

Platinum-iron alloy (Pt₃Fe) in kimberlite from Fayette County, Pennsylvania

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ABSTRACT

Samples of kimberlite from Fayette County, Pennsylvania, contain bleb-like aggregates of pyrrhotite, pentlandite, and chalcopyrite, which occur in olivine megacrysts (Fo₉₀). Two of the six sulfide blebs observed in olivine megacrysts, designated A and B, each contain a grain of Pt-Fe alloy (Pt₃Fe) in chalcopyrite within the bleb margin, as well as pentlandite, pyrrhotite, and trace amounts of Pd and Ru. The bulk Pt and Pd contents of sulfide bleb A are 27000 and 5000 ppm, respectively, whereas those of sulfide bleb B are 3000 and about 100 ppm, respectively.

The heterogeneous distribution of platinum-group elements (PGE) among sulfide blebs, nonchondritic bulk Pt-Pd ratios, and depleted bulk Ni contents are inconsistent with equilibration at high temperature and therefore with an origin by sulfide-liquid immiscibility, during either residence in the upper mantle or the early stage of kimberlite magmatism. Alternatively, late magmatic high-temperature subsolidus processes, such as degassing of S and sulfide metasomatism, before, during, or after emplacement of the kimberlite may have been important. The presence of PGM-bearing sulfide blebs in upper-mantle megacrysts and xenoliths is not necessarily evidence for PGE-enriched immiscible sulfide liquid in the mantle.

INTRODUCTION

In the crust of the earth, platinum-group elements (PGE) are concentrated in basic and ultrabasic rocks in quantities ranging from rare micrometer-sized bleb-like inclusions to ore bodies with abundant Ni-Cu sulfides (Naldrett and Cabri, 1976; Cabri and Laflamme, 1976). Sulfide blebs have been reported in numerous megacrysts and xenoliths from the upper mantle and, in one instance, platinum-group minerals (PGM) have been shown to be associated with them (Keays et al., 1981). Although some of the highest whole-rock PGE values have been reported from kimberlite (e.g., Crocket, 1981), to our knowledge, PGM have not been reported previously in association with sulfides in kimberlite.

In this paper, an occurrence of PGM in sulfide blebs within a sample of kimberlite from Fayette County, Pennsylvania (Hunter and Taylor, 1984), is described, and its origin is discussed. The PGM is platinum-iron alloy (Pt₃Fe) (e.g., Cabri and Feather, 1975) with minor Pd and traces of Rh and Ru. It occurs in chalcopyrite at the margin of two sulfide blebs that consist largely of pentlandite and pyrrhotite with minor or trace amounts of Pd and Ru. The PGM from Fayette County presents an opportunity to increase knowledge of the distribution of PGE (and the origin of PGM in upper-mantle rocks), which is crucial to an understanding of PGE abundance and concentration in the crust.

ANALYTICAL METHODS

The PGM and sulfide mineral grains were analyzed with a JEOL 8600 Superprobe at the University of Western Ontario, with pure metals of Pt, Pd, Ru, Os, Ir, and Rh, synthetic NiS and FeS, natural chalcopyrite, and natural olivine as standards. Analyses were made at 20 kV for 20 s or 20000 total counts, with a beam diameter of 2 μm and a beam current of 1 nA. The following analytical lines were used: FeKα, SKα, NiKα, CuKα, PtLα, PdLβ, RuLα, RhLα, OsLβ, IrLα and SiKα. Matrix corrections were made on-line using the Tracor-Northern 1989 version of the ZAF program, and corrections were made for minor interference from Pt and Rh. The analyzed phases were checked by qualitative EDS analysis with a count time of 30 s. Replicate analyses of the standards indicate an accuracy relative to the absolute element concentrations within 1 wt% for Fe, S, Ni, and Cu and within 1.5 wt% for Pt, Pd, Ru, and Rh. Bulk compositions of the sulfide blebs were derived from the modal proportions of the phases present.

