Ir, Ru, Rh) ratios. Thus, if either the temperature is not high enough to melt the sulfides, or if the Ni and Cu contents of the donor sulfides are low, the order of vapor mobility is Au > Cu–Ni > Pt–Pd > Rh–Ru–Ir. Ores formed from this vapor would be Au-rich, with minor Cu, Ni, Pt, Pd and IPGE. If the temperature is high enough and composition is rich enough in Ni and Cu for a sulfide melt to form, then the order of mass transfer by vapor changes to Ni > Cu > Au–Pt–Pd > Rh–Ru–Ir.

5. Conclusions

Mass transfer of significant amounts of Ni, Cu, Au, Pt and Pd occurs in an S-vapor at magmatic temperatures. The mass transfer of Rh, Ru and Ir in an S-dominated vapor is negligible. For all of the metals, the longer the run the larger the quantity of the metal transferred. Copper did not appear to be influenced by temperature, S-fugacity or phase assemblage. Inasmuch

as the S-fugacity and the phase assemblage appeared to have very little effect on the amount of transferred Cu, it is thought to be transferred as a metal. Temperature did not appear to be important for Au mobility. The most important factor for the mass transfer of Au appeared to be the phase assemblage. The presence of base metal sulfide liquid reduces the Au mobility by an order of magnitude. Changes in the S-fugacity appear to have no effect on Au mobility and, hence, thought to be transferred as a metal. The vapor mass transfer of Pd and Pt is controlled by phase assemblage and S-fugacity. Thus, it is thought that Pt and Pd are transferred as S-species. The presence of base metal sulfide liquid reduces the mobility of Pt and Pd by a factor of 3–10. The amount of Ni, Ir, Ru and Rh transferred is controlled by temperature and the phase assemblage. In addition, the S-fugacity may be important. The presence of a sulfide liquid enhances the Ni, Rh, Ru and Ir mobility, but the presence of a sulfide liquid also raises the S-fugacity so it is difficult to distinguish the two effects. Possibly these elements are also transferred as S-species.

Direct application of these results to natural systems should be tempered by two points: Firstly, the vapor contained only S and metals; natural systems would contain many more components (e.g. Cl, H₂O, CO₂) which will influence the solubility of the metals in the vapor. Secondly, the PGE and Au were present in the donor assemblage dissolved in a base metal sulfide; in natural systems PGE and Au are present not only dissolved in base metal sulfide, but are also present in variety of alloys and in combination with various metalloids such as As, Te and Bi. Nonetheless the S-dominated vapor experiments can be used to suggest that PGE deposits enriched Cu, Pd and Au may have formed by desulfurization of base metal sulfides at depth. The S-rich fluid could transport the Cu, Pd and Au and deposit the metals when in an S-rich fluid dissolved in a silicate magma or when the temperature dropped. The experiments could also be used to explain S and Pd loss in mantle nodules.

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