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## Distribution of Pd, Rh, Ru, Jr, Os, and Au between sulfide and silicate melts

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**Abstract**—Experiments have been conducted on the partitioning of noble metals in the presence of an H–O–C–S fluid in a high pressure gas apparatus at 1200–1300°C and 1–4 kbar fluid pressure. The fugacities of oxygen and sulfur, and the chemical species in the fluid phase, were controlled by the presence of graphite and of a sulfide melt of pyrrhotite composition and by external control of the fugacity of hydrogen. It has been found that PGE and Au partition strongly into a sulfide liquid in equilibrium with a silicate melt. The compositions of the sulfide and silicate melts as well as the redox conditions have only weak effects on the partitioning.

The following partition coefficients have been obtained:

$$D_{\text{Pd}} = (5.5 \pm 0.7) \times 10^4; \quad D_{\text{Rh}} = (2.7 \pm 0.6) \times 10^4; \quad D_{\text{Ru}} = (2.5 \pm 0.7) \times 10^3;$$

$$D_{\text{Ir}} = (3.1 \pm 0.8) \times 10^5; \quad D_{\text{Os}} = (2.3 \pm 0.3) \times 10^2; \quad D_{\text{Au}} = (1.6 \pm 0.4) \times 10^4.$$

These values are significantly higher than those reported in the recent literature (FLEET et al., 1991; CROCKET et al., 1992); this is attributed to their having been obtained under hydrous conditions. Their magnitudes demonstrate that the segregation of sulfide liquid from silicate magma is an effective mechanism for concentrating PGE and Au, as has been concluded from the study of deposits of believed magmatic origin.

### INTRODUCTION

THERE HAS BEEN CONSIDERABLE interest in the recent literature concerning the genesis of PGE deposits. As a rule, these are magmatic deposits occurring in differentiated basic-ultrabasic layered complexes, where concentrations of PGE are associated with chromite and/or sulfide. The largest and richest concentrations of PGE and Au in these layered complexes occur as stratabound sheets at or near the base of cyclic units which have developed above the level at which plagioclase cumulates first appear in the intrusions (see NALDRETT et al., 1987; BOUDREAU and MCCALLUM, 1992; CZAMANSKE and ZIENTEK, 1985; for contrasting viewpoints as to their origin); important resources also occur in the upper part of the ultramafic zone of some intrusions including the Great Dyke of Zimbabwe (see WILSON et al., 1989; PRENDERGAST, 1988).

The noble metal minerals in these deposits are present either in solid solution in the base metal sulfides or as finely dispersed aggregates of grains (<0.1–0.2 mm diam.), spatially related to the sulfides. The magmatic hypothesis of ore formation stipulates that a sulfide liquid segregates from silicate magma, carrying the noble metals with it, and that discrete noble metal minerals subsequently form from this, or from crystallization products of this. The low sulfide contents (1–3 vol%) that characterize ore horizons of this type call for high partition coefficients for the noble metals between sulfide and silicate melts ( $D = \text{metal in sul./metal in sil.}$ ). The calculations carried out by various authors (NALDRETT, 1981; SHARPE, 1982; CAMPBELL and BARNES, 1984; NALDRETT et al., 1987) indicate that the partition coefficients for noble

metals must be extremely high, of the order of  $10^5$ , if the magmatic hypothesis is to be sustained.

In any experimental study of PGE partitioning, one of the major experimental difficulties is that of separating the co-existing phases in order to analyze them for PGE at low concentrations. Nevertheless, a number of experimental studies have been concluded. JONES and DRAKE (1986) found partition coefficients of  $2 \times 10^3$  and  $2 \times 10^5$  for Ir and  $3.3 \times 10^3$  and  $2 \times 10^4$  for Au between Fe–FeS liquid and basaltic melt. The metal-rich nature of the sulfide liquid in their experiments meant that they were working at very low oxygen fugacities. STONE et al. (1990) obtained values of  $(9 \pm 7) \times 10^4$  for Pd,  $(1 \pm 0.7) \times 10^5$  for Ir,  $(9 \pm 6) \times 10^3$  for Pt, and  $(1 \pm 0.1) \times 10^3$  for Au. They controlled  $f_{\text{O}_2}$  in a 1 atmosphere gas mixing furnace using CO–CO<sub>2</sub> mixtures. Subsequently, FLEET et al. (1991) obtained values of about  $3 \times 10^3$  for Ir and  $2 \times 10^3$  for Pt and Pd, and CROCKET et al. (1992) obtained values of  $3.2 \times 10^3$ ,  $3.0 \times 10^3$ , and  $3.7 \times 10^3$  for Ir, Au, and Os, respectively, over a range of  $f_{\text{O}_2}$ ; in both of these studies,  $f_{\text{O}_2}$  was controlled by pre-heating the silicate charges, at 950°C and oxygen fugacities corresponding to those of known buffer curves, for two days in a controlled atmosphere furnace. Both FLEET et al. (1991) and CROCKET et al. (1992) noted that the partition coefficients appeared to decrease with increasing  $f_{\text{O}_2}$ .

Recent work on the  $f_{\text{O}_2}$  likely to have existed in basaltic magmas prior to their eruption suggests that this may be about 2.5 log units lower than the Ni–Ni oxide buffer (CHRISTIE et al., 1986). Figure 1 indicates that the IW buffer is close to the suggested  $f_{\text{O}_2}$ . It is for these reasons that the experiments in this study have been undertaken under the intensive pa-

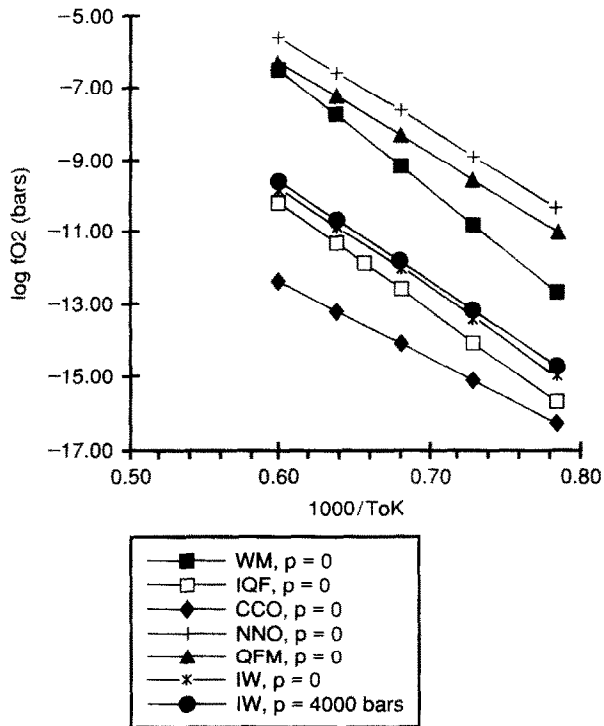


FIG. 1. Plot of  $\log f_{O_2}$  vs.  $1/T$  for a series of buffers. It can be seen that the conditions of this study (see Table 4) are comparable to those used by CROCKET et al. (1992) [IQF], FLEET et al. (1991) [IQF, CCO, IW], and STONE et al. (1990) [ $\log f_{O_2} = -9.2$  at  $1200^\circ\text{C}$ ]. The curves have been calculated from thermodynamic data from the following sources: IW, WM—EUGSTER and WONES (1962), DARKEN and GURRY (1945); IQF—Haas as quoted by CHOU (1987); CCO—HOLLAND (1965); NNO—HUEBNER and SATO (1970); QFM—SCHWAB and KÄSTNER (1981).

