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## Collectors of Pt, Pd and Rh in an S-poor Fe-Ni-Cu-sulfide system at 760°C: Experimental Data and Application to PGE Deposits

Anna Peregoedova<sup>1</sup> and Maryse Ohnenstetter<sup>2</sup>

<sup>1</sup>Institute of Mineralogy and Petrography, RAS Novosibirsk, Russia

<sup>2</sup>Centre de Recherches Pétrographiques et Géochimiques, CRPG, France  
e-mail: aperegoe@eps.mcgill.ca

We present results of a study of PGE distribution in the Fe-Ni-Cu-S system at intermediate temperatures at which a sulfide liquid no longer exists. We chose to investigate a metal-rich section of the system Fe-Ni-Cu-S, corresponding to the metal/S ratio of pentlandite (Me<sub>9</sub>S<sub>8</sub>), at 760°C. At this temperature, it is unknown whether pentlandite (Pn), the main collector of light platinum group elements in natural Cu-Ni deposits, appears as a magmatic phase or during subsolidus reaction. Two sets of experiments were performed: the first, without PGE, was carried out to determine the sulfide assemblages stable at 760°C in the compositional field of interest; the second, with PGE added, was done to study how Pt and the light PGE (Pd and Rh) partition into these phases. PGE were added in minor amounts (0.5 - 1 wt. %) to be close to natural analogs while allowing the use of the electron microprobe technique to analyze run products. Microscopic examination, electron microprobe, thermal analysis and X-ray diffraction were also used to study the compositions of associated phases and the temperature of the reactions. The sulfur fugacity ( $f_{S_2}$ ) of the samples was determined with the use of a “tube-in-tube” technique and pyrrhotite as indicator.

### Experimental results

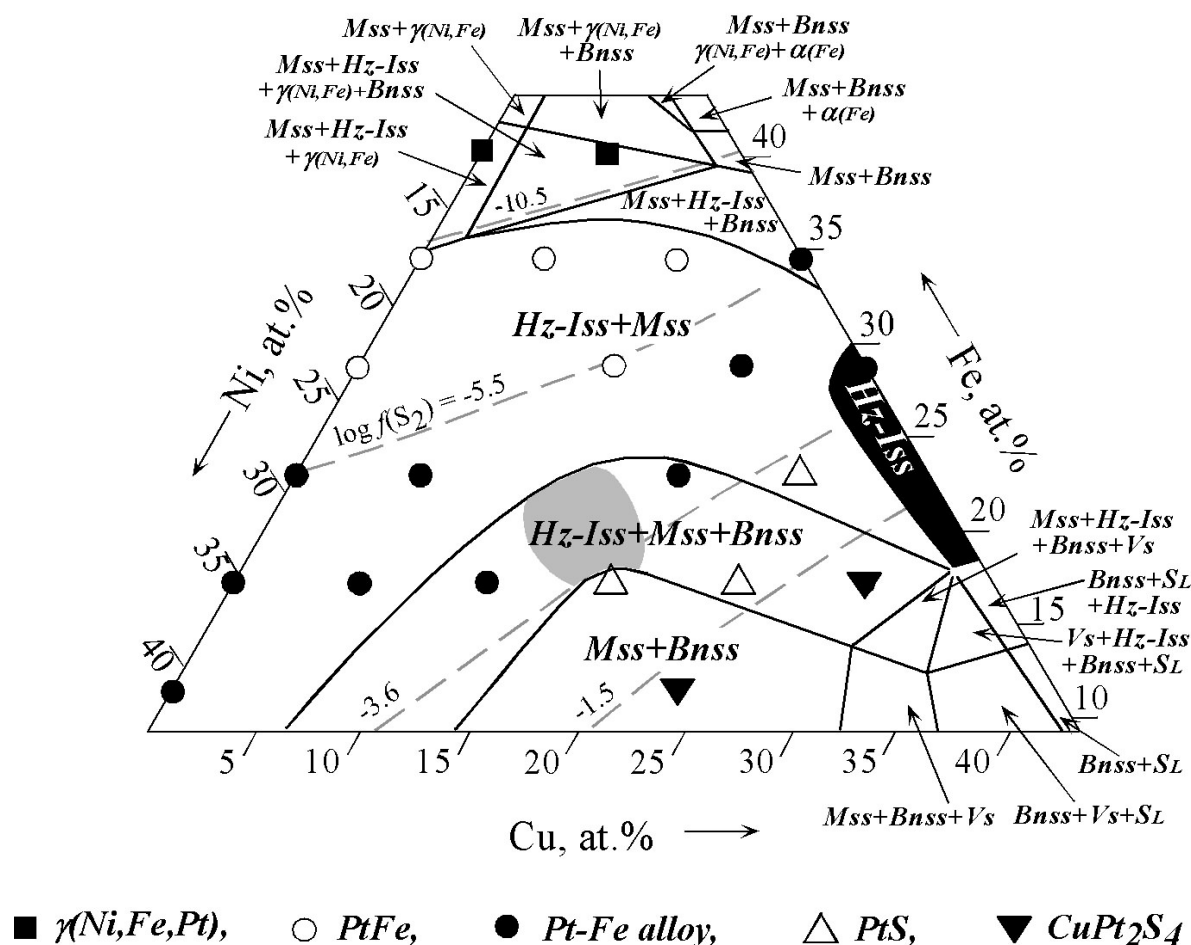
One important result of this study bears on the existence of a high-temperature Hz-Iss phase that coexists with monosulfide solid solution (Mss) in most of the Me<sub>9</sub>S<sub>8</sub> section at 760°C (Fig. 1). The composition of the Hz-Iss phase, a complete range between heazlewoodite (Ni,Fe)<sub>3±x</sub>S<sub>2</sub> and intermediate Cu<sub>1±x</sub>Fe<sub>1±y</sub>S<sub>2</sub> solid-solutions, changes from Ni-rich to Cu-rich according to the initial proportion of base metals. No evidence of primary crystallization of Pn from sulfide liquid was found in the part of the system Fe-Ni-Cu-S. Pn only forms where Mss reacts with the Hz-Iss solid-solution during quenching. Pn appears at subsolidus temperatures lower than 760°C as shown by Cu-containing sulfide associations. Such Pn, together with secondary alloys or sulfides, may collect the light PGE exsolved from their high-temperature collectors (Mss, Hz-Iss or Bn<sub>ss</sub>).