Averaged PGM and sulfide compositions are in Table 1. The standard deviation for the averaged compositions of the phases is a maximum of 6.1 wt% for those elements present in amounts in excess of 40 wt%, a maximum of 2.9 wt% for those elements present in amounts between 10 and 40 wt%, a maximum of 2.8 wt% for elements present in the range of 1 to 10 wt%, and a maximum of

TABLE 1. Composition of platinum-iron alloy and coexisting sulfide phases in sulfide blebs A and B, Fayette County kimberlite

	Sulfide bleb A				Sulfide bleb B			
	pia	pn	po-pn	cp	pia	pn	po-pn	cp
	Raw data (wt%)							
Fe	11.61	25.93	45.61	28.26	17.96	30.35	57.65	30.33
S	4.34	34.86	37.95	33.02	18.75	33.80	39.56	33.94
Ni	1.09	37.68	13.22	1.37	1.02	33.96	3.16	1.59
Cu	3.73	0.18	0.00	30.18	15.30	0.00	0.00	29.74
Pt	63.90	0.00	0.00	0.00	8.61	0.00	0.00	0.00
Pd	2.96	0.59	0.00	0.00	0.26	0.00	0.00	0.00
Ru	0.38	0.51	0.27	0.00	0.00	0.16	0.19	0.00
Rh	0.31	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Os	n.d.	n.d.	n.d.	n.d.	0.00	n.d.	0.00	n.d.
Ir	n.d.	n.d.	n.d.	n.d.	0.00	n.d.	0.00	n.d.
Si	n.d.	n.d.	n.d.	n.d.	5.03	n.d.	0.00	n.d.
Total	88.32	99.56	97.04	92.83	66.93	98.26	100.56	95.59
n	8	4	3	4	5	3	2	3
	Recalculated (wt%)							
Fe	9.84	26.68	47.00	30.90	9.58	31.44	57.33	31.22
S	0.00	33.22	39.10	36.10	0.00	33.22	39.34	36.66
Ni	0.00	38.97	13.62	0.00	0.00	35.18	3.14	0.00
Cu	0.00	0.00	0.00	33.00	0.00	0.00	0.00	32.12
Pt	85.31	0.00	0.00	0.00	87.77	0.00	0.00	0.00
Pd	3.93	0.61	0.00	0.00	2.65	0.00	0.00	0.00
Ru	0.49	0.52	0.27	0.00	0.00	0.16	0.19	0.00
Rh	0.41	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Recalculated (at%)							
Fe	26.73	21.83	36.66	25.17	26.54	25.54	44.46	25.32
S	0.00	47.35	53.12	51.21	0.00	47.10	53.14	51.79
Ni	0.00	30.33	10.10	0.00	0.00	27.24	2.32	0.00
Cu	0.00	0.00	0.00	23.62	0.00	0.00	0.00	22.89
Pt	66.33	0.00	0.00	0.00	69.61	0.00	0.00	0.00
Pd	5.60	0.26	0.00	0.00	3.85	0.00	0.00	0.00
Ru	0.73	0.23	0.12	0.00	0.00	0.07	0.08	0.00
Rh	0.61	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Note: Sulfide bleb A is the sulfide bleb with the larger PGM grain; pia is platinum-iron alloy; pn is pentlandite; po-pn is intergrown pyrrhotite and pentlandite; cp is chalcopyrite; n is the number of analyses obtained.

0.1 wt% for elements present in amounts of less than 1 wt%. The relatively large maximum standard deviations for the elements present in amounts of less than 1 wt%, in particular, reflect variation in the extent of X-ray fluorescence interference from adjacent phases during repeat analysis.

The low totals obtained for most of the analyses are attributable to small grain size. S, Ni, Cu, and Si are present in analyses of the PGM, Cu in analyses of pentlandite, and Ni in analyses of chalcopyrite. Analyses of pentlandite contain an excess of S relative to nominal $(\text{FeNi})_9\text{S}_8$. The anomalies were not detected by qualitative EDS analyses, and therefore they are attributed to fluorescence excitation of elements concentrated in the surrounding sulfides and olivine. The analyses were corrected for these effects by subtracting the proportion of Si, Fe, S, Ni, and Cu present in the adjacent phases, subtracting the excess S from pentlandite, and normalizing totals to 100 wt%. It is assumed that the content of Cu in the pentlandite and Ni in chalcopyrite is minimal, which is consistent with the apparently low temperature of equilibration in the blebs (e.g., the lack of monosulfide solid solution and intermediate solid solution). The corrected compositions approximate the nominal stoichiometries, and therefore the correction procedure appears to

be acceptable (e.g., Stockman and Hlava, 1984; Augé, 1988).