rameters of  $P_{(\text{total})} = 1\text{--}4$  kbar,  $T = 1200\text{--}1350^\circ\text{C}$ ,  $f_{O_2} = 10^{-9.9}$  to  $10^{-12.0}$  atm, close to and just above IW. The chemical potentials of other gases in our experimental charges have been controlled by the presence of native C and a high-Fe pyrrhotite liquid. It should be noted that our experiments were conducted under wet conditions, which allowed us to control the  $f_{O_2}$  fugacity directly. The studies of FLEET et al. (1991) and CROCKET et al. (1992), cited above, relied on the equilibration of the silicate charges at controlled  $f_{O_2}$  (mostly IQF which lies just below IW, see Fig. 1) prior to the experiments for control of  $f_{O_2}$ . This requires the silicate charge to buffer the experiment. Since, as these authors state, the Fe content of their silicate charges changed due to the diffusion of Fe into the sulfide melt, and since the  $f_{O_2}$  of a silicate melt is critically dependent on the Fe/ $O_2$  ratio, we believe that our experiments provide a much surer indication of the effect of  $f_{O_2}$  on the partition coefficient than these earlier studies.

Another factor potentially contributing to the magnitude of the partition coefficients is that at these low  $f_{O_2}$  values,  $H_2$ ,  $CH_4$ , and other reduced gases must be present in the fluid phase. Some of these species have been identified in gas inclusions from the Merensky Reef of the Bushveld complex (BALLHAUS and STUMPFL, 1985), although other inclusions studied by them were lacking in these gases and contained

$CO_2$ , indicative of a more oxidized fluid. Another indication of the reduced conditions existing within the intrusion is that fluids penetrating into the enclosing rocks have caused contact metamorphism which is characterized by more reducing condition than that characteristic of the regional metamorphism (VANIMAN et al., 1980). The high  $H_2$  content of the fluid in our experiments (which would also characterize the fluid in equilibrium with, or dissolved within natural magmas) means that considerable hydrogen may dissolve within the sulfide melt, and in this way affect the magnitude of the sulfide-silicate partition coefficient.

#### EXPERIMENTAL DETAILS

The experiments were conducted in the system H–O–C–S in a high pressure gas apparatus under conditions of known gas speciation and controlled fugacities. A sketch of the reaction vessel together with a charge capsule is shown in Fig. 2.

Reagent-grade oxides were used to prepare the silicate compositions (Table 1). Before mixing the oxides, they were completely dried at  $1000^\circ\text{C}$  for 12 h. Sodium and potassium were added in the form of dry  $NaAlO_2$  and  $K_2CO_3$ . Mixtures were melted in carbon-glass crucibles in a vacuum furnace at  $1600\text{--}1700^\circ\text{C}$  for 25 min to produce homogeneous glasses. Losses of alkalis amounted to 15–20 wt% of that originally present. The glasses were analysed with the microprobe, ground to a powder, the alkali deficiency was augmented by adding  $Na_2O$  and  $K_2O$  in the form of their carbonates, and aliquots were pressed into 7 mm diam. Pt (99.93 wt% Pt) capsules. The silicate glass was remelted in the gas pressure apparatus at 5 kbar water pressure and  $1300^\circ\text{C}$  at an oxidation state corresponding to the hematite-magnetite buffer. No loss of Fe was observed as a result of diffusion into the Pt capsule. Initial silicate charges for our experiments con-

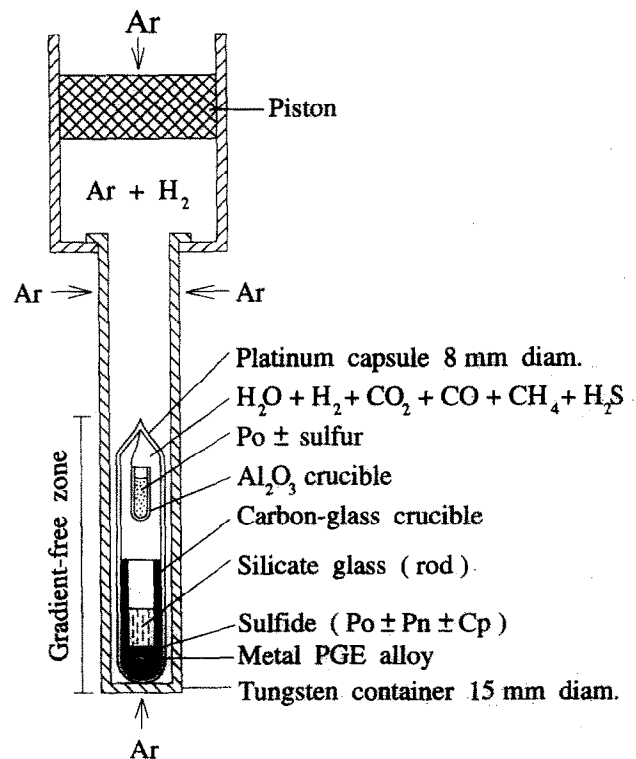


FIG. 2. Reaction vessel of high-pressure gas apparatus showing the design of the capsule containing the charge. Fugacities of gaseous species in the system H–C–O–S can be controlled as described in the text.

TABLE 1. Initial compositions of silicate glasses (in wt%)

Oxides	A	B	C	D	E
SiO <sub>2</sub>	56.06	47.65	51.98	45.54	49.90
TiO <sub>2</sub>	—	0.19	—	1.01	0.90
Al <sub>2</sub> O <sub>3</sub>	12.90	7.34	17.51	15.18	8.10
FeO	11.24	14.40	6.40	12.62	12.50
MnO	—	0.16	—	0.19	0.21
MgO	9.75	22.12	14.36	11.95	14.70
CaO	7.01	4.39	8.56	9.61	11.80
Na <sub>2</sub> O	2.03	0.69	1.18	1.83	1.86
K <sub>2</sub> O	1.03	0.11	—	0.92	0.07

A = Bulk composition of the Bushveld Complex (BARNES, 1986)

B = Average composition of the Merensky reef (LEE and SHARPE, 1980)

C = melt of bronzite (Fs<sub>25</sub>)-plagioclase (Ab<sub>20</sub>) composition (75 mole % Opx, 25 mole % plag)

D = typical bulk composition of a mineralized massif at Noril'sk (ZOLOTUKHIN et al., 1975)

E = bulk composition of Theo's flow in tholeiite-komatiite complex of Munro Township, Abitibi belt, Canada (ARNDT et al., 1977)

sisted of columns of this glass, 6 mm in diameter and 6 mm in height, weighing 300–350 mg.