The phase assemblage and the mineral composition obtained from the experiments can be expressed as a function of  $f_{S_2}$ , as shown in Table 1. Under conditions of constant sulfur content in the section Me<sub>9</sub>S<sub>8</sub>, the starting proportions of the base metals (Fe, Ni and Cu) control the sulfur fugacity and the formation of the different PGE-phases. Pt forms Pt-Fe alloys in association with Fe-rich base-metal sulfides (BMS) and Pt-sulfides in Ni- and Cu-rich assemblages. The morphology of platinum grains is usually characterized by well-developed faces, testifying to their direct crystallization from a sulfide liquid, commonly before the crystallization of Mss.

In contrast to Pt, Pd is distributed mainly among the sulfide solid-solutions, with the quaternary solid-solution Hz-Iss being its principal collector (Table 1). In only the most Fe-rich part of the Me<sub>9</sub>S<sub>8</sub> section, a (Ni,Fe,Pd) alloy (up to 18.1 at.% Pd) occurs, and the in this case partitioning of Pd into the base-metal sulfide solid-solutions is very limited. Similarly, a Pd(Cu,Fe) alloy is formed in Fe-rich bulk compositions lying on the Fe<sub>9</sub>S<sub>8</sub>-Cu<sub>9</sub>S<sub>8</sub> join. The Pd-content of Hz-Iss ranges from 0.1 at.% up to 1.5 at.%, increasing as Ni and Cu increase in Hz-Iss. The morphology of Pd-bearing phases exsolved from the Hz-Iss matrix indicates that Pd entered into the Hz-Iss structure at 760°C. Exsolved Pd-bearing phases include Pn (Pd up to 1 at.%), lamellar complex (Pd,Cu,Fe,Ni) sulfide and a Pd(Cu,Fe) alloy that occurs along boundaries of the macrograins of Hz-Iss. Besides Hz-Iss, Pd also partitions into Mss; up to 0.9-1.1 at. % of Pd was fixed in Ni- and S-rich Mss from the assemblages richest in Cu, where an equal distribution of Pd between Mss and Hz-Iss is observed. Pd was not found in bornite solid-solution, but lamellar exsolution-induced blebs of Pd-rich phases in the Bn<sub>ss</sub> matrix indicate its capacity to contain some Pd at elevated temperatures.