PETROGRAPHY AND COMPOSITION

Sulfides in samples of the Fayette County kimberlite occur as (1) rare polyminerale sub-spherical blebs in or adjacent to fractures within olivine megacrysts (Fo_{90}) and phenocrysts (Fo_{88}), (2) pyrite within fractures crosscutting olivine grains, and (3) disseminated grains of pyrrhotite in the rock matrix, which locally constitute 10 modal percent of thin sections. The sulfide blebs range from < 1 to 70 μm in diameter and consist of a core of lamellar-intergrown pyrrhotite and pentlandite, which is surrounded by single-phase pentlandite and a variably developed margin of chalcopyrite. Locally, the chalcopyrite is associated with a PGM (Fig. 1).

The PGM has only been observed as two single grains, one each in two sulfide blebs, labeled A (Fig. 1a) and B within an olivine megacryst 2 mm in diameter. The single PGM grain in sulfide bleb A (Fig. 1b) is rectangular and $1 \times 3 \mu\text{m}$ in size. It is partly within chalcopyrite at the bleb margin, near a chromite grain, and partly within the surrounding olivine. The single PGM grain in sulfide bleb B (800 μm from bleb A) is about 0.5 μm in diameter and occurs at the contact between chalcopyrite in the bleb

margin and the surrounding olivine. Back-scattered electron images of the two PGM grains are similar in brightness, suggesting similarity in bulk composition.

The corrected microprobe analyses (Table 1) indicate that the PGM grains in sulfide blebs A and B contain 66.3 and 69.6 at% Pt, 73.3 and 73.5 at% Σ PGE, and 26.7 and 26.5 at% Fe, respectively, and therefore the grains are platinum-iron alloy (Cabri and Feather, 1975). Whether these grains are actually isoferroplatinum (primitive cubic) or ferroan platinum (face-centered cubic) (Cabri and Laflamme, 1981) is as yet undetermined. Also, the PGM grain in sulfide bleb A contains 5.6 at% Pd and trace amounts of Ru and Rh, and that in sulfide bleb B contains 3.9 at% Pd.

The corrected averaged analysis of the pentlandite in sulfide bleb A suggests that it contains approximately 0.3 at% Pd, 0.2 at% Ru, and 30.3 at% Ni, and it has a metal-to-sulfur ratio of 1.1. The pentlandite in the sulfide bleb B appears to lack Pd but contains 0.1 at% Ru and 27.2 at% Ni and has a metal-to-sulfur ratio of 1.1. Intergrown pyrrhotite and pentlandite in both PGM-bearing sulfide blebs contains about 0.1 at% Ru. Chalcopyrite in both of the blebs appears to be S-rich, slightly Cu-depleted relative to Fe, and devoid of PGE. The apparent excess of S in the chalcopyrite probably reflects fluorescence by nearby pyrrhotite. Platinum-group elements were not detected by either quantitative WDS or qualitative EDS electron-microprobe analysis of four other blebs found in olivine, including a large multiphase bleb in the olivine megacryst that also contains inclusions A and B, one pyrite inclusion in olivine, and nine grains of pyrrhotite ($\text{Fe}_{0.860}\text{S}$) found in the rock matrix.

On the basis of modal and electron microprobe analyses, the inferred bulk Pt and Pd contents of sulfide bleb A are 27000 and 5000 ppm, respectively, whereas those of sulfide bleb B are 3000 and about 100 ppm, respectively (Table 2). However, the area occupied by each mineral, particularly the PGM, is probably not representative of the volume of each in the blebs, and hence the bulk compositions reported in Table 2 are regarded as