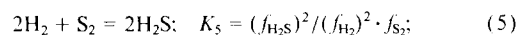
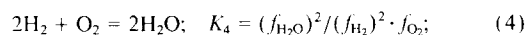
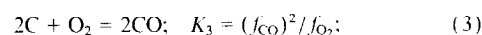
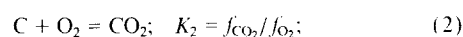
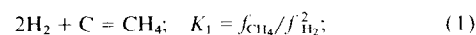
Sulfides of stoichiometric composition were synthesized from high purity elements in evacuated quartz capsules. Pyrrhotite (po) mixtures were kept at 900°C for two days, those of chalcopyrite (cp) at 700°C for seven days and those of pentlandite (pn) at 500°C for fourteen days. Initial sulfide charges (100 mg) consisted either of pure pyrrhotite or mixtures of po, pn, and cp in proportions similar to averages typical of a variety of geologic settings (Table 2).

Alloys of PGE and Au of different proportions (Table 3), prepared by melting the metals in an alumina crucible in the flame of a gas burner ( $T = 2000^\circ\text{C}$ ), were used as starting materials for these components.

To avoid Fe loss, experiments were performed in carbon-glass crucibles which were placed in a Pt capsule, 8 mm in diameter and of 50 mm long. The PGE-Au alloy was placed at bottom of the crucible, followed by a column of sulfide prepared by compressing powdered sulfide at 200 atm. This was followed by the silicate glass column (Fig. 2). An alumina container containing 100 mg of pure (previously synthesized) pyrrhotite or a mixture of this with S (5–10 mg) was suspended on Pt wire to serve as an indicator of  $f_{\text{S}_2}$ . Water or a solution of weak acid (1.5 wt% HCl), amounting to 80–200 mg, was poured into the capsule. In order to accelerate the achievement of reducing conditions 50 mg of paraffin, ( $\text{C}_n\text{H}_{n+2}$ ), was also placed in the Pt capsule.

The pressure of hydrogen in the reaction vessel was controlled by introducing an Ar-H<sub>2</sub> mixture as the pressure medium. Hydrogen diffused through the wall of the Pt capsule, resulting in control of the hydrogen fugacity and of the fugacities of the other gaseous species in the system H-C-O-S in the capsule.

The welded Pt capsule was placed in a tungsten reaction vessel (Fig. 2) which was filled with an Ar-H<sub>2</sub> mixture consisting of 0.1 or 0.2 mole fraction of H<sub>2</sub> under a pressure of 100 atm. The reaction vessel was inserted into the high pressure gas apparatus, inside the furnace, so that the Pt capsule with the charge being studied and the indicator for the system were in the zone that was essentially free of thermal gradients. Thermocouples, calibrated at the melting temperature of pure Au, gave a temperature measurement accurate to  $\pm 7^\circ\text{C}$ . The inner reaction vessel is separated from the gas (Ar) transmitting the pressure by a separating piston which is situated outside the hot zone. Pressure is measured using a Bourdon gauge with an accuracy of  $\pm 50$  atm. Because, even at high temperatures, diffusion of hydrogen through the walls of the tungsten reaction vessel is negligible (BEZMEN, 1989, 1992a,b), the fugacities of hydrogen and the other species in the fluid phase remained constant during the course of an experiment. Relationships between gaseous species in the system H-O-C-S in presence of free Ca are defined by the reactions coupling them:



where  $f$  = fugacities of gases and  $K$  = equilibrium constants of the reactions. Taking into account that

$$P_{\text{tot}} = P_{\text{H}_2\text{O}} + P_{\text{H}_2\text{S}} + P_{\text{CO}_2} + P_{\text{CO}} + P_{\text{CH}_4} + P_{\text{H}_2} + P_{\text{O}_2} + P_{\text{S}_2}$$

$$= \frac{f_{\text{H}_2\text{O}}}{\gamma_{\text{H}_2\text{O}}} + \frac{f_{\text{H}_2\text{S}}}{\gamma_{\text{H}_2\text{S}}} + \frac{f_{\text{CO}_2}}{\gamma_{\text{CO}_2}} + \frac{f_{\text{CO}}}{\gamma_{\text{CO}}} + \frac{f_{\text{CH}_4}}{\gamma_{\text{CH}_4}} + \frac{f_{\text{H}_2}}{\gamma_{\text{H}_2}}$$

$$+ \frac{f_{\text{O}_2}}{\gamma_{\text{O}_2}} + \frac{f_{\text{S}_2}}{\gamma_{\text{S}_2}}, \quad (6)$$

where  $P$  and  $\gamma$  are the partial pressures and fugacity coefficients of the corresponding gases.

By presetting the mole fraction of H<sub>2</sub> in the fluid phase, and solving the six equations with six unknowns, we can determine the fugacities, and thus the mole fraction of H<sub>2</sub>O, H<sub>2</sub>S, CO<sub>2</sub>, CO, CH<sub>4</sub>, and the value of log  $f_{\text{O}_2}$ . The thermodynamic constants given by ROBIE et al. (1978) have been used in the calculations together with data on gas fugacities at high pressure from MELNIK (1978) and SHMULOVICH et al. (1982). In all calculations it has been assumed that, at the temperatures and pressures of the experiments, the gas mixtures behave as ideal solutions of real gases. Sulfur fugacity was defined from the composition of the iron sulfide melt (BURGMANN et al., 1968). Hydrogen dissolving in sulfide melt can affect the relationship between Fe and S, owing to the resulting increase in Fe activity, as has been observed for the equilibrium between wustite and metallic Fe (BEZMAN and SUK, 1990). However, as can be seen from Fig. 3, large changes in  $f_{\text{S}_2}$  produce only small changes in  $f_{\text{O}_2}$ , and errors in the determination of  $f_{\text{O}_2}$  (which would result from dissolved H<sub>2</sub>) do not have a major effect on the calculation of log  $f_{\text{O}_2}$ . Thermodynamic parameters for the runs are given in Table 4.

