

Partitioning of Platinum Group Elements in the Fe-O-S System to 11 GPa and Their Fractionation in the Mantle and Meteorites

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The partitioning of minor amounts of platinum group elements (PGE: Ru, Rh, Pd, Os, Ir, Pt) in the Fe-O-S system has been investigated to 11 GPa. The marked fractionation of Pt from Pd in the presence of coexisting alloy and sulfide liquid, reported earlier for the Fe-Ni-S system at low pressure, is extended to high pressure. The experiments were carried out at 1000°–1375°C and 4.5–11 GPa with graphite capsules using 18-mm octahedral pressure cells in a uniaxial split-sphere multianvil apparatus. Oxygen fugacities corresponded to wustite stability. Phases present included sulfide liquid (close to M_3S_2 stoichiometry), FeS (troilite, pyrrhotite, HPP), alloys (PtFe, PtFeIr, OsIr, FePtIrOs, OsFeIr), and wustite. Partition coefficients for OsIr alloy/ $Fe_{1-x}S$ at 1200°C, 11 GPa are Os (1400), Ir (160), Pt (32), Ru (0.6), Rh (0.2), and Pd (0.04) and for FePtOs alloy/liquid at 1100°C, 8.5 GPa are Os (120), Ir (82), Pt (20), Ru (5.0), Rh (1.6), and Pd (0.1). Geochemical processes which involve separation of a metal-rich phase from sulfide therefore would result in fractionation of PGE, with Os, Ir, and Pt concentrated in the former phase and Pd in the latter. These results are further support for the presence of a discrete metal-sulfide liquid during the primary differentiation of planetary material and preclude an explanation for the fractionation of PGE in chromitites and mafic crustal rocks based on equilibrium partitioning between refractory alloys in residual assemblages and immiscible sulfide liquid in silicate melts.

INTRODUCTION

Recent study of the partitioning of the platinum group elements (PGE) in the Fe-Ni-S system at 1000°–1400°C and low pressure [Fleet and Stone, 1991] revealed distinctly different behavior for heavy (Os, Ir, Pt) and light (Ru, Rh, Pd) platinoids. Os, Ir, and Pt are preferentially concentrated in alloy phases, and Ru, Rh, and Pd are concentrated in sulfide phases. Pd, in particular, is depleted in alloys and relatively enriched in sulfide liquid. This marked fractionation of Pt from Pd in the presence of coexisting alloy and sulfide liquid was contrasted with the minimal fractionation of PGE in the primary differentiation of planetary material [Chou, 1978; Sun, 1982; Schmitt *et al.*, 1989] and of Pt from Pd in the generation of basic magmas in the upper mantle [e.g., Crocket, 1979].

Fractionation of PGE does indeed occur in nature and is revealed by plots of chondrite-normalized values [Naldrett *et al.*, 1979; Naldrett and Duke, 1980]. PGE patterns for chromitites from ophiolitic complexes [Page and Talkington, 1984] and other chromite-rich lithologies [e.g., Von Gruenewaldt *et al.*, 1989] are relatively enriched in Os, Ir, and Ru, whereas patterns for both mafic rocks and ore deposits associated with mafic and ultramafic intrusions are relatively enriched in Pt, Pd, and Au [Naldrett *et al.*, 1979; Naldrett, 1981]. Also, metal zoning is observed among some

Ni, Cu-sulfide ore deposits at Sudbury, Ontario, with Pt, Pd, and Au increasing away from the Irruptive hanging wall into the footwall [Naldrett *et al.*, 1982]. However, with the single exception of the study of Distler *et al.* [1977], these fractionations are not consistent with the existing laboratory experimentation on the partitioning of PGE in alloy/sulfide/silicate systems (reviewed by Stone *et al.* [1990] and Fleet and Stone [1991]).

Various aspects of the Fe-Ni-O-S system have been investigated up to about 20 GPa [Ryzhenko and Kennedy, 1973; Usselman, 1975; Urakawa *et al.*, 1987; Kato and Ringwood, 1989; Ringwood and Hibberson, 1990]. The most significant effects of high pressure for the present study are the progressive shift in the eutectic composition in the Fe-FeS system with pressure from 31.2 wt % S at low pressure [Jensen, 1942] to 23.6 wt % S at 10 GPa [Ryzhenko and Kennedy, 1973; Usselman, 1975] and the appearance of a high-pressure FeS phase of uncertain symmetry and structure [Mao *et al.*, 1981; King and Prewitt, 1982] at about 5.2 GPa (and 1000°C) [Usselman, 1975]. The room-temperature high-pressure phase has a distorted NaCl-type structure [Mao *et al.*, 1981]. Very recently, using a laser-heated diamond cell, Williams and Jeanloz [1990] have studied the melting relations in the Fe-S system at ultrahigh pressures (to 120 GPa) and have confirmed the eutecticlike behavior to core-mantle boundary conditions.

In the present paper the partitioning of PGE in the Fe-O-S system is investigated from 4.5 to 11 GPa (and from 1000° to 1375°C) to extend the experimental results of Fleet and

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TABLE 1. Experimental Details and Product Compositions

