
The Formation of Pt and Ir Minerals in Base Metal Sulfides: Effect of Sulfur Fugacity and Composition

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There are a number of examples of PGE ore deposits where it has been proposed that after sulfides have collected PGE to form the proto-ore, sulfur has been removed from the system by vapour or by fluids [e.g. UG-2 and Merksky Reef (Gain, 1985; Merkle, 1992; Barnes and Maier, 2002)]. This removal of S by vapour should change the mineralogy and potentially remove some metals. Another example where S loss could be important is from entrained sulfide droplets during magma ascent (Barnes et al., 2002). This could occur because S solubility decreases with pressure (Mavrogenes and O'Neill, 1999). Vapour transport of S and possibly other metals is potentially important when S is transferred from country rocks into an intrusion [e.g. Duluth (Ripley and Alawi, 1998); Noril'sk (Grinenko, 1985)]. With this in mind we have started a series of experiments to investigate the possibility of S and metal transport in vapour. Initial experiments, by Baker et al. (2001), show that S, Pt, Cu and Ni can be transferred by vapour at 1100°C and 1300°C. The present experiments were carried with the aim of investigating the role of sulfur fugacity on the formation of platinum-group minerals (PGM) with variable bulk base-metal (BM) ratio.

The system Fe-Ni-Cu-S was studied with 0.2 wt.% of Pt and Ir added and sulfur fugacity buffered by pyrrhotites of different composition. Experiments were performed using the "tube in tube" technique to control and determine sulfur fugacity of the sample by the pyrrhotite method of Toulmin and Barton, 1964. The initial Pt- and Ir-bearing sulfide assemblages were synthesized by melting of a mixture of pure elements at 1200°C in vacuum. In the first series of experiments, the sulfur fugacity of the samples equilibrated at 1000°C and 980°C was determined by use of pyrrhotite as the indicator. In these experiments, the quantity of powdered pyrrhotite (Po) placed inside the evacuated and sealed silica glass tube in the open inner tube, was much less than that of the main charge. Sulfide assemblages were initially undersaturated in Pt and Ir at the run temperature and all 0.2 wt.% of PGE added were dissolved in base-metal sulfides. In the second series of

experiments pyrrhotites with variable Fe/S ratio were used to buffer the sulfur fugacity of the samples, and 30-40 times more buffer than sample was used to ensure that the pyrrhotite remained constant in composition and not modified by S or metal transport in the vapour phase. Two pyrrhotite buffers were used: Fe (63.5 wt.%), S (36.5 wt.%) and Fe (61.2 wt.%), S (38.8 wt.%). The samples were then equilibrated at 1000°C or 980°C for 7 days and quenched in an ice salted water.

The products of experiments were studied by electron microprobe. The sulfides CuFeS₂ and FeS as well as Ni, Pt, Ir metals were used as standards. The analytical conditions were as follows: accelerating voltage 20 kV, beam current 30 nA, counting times up to 120 s, spot diameter of 2 µm. A defocused electron beam of 30 µm in diameter was used to determine the bulk compositions of sulfide liquid and base-metal sulfides containing exsolved PGM when the size of the metals was too small to analyze them individually. The detection limits of Pt and Ir were <0.1 wt.% depending on PGE-composition of the phase analyzed. The conditions and main results of three most representative experiments are listed in the table and in the back-scattered images of the samples synthesized.

The experiments show that the sulfur fugacity plays an extremely important role in the formation of individual PGE minerals as the variation of f_{S_2} directly controls the bulk metal/S ratio of sulfide assemblages and leads to a change in stable BM sulfides and PGE minerals. Thus, the Cu-, and Ni-free sample FS1 at 1000°C represents a homogeneous high-temperature pyrrhotite containing 0.16 wt.% of Ir and 0.18 wt.% of Pt in solid solution (Table 1). The estimated sulfur fugacity of the sample is -0.02 ± 0.35 (in $\log f_{S_2}$). Decreasing $\log f_{S_2}$ to -0.3 does not change the phase relationships in the sample, but when the sulfur fugacity is reduced to -4.8 , the metal/sulfur ratio (atomic) of pyrrhotite changes from 0.9 to 0.98 and lamellar PGM exsolutions appear in the matrix of pyrrhotite (Fig. 1B). The electron microprobe analysis of the exsolutions shows that

they represent Fe-Ir-Pt alloy but their small size did not allow quantitative analysis. It is interesting that although when the sample FS1 is quenched from 1000°C it consists only of PGE-bearing pyrrhotite, the same sample after slow cooling from melting to room temperature contains large grains of cooperite (PtS) in association with Po (Fig. 1A). This is interpreted to mean that Pt can be dissolved at high temperature in the sulfur-rich pyrrhotite, but it will exsolve from the matrix of Po in the form of cooperite at lower temperature. The euhedral well shaped crystals belies the secondary nature of PtS, showing that subsolidus reequilibration and

recrystallization could produce the PGM crystals very similar to those crystallized directly from sulfide liquid.