It was found that at the termination of the experiments, sulfide droplets adhered to the surface of the silicate glass column (Fig. 4), but were completely absent within it. The sulfide droplets were removed by boiling the column in 10 wt% HCl solution (3–4 times). The silicate column was then boiled in double-distilled water and was powdered in a jasper mortar. The content of the PGE and Au in silicate phase was analyzed by neutron-activation analysis according to the technique of BRÜGMANN et al. (1987). The sulfide composition was analyzed on the Camebax SX50 microprobe by scanning with a wide beam (20–20  $\mu\text{m}$ ) over the whole of the area of sulfide at 25 keV and 30 nA. The sulfur and iron concentrations in the indicator pyrrhotite (Table 4) were also determined by electron probe micro-

TABLE 2. Initial composition of sulfide phases (wt %)

Element	Po	Cp	X	Y	Z
Fe	63.53	30.42	47.67	50.61	49.60
Ni	—	—	11.29	5.13	17.11
Cu	—	34.64	6.24	8.66	1.73
S	36.47	34.94	34.8	35.60	34.26
Po	100	—	49	60	45
Pn	—	—	33	15	50
Cp	—	100	18	25	5

Po—pyrrhotite of stoichiometric composition (FeS)

Cp—chalcopyrite (CuFeS<sub>2</sub>)

X—average composition of sulfide Merensky reef ores (DISTLER et al., 1988)

Y—average composition of sulfide Talnakh ores (DISTLER et al., 1988)

Z—average composition of sulfide ores in komatiites of Kambadla Australia (DONALDSON and BROMLEY, 1981)

TABLE 3. Composition of the initial charges for the runs

N sample	Melt type		Composition of the alloy, mg							Composition of fluid phase	
	Silicate (300–350 mg)	Sulfide (100 mg)	Fe	Pd	Rh	Ir	Ru	Os	Au	S, mg.	Solution wt%
Pt-37	A	Po	20	5	3	—	—	—	—	10	H <sub>2</sub> O
Pt-41		Po	20	10	2	—	—	—	—	5	"
Pt-42		Po	20	10	2	—	—	—	—	10	"
Pt-54		X	20	10	2	—	—	—	—	5	"
Pt-58		Po	20	5	3	—	—	—	—	5	"
Pt-59		X	20	5	3	—	—	—	—	—	"
Pt-61		X	20	1	2	—	—	—	—	5	"
Pt-63		X	20	5	3	—	—	—	—	5	"
Pt-56		Po	20	5	2	3	1	3	3	5	"
Pt-62		Po	20	5	2	3	1	3	3	10	"
Pt-64		Po	20	5	2	3	1	3	3	5	1.5% HCl
Pt-65		Po	20	3	10	5	4	10	1	5	"
Pt-60		Cp	20	15	2	3	1	3	3	5	"
Pt-47		Po	20	—	—	—	—	1	—	5	H <sub>2</sub> O
Pt-48		Po	20	—	—	—	—	3	—	5	"
Pt-49		Po	20	—	—	—	—	5	—	5	"
Pt-20	B	X	20	—	—	1	3	—	3	5	1.5% HCl
Pt-6	C	Po	15	—	—	3	3	—	3	10	H <sub>2</sub> O
Pt-7		Po	15	—	—	5	1	—	5	10	"
Pt-12		Po	15	—	—	1	5	—	2	10	1.5% HCl
Pt-13		X	15	—	—	2	7	—	2	10	1.5% HCl
Pt-17		Po	15	—	—	1	2	—	1	10	H <sub>2</sub> O
Pt-18		Po	15	—	—	3	2	—	2	10	"
Pt-25		Po	15	—	—	2	3	—	3	10	"
Pt-15	D	Y	20	—	—	2	—	—	—	5	"
Pt-24		Y	20	—	—	2	4	—	5	10	1.5% HCl
Pt-26	E	Z	20	—	—	1	3	—	2	5	"

analysis (EPMA). PGE and Au, which were present in sulfide at trace levels, were analysed using a single channel pulse height analyser in order to remove interference by 2nd and higher order lines. Analytical lines and background were measured using blank standards, taking into account the average difference in atomic number between the blank standards, reference standards, and unknown samples (ROMANENKO, 1982). Table 5 shows the necessary data on reference standards and the analytical lines used for PGE and Au EPMA in sulfides with nickel-iron matrix.

A series of runs of different duration were carried out in order to determine the time necessary to attain equilibrium and to optimise

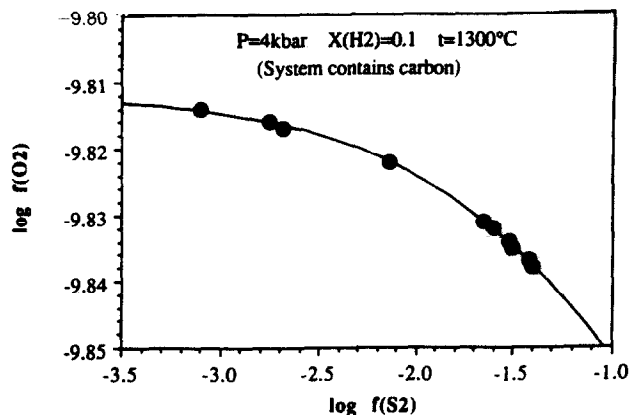


FIG. 3. Relationship between sulfur and oxygen fugacities in the fluid phase of the system H-O-C-S at 1300°C, 4 kbar and  $X_{H_2} = 0.1$  in the presence of carbon (calculated data).

the concentrations of PGE, Au, and Fe in the initial charges. Bronzite-anorthite glasses (Table 6) were used as starting compositions. Figure 5 shows the dependence of Ir, Ru, and Au partition coefficients on run time. The silicate column obtained initially by synthesis from the oxides in an alumina crucible followed by melting in a Pt capsule typically contains PGE in the following concentrations (ppb): Pt = 739,566; Pd = 0; Rh = 277.5; Ru = 870.9; Ir = 24; Os = 2813; Au = 67.2; these are thought to have been derived from the Pt capsule.

As seen in Fig. 5, PGE enter the silicate melt in high concentrations that do not reflect the final equilibrium state during the first few hours of an experiment. However, with time PGE and Au are redistributed into the sulfide melt and after 30–48 hours the partition coefficients remain constant.

Thus, the conditions of an experiment were held constant for 48 h, and the runs were then quenched by switching off the power. Quenching rate was 2000°C per min. The preliminary runs also demonstrated that, unfortunately, it is impossible to obtain Pt distribution data using our technique, since a Pt capsule is used and as a result, a disequilibrium saturation of silicate melt by Pt takes place. Moreover, it was shown that under reducing conditions, in accordance with the diagram of the system Fe-S (BURGMANN et al., 1968), the sulfide phase is enriched with Fe from the silicate melt. As a result, the silicate melt is depleted in some runs by as much as 50 wt% of its initial Fe content. To circumvent this, additional native Fe was added to the metallic starting phase; the precise amount depended on the composition of the silicate melt and amounted to 15–20 mg (Table 3).