Rhodium is characterized by a dual behavior. Like palladium, it partitions readily into the BMS, but at conditions of very low or very high  $f_{S_2}$ , it forms Rh minerals, as does platinum (Table 1). (Fe,Rh) alloys are stable when  $\log f_{S_2}$  is equal to or less than -10.5 whereas sulfides (CuRh<sub>2</sub>S<sub>4</sub> or (Rh,Ni)<sub>2</sub>S<sub>2</sub>) appear when  $\log f_{S_2}$  is equal to or

### Partition coefficients of Ni between Mss



**Figure 1.** Diagram showing schematically the domains of stability of PGE-bearing BMS phase assemblages in the  $\text{Me}_9\text{S}_8$  section of the Fe-Ni-Cu-S system at  $760^\circ\text{C}$ . Phase relationships are still uncertain in the black region within the three phase field (Hzss-Mss-Bnss).

**Table 1.** The forms of PGM and distribution of PGE in base metal sulfide associations stable at 760° C.

Log f(S <sub>2</sub> )	Base metal sulfide association	The forms of presence of platinum group elements (at. %)		
		Pt	Pd	Rh
-10.5	Fe-Mss*, Hz-Iss with Fe>Ni>Cu	Fe-Ni-Pt alloy	Fe-Ni-Pd alloy or Pd(Cu,Fe)	Fe-Ni-Rh alloy or FeRh
-7.5	Fe-Mss, from Hz-Iss with Fe>Ni>Cu to Ni-rich Hz-Iss	(Fe,Ni) <sub>1-x</sub> Pt	≥ 2.2 % in (Fe,Ni) <sub>1-x</sub> Pt	0.6-0.9 % in Mss ≥ 0.2 % in Hz-Iss
-5.5				
-5.7	from Fe-Mss to Ni-Mss, from Hz-Iss with Fe□Cu>>Ni	(Pt,Ni) <sub>3-x</sub> Fe	≥ 1,5 % in Hz-Iss ≥ 0,1 % in Mss	≥ 0.9 % in Mss
-3.7	to Ni-rich Hz-Iss		≥ 2.4 % in (Pt,Ni) <sub>3-x</sub> Fe	
-3.6	Ni-Mss, Bn <sub>SS</sub>	PtS	≥0.9 % in Mss and Hz-Iss ≥ 4.8 % in PtS	≥ 2.6 % in Ni-Mss
-1.7	Hz-Iss(Cu>Fe>>Ni)			
> - 1.4	Ni-Mss, Bn <sub>SS</sub> , Hz-Iss(Cu>Fe>>Ni)	Cu(Pt,Ni) <sub>2</sub> S <sub>4</sub>	2 % in Ni-Mss 0.1 % in Hz-Iss 0.1 % in Cu(Pt,Ni) <sub>2</sub> S <sub>4</sub>	CuRh <sub>2</sub> S <sub>4</sub>
>0	Vs, Bn <sub>SS</sub>	no data	0.2 % in Bn <sub>SS</sub> 0.1 % in Vs	(Rh,Ni)S <sub>2</sub>

\* - Fe-Mss – Fe-rich monosulfide solid solution; Bn<sub>SS</sub> – bornite solid solution; Vs – vaesite.