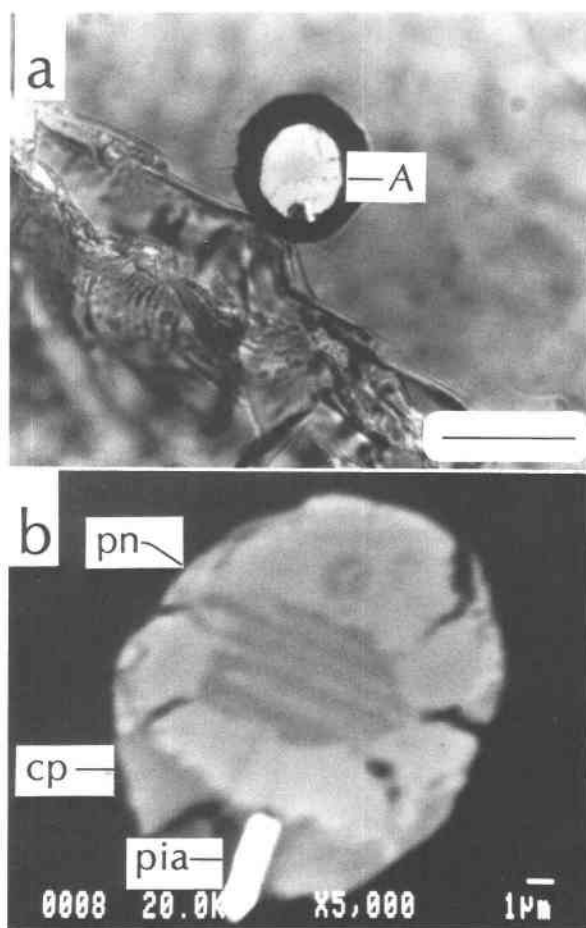


Fig. 1. (a) Photomicrograph of sulfide bleb A in fractured olivine megacryst. Subsurface extent of bleb A indicated by dark margin. Combined reflected and transmitted light, crossed polars, oil; scale bar represents 25 μm . (b) Back-scattered electron image of sulfide bleb A, consisting of intergrown pyrrhotite and pentlandite (center), single-phase pentlandite (light gray, labeled pn), chalcopyrite (medium gray, labeled cp), and platinum-iron alloy (white, labeled pia) in olivine megacryst.

TABLE 2. Estimated high-temperature sulfide compositions (wt%) and partition coefficients

	Sulfide bleb A					Sulfide bleb B				
	Bulk sulfide*	Cu-rich sulfide liquid	mss	D'	D''	Bulk sulfide**	Cu-rich sulfide liquid	mss	D'	D''
Fe	31.2	27.8	32.1	0.3	0.9	40.4	30.6	41.5	0.2	0.7
S	33.9	30.7	34.8	—	—	35.6	35.6	35.6	—	—
Ni	25.4	0.0	32.2	—	—	20.3	0.0	22.7	—	—
Cu	5.9	28.1	0.0	—	—	3.2	31.2	0.0	—	—
Pt	2.7	12.7	0.0	>8000	>1200	0.3	2.6	0.0	>8000	>200
Pd	0.5	0.6	0.5	10.9	1.3	0.0	0.1	0.0	>200	>8
Ru	0.4	0.1	0.5	1.3	0.2	0.2	0.0	0.2	<20	<0.1
Rh	0.0	0.1	0.0	>40	>6	0.0	0.0	0.0	—	—

Note: D' is the partition coefficient for the given element between Pt-Fe alloy and bulk sulfide; D'' is the partition coefficient for the given element between hypothesized Cu-rich liquid and mss.

* Bulk sulfide based on following modal analysis: Pentlandite, 57.9%; pyrrhotite-pentlandite intergrowth, 21%; chalcopyrite, 18.0%; and Pt-Fe alloy, 3.1%.

** Bulk sulfide based on following modal analysis: Pentlandite, 54.7%; chalcopyrite, 35.0%; pyrrhotite-pentlandite intergrowth, 10%; and Pt-Fe alloy, 0.3%.

only crude estimates. The bulk Pt and Pd contents of bleb B resemble those calculated for some sulfide liquids (Naldrett and Cabri, 1976; Sharpe, 1982; Naldrett, 1981), whereas those of bleb A are significantly greater than calculated values for the most PGE-enriched sulfide liquids (Campbell and Barnes, 1984). Moreover, the bulk Pt/Pd ratios (5.4 and 30.0, respectively) of the sulfide blebs are much larger than the chondritic value (1.8) (Crocket et al., 1967).