The bulk composition of sample FS2 contains 2 wt.% of Cu and Ni and after slow cooling consists of monosulfide solid solution (Mss), intermediate solid solution (Iss) and Pt-rich exsolutions in the matrix of Mss. In contrast, when quenched from 980°C, this sample consists of homogeneous PGE-bearing Mss and is characterized by a slightly lower, -0.2 (in log f_{S_2}), sulfur fugacity when compared with Cu-, and Ni-free sample FS1 at 1000°C.

Table 1. Results of experiments.

Sample	T, °C	-lg f_{S_2} , atm.	Phase association	Chemical composition, wt. %						
				Fe	Cu	Ni	Ir	Pt	S	Total
FS1			Starting	60.6			0.2	0.19	39	100
FS1-0	Slow cooling	-	Fe _{1-x} S	59.6			1.52	0.17	38.8	100.1
			PtS	1.3			bdl	83.7	14.2	99.2
FS1-1	1000°C	0.02	Fe _{1-x} S	60.7			0.16	0.18	38.9	99.9
FS1-3	1000°C	0.3	Fe _{1-x} S	61			0.18	0.17	38.8	100.1
FS1-2	1000°C	4.8	Fe _{1-x} S	63.4			bdl*	bdl	37	100.4
			Lamellar PGM exsolutions in the matrix of Fe _{1-x} S							
FS2			Starting	56.7	2	2	0.2	0.19	38.9	100
FS2-0	Slow cooling	-	Mss	57.8	0.9	2.3	0.21	bdl	39.2	100.4
			Iss	39.8	26.1					
			Pt-rich exsolutions in the matrix of Mss							
FS2-1	980°C	0.2	Mss	57.1	3.1	2	0.15	0.19	38.5	101
FS2-3	980°C	0.6	Mss	57.3	2.7	2	0.21	0.2	38.3	100.7
			PGM exsolutions in the matrix of Mss							
FS2-3	1000°C	1	Mss	54.9	3.6	4.2	0.15	0.1	37.9	100.9
			Mss + PGM exsolutions	53.7	4.8	4.1	0.17	0.21	37.8	100.8
FS2-2	980°C	6.2	Mss	62.3	1.3	0.4	bdl	bdl	36.7	100.7
			PGE alloy	45.3	0.4	2.5	28.5	23.7	0	100.4
			Liquid	56.3	12	5.4	bdl	bdl	30.6	104.3
FS3			Starting	52.8	4	4	0.2	0.2	38.7	100
FS3-0	Slow cooling	-	Mss	55.6	0.9	4.5	0.23	bdl	39.3	100.5
			Mss + PGM exsolutions	54.7	1.2	4.5	0.24	0.29	39.2	100.13
			Iss	39.9	25.8	0.6	bdl	bdl	35.4	101.7
FS3-1	1000°C	0.1	Mss	53.7	4.4	4	0.17	0.17	38.5	100.9
FS3-3	1000°C	0.6	Mss	57.2	2.53	2.1	0.2	0.17	38.4	100.6
FS3-2	1000°C	4.9	Mss	61.8	3	0.8	bdl	bdl	36.4	102
			PGE alloy	36	1.2	2.9	32	28.4	0.1	100.6
			Liquid	55.6	11.7	6.7	bdl	bdl	30.5	104.5

*bdl - below the detection limits.