	Phase	Run Products								
		Fe	S	Ru	Rh	Pd	Os	Ir	Pt	Total
<i>S-Rich Assemblage</i>										
Starting Composition		59.9	34.4	1.04	0.97	0.96	0.92	0.96	0.94	100.0
Run 801* (1375°C, 5 GPa, 35 min)	bulk†	62.7	32.4	0.75	1.00	0.99	0.51	0.84	1.29	100.5
	FeS‡	58.2	36.1	1.01	1.11	1.08	0.71	0.98	0.22	99.5
	PtFe§	11.7	...	0.0	0.0	1.82	0.0	0.0	86.5	100.0
	FePt§	64.2	...	0.0	0.0	0.0	0.0	0.0	35.9	100.0
Run 851 (1100°C, 4.5 GPa, 150 min)	FeS	59.8	36.4	1.03	1.15	0.88	0.24	0.78	0.15	100.4
	PtFe	14.4	...	0.09	0.67	1.47	0.54	9.2	74.1	100.6
	OsIr	2.7	...	1.06	0.13	0.01	75.7	22.1	1.54	103.2
	OsFeIr	35.2	...	1.9	0.9	0.6	36.0	17.2	8.1	100.0
Run 934 (1100°C, 11.0 GPa, 100 min)	FeS	59.9	36.1	1.09	0.93	0.84	0.14	0.68	0.06	99.7
	s.d.	0.9	0.8	0.15	0.04	0.03	0.03	0.08	0.04	
	IrOs	7.2	...	2.32	0.25	0.15	42.1	45.6	2.43	100.0
	s.d.	1.6	...	0.41	0.05	0.04	7.0	6.1	0.71	
	OsIr	2.6	...	0.83	0.17	0.17	84.1	10.9	1.15	100.0
	s.d.	0.1	...	0.10	0.04	0.02	2.2	1.1	0.27	
Run 838 (1200°C, 4.5 GPa, 75 min)	FeS	60.8	36.1	0.98	0.95	0.26	0.0	0.0	0.0	99.1
	OsIr	3.0	...	1.62	0.25	0.14	68.8	24.0	1.87	99.8
	PtIrFe	15.8	...	0.40	1.32	0.94	1.10	18.7	59.4	97.7
Run 860 (1200°C, 8.5 GPa, 105 min)	FeS	60.3	35.9	1.08	0.83	0.67	0.0	0.0	0.0	98.8
	liquid¶	44.1	26.3	0.5	2.7	18.6	0.7	2.5	13.6	109.0
	PtIrFe	16.2	...	0.27	0.83	1.69	2.78	20.5	57.9	100.2
	OsIr	8.0	...	1.09	0.26	0.08	53.7	36.1	3.4	102.4
Run 930 (1200°C, 11.0 GPa, 150 min)	FeS	60.4	35.8	1.46	0.63	0.47	0.05	0.14	0.01	99.0
	liquid	53.4	27.2	1.0	3.6	11.5	0.5	2.1	6.0	105.2
	OsIr	4.38	0.2	0.91	0.13	0.02	71.2	23.0	0.32	100.1
	PtIrFe	20.0	0.0	0.82	1.44	1.22	6.2	33.0	36.4	99.1
<i>Fe-Rich Assemblage</i>										
Starting Composition		71.9	24.6	0.62	0.58	0.57	0.55	0.58	0.56	100.0
Run 863 (1000°C, 4.5 GPa, 225 min)	liquid	69.3	26.7	0.59	0.79	1.41	0.09	0.09	0.25	99.2
	FeS	63.6	35.8	0.04	0.0	0.0	0.0	0.03	0.0	99.5
	FePtIr	53.7	0.0	7.4	2.78	0.25	9.6	13.3	11.7	98.7
	FeOsIr	44.1	0.0	4.7	1.08	0.08	26.4	20.0	3.73	100.1
Run 877 (1100°C, 8.5 GPa, 150 min)	liquid	69.0	27.0	0.62	0.70	1.03	0.17	0.19	0.87	99.6
	FeS	63.7	36.2	0.07	0.0	0.0	0.0	0.0	0.0	99.9
	FePtIrOs	43.0	0.0	3.12	1.12	0.11	19.6	15.6	17.8	100.4
	OsFeIr	22.1	0.0	2.22	0.15	0.05	59.9	17.6	2.36	104.4
Run 972 (1100°C, 11.0 GPa, 180 min)	liquid	68.2	25.6	0.68	1.08	1.14	0.08	0.09	1.37	98.3
	FeS	63.9	36.3	0.16	0.05	0.02	0.06	0.01	0.03	100.5
	FePtOs	42.6	0.0	2.14	1.73	0.75	11.3	8.4	33.4	100.4
	OsFeIr	20.9	0.0	1.79	0.21	0.10	61.7	16.3	3.06	104.0
Run 938 (1200°C, 11.0 GPa, 140 min)	liquid	67.1	26.7	0.59	0.86	0.87	0.15	0.15	2.59	98.9
	s.d.	1.7	1.6	0.05	0.09	0.17	0.07	0.11	1.03	
	FeS	63.8	36.5	0.21	0.06	0.04	0.08	0.01	0.10	100.8
	s.d.	0.4	0.1	0.02	0.01	0.01	0.01	0.01	0.04	
	OsFeIr	20.8	0.0	1.44	0.27	0.16	62.3	12.6	2.48	100.0
	s.d.	2.0	...	0.03	0.04	0.10	2.3	0.9	0.38	

All run product values are in weight percent.

**T*, *P*, and time are given in parentheses for each run.

†Broad beam analysis of quenched liquid with minor equilibrium alloy.

‡Equilibrium FeS, monosulfide solid solution (Fe_{1-x}S) or HPP.

§Equilibrium alloy.

||Standard deviation.

¶Quenched equilibrium liquid.

Stone [1991] to upper mantle conditions and to evaluate their extrapolation to core-mantle differentiation.

EXPERIMENTAL PROCEDURES

The present series of experiments were based on two starting compositions, selected to correspond to the S-rich and metal-rich assemblages of Fleet and Stone [1991]. Starting materials were prepared from Fe and S (both 5*N* purity) and PGE metals (2–3*N* purity), as was done by Fleet and Stone [1991]. A PGE standard composition (PGS11) with

about 1 wt % of individual PGE was prepared from a mixture of PGE metals and iron monosulfide (FeS) contained in an alumina crucible within a sealed silica glass tube and heated at 1200°C. The products, consisting of troilite with dispersed alloy, were removed with a hardened steel drill bit and ground under methanol in an agate mortar. Starting material for the present S-rich assemblage (Table 1) consisted of PGS11 alone. For the Fe-rich assemblage (Table 1) the starting material consisted of PGS11 mixed in the ratio 6:4 with an iron-sulfide preparation containing 90 wt % Fe, 10 wt % S.

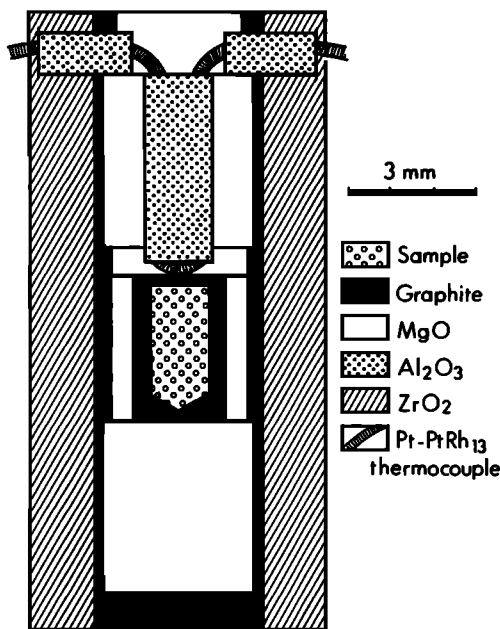


Fig. 1. Cross section of the cylindrical furnace assembly (un-compressed condition). A segmented graphite heater with wall thickness of 0.35 mm and 0.20 mm in the central and end segments, respectively, provides very low thermal gradients throughout the central segment (see text) and very steep axial thermal gradients over the end segments. The Al_2O_3 thermocouple rod (two-hole) and sleeves are fully sintered, and the MgO and Ca-stabilized ZrO_2 are semisintered.