## DISCUSSION OF RESULTS

At the termination of the experiments, the silicate phase consisted of a transparent glass, devoid of liquidus crystals, except for the melt with the composition corresponding to that of the Merensky reef. The latter developed a layering

TABLE 4. Thermodynamic conditions of the runs

N sample	Composition of silicate phase	T°C	P, kbar	Indicat. $f_{S_2}$	$-\lg f_{S_2}$	$-\lg f_{O_2}$	Mol. fraction of gases in fluid ( $X_i^p$ )						Duration of the run, h
							H <sub>2</sub>	H <sub>2</sub> O	H <sub>2</sub> S	CO <sub>2</sub>	CO	CH <sub>4</sub>	
Pt-6	C*	1250	4	FeS <sub>0.993</sub>	2.02	10.27	0.1	0.367	0.019	0.216	0.207	0.087	48
Pt-7	"	"	4	FeS <sub>1.035</sub>	1.15	10.30	0.1	0.355	0.054	0.202	0.200	0.087	8
Pt-12	"	"	3	FeS <sub>1.079</sub>	0.27	10.77	0.1	0.200	0.323	0.113	0.190	0.072	54
Pt-13	"	"	4	FeS <sub>0.988</sub>	1.80	11.09	0.2	0.284	0.051	0.032	0.080	0.350	72
Pt-17	"	"	4	FeS <sub>0.973</sub>	2.42	10.26	0.1	0.370	0.012	0.202	0.209	0.012	12
Pt-18	"	"	4	FeS <sub>0.99</sub>	2.00	10.27	0.1	0.367	0.020	0.216	0.207	0.087	6
Pt-25	"	"	4	FeS <sub>0.984</sub>	2.22	10.27	0.1	0.369	0.015	0.218	0.208	0.087	24
Pt-37	A	1300	4	FeS <sub>1.033</sub>	1.52	9.83	0.1	0.313	0.027	0.225	0.264	0.068	48
Pt-41	"	"	4	FeS <sub>0.978</sub>	2.14	9.82	0.1	0.317	0.013	0.232	0.267	0.068	48
Pt-42	"	"	4	FeS <sub>1.063</sub>	1.42	9.84	0.1	0.312	0.031	0.224	0.263	0.068	48
Pt-47	"	"	4	FeS <sub>0.931</sub>	2.68	9.82	0.1	0.319	0.007	0.234	0.269	0.068	48
Pt-48	"	"	4	FeS <sub>0.904</sub>	3.10	9.81	0.1	0.320	0.004	0.236	0.270	0.068	48
Pt-49	"	"	4	FeS <sub>0.904</sub>	3.10	9.81	0.1	0.320	0.004	0.236	0.270	0.068	48
Pt-54	"	"	4	FeS <sub>0.981</sub>	1.99	10.45	0.2	0.308	0.032	0.054	0.129	0.274	48
Pt-56	"	"	4	FeS <sub>0.965</sub>	2.21	10.43	0.2	0.312	0.025	0.056	0.131	0.274	48
Pt-58	"	"	4	FeS <sub>0.911</sub>	2.98	10.41	0.2	0.320	0.010	0.059	0.135	0.274	48
Pt-59	"	"	4	FeS <sub>0.796</sub>	4.00	10.40	0.2	0.324	0.003	0.060	0.136	0.274	48
Pt-60	"	"	4	FeS <sub>0.992</sub>	1.72	10.47	0.2	0.301	0.044	0.052	0.127	0.274	48
Pt-61	"	"	4	FeS <sub>0.995</sub>	1.68	10.47	0.2	0.300	0.046	0.051	0.126	0.274	48
Pt-62	"	"	4	FeS <sub>1.017</sub>	1.24	10.52	0.2	0.282	0.077	0.045	0.119	0.274	48
Pt-63	"	"	4	FeS <sub>0.927</sub>	2.80	10.42	0.2	0.318	0.012	0.058	0.134	0.274	48
Pt-64	"	"	4	FeS <sub>0.972</sub>	2.12	10.44	0.2	0.310	0.028	0.055	0.130	0.274	48
Pt-65	"	"	4	FeS <sub>0.915</sub>	2.94	10.41	0.2	0.320	0.010	0.058	0.134	0.274	48
Pt-20	B	1350	4	FeS <sub>0.790</sub>	3.70	9.90	0.2	0.310	0.003	0.077	0.190	0.218	72
Pt-15	"	1250	1	FeS <sub>0.940</sub>	2.95	11.45	0.2	0.165	0.021	0.113	0.400	0.091	54
Pt-24	"	1200	1	FeS <sub>1.033</sub>	1.50	12.03	0.2	0.168	0.143	0.086	0.284	0.117	72
Pt-26	"	1350	1	FeS <sub>0.917</sub>	2.45	10.54	0.1	0.068	0.011	0.134	0.671	0.014	48

\* A series of runs of variable duration which were performed in order to understand the kinetics of the achievement of equilibrium during the experiments (Fig. 5).

due to liquid cluster differentiation (BEZMEN, 1992a,b) under the influence of a high H-bearing fluid pressure; the layering consisted of a thin (0.4 mm) band of liquid of peridotite composition, occupying not more than 5 vol% of the silicate phase, at the top of the mass of silicate liquid. Microprobe analysis of some of the run products has shown that the Fe content of the silicate glass is close (within  $\pm 1$  wt%) to the initial content and that the glass contains about 0.25 wt% S

(BEZMEN et al., 1991b). In runs involving a Cp-Pn-Po initial sulfide assemblage, the run product contained quenched dendritic aggregations of copper sulfide within nickeliferous pyrrhotite (Mss). In some runs with a high Os content, OsS<sub>2</sub> crystallized as a liquidus phase in the sulfide liquid. As a rule, the metallic phase remained in the lower part of the sulfide melt with the form of individual grains of uniform composition.

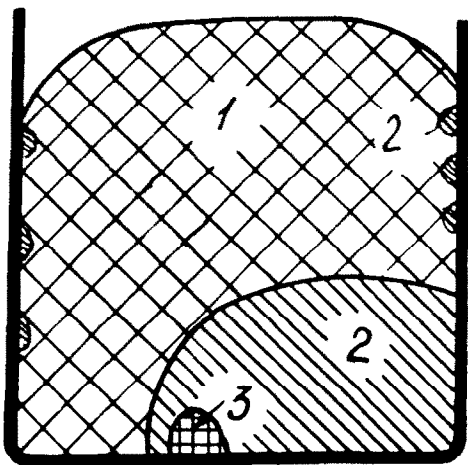


FIG. 4. Section through a typical sample after a run. 1 = silicate melt, 2 = sulfide melt, 3 = metal alloy.