### Application to Ore Deposits

According to experiments done under conditions of extremely low sulfur fugacity, a low-S (47 at.%) but Fe-rich sulfide melt should induce fractionation of PGE as a result of separation of a metal-rich solid from the sulfide liquid, with Pt partitioning into alloy and Pd into the sulfide liquid. Consequently, the present experimental results are especially relevant to PGE deposits hosting abundant Pt-Fe alloys. The preponderance of Pt-Fe alloys among other PGE mineral species generally skews the Pt/Pd ratio towards high values, a feature characteristic of the alloy type of platiniferous mineralization. The latter can be found in diverse settings ranging from mantle rocks to layered complexes and ophiolites. In all of these PGE deposits, the proportion of base-metal sulfides is low, below 2%, and soetimes nearly absent as in Pt deposits located in the crustal sequence of ophiolites.

In mantle peridotites, among the first PGM described are Pt-Fe alloy grains (Pt<sub>3</sub>Fe) found in peridotite nodules of kimberlite and in ophiolitic peridotites from Corsica. Further PGM found in ophiolitic mantle peridotites are diverse, occurring within BMS, or as satellite grains around BMS. Based on the present experiments, preliminary comparison of PGM occurrences within mantle rocks suggest derivation from magmatic sulfide liquids of distinct composition, crystallizing under different fS<sub>2</sub>. Sulfide melt with high Me/S ratio

(Me/S>1), close to that used in the present experiments, but lower than that supposed to be parental to massive sulfide deposits, may be present in different geotectonic settings, from Mid-Oceanic Ridges to Island-arcs, as suggested by the composition of trapped sulfide globules in lavas.

In the Bushveld Complex, the close similarity between the PGE mineral assemblage observed along the Merensky Reef and the UG2 (where dominated by Pt-Fe alloys and sulfides), and that produced by the present experiments provides good evidence for a common primary magmatic origin of BMS and PGM. An early-stage deposition of Pt is suggested when Pt-Fe alloy is associated with mss, and a later-stage when cooperite is associated with Fe- and Ni-rich sulfides; deposition of Pt could have occurred even later when arsenides and or tellurides are associated with Cu-rich sulfides. The change in the mineral form hosting Pt as well as the different time of deposition of Pt with respect to the associated BMS, underline the important variation of sulfur fugacity during the deposition of PGE along the mineralized layers. The scarcity of Pd minerals and the preferential concentration of Pd in Pn reflects the incompatible behaviour of Pd which has accumulated in the residual Cu-rich sulfide liquid.

The alloy-type of platiniferous mineralization is well exposed in some chromitites from cumulative sequences of ophiolites (Albania, New Caledonia, Thetford) and alaskan-type complexes

(Tulameen). For example, the main phases reported from the Tropoja deposit in Albania consist of 73% alloys and 21% PGE sulfides. Pt-Fe alloys are the preponderant Pt carrier, which are generally included in chromite grains. Other mineral species are sulfoarsenides, arsenides and tellurides. However, direct application of the present experiments is prevented by the extremely low amount of BMS, and the uncertain origin of the Pt-Fe alloys which may have been derived directly from a silicate magma or from a sulfide melt segregated from a silicate magma. Silicate-glass inclusions together with round polyphase sulfide inclusions in Pt-Fe nuggets indicate that a silicate magma and a sulfide melt were present but incompletely separated at the time of PGE deposition. Locally, the composition of some inclusions testifies to the presence of a Cu-rich melt hosting the light platinoids, besides Pt. The wide range of compositions shown by the Pt-Fe alloys within and between deposits is related to variations

of  $fS_2$ , in agreement with the present experiments, but also of  $fO_2$ .

In summary, according to experiments done under conditions of extremely low  $fS_2$ , a low-S (47 at.%) but Fe-rich sulfide melt should involve fractionation of PGE as a result of separation of a metal-rich phase from sulfide liquid, with Pt partitioning into alloy and Pd into sulfide liquid. This would result in zoned mineralizations with a Fe- and Pt-rich core characterized by the predominance of Pt-Fe alloys, surrounded by Ni, Cu and Pd richer margins formed at a later stage. PGE deposits with a predominance of Pt-Fe alloys, such as those occurring in mantle rocks, layered complexes and ophiolites, are consistent with derivation from a S-poor sulfide melt. Even in these low-S deposits, high  $fS_2$  may be reached locally as a result of the appearance of a Cu-rich sulfide liquid derived by fractionation or by immiscibility from an original Fe-rich sulfide melt.