The experiments were performed in a 2000-t uniaxial split sphere apparatus, using semisintered $\text{MgO}/5\%\text{Cr}_2\text{O}_3$ octahedral pressure media between 8 WC-anvils with truncated corners (18-mm octahedral edge lengths and 11-mm truncation edge lengths). The furnace assembly with a variable thickness graphite heater is shown in Figure 1.

The sample pressure was calibrated at room temperature with the phase transitions Bi(I-II) at 2.55 GPa [Hall, 1971] and Bi(III-V) at 7.7 GPa [Homan, 1975], and at 1000°C with the following phase transitions: quartz-coesite at 2.95 GPa [Bohlen and Boettcher, 1982], fayalite- γ -spinel at 5.27 GPa [Yagi et al., 1987], garnet-perovskite in CaGeO_3 at 6.1 GPa [Susaki et al., 1985], and coesite-stishovite at 9.1 GPa [Yagi and Akimoto, 1976]. The estimated pressure uncertainty is ± 0.5 GPa.

Temperature was measured with a Pt-PtRh₁₃ thermocouple, and no correction was used for the pressure effect on the EMF. The temperature was controlled to within $\pm 5^\circ\text{C}$ of the set point. All charges except 801 (Table 1) were preheated at 1375°C and run pressure for 6 min prior to slow cooling (20–30°C per minute) to the run temperature. The preheating step melted and homogenized the starting materials except for minor OsIr alloy which was apparently present in all runs at 1375°C (see below). The experiments were quenched by shutting off the power, and the temperature dropped from about 1200°C to 200°C in less than 1–2 s. Independent measurements of the axial temperature profile within the central segment of the furnace containing the sample capsule indicated that the center of the furnace (and sample capsule) was about 10°C hotter than the upper and lower ends of the central furnace segment (Figure 1).

The experimental products were analyzed with a JEOL

JXA-8600 electron microprobe, with the procedures reported by Fleet and Stone [1991]. The results are summarized in Table 1. Typical values for standard deviations of up to 12 replicate spot analyses are given in Table 1 for runs 934 and 938. Relatively large values reflect small grain size, low abundance, and inhomogeneity. Uncertainties in the partition coefficients are reflected in the number of significant figures reported in Table 2; these conservatively range from less than $\pm 10\%$ to greater than $\pm 50\%$ for elements present in abundances close to detection limits.

EXPERIMENTAL RESULTS

Products

The experimental products generally corresponded to those of the portion of the PGE-bearing Fe-Ni-S system investigated by Fleet and Stone [1991]. Sulfidation of MgO in the furnace assembly (Figure 1) was not anticipated under the present high-pressure experimental conditions [cf. Fleet and MacRae, 1987]. However, there was sufficient oxygen within the high-pressure cells to produce a significant quantity of iron oxide phases, particularly in the Fe-rich assemblage. Hence the investigated system changed from PGE-bearing Fe-S to PGE-bearing Fe-O-S. PGE were not detected by electron microprobe analysis in the oxide phases, and the principal effect of the addition of oxygen to the experimental system was to shift all alloy/sulfide equilibria to the FeS side of the eutectic in the Fe-FeS system [cf. Shunk, 1969]. FeS was the principal solid phase in all runs except 801 (1375°C, 5GPa), which was consistent with the bulk alloy/sulfide compositions and the elevation of the melting curves of FeS and pyrrhotite at high pressure [Ryzhenko and Kennedy, 1973; Williams and Jeanloz, 1990]. For the Fe-rich assemblage the bulk Fe-S composition corresponded to the field of Fe-rich liquid + FeS [Fleet and Stone, 1991, Figure 1] and these experiments quenched to liquid + FeS + iron oxide + alloy (see below). However, for the S-rich assemblage the bulk Fe-S composition was shifted beyond the influence of the eutectic and corresponded to the field of Fe_{1-x}S solid solution. These latter experiments therefore quenched to FeS + iron oxide + alloy (Table 1). The liquid reported for runs 860 and 930 is Pd and Pt rich and of uncertain origin and does not correspond to the Fe-rich liquid of the Fe-S system.

The iron oxide assemblage in the quenched products consisted of rounded bleblike grains of wustite in ragged intergrowth with minor magnetite (Figure 2a), which was usually in the form of a narrow grain margin. This texture is interpreted to represent wustite stability for the C-CO-CO₂ oxygen buffer during the conditions of the experiments, crossing into the magnetite stability field during the temperature quench [cf. Lindsley, 1976, Figure L-20]. The wustite of run 863 (1000°C, 4.5 GPa) has a composition of $\text{Fe}_{0.88}\text{O}$ and that of run 877 (1100°C, 8.5 GPa) a composition of $\text{Fe}_{0.94}\text{O}$, both within the composition range of wustite at low pressure [e.g., Lindsley, 1976] and high pressure [Knittle and Jeanloz, 1991].

A second problem encountered, and not anticipated when the experiments were designed, was contamination of the charge by Pt from the thermocouple. This is particularly evident in runs containing a large fraction of liquid and annealed at high temperature (runs 801, 877, 972, and 938).