TABLE 5. Standards and conditions for microprobe analysis

Element	Line	Analyser	Standards		
			1	2	3
Fe	K $\alpha$	LiF	Fe		Ni(Fe), Pt
Ni	K $\alpha$	LiF	Ni		Fe(Ni), Pt
Cu	L $\alpha$	TAP (RAP)	Cu		Fe(Cu), Pt
Ru	L $\alpha$	PET	Ru		Rh(Ru), Ir
Rh	L $\alpha$	PET	Rh	Ru, Cu	Pt
Pd	L $\alpha$	PET	Pd	Ru, Rh	Pt
Os	M $\alpha$	PET	Os		Ir
Ir	L $\alpha$	LiF	Ir		Pt
Pt	L $\alpha$	LiF	Pt		Os
Au	L $\alpha$	LiF	Au		Ir
S	K $\alpha$	PET	FeS <sub>2</sub>		Fe(S), Os

1 = Reference Standards

2 = Standards for elements with interference

3 = Standards used in measuring background

"Ni(Fe), Pt" denotes the use of Ni as the background standard for the FeK $\alpha$  line and Pt as the background standard for the unknown.

TABLE 6. Distribution of Ru, Ir and Au between sulfide and silicate melts at 1250°C and 4 kbar depending on the duration of the runs

N sample	Melt type		Ru			Ir			Au			
	Silicate	Sulfide	Duration run, h	Silicate melt	Sulfide melt	Silicate melt	Sulfide melt	Silicate melt	Sulfide melt	Silicate melt	Sulfide melt	
				δ*, ppb	wt%	δ, wt%	D <sub>Ru</sub>	δ, ppb	wt%	δ, ppb	wt%	δ, ppb
Pt-18	C	Po	6	2805	1.42	0.15	5.1 × 10 <sup>3</sup>	52	0.15	3128	0.05	1.9 × 10 <sup>1</sup>
Pt-7	"	Po	8	5987	2.24	0.31	3.7 × 10 <sup>3</sup>	74	0.03	12475	0.31	2.5 × 10 <sup>2</sup>
Pt-17	"	Po	12	0	0.05	—	67	7.1	0.12	87.6	0.002	7.9 × 10 <sup>2</sup>
Pt-25	"	Po	24	2304	0.18	0.02	7.8 × 10 <sup>2</sup>	13	0.52	1051	1.1	1.5 × 10 <sup>2</sup>
Pt-6	"	Po	48	3553	1.31	0.14	3.7 × 10 <sup>3</sup>	22	0.50	607	0.15	1.5 × 10 <sup>4</sup>
Pt-12	"	Po	54	0	0.05	—	34.5	3.5	1.28	465	0.10	1.8 × 10 <sup>4</sup>
Pt-13	"	X	72	1004	0.21	0.02	2.1 × 10 <sup>3</sup>	74.1	2.18	226	0.04	1.2 × 10 <sup>4</sup>
								8.1	0.21	27	0.05	1.3 × 10 <sup>4</sup>

\* Here and everywhere a relative error of the analysis.

Our experimental results are given in Tables 7–9 and are illustrated in Figs. 6–8. Palladium is the metal with the highest concentrations in the sulfide melt in the presence of an iron-bearing metallic phase, followed by Rh, then Ir, Ru, and Au with Os showing the lowest concentration. The addition of HCl to the fluid phase of the experiments increases the concentration of the PGE and Au in the sulfide phase (for example, experiments #Pt-64, Pt-65, Table 7–9) but it also increases their solubility in the silicate melt, so that the partition coefficients show little change.

PGE and Au greatly favour the sulfide over the silicate melt. In the range of temperatures, pressures, and oxygen fugacities (Table 4) covered in this study, the following average partition coefficients were obtained:

$$D_{Pd} = (5.5 \pm 0.7) \times 10^4;$$

$$D_{Rh} = (2.7 + 0.6) \times 10^4;$$

$$D_{Ru} = (2.5 \pm 0.7) \times 10^3;$$

$$D_{Ir} = (3.1 \pm 0.8) \times 10^5;$$

$$D_{Os} = (2.3 \pm 0.3) \times 10^2;$$

$$D_{Au} = (1.6 \pm 0.4) \times 10^4;$$

where the uncertainty is the standard deviation.

We did not discern any significant effect of the presence Ni in the sulfide liquid (Table 2) on partitioning, which is contrary to the suggestion of FLEET et al. (1991) that the difference between their results and those of STONE et al. (1990) might be due to the difference in the Ni contents of the sulfide melts involved. Very likely, because of their similar properties, Fe and Ni behave identically in sulfide melts with respect to influencing the partitioning of PGE and Au.

The partition coefficients for Pd, Rh, and Ir appear to be lower for melts of chalcopyrite composition (Figs. 6, 7a) than for those with other compositions. The partition coefficient for Au, on the other hand, appears to be higher for the melt of chalcopyrite composition (Fig. 7c); this probably indicates a greater similarity between the chemical properties of Cu and Au than between Cu and the PGE under these conditions, something that is suggested by their respective positions in the periodic table.

It is important to note that during crystallization of the sulfide liquid and the subsequent breakdown of the initial products of this crystallization, as phases with different structures are formed (po, pn, cp) a low temperature redistribution of elements occurs between them. It is known, for example, that Pd prefers to be concentrated in Pn in the presence of Po (CHYI and CROCKET, 1976; DISTLER et al., 1988; CHAI and NALDRETT, 1992; LI et al., 1992).

Our data do not indicate any dependence of the partition coefficients on the concentration of the PGE in the sulfide melt, which is contrary to the observations of FLEET et al. (1991), but consistent with those of CROCKET et al. (1992).

It has been suggested previously (PEACH et al. 1990; FLEET et al. 1991; CROCKET et al. 1992) that redox processes will have an important effect upon noble metal partitioning. We (BEZMEN et al., 1991a) proposed that since, under reducing conditions, the sulfide melt is enriched in Fe relative to S,

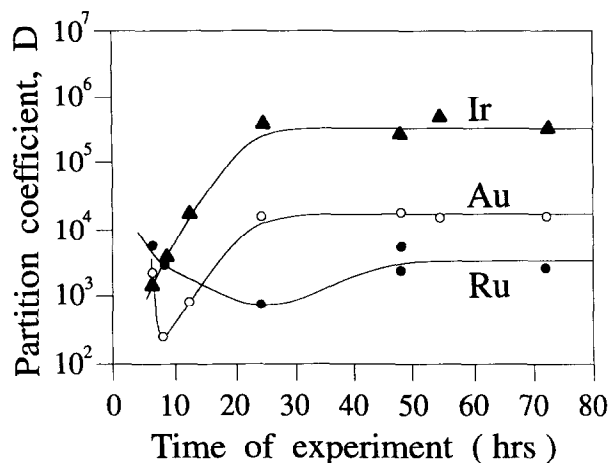


FIG. 5. Variation of partition coefficients of Ir, Ru, and Au between sulfide and silicate melts with duration of experiment.

this will aid the concentration of siderophile elements such as the platinoids. However, it was only possible to discern the influence of oxidation state on Pd distribution, and this was found to be less than had been anticipated. A decrease in  $f_{O_2}$  of 0.71 log units causes a 1.11 times increase in the partition coefficient (Fig. 6a).

