

Platinum-Group Element Concentrations in Pyrrhotite, Pentlandite, Chalcopyrite and Pyrite from the Aguablanca Ni-Cu Ore Deposit (Southwest Spain)

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ABSTRACT. A detailed LA-ICP-MS study has been carried out on base-metal sulfides (BMS) from the Aguablanca deposit (Spain) in order to establish the role of the BMS as carriers of PGE and the processes controlling their distribution. The distribution of the PGE is largely governed by the fractionation of the sulfide liquid. IPGE and Rh are concentrated in pyrrhotite and pentlandite of the semi-massive ore (i.e., mss cumulate). These phases have lower IPGE and Rh values in the disseminated and chalcopyrite-veined ores, but pentlandite and chalcopyrite host higher Pd contents. Laser ablation analyses support the interpretation of chalcopyrite veinlets as representing a Cu-rich sulfide liquid. Palladium is present in solid solution within pentlandite, whose concentrations are a function of the textural type (flames host lesser amounts than the granular pentlandites) and the presence of chalcopyrite in the samples (pentlandites related to chalcopyrites are enriched in Pd). Pd diffusion into pentlandite from mss and possibly iss was the key mechanism in its enrichment in pentlandite. Finally, this study demonstrates that pyrite hosts appreciable amounts of Rh and Pt, and therefore pyrite should not be overlooked as a potential carrier of PGE in Ni-Cu-(PGE) ore deposits.

1 INTRODUCTION

The Aguablanca Ni-Cu-Platinum-Group Elements (PGE) sulfide deposit occurs in the form of a magmatic breccia with three ore types: semi-massive, disseminated and minor chalcopyrite-veined ore (Tornos et al. 2001; Ortega et al. 2004; Piña et al. 2006, 2008 and 2010). Based on the base-metal sulfides (BMS) mineralogy and whole rock metal abundances, these ore types have been interpreted to be the result of the fractionation and crystallization of an immiscible sulfide liquid (Piña et al. 2008). The semi-massive ore is interpreted to represent monosulfide solid solution (mss) cumulate, and the chalcopyrite veinlets to represent fractionated Cu-rich liquid. The disseminated ore could represent either the crystallization of a fractionated sulfide liquid or an original, unfractionated sulfide liquid. According to the partition coefficients between mss and Cu-rich liquid, if the fractionation of the sulfide liquid were the key factor in the distribution of the PGE, then Os, Ir, Ru, and Rh should be enriched in the products of mss (pyrrhotite and pentlandite), whereas Pt, Pd, and Au could be concentrated in intermediate solid solution (iss) (Li et al. 1996).

At Aguablanca, the phases hosting PGE have not been clearly established. Previous studies have identified Pd-Pt bismuthotellurides and Pt arsenides largely within BMS (Ortega et al. 2004; Piña et al. 2008), but these PGM grains are not abundant enough to account for the whole rock concentrations of the samples. *In situ* concentrations of PGE and other chalcophile elements in the BMS have been determined by LA-ICP-MS in order to identify the PGE-hosting BMS and to better understand the relevant processes controlling their distribution in the deposit.

2 SAMPLE DESCRIPTIONS AND ANALYTICAL METHODS

We have studied 5 representative samples from the semi-massive ore, 3 from the disseminated ore and 1 from the chalcopyrite veinlets. The semi-massive ore samples are made up of early-

crystallized silicates (pyroxene, plagioclase and/or olivine) with a matrix of BMS. Sulfides are mostly pyrrhotite (34-77 modal % of the sulfides), pentlandite (11-34 modal %) and minor chalcopyrite (< 11 modal %). Pentlandite largely occurs as granular aggregates or as minor flames within pyrrhotite. Hydrothermal pyrite is locally relatively abundant (5-10 modal %) and occurs replacing pyrrhotite as large idiomorphic crystals and as ribbon-like crystals. The disseminated ore samples contain interstitial BMS in medium-grained gabbro-norites and norites. BMS are pyrrhotite (21-68 modal %), chalcopyrite (12-58 modal %) and pentlandite (3-18 modal %). Pentlandite forms granular aggregates and flames are not common. The chalcopyrite veinlets (< 10 cm wide) are mostly made up of massive chalcopyrite with minor amounts of pyrrhotite and pentlandite.

The PGE and other chalcophile element concentrations were determined by LA-ICP-MS at the Université du Québec à Chicoutimi (Canada) using a New Wave 213 nm laser and Thermos X-7.

3 RESULTS

3.1 Pyrrhotite, Pentlandite and Chalcopyrite

The PGE concentrations vary as a function of the BMS and the ore type (Table 1). Osmium, Ir, Ru, and Rh values in the pyrrhotite and pentlandite from the semi-massive ore are the highest. These values decrease in the disseminated ore and more notably in the chalcopyrite-veined ore (below the detection limit, ~ 7-14 ppb, depending on the BMS) (Figure 1a-c). These elements are positively correlated, suggesting a similar control in their distribution.

Table 1. Ranges and average PGE contents of the BMS by LA-ICP-MS analyses.

	¹⁸⁹ Os	¹⁹³ Ir	¹⁰¹ Ru ¹	¹⁰³ Rh ¹	¹⁹⁵ Pt	¹⁰⁵ Pd ²
SM. ore	Range; Avg	Range; Avg	Range; Avg	Range; Avg	Range; Avg	Range; Avg
Po (n=38)	16-189; 78	43-314; 136	20-238; 82	28-199; 81	< 11	< 46
Pn (n=27)	24-152; 56	47-259; 103	16-258; 122	30-150; 65	< 8	466-5218; 2212
Pn-f (n=3)	33-125; 66	61-244; 124	67-152; 106	16-137; 66	< 7	43-149; 64
Ccp (n=8)	< 6-87; 31	< 13			< 8	< 17-82; 45
Py1 (n=4)	27-292	98-622	46-719	4206-30570	41-15030	< 46
Py2 (n=8)	45-112;105	84-358;191	32-225;119	62-220;115	< 10	< 40
D. ore						
Po (n=16)	< 5-40; 16	< 5-45; 13	< 19-81; 22	< 15-76; 22	< 9	< 41
Pn (n=13)	< 5-36; 11	< 4-22; 9	< 16-71; 24	< 12-129; 29	< 7	539-7087; 2771
Ccp (n=16)	< 10	< 5			< 5	68-407; 133
Ccp. v.						
Po (n=3)	< 7	< 3	< 12	< 12	< 7	< 39
Pn (n=3)	< 6	< 4	< 14	< 12	< 7	3592-6770, 5053
Ccp (n=7)	< 7	< 3			< 5	30-191; 83

Values are in ppb. SM. ore: semi-massive ore; D. ore: disseminated ore; Ccp. v.: chalcopyrite veinlet. Pn-f: pentlandite flames; Py1: large idiomorphic pyrite; Py2: ribbon-like pyrite. ¹Ru and Rh in chalcopyrite not reported due to interferences. ²In chalcopyrite, ¹⁰⁸Pd was used instead of ¹⁰⁵Pd to avoid Cu interference. ¹⁰⁸Pd was corrected for ¹⁰⁸Cd.

Palladium has been detected in pentlandite (> 85% of the total content of PGE in this phase). Pd values are slightly higher in the pentlandite from disseminated and chalcopyrite-veined ores relative to that from the semi-massive ore (Figure 1b-c). Moreover, most pentlandites in contact with chalcopyrite have higher Pd values than those pentlandites not in contact with chalcopyrite. Palladium is strongly depleted in the flame-textured pentlandites, containing ~ 95% less Pd than co-existing granular pentlandites. In the chalcopyrite, Pd values are slightly higher in the disseminated ore than in the semi-massive ore (Figure 1c). Pd in pyrrhotite is below detection limit (~ 40 ppb) in all ore types. Except in pyrite, Pt occurs below the detection limit (~ 6-7 ppb) in all the analyzed BMS.

Cobalt is found within pentlandite (0.28-1.36 wt%). For a given sample, flames contain less Co than granular pentlandites. Chalcopyrite hosts the majority of the Ag detected (6-47 ppm), and pentlandite and pyrrhotite have lower contents (from 0.4 to 9 ppm, and less than 1 ppm, respectively). Gold is preferentially partitioned in chalcopyrite from the disseminated and chalcopyrite-veined ores (10-170 ppb) (Figure 1c). Gold values in chalcopyrite from the semi-massive ore are close to the detection limit (~ 4-6 ppb). Pentlandite Au values are approximately equal for the three ore types (up to 70 ppb), and in pyrrhotite Au is below the detection limit (~ 4-6 ppb).

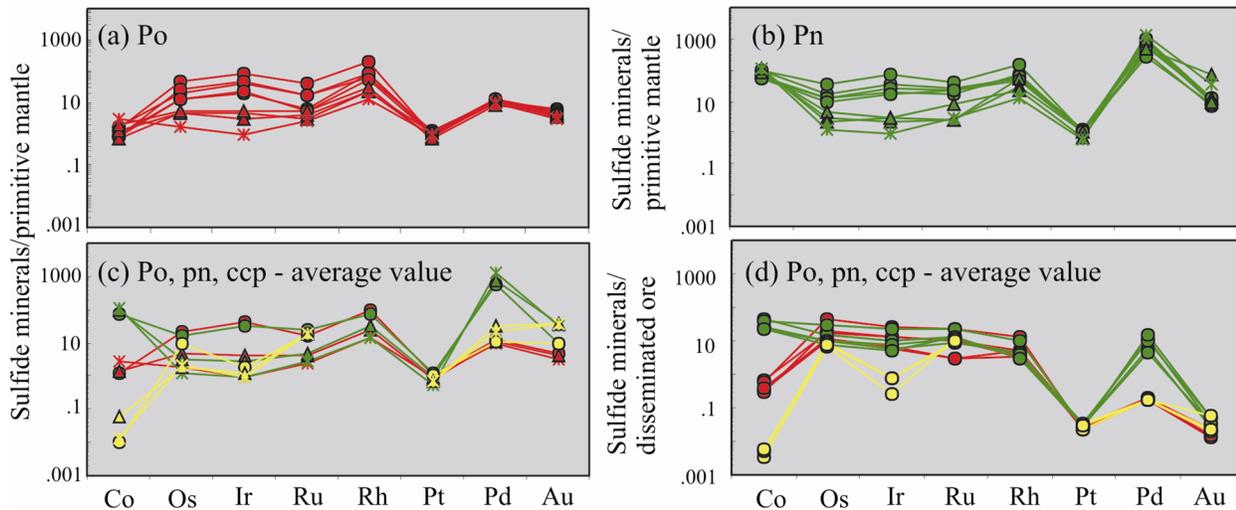


Figure 1. Primitive-mantle-normalized metal patterns for (a) pyrrhotite, (b) pentlandite, and (c) average values of pyrrhotite, pentlandite and chalcopyrite from the three ore types. (d) Disseminated ore normalized metal patterns for average values of pyrrhotite, pentlandite and chalcopyrite from the semi-massive samples. Circles: semi-massive samples; triangles: disseminated samples; cross: chalcopyrite-veined sample. When data are below the detection limit, these values were employed.

3.2 Pyrite

The large idiomorphic pyrites have relatively high concentrations of Pt and Rh (Table 1), low Ni (0.049-0.15 wt%) contents, and high Co (0.59-0.99 wt%) and As (42-208 ppm) values. In contrast, ribbon-like pyrites have low values of Pt, Rh, Co (< 0.58 wt%) and As (close to the detection limit, ~ 2 ppm), but higher values of Ni (1.19-7.67 wt%), Au (16-418 ppb), Ag (2-17 ppm) and Te (2-17 ppm) than the idiomorphic pyrites. Osmium, Ir and Ru concentrations are similar in both pyrites (Table 1).

4 INTERPRETATION OF THE LASER RESULTS

At Aguablanca, the distribution of the PGE is primarily controlled by their partitioning behaviour during the fractional crystallization of the parent sulfide liquid. Osmium, Ir, Ru, and Rh are largely accommodated in pyrrhotite and pentlandite from the semi-massive ore (i.e., mss cumulate). Mass balance calculation indicates that these BMS host the majority of these PGE, in agreement with the almost total absence of IPGE-Rh-bearing discrete PGM in such ore. As is shown in Figure 1d, Os to Rh are enriched in pyrrhotite and pentlandite by a factor of 3 to 15 relative to the disseminated ore. If pyrrhotite and pentlandite retained the PGE budget of the mss, these data are consistent with the initial hypothesis of the disseminated ore representing an original sulfide liquid from which mss crystallized. The extremely low IPGE and Rh values in pyrrhotite and pentlandite (below the detection limit) and the relatively high Pd and Au values in pentlandite and chalcopyrite from the chalcopyrite veinlets support the suggestion that this ore type represents the Cu-rich sulfide liquid.

Although Pd concentrations are highest in the chalcopyrite veinlet, Pd is not concentrated in chalcopyrite, but rather in pentlandite in all ore types. Unlike IPGE and Rh, the distribution of Pd must be controlled by a process other than fractionation of the sulfide liquid, because Pd is incompatible in mss and should be concentrated in the fractionated liquid. Palladium contents in pentlandite from Sudbury and Noril'sk Ni-Cu deposits have been attributed to Pd diffusion into pentlandite from Cu-minerals and mss during cooling (Barnes et al. 2006; Dare and Barnes 2009). The evidence observed by these authors pointing out this interpretation has been also found at Aguablanca, namely: flame-textured pentlandites are much poorer in Pd (and Co) than co-existing granular pentlandites, and pentlandites with textural relationship with chalcopyrite have usually higher Pd values than those grains without any relationship. The diffusion of Pd into pentlandite is probably conducted by the rejection of Pd from mss and chalcopyrite at low temperature (Dare and Barnes 2009). Mass balance calculation indicates that Pd in pentlandite only accounts for ~ 17-26% of the total Pd, so the majority of the Pd was probably exsolved from BMS at low temperature to form the observed assemblage of Pd-bismuthotellurides. The identification of tiny inclusions enriched in Pd-Bi-Te during laser ablation points out to exsolution processes during cooling (Helmy et al. 2007). Finally, Pt is only present in the idiomorphic pyrites. Recently, Dare et al. (2010) have also found significant Pt values in pyrites from McCreedy mine of the Sudbury ore. Further work will be needed to evaluate the role of the pyrite as a carrier of PGE and the distribution of these elements among the different pyrite textures.

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