TABLE 2. Partition Coefficients

Phase Assemblage	Run (°C, GPa)	Ru	Rh	Pd	Os	Ir	Pt
<i>S-Rich Assemblage</i>							
PtFe/FeS	851 (1100, 4.5)	0.1	0.6	1.7	2.3	12	490
	838 (1200, 4.5)	0.4	1.4	3.6			
	860 (1200, 8.5)	0.3	1.0	2.5			
	930 (1200, 11.0)	0.6	2.3	2.6	120	240	3600
OsIr/FeS	851 (1100, 4.5)	1.0	0.1	0.01	320	28	10
	934 (1100, 11.0)	0.8	0.2	0.2	600	16	19
	838 (1200, 4.5)	1.7	0.3	0.5			
	860 (1200, 8.5)	1.0	0.3	0.1			
(Pd, Pt)-Liquid/FeS	930 (1200, 11.0)	0.6	0.2	0.04	1400	160	32
	860 (1200, 8.5)	0.5	3	28			
	930 (1200, 11.0)	0.7	6	24	10	15	600
<i>Fe-Rich Assemblage</i>							
FePtOs/FeS	972 (1100, 11.0)	13	30	40	200		1000
OsFeIr/FeS	972 (1100, 11.0)	11	4	5	1000		100
	938 (1200, 11.0)	6.9	5	4	800		25
Liquid/FeS	972 (1100, 11.0)	4	20	60	1		50
	938 (1200, 11.0)	2.8	14	22	1.9	15	26
FePtOs/Liquid	863 (1000, 4.5)	13	3.5	0.2	110	150	47
	877 (1100, 8.5)	5.0	1.6	0.1	120	82	20
	972 (1100, 11.0)	3.1	1.6	0.7	140	93	24
OsFeIr/Liquid	863 (1000, 4.5)	8.0	1.4	0.06	290	220	15
	877 (1100, 8.5)	3.6	0.2	0.05	350	93	2.7
	972 (1100, 11.0)	2.6	0.2	0.09	770	180	2.2
	938 (1200, 11.0)	4.1	0.3	0.2	420	84	1.0
<i>Low Pressure*</i>							
Liquid/FeS	PGX11 (1000)	0.8	3	50			
FePt/Liquid	PGX11 (1000)	7	3	0.4		600	170
Fe/Liquid	PGX16 (1000)		60	1.3			

*Data are from *Fleet and Stone* [1991].

The thermocouple is in direct contact with the sulfide liquid in the polished section of run 938. Contamination by Rh from the thermocouple was not significant.

In the temperature range 1100°–1200°C the S-rich assemblage [cf. *Fleet and Stone*, 1991] consisted of an FeS phase, iron oxide (wustite under the experimental conditions), small amounts of alloy phases dispersed within the FeS phase (principally, OsIr, PtFe, IrOs, and PtIrFe), and (in runs 860 and 930) sulfide liquid. We did not detect any characteristic change in the composition of the FeS phase that was attributable to pressure in the pressure interval investigated. The S and PGE contents of FeS appeared to be independent of structural state. Phase transitions also have little effect on the melting curve of FeS [*Williams and Jeanloz*, 1990]. Therefore both the NiAs-type phase (which quenched to troilite or pyrrhotite) and the high-pressure phase stable at about 5.2 GPa [*Usselman*, 1975; *King and Prewitt*, 1982] are presently referred to collectively as “FeS”. OsIr alloy is heterogeneously distributed and not present in all sections, occurring as either spongy/porous masses or anvil-shaped grains partly rimmed by Pt alloys (Figure 2b). It appears that OsIr alloy is the liquidus phase in all of the present experiments and was present during the preheating stage (at 1375°C). Run 801 (1375°C, 5 GPa) yielded liquid with minor OsIr alloy and quenched to fine-grained nonstoichiometric FeS (Fe_{0.96}S) with Pt alloys; iron oxide precipitated at incipient grain boundaries. The bulk analysis for this run (Table 1) generally reproduces the starting composition except for loss of Os to OsIr alloy (which was not present in the polished section but was indicated by the low bulk Os content). The textures of runs 851 and 934, which were

cooled slowly from 1375°C to the 1100°C annealing temperature, are coarser-grained variants of the texture in run 801, with some segregation of alloys and oxides to the cooler ends of the charges [cf. *Herzberg et al.*, 1990]. The FeS phase of run 851 also contains fine-scale lamellae of OsFeIr alloy (Table 1) which appear to be a quench product. The 1200°C runs (838, 860, 930) contain coarse-grained FeS, and the alloy phases and oxide phase are segregated to the cooler ends of the charges. They also contain evidence of small amounts of a late Pd- and Pt-rich sulfide liquid that is apparently equivalent to the liquid reported at low pressure in the Fe-Ni-Pd-S system [*Distler et al.*, 1977]. The present electron microprobe analyses are not fully quantitative (Table 1) but indicate about 42–43 at. % S. In runs 860 and 930 this (Pd,Pt)-rich liquid had been squeezed to the edge of the charge (Table 1 and Figure 2c), bulging the enclosing graphite capsule of run 860, whereas in 838 it is present only as veinlets filling fractures within the lid to the capsule. The (Pd,Pt)-rich liquid may have been present under the experimental conditions, but formation during quenching cannot be excluded.

In runs of the Fe-rich assemblage [cf. *Fleet and Stone*, 1991] the products consisted of Fe-rich sulfide liquid, an FeS phase, iron oxide and alloy phases (principally, FePtIr and OsFeIr). In all four runs (Table 1) the phases segregated in response to the thermal gradient across the charges (about 10°C), with the FeS phases crystallizing at the cool ends and the sulfide liquid in the middle. Wustite and alloy phases tend to concentrate at the interface (Figure 2d). The alloy/sulfide liquid assemblage is generally similar to that in the metal-rich assemblage of *Fleet and Stone* [1991], except that the phases are less Fe-rich. Evidently, addition of oxygen