We suggest that in equilibrium between coexisting silicate and sulfide melts, hydrogen may concentrate in the sulfide phase. If so, this will raise the activity of Fe (BEZMEN and SUK, 1990; BEZMEN, 1992b), and contribute to PGE concentrating in the sulfide melt. This may be the reason why the partition coefficients presented here, with the exception of Os (see below), are higher by one to two orders of magnitude than those obtained in the absence of a fluid phase (FLEET et al., 1991; CROCKET et al., 1992). While most magmas that have given rise to PGE concentrations are unlikely to have been saturated with a volatile phase, they undoubtedly contained volatiles (MATHEZ, 1990; BOUDREAU and

TABLE 7. Distribution of palladium and rhodium between silicate and sulfide melts at 1300°C and 4 kbar

N sample	Melt type		Pd				$D_{Pd}$	Rh				$D_{Rh}$
			Silicate		Sulfide			Silicate		Sulfide		
	Silicate	Sulfide	ppb	$\delta$ , ppb	wt%	$\delta$ , wt%	ppb	$\delta$ , ppb	wt%	$\delta$ , wt%		
Pt-37	A	Po	695	472	3.86	0.31	$5.6 \times 10^4$	281	21	0.59	0.06	$2.1 \times 10^4$
Pt-41	"	Po	1453	567	7.08	0.52	$4.9 \times 10^4$	155	22	0.37	0.04	$2.4 \times 10^4$
Pt-42	"	Po	1242	621	6.01	0.58	$4.8 \times 10^4$	416	23	1.15	0.11	$2.8 \times 10^4$
Pt-54	"	X	1039	558	5.71	0.49	$5.5 \times 10^4$	347	16	0.75	0.07	$2.2 \times 10^4$
Pt-56	"	Po	561	111	3.20	0.31	$5.7 \times 10^4$	154	93	0.53	0.05	$3.4 \times 10^4$
Pt-58	"	Po	407	93	2.10	0.28	$5.2 \times 10^4$	64.1	11.8	0.15	0.02	$2.3 \times 10^4$
Pt-59	"	X	419	90	2.31	0.25	$5.5 \times 10^4$	519	39	1.05	0.11	$2.0 \times 10^4$
Pt-60	"	Cp	2563	381	10.11	1.05	$3.9 \times 10^4$	640	74	0.54	0.04	$8.4 \times 10^3$
Pt-61	"	X	0	—	0.21	0.02	—	113	12	0.39	0.04	$3.5 \times 10^4$
Pt-62	"	Po	487	68	2.47	0.25	$5.0 \times 10^4$	127	11	0.42	0.04	$3.3 \times 10^4$
Pt-63	"	X	764	56	4.08	0.39	$5.3 \times 10^4$	377	15	1.21	0.13	$3.2 \times 10^4$
Pt-64	"	Po	842	102	4.47	0.41	$5.3 \times 10^4$	177	26	0.62	0.06	$3.5 \times 10^4$
Pt-65	"	Po	195	22	1.48	0.15	$7.3 \times 10^4$	3617	50	8.13	0.55	$2.2 \times 10^4$

TABLE 8. Distribution of ruthenium, iridium and osmium between silicate and sulfide melts

N sample	Melt type		Ru				$D_{Ru}$	Ir				$D_{Ir}$	Os				$D_{Os}$
			Silicate		Sulfide			Silicate		Sulfide			Silicate		Sulfide		
	Silicate	Sulfide	ppb	$\delta$ , ppb	wt%	$\delta$ , wt%	ppb	$\delta$ , ppb	wt%	$\delta$ , wt%	ppb	$\delta$ , ppb	wt%	$\delta$ , wt%			
Pt-56	A	Po	958	45	0.21	0.02	$2.2 \times 10^3$	34.7	14.6	0.82	0.09	$2.4 \times 10^5$	3098	991	0.075	0.01	$2.4 \times 10^3$
Pt-62	"	Po	211	22	0.07	0.01	$3.3 \times 10^3$	4.9	3.5	0.19	0.02	$3.9 \times 10^5$	39.1	—	0.01	—	—
Pt-64	"	Po	0	—	—	—	—	29.2	9.0	0.95	0.11	$3.2 \times 10^5$	117	—	0.01	—	—
Pt-65	"	Po	1959	202	0.41	0.04	$2.7 \times 10^3$	52.1	12.5	1.61	0.12	$3.1 \times 10^5$	347693*	3477	0.150	0.02	—
Pt-60	"	Cp	0	—	—	—	—	40.3	5.6	0.89	0.09	$2.2 \times 10^5$	18461	369	0.090	0.01	48.8
Pt-47	"	Po	—	—	—	—	—	—	—	—	—	—	626	200	0.012	0.003	$1.9 \times 10^2$
Pt-48	"	Po	—	—	—	—	—	—	—	—	—	—	2758	82	0.070	0.001	$2.5 \times 10^2$
Pt-49	"	Po	—	—	—	—	—	—	—	—	—	—	5789	58	0.131	0.02	$2.2 \times 10^2$
Pt-20	B	X	1205	112	0.26	0.02	$2.2 \times 10^3$	7.3	1.2	0.20	0.02	$2.7 \times 10^5$	—	—	—	—	—
Pt-24	D	Y	3647	201	0.66	0.06	$1.8 \times 10^3$	15.4	2.3	0.49	0.07	$3.2 \times 10^5$	—	—	—	—	—
Pt-15	D	Y	—	—	—	—	—	13.0	2.0	0.61	0.07	$4.7 \times 10^5$	—	—	—	—	—
Pt-26	E	Z	1856	157	0.37	0.04	$2.0 \times 10^3$	10.2	0.8	0.21	0.02	$2.1 \times 10^5$	—	—	—	—	—

\* Discrete grains of Os<sub>2</sub>S<sub>3</sub> are present in the sulfide phase of this sample and have affected the analysis. This particular value has been ignored in calculating the average partition coefficient.



TABLE 9. Distribution of gold between silicate and sulfide melts

N sample	Melt type		Au				
			Silicate		Sulfide		$D_{Au}$
	Silicate	Sulfide	ppb	$\delta$ , ppb	wt%	$\delta$ , wt%	
Pt-62	A	Po	812	8	1.12	0.12	$1.4 \times 10^4$
Pt-64	"	Po	43.4	1.7	0.05	0.01	$1.2 \times 10^4$
Pt-65	"	Po	135	3	0.18	0.02	$1.3 \times 10^4$
Pt-60	"	Cp	242	2.4	0.52	0.07	$2.1 \times 10^4$
Pt-20	B	$\lambda$	52.9	3.0	0.12	0.02	$2.3 \times 10^4$
Pt-15	D	$\gamma$	129	2.7	0.22	0.03	$1.7 \times 10^4$
Pt-26	E	Z	43.4	1.4	0.07	0.01	$1.6 \times 10^4$

MCCALLUM, 1992) and we believe that our partition coefficients, obtained under wet conditions, are likely to be closer to those operative in nature than those observed in totally dry systems. PEACH et al. (1989) obtained partition coefficients for Au, Ir, and Pd between sulfide and mid-oceanic

