Weathering of Platinum-Group Minerals in the Aguablanca Ni-Cu Gossan(SW Spain)

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INTRODUCTION.

It is known that platinum-group elements (PGE) are variably mobile in low temperature conditions (e.g. Fuchs and Rose, 1974; Prichard and Lord, 1994), but processes of PGE redistribution during the exogenic cycle are still much debated. Disintegration of primary platinum-group minerals (PGM) with later dispersion of PGE or reconcentration as new secondary phases have been proposed in the supergene domain (i.e. during lateritisation processes, in eluvial and alluvial placers or in soils).

This work examines the stages of PGM formation and variations in PGE distribution during development of the gossan overlying the Aguablanca Ni-Cu-(PGE) magmatic deposit (Badajoz, SW Spain) (e.g. Tornos et al., 2001 and references therein). Primary PGM associated with the sulfide ores at Aguablanca have been studied extensively by Ortega et al. (2004). The PGM assemblage mostly consists of Pt- and Pd-tellurides and bismuthotellurides generated as result of subsolidus recrystallization of the ore during postmagmatic evolution of the sulfides. These authors also proposed some redistribution of the PGM related to the skarn processes in the nearby country-rocks and the circulation of hydrothermal fluids restricted to channel ways through the deposit.

The objectives of this work were to identify the stages of alteration of primary PGM formed by different degrees of oxidation throughout the gossan profile, and study the secondary PGE-oxides developed, in order to recognize their precursors and so establish their origin. This study shows how PGM are weathered in a gossan and so describes a part of the PGE cycle in the supergene domain.

MATERIALS AND METHODS

For this study 31 samples were selected from different levels of the gossanous outcrops overlying the main orebody (southern orebody) at the Aguablanca deposit. A subset of 17 samples was chosen for whole-rock analysis for all six PGE and Au. Six samples belong to the highly oxidised top layer of the gossan (*Upper Gossan*; 490-482m); five to the lower part of the gossan, which is less weathered and shows better preserved relicts of sulfides (*Lower Gossan*; 482-478m); four samples are from gossan in fractures cross cutting the underlying weathered gabbro and six samples are from weathered gabbroic rocks (475-476m). The analyses were obtained using a nickel sulfide fire assay method combined with ICP-MS analysis. PGE and chemical characterization of the whole rock samples was achieved by using a Multielemental Scan Analysis by ICP-MS (Ultratrace Pty. Ltd. Analytical Laboratoires, Australia).

PGM grains were searched for in 18 polished blocks (30mm in diameter) from the *Upper* and *Lower Gossan* using a scanning electron microscope (SEM) (at the School of Earth and Ocean Sciences, University of Cardiff, U.K.). The SEM is a Zeiss SMT S360 Scanning Electron Microscope (SEM) with an attached Oxford Instruments INCA Energy + Energy Dispersive X-ray (EDX) analyser. Those grains larger than 5µm were analysed quantitatively using beam conditions of ~1nA at 20 kV and a working distance of 25mm. Standards used were pure metals.

DISTRIBUTION OF PGE

Average total PGE concentrations for all the samples in each area are as follows: 1723ppb in the upper gossan, 3418ppb in the lower gossan, 335ppb in gossan within fractures and only 80ppb in the weathered gabbro. Au contents are greater in the upper and lower gossan ($\leq$244ppb) than in the other sampled areas (<20ppb). As a rule, Pt and Pd are dominant over Rh and IPGE (Ru, Ir, Os).

PGE are associated with the presence of base metal sulfides in the weathering profile but relatively weak correlations between chalcophyle elements and PGE might reflect some redistribution of metals (including the PGE) in the ore. This redistribution could be due to hydrothermal processes and moreover, to diffusion of elements in response to the on-going supergene alteration. This is also reflected in the Pt/Pd ratios which range from 1.16-3.34, showing sporadic values of up to 10 in the more leached areas of the oxide zone, whereas the weathered gabbro displays values <0.5. The increasing Pt/Pd ratios from the lower gossan to the upper gossan and from the weathered gabbro to the material within fractures may reflect greater Pd mobility compared to that of Pt. (Pt+Pd)/IPGE ratios are $\geq$14.0 and these values are unlikely to be a magmatic feature (Naldrett and Duke, 1980).