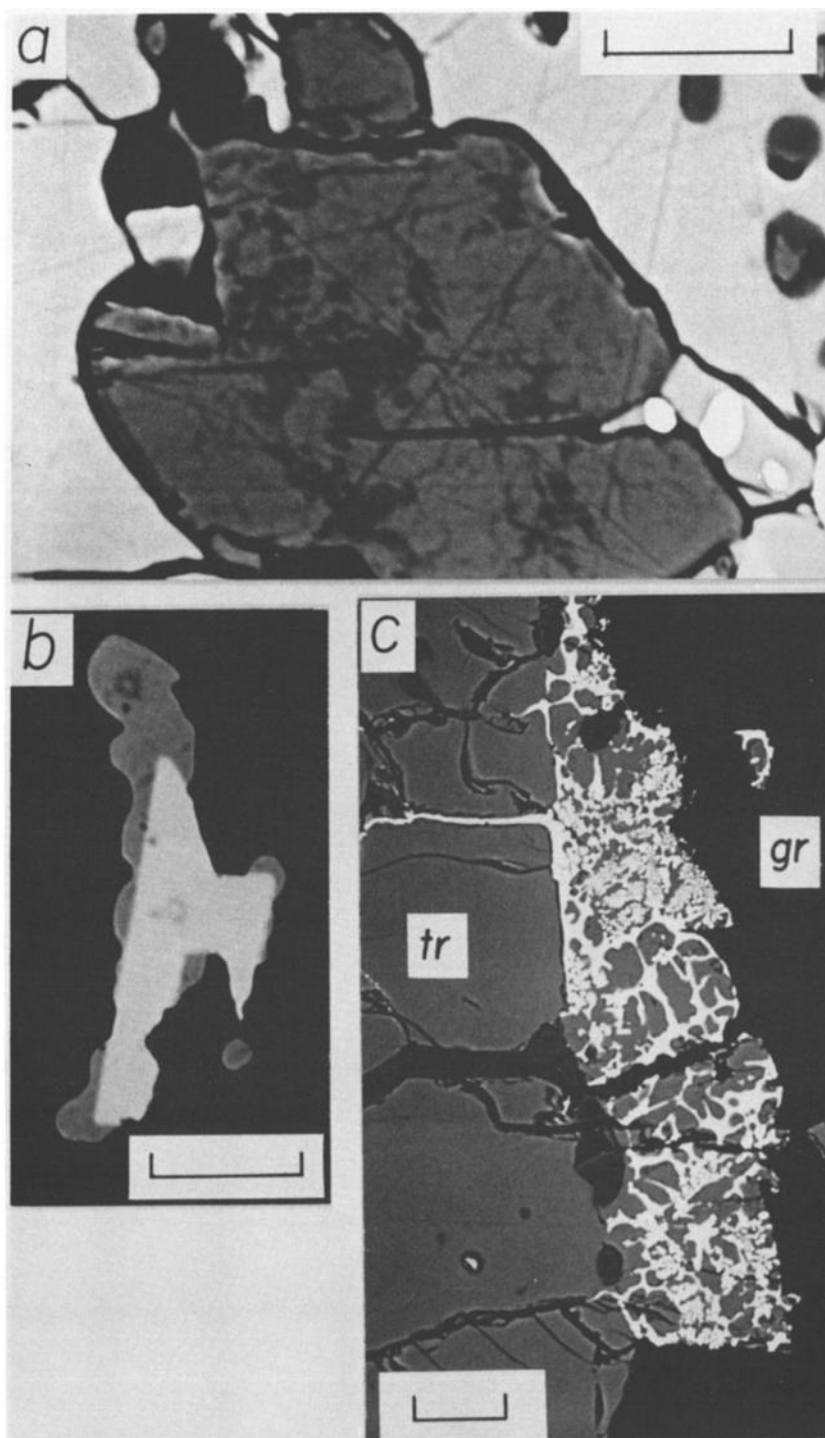


Fig. 2. Micrographs of textural relationships. (a) Wustite (grey) with ragged, patchy replacement by magnetite (dark grey), within pyrrhotite (light); run 851, scale bar is $10\ \mu\text{m}$. (b) OsIr alloy (light) partly rimmed by PtFe alloy (light grey), within pyrrhotite (dark); run 851, scale bar is $10\ \mu\text{m}$. (c) Unmixed late (Pd,Pt)-rich liquid adjacent to troilite (tr) and capsule wall (gr); run 860, scale bar is $20\ \mu\text{m}$. (d) Phase segregation in Fe-rich assemblage with troilite (tr) at cool end of charge, Fe-rich sulfide liquid (lq) in middle and wustite (dark blebs) and alloys (light); run 863, scale bar is $0.1\ \text{mm}$. (e) Rounded grains of FePtIr alloy (pale grey) with FeOsIr alloy core (light) and diffuse boundary, within troilite (dark); run 863, scale bar is $20\ \mu\text{m}$. (f) Rounded grains of FePtIrOs alloy (pale grey) with polygonal OsFeIr core (light), within troilite (dark); run 877, scale bar is $10\ \mu\text{m}$. Figures 2a–2c, 2e, and 2f are backscattered electron (BSE) images; Figure 2d is a plane-polarized, optical micrograph.

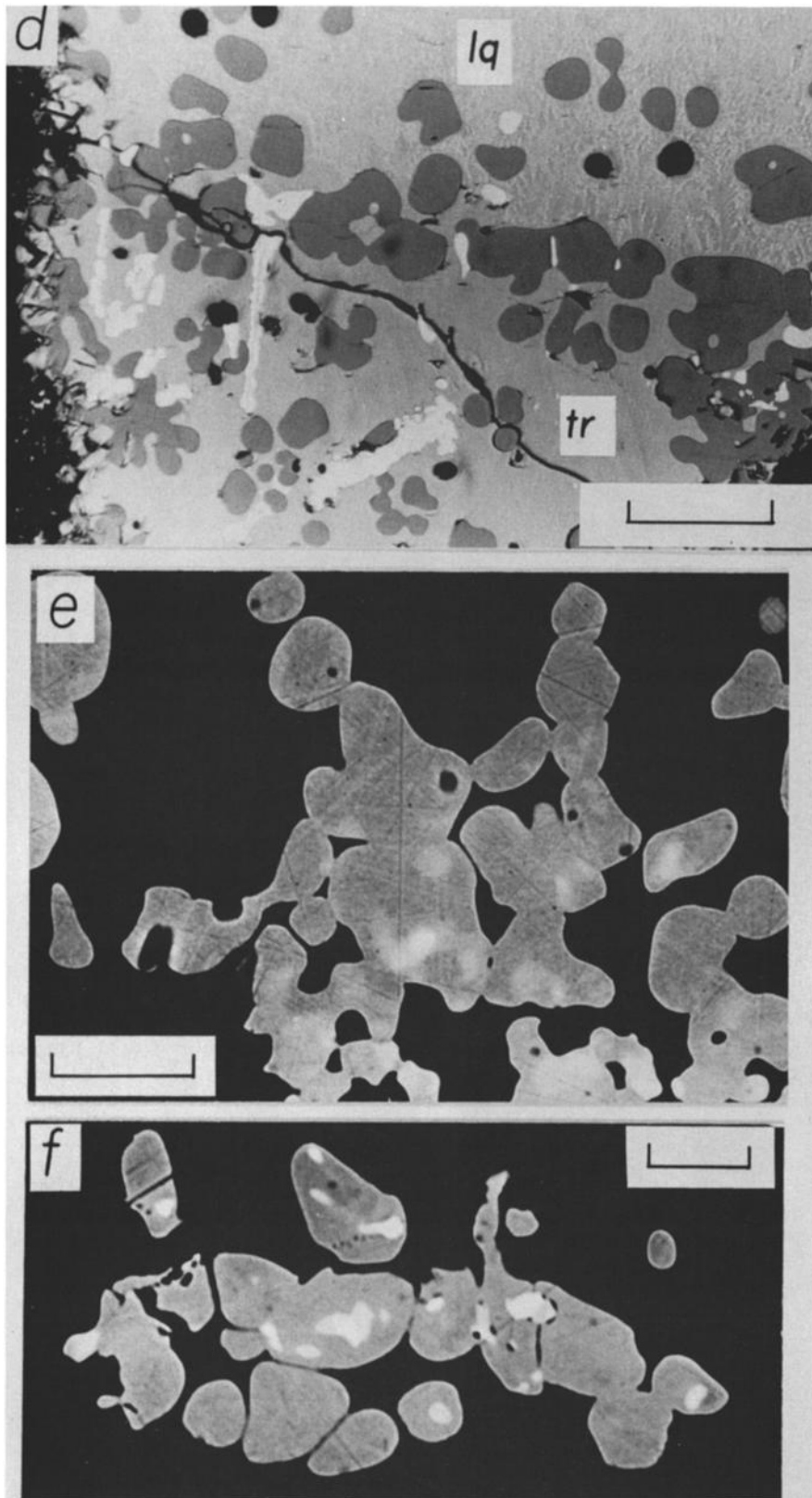


Fig. 2. (continued)

shifted the alloy/sulfide equilibria to a field of Fe_{1+x}S liquid + FeS + (Fe and PGE) alloy. As in the earlier study, the Fe-rich alloys are compositionally zoned, with an Os- and Ir-rich core. In run 863 (1000°C) the minor FeOsIr alloy core has a diffuse boundary with the FePtIr alloy phase (Figure 2e). This is very similar to the perplexing intergrowth texture of the PGE-bearing Fe-alloys at low pressure [Fleet and Stone, 1991]. The Fe-alloy textures of the earlier low-pressure study were seemingly dependent only on bulk composition and final annealing temperature, and not on duration of annealing (up to 14 days), preheating history, or quenching procedure. Os-rich alloy is a liquidus phase for the preheating conditions of the present experiments and those of Fleet and Stone [1991]. Quenched Os-rich alloy certainly tends to be inhomogeneous relative to the other experimental products (cf. standard deviations in Table 1) but, on balance, we believe that it remains a discrete stable phase at 1000°C. However, Os-rich alloy has a low rate of recrystallization so that further precipitation at this lower temperature takes the form of a fine-scale intergrowth with more Fe-rich alloy. On the other hand, at 1100°C the Os-rich alloy is in abrupt contact with surrounding Fe-rich alloy and clearly behaves as a discrete phase (Figure 2f). At 1200°C the only alloy phase present is OsFeIr in the form of fine-scale discoid grains, about 5 μm in length.

Carbon was not analyzed but may be present as a very minor constituent in the FePtIr alloy. Isolated flakes of graphite at the margins of the charges (e.g., Figure 2d) are present as inclusions in all phases (liquid, FeS , iron oxide, alloys). Therefore they represent capsule material physically incorporated into the charges, not carbon precipitated during quenching.

Partition Coefficients

The solubility of metals in alloys and sulfide phases is understandably dependent on bulk composition [e.g., Jones and Malvin, 1990], phase composition, nature of coexisting alloy phases, and proximity to the liquidus. Although the compositions of the experimental products (Table 1) do reveal a preferential concentration of Os, Ir, and Pt in alloy phases and Ru, Rh, and Pd in sulfide phases, as in the product compositions of Fleet and Stone [1991], this qualitative difference in affinity is somewhat obscured by the relatively high levels of Os, Ir, and Pt in the sulfide phases. The latter may be attributed to the dependence of the solubility of PGE in the FeS phase on S content and the generally lower metal/S ratios of the sulfide phases in the present series of experiments. For example, in the Fe-rich assemblage the FeS phase is slightly metal excess (S contents vary from 49.5 to 49.8 at. %), and Ru is the only PGE consistently present above background levels. In contrast, in the S-rich assemblage the FeS phase is metal (M) deficient (M_{1-x}S). The S content of the FeS phase in run 801 (quenched from 1375°C) is 51.0 at. %, and the FeS phase appears to readily dissolve most of the Ru, Rh, Pd, and Ir in the charge. The S content of the FeS phase decreases to 50.5–50.7 at. % in the 1100°C runs and to 50.2–50.3 in the 1200°C runs, and the solubilities of the PGE decrease proportionally. The preferential partitioning of Ru into Ni-bearing troilite at low pressure [Fleet and Stone, 1991] is probably also attributable more to a lower metal/S ratio rather than to the Ni substitution itself.

The increased concentrations of PGE in the sulfide phases allow an extended range of partition coefficients to be derived for coexisting phases in the present series of experiments (Table 2 and Figure 3). The strong siderophile affinities of Os, Ir, and Pt and chalcophile affinity of Pd are now clearly evident. For example, in the S-rich assemblage, partitioning between OsIr alloy and FeS in run 930 reveals a siderophile tendency of $\text{Os} > \text{Ir} > \text{Pt} \gg \text{Ru} > \text{Rh} > \text{Pd}$. In the Fe-rich assemblage, siderophile tendencies for run 877 are $\text{Os} > \text{Ir} \gg \text{Pt} \approx \text{Ru} > \text{Rh} > \text{Pd}$ for OsFeIr /liquid and $\text{Os} > \text{Ir} \gg \text{Pt} > \text{Ru} > \text{Rh} \gg \text{Pd}$ for FePtOs /liquid. In partitioning between crystalline FeS and sulfide liquid, Pt, Pd, Ir, Os, and Rh favor the liquid phase in the S-rich assemblage, and all PGE favor the liquid phase in the Fe-rich assemblage.

DISCUSSION

Phase Relations

The Fe-O-S phase relations of the present high-pressure experiments (1000° to 1200°C, 4.5 to 11 GPa) are consistent with previous studies [Ryzhenko and Kennedy, 1973; Usselman, 1975; Urakawa et al., 1987; Kato and Ringwood, 1989; Williams and Jeanloz, 1990]. Also, the present alloy phases are generally similar to those in the PGE-bearing Fe-Ni-S system at low pressure [Fleet and Stone, 1991]. In view of the lower Fe content of the present bulk alloy/sulfide fraction, the differences in alloy assemblage that do exist cannot be readily ascribed to the effects of high pressure. We have already noted that the composition of the FeS phase does not reflect the phase change at about 5.2 GPa [Usselman, 1975; King and Prewitt, 1982]. Evidently, the nonstoichiometry and chemical specificity of the as yet uncharacterized high-pressure FeS phase are similar to NiAs-type FeS , and this would be consistent with a NiAs-type derivative crystal structure for the former [cf. King and Prewitt, 1982]. The NiAs-type structure permits short metal-metal interactions, parallel to the *c* axis, which tend to stabilize transition-metal substituents. On the other hand, transformation to a NaCl-type derivative structure, as observed by Mao et al. [1981] at room temperature, would result in a diminished site preference for siderophile elements. In summary, the principal effect of these high pressures on the phase relations in the present complex PGE-bearing Fe-O-S system is to shift the minimum melting to more Fe-rich compositions.

The liquidus surface in the vicinity of the minimum-melting composition evidently has a very steep (dT/dX) gradient at high pressure. The liquids in the Fe-rich assemblage, which contain several wt % total PGE (Table 1), have S contents in the range 38.9–40.2 at. % and closely approximate M_3S_2 stoichiometry. Consequently, the high-pressure sulfide liquid in the vicinity of the minimum melting composition may be extensively prestructured. In addition, the two liquid compositions for the S-rich assemblage at 1200°C, which contain about 35 and 23 wt % total PGE when the analyses are normalized to 100% (Table 1), also have stoichiometries close to M_3S_2 . Interestingly, Williams and Jeanloz [1990] calculated that the eutectic composition in the pure Fe-S system increases in S content from a minimum at about 35 GPa to the 3:2 stoichiometry at about 120 GPa.

Partition Coefficients

Although the strong siderophile affinities of Os, Ir, and Pt and the chalcophile affinity of Pd are unchanged from the

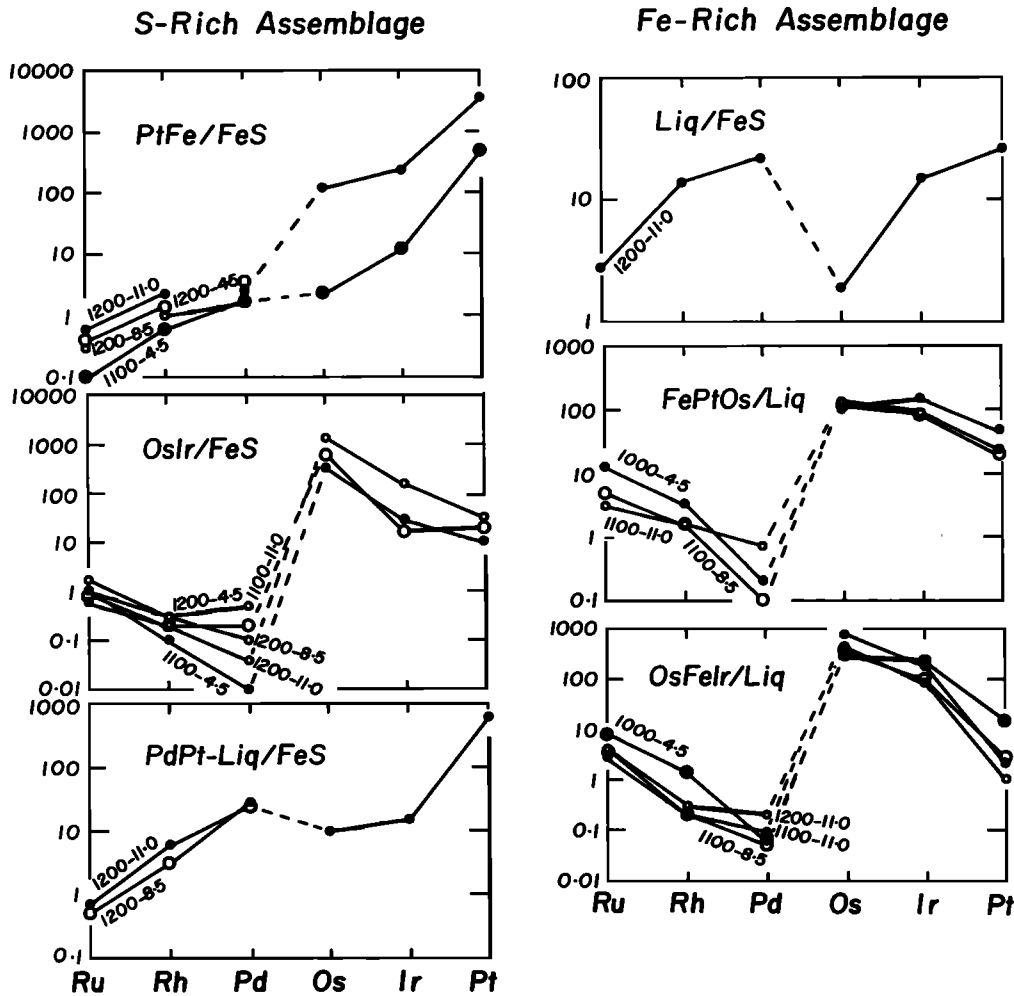


Fig. 3. Partition coefficients from Table 2 plotted on a logarithmic scale, emphasizing the separate chemical affinities of heavy and light platinumoids (strong siderophile affinities of Os, Ir, and Pt and chalcophile affinity of Pd). Platinum group elements are plotted in sequence of increasing atomic number.

low-pressure study of *Fleet and Stone* [1991], there are discernible differences in the compositions of corresponding alloy and sulfide phases at high pressure. Pressures of 4.5–11 GPa appear to increase slightly the coherence of Ru, Rh, and Pd in the sulfide fraction and to enhance the siderophile affinity of Os relative to Ir (Tables 1 and 2 and Figure 3). Also, high pressure appears to increase slightly the solubility of the light platinumoids in the sulfide liquids, and their partition coefficients (D values) for partitioning between alloy and sulfide liquid in the Fe-rich assemblage are correspondingly reduced. In summary, high pressure appears to enhance the distinct and separate chemical behavior of the heavy and light platinumoids first reported in the low-pressure study of *Fleet and Stone* [1991].

The extrapolation of partition coefficients for laboratory experimentation with minor amounts of PGE to natural assemblages was discussed by *Fleet and Stone* [1991]. The presently investigated range in temperature and pressure does fall below even a cratonic mantle geotherm at the high-pressure end [cf. *Boyd and Gurney*, 1986; *Wyllie*, 1988] but nevertheless extends the conclusions of *Fleet and Stone* [1991] to upper mantle temperature-pressure conditions. Also, the C-CO-CO₂ oxygen buffer is generally applicable to

redox conditions in the upper mantle [e.g., *Kadik*, 1990]. Extrapolation to the order-of-magnitude higher pressures and higher temperatures applicable to core-mantle differentiation in the Earth is problematical. However, this study has shown that the tendency for the light platinumoids to be chalcophile in S-bearing systems increases with pressure, at least to 11 GPa. The extrapolation from minor amounts of PGE to trace (parts per billion) levels is also problematical, especially since the presence of minor substituents may modify the solubility of trace metals.

Additionally, the light platinumoids (Ru, Rh, and Pd) are well known to behave as highly siderophile metals in meteorites, being coherent with Os, Ir, Pt, and Au [e.g., *Crocket*, 1969; *Chou*, 1978]. This apparent discrepancy with the present study may be rationalized in terms of the association of Ru, Rh, and Pd with the combined alloy/sulfide fraction of meteorites. However, the distribution of PGE between troilite and (Fe,Ni)-alloy in meteorites [e.g., *Crocket*, 1969] does not reflect the presently determined high-temperature, high-pressure partitioning. On the other hand, the troilite of meteorites is stoichiometric FeS with very minor atomic substitution [e.g., *Kruse and Ericsson*, 1988], and, presumably, its PGE contents reflect equilibration at lower temper-

atures and pressures. We suggest that the geochemical affinities of metals deduced from abundances in meteorites are not necessarily appropriate to geochemical processes at high temperatures and pressures.

Primary Differentiation of Planetary Material

The conclusion of *Fleet and Stone* [1991] on the consequences of alloy/sulfide partitioning studies for the primary differentiation of planetary material is unchanged. The present study is further support for the suggestion that core formation involves chemical equilibration between refractory mantle material and segregating metal-sulfide liquid [e.g., *Urakawa et al.*, 1987]. Platinum group elements are not significantly fractionated during core formation. Therefore primary differentiation of accreted planetesimals must involve the separation of a discrete metal-sulfide liquid from the silicate fraction. Early separation of a metal-rich liquid appears to be quite feasible [*Urakawa et al.*, 1987; *Williams and Jeanloz*, 1990], and indeed separation of core material should have commenced during the accretion phase itself [*Urakawa et al.*, 1987]. If a sulfide liquid separated from Fe-alloy during the early history of planetary bodies, the light platinumoids would have been fractionated from the heavy platinumoids, depleting Pd in the metal-rich phase.

In the inhomogeneous accretion model for the formation of the Earth, the low absolute abundances and chondritic ratios of PGE in the upper mantle are interpreted to indicate the presence of 1% of a chondritic component reflecting the last spike of accretion [*Chou*, 1978; *Jagoutz et al.*, 1979]. As noted by *Lodders and Palme* [1991], if the abundances of PGE were established by a late accretionary component, the upper mantle must have been previously essentially free of these elements. This would require very efficient scavenging of the highly siderophile elements by the metal-sulfide liquid during the early separation event. Alternatively, a subsequent phase of separation of metal-sulfide material may have occurred. For a subsolidus mantle a minimum-melting metal-sulfide liquid would tend to percolate downward toward the core [*Urakawa et al.*, 1987] (see below) removing excess Fe alloy from the early mantle. However, the present experiments show that a minimum-melting liquid in equilibrium with solid FeS would not result in uniform removal of PGE from the mantle. Additionally, separation of a higher temperature liquid, above the sulfide liquidus, would also fractionate PGE if a residual refractory alloy phase were present.

PGE in Partial Melts

The abundances of PGE in partial melts from the upper mantle are diminished by 1–2 orders of magnitude compared to source rocks but apparently only weakly fractionated [e.g., *Crocket*, 1979]. Platinum group elements are depleted in crustal mafic rocks and (Ni,Cu)-sulfide ore deposits in the approximate sequence $Os \approx Ir < Ru < Rh < Pt \approx Pd$, which corresponds to a positive PGE pattern [e.g., *Naldrett et al.*, 1979; *Naldrett*, 1981; *Page and Talkington*, 1984; *Von Gruenewaldt et al.*, 1989]. The principal discrepancy with the sequence predicted from experimental partitioning between alloys and coexisting sulfide liquid (approximately $Os < Ir \ll Pt < Ru < Rh \ll Pd$) lies in the coherence of Pt, which

is clearly associated with the other heavy platinumoids in the laboratory experiments.

Fleet and Stone [1991] suggested that the combination in the upper mantle of immiscible sulfide liquid in a partial melt with various refractory alloy phases in the residual assemblage is precluded by the laboratory results for alloy/sulfide partitioning. Pd would be enriched in the melt and Pt strongly depleted in it. Also, if an immiscible sulfide liquid were present in upper mantle partial melts, and alloys were not present in the residual assemblages, crustal mafic/ultramafic rocks would tend to be enriched in all PGE rather than depleted. Moreover, any scenario with an immiscible sulfide liquid associated with partial melt in the upper mantle is additionally disfavored on buoyancy grounds: with the approximate density values of 2.8 g cm^{-3} for partial melt, 3.3 for residual assemblage, and >4.0 for sulfide liquid, an immiscible sulfide liquid is more likely to percolate downward toward the core than rise with the partial melt. Indeed, the negative buoyancy of immiscible sulfide liquid argues against any model for genesis of magmatic sulfides that involves the slow rise of sulfide-laden magma, either within the upper mantle or more generally within the crust.

Beyond the constraints imposed by the present alloy/sulfide partitioning study, the influence of siderophile and/or chalcophile phases in controlling the abundances of PGE in partial melts is unclear at the present time. Processes involving separation of alloys from sulfide phases would certainly result in fractionation of PGE, but any successful model must include phases that concentrate PGE in the residual assemblage relative to the partial melt. Recent study of the partitioning of PGE between sulfide liquid and basalt melt [*Fleet et al.*, 1991] has revealed fairly uniform sulfide/silicate partition coefficients with values close to 10^3 . Thus for equilibrium partitioning, 1 wt % of sulfide liquid in the residual assemblage and containing 1 ppm individual PGE would limit the abundance of individual PGE in a partial melt to 0.1–1 ppb, the approximate concentration range for PGE in ocean floor basalts [*Crocket*, 1979]. However, this proportion of sulfide is far in excess of that commonly associated with the upper mantle [*Lorand*, 1988; *Peach et al.*, 1990].

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