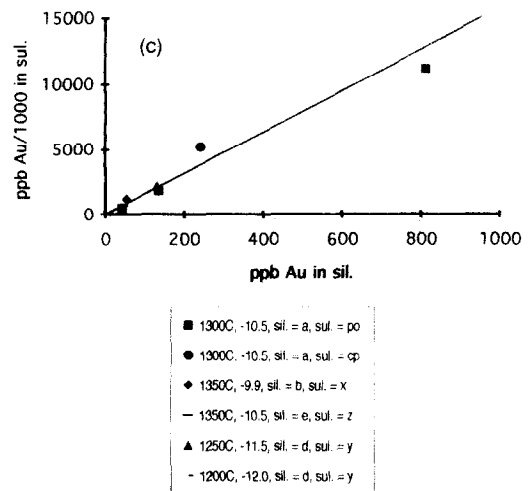
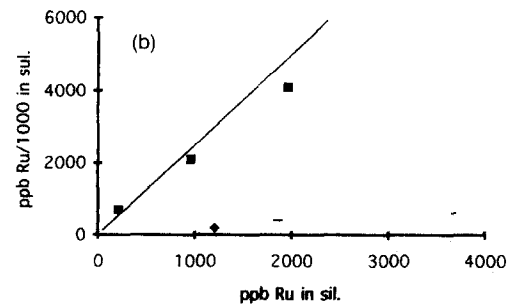
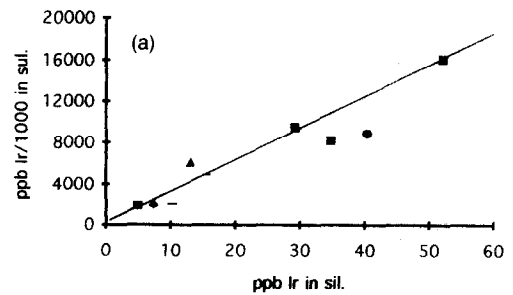
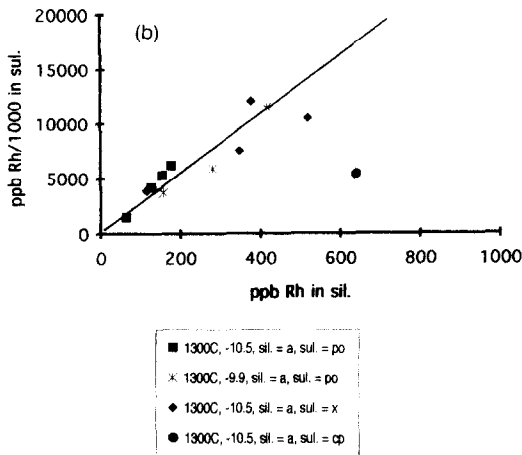
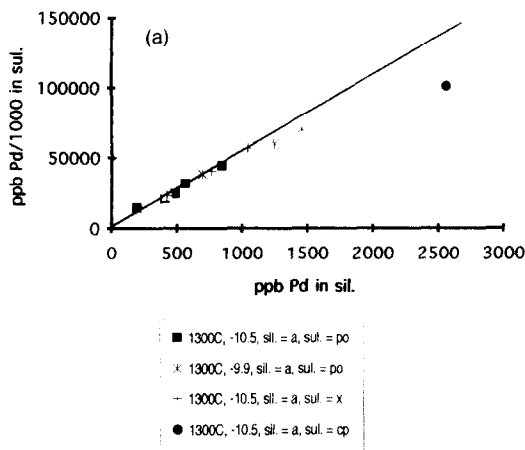


FIG. 6. Experimental data for (a) Pd and (b) Rh between sulfide and silicate melts. The lines represent  $D_{Pd} = 5.5 \times 10^4$  and  $D_{Rh} = 2.7 \times 10^4$ . Temperature is in degrees celcius, the figure after temperature is  $\log f_{O_2}$ . See Table 2 for compositions of sulfide and silicate melts.

FIG. 7. Experimental data for (a) Ir, (b) Ru, and (c) Au between sulfide and silicate melts. The lines represent  $D_{Ir} = 3.1 \times 10^5$ ,  $D_{Ru} = 2.5 \times 10^3$ , and  $D_{Au} = 2.7 \times 10^4$ . Temperature is in °C, the figure after temperature is  $\log f_{O_2}$ . See Table 2 for compositions of sulfide and silicate melts.

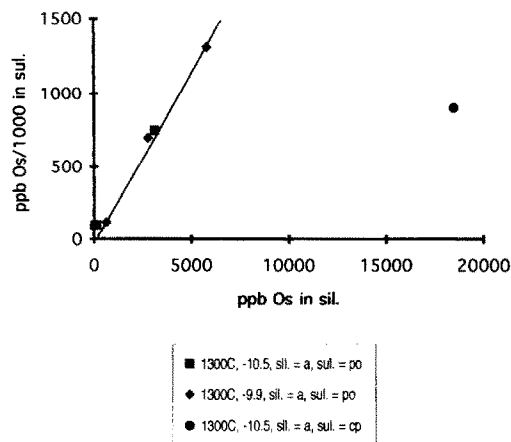


FIG. 8. Distribution Os between sulfide (Po) and silicate melts. The line represents  $D_{Os} = 2.3 \times 10^2$ . Temperature is in  $^{\circ}\text{C}$ , the figure after temperature is  $\log f_{O_2}$ . See Table 2 for compositions of sulfide and silicate melts.

ridge basalt in the glassy rim of a pillow of  $1.5$  to  $1.9 \times 10^4$ ,  $1.2$  to  $1.6 \times 10^4$  and  $>2.3 \times 10^4$ , respectively. Their value for Au is essentially the same as that given here, their value for Ir is a factor of 22 less, and their minimum value for Pd is a factor of 2.2 less than that determined in our study.

Thus, on the basis of the experimental data obtained, it follows that the segregation of sulfide melt from silicate liquid is an effective mechanism for concentrating PGE and Au concentration. Rather small amounts of segregating sulfide can significantly deplete silicate magmas and, at the same time, give rise to high PGE and Au concentrations in the sulfides, as observed in many deposits of the low-sulfide type. One aspect of our data remains puzzling. The partition coefficients determined by us for Os ( $2.3 \times 10^2$ ) and Ru ( $2.5 \times 10^3$ ) are, respectively,  $10^3$  and  $10^2$  lower than that determined for Ir ( $3.1 \times 10^5$ ). This would lead one to predict that sulfide segregation would give rise to strong fractionation of Ir from Os and Ru. This is never observed; observations on natural materials (for example BARNES et al., 1985) indicate that Ir, Os, and Ru are not fractionated from each other during processes thought to involve the segregation of a sulfide liquid. We have no solution to suggest for this enigma at the present time.

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