PLATINUM GROUP-BEARING MINERALS

More than 400 PGM grains have been identified in the Aguablanca gossan (Table 1). Most of them (n=397) were found in the lower gossan whereas only 24 grains were found in the upper gossan. Largest PGM (n=234) are commonly 7-14µm in size but they can reach up to 27-31µm. The remaining PGM (n=187) are small Pd-Pt-Cu oxides (<5µm) concentrated in clusters within soft goethite in the lower gossan. PGM are mainly associated with massive goethite and silicates, but also appear enclosed in sulfides. They are mostly observed included in large hydrothermal pyrite crystals and associated with chalcopyrite, which are the best preserved sulfides.

PGE-bearing minerals can be divided into four groups revealing an *in situ* alteration sequence of the earlier PGM:

1) Least altered PGM. These are inherited grains formed prior to the gossan and occur mainly associated with the remaining base-metal sufide assemblage in the lower gossan. This group mostly consists of arsenides and tellurides. Sperrylite is the most stable PGM but is frequently present as broken and irregular "C-shaped" grains within goethite and silicates or as small relicts in PGE-oxides. Pd-Pt tellurides are mainly associated with chalcopyrite and occur as large sub-rounded grains with homogeneous and flat surfaces. Moncheite only occurs as euhedral elongated laths within pyrite. Conversely, bismuthotellurides are commonly oxidised and only a few fresh minerals are observed including michenerite, and a rare PGM with a high Pd and Pt content having a formula of $(Pd,Pt)_4BiTe$. In general, sperrylite breaks down more slowly than Pd-bearing minerals.

2) Partially oxidised PGM. These represent the initial stage of oxidation that has produced partially oxidised Pt-Pd-PGM and Pt-Pd-Fe and Cu-bearing PGM. The oxygen content is always ≤10%. The majority of these grains occur in the lower gossan, in areas of massive goethite with silicates.

3) PGE-oxides. These are the most abundant group of PGM. They have irregular shapes, are often mottled, and appear fractured or cross cut by silicates or later Fe-oxide veins. They have variable compositions (see Table 1) containing Pt and/or Pd, variable amounts of Fe, Cu, and Ni and oxygen in the range of [11.6-30.0%]. They usually appear surrounding PGM precursors but Pt- and Pd-oxides can also occur in clusters of either Pd±Pt-Cu-O or Pt±Pd-Fe-O. It is remarkable that the majority of the PGE-oxides in the upper gossan are Cu- Te- and Bi-poor compared with the lower gossan. This suggests that these elements are probably being removed from this more leached area of the profile.

4) Fe/Cu-PGE oxides and hydroxides. These are developed during the advanced stages of PGE dispersal, when PGE-oxides start to disintegrate. These Fe- or Cu-rich oxides occur as mottled patches mainly associated to Mg-Fe silicates and quartz. Several of these patches retain very small relicts of PGM in their cores. Contents of up to 17.4% Pd, 16.3% Pt, 5.3% Bi or 4.2% Te are recorded in these patches. Iron oxides and oxyhydroxides surrounding oxidised PGM can retain up to 3% Cu or Ni, and

Group	PGM Type Type	Composition	Size (µm)	PGM number LG	PGM number UG	Total
1. Arsenides	Sperrylite	Pt As₂	[2.7-17.2]	60	3	63
Tellurides	Moncheite	Pt Te₂	[10 -23.2]	18	0	18
**	Merens-Mon	(Pd,Pt) Te₂	[6 -13]	7	0	7
	Michenerite	Pd Bi Te	[3.2 -13.4]	9	1	10
	Unnamed PGM	(Pd, Pt)₄BiTe	[4.4 -11.7]	7	0	7
2. Partially		Pt-Pd PGM	[6.6 - 28.9]	2	0	2
oxidised PGM		Pt-Pd-Fe-Cu PGM	[3.5 - 21.5]	9	1	10
3. Oxidised PGM		Pd-Pt±Bi