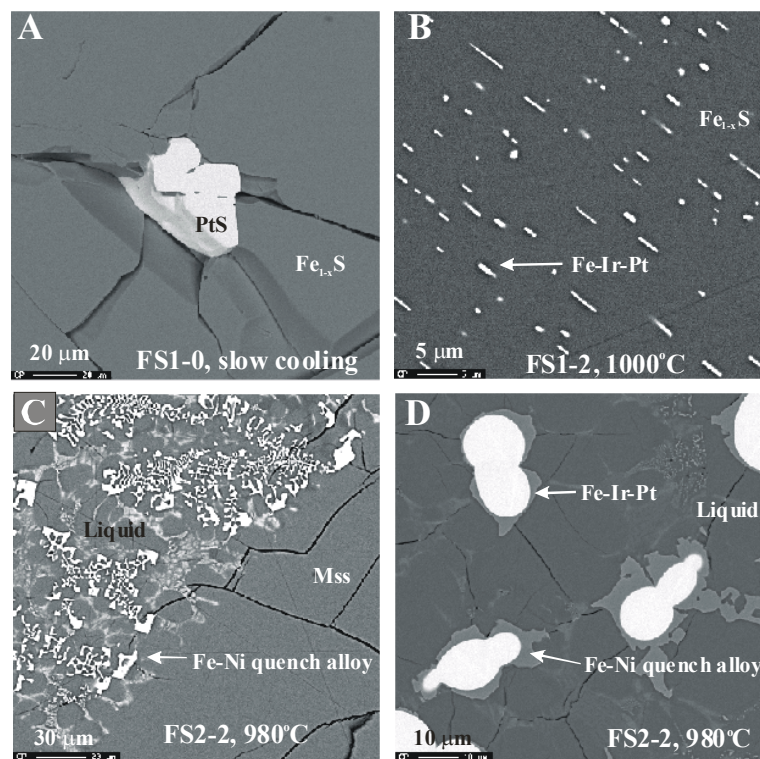


Figure 1. BSE images.

When the sulfur fugacity was reduced to -0.6 (in $\log fS_2$) at the temperature 980°C, and to -1 at 1000°C, very tiny exsolutions of higher mean atomic number have appeared on the boundaries of the grains of Mss. Slightly higher Pt and Ir concentration in the analyses of Mss made with a defocused electron beam demonstrates enrichment in PGE of these exsolutions. It was, however, impossible to determine whether the exsolutions are PGE-bearing alloys or sulfides.

The decrease of sulfur fugacity down to -6.2 (in $\log fS_2$) at the temperature 980°C leads to critical changes in the phase relationships as sulfide liquid and Fe-Ir-Pt alloy form in association with monosulfide solid solution (Table 1, Fig. 1C-D). A third composition was investigated that is richer in Cu and Ni (4 wt.%), sample FS3. This sample produces the same results as FS2 described above. The only difference is that it is necessary to reduce the sulfur fugacity to -4.9 (in $\log fS_2$) to provoke the formation of the Fe-Ir-Pt alloys and sulfide liquid, which is more than one order higher than the fS_2 needed for the formation of Mss+alloy+liquid association in poorer in Cu and Ni sample FS2.

To summarize, the bulk metal/S ratio of the sulfide association can be easily affected by

changes in the sulfur fugacity. The dependence of S composition of sulfide on sulfur fugacity in the mineralizing system is extremely important in the light of recent studies showing the dependence of Mss/L PGE partition coefficients on sulfur content of the system (Fleet et al., 1993, Barnes et al., 1997, Li et al., 1996). Reduction in the sulfur fugacity of a sulfide can produce the exsolution of Pt and Ir from base-metal sulfide solid solutions in the form of PGE-alloys and, possibly, sulfides. Alternatively, reduction of the sulfur fugacity may provoke melting of the sample with the formation of association [Mss + sulfide liquid + Fe-Ir-Pt alloy] stable in low-sulfur part of the system Fe-Ni-Cu-S. It is interesting to note that this liquid is Cu rich and we speculate that in natural samples this Cu-rich liquid could migrate away from the alloys and Mss thus spatially decoupling the Ir, Pt and Cu, as observed in the Merensky Reef (Barnes and Maier, 2002). Other examples may be Lac des Iles (Watkinson and Dunning, 1979), Platinova reef, Skaergaard (Andersen et al., 1998). The question is whether or not reduction in sulfur fugacity resulting in the crystallization of PGE minerals occurs under natural conditions. And if so, which natural processes control the sulfur fugacity and play the

role of fS_2 buffer, similar to pyrrhotite buffer in the present experiments. The two most likely mechanisms responsible for reducing sulfur fugacity in natural sulfide ore are the volatile transport of sulfur in the direction of undersaturated sulfur magma (Willmore et al., 2000) and fS_2 buffering by oxygen activity (Naldrett, 1969; Kress, 1997).

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