PETROGENESIS

Platinum-group minerals in sulfide blebs within megacrysts and xenoliths from the upper mantle (Keays et al., 1981), as well as in Ni-Cu sulfide ores (Cabri and Laflamme, 1976; Mostert et al., 1982), generally have been considered to form by the separation of an immiscible sulfide liquid from silicate magma. The Pt-Fe alloy commonly occurs as inclusions in chromite, pentlandite, and pyrrhotite and generally is considered to form at high temperature (e.g., at 1000 °C; Kingston and El-Dosuky, 1982; Mostert et al., 1982), although formation at relatively low temperature, about 600 °C, by desulfurization or hydrothermal alteration has been suggested as well (Kinloch, 1982; Schiffries, 1982; Stockman and Hlava, 1984). Commonly, PGM included in chalcopyrite are tellurides, bismuthides, arsenides, and stannides and are widely considered to have formed during cooling of the Cu-rich liquid residual remaining after crystallization of a monosulfide solid solution (mss) (Keays and Crocket, 1970; Cabri and Laflamme, 1976).

In the case of the Fayette County kimberlite, the heterogeneous distribution of Pt and Pd, nonchondritic bulk Pt-Pd ratios, and the occurrence of the PGM-bearing sulfide blebs in or adjacent to fractures, coupled with the sporadic occurrence of the sulfide blebs and depleted Ni content of the sulfide aggregates relative to the host olivine megacryst (Fleet and Stone, unpublished data), are inconsistent with equilibration at high temperature. Hence, it appears unlikely that the petrogenesis of the PGM and the sulfides involved sulfide liquid immiscibility during either residence in the upper mantle or the early stage of kimberlite magmatism.

Alternatively, the PGM-bearing sulfide blebs in the Fayette County kimberlite could have been formed by high-temperature fluids during degassing and sulfide metasomatism prior to (e.g., MacRae, 1979), during, or following (e.g., Stone et al., 1989) kimberlite emplacement, wherein equilibration of the PGE and Ni might not be expected. In this context, S released by degassing in the late-magmatic high-temperature subsolidus stage of the kimberlite could have infiltrated the megacrysts and xenoliths along fractures or other permeable pathways, and metals scavenged from the megacrysts, xenoliths, and matrix (interstitial silicate melt or glass) combined with S to form blebs of sulfide liquid which, locally, were relatively enriched in PGE, particularly Pt. Consequently, the presence of PGM in upper-mantle megacrysts and xenoliths, in general, does not necessarily con-

stitute conclusive evidence for PGE-rich immiscible sulfide liquid in the upper mantle.

Certainly, PGE may be mobilized by metamorphic and hydrothermal fluids (e.g., Leshner and Keays, 1984). Hydrothermal alteration phases, particularly serpentine, are present in the Fayette County kimberlite, and the presence of pyrite and disseminated pyrrhotite (above) is certainly evidence that sulfide metasomatism occurred during the later cooling history of the kimberlite. The pyrrhotite-pentlandite intergrowth and restriction of the chalcopyrite to the bleb margins, however, suggest a high-temperature history for the two PGM-bearing sulfide blebs, and sulfide blebs found in the olivine megacryst in general.

Little direct evidence has been recognized that indicates that the temperature of sulfide formation exceeded the sulfide solidus. The association of Pt-Fe alloy grains with chalcopyrite in blebs A and B suggests that Pt and Rh and much of the Pd and Ru in the precursor sulfide liquid may have been partitioned into a Cu-rich sulfide liquid residual of mss crystallization during cooling (cf., Keays and Crocket, 1970; Cabri and Laflamme, 1976). However, the calculated compositions for the possible Cu-rich residual sulfide liquids (Table 2) are inordinately enriched in PGE. Sulfide bleb A, in particular, contains about 13 wt% Pt and might not represent a stable liquid composition for the temperature range in question. Concentration of Pt as Pt-Fe alloy grains in chalcopyrite is consistent with the incompatibility of Pt in solid solution in pentlandite, pyrrhotite, and chalcopyrite (Cabri and Laflamme, 1981; Makovicky et al., 1986). Occurrence of the PGM as Pt-Fe alloy in the Fayette County kimberlite rather than as telluride, bismuthide, stannide, or arsenide (cf., Cabri and Laflamme, 1976; Schiffries, 1982; Kinloch, 1982; Mostert et al., 1982) might reflect the bulk rock composition (e.g., paucity of Te, Sb, Bi, As, etc., in kimberlite), lack of a large-scale hydrothermal system, and a relatively high temperature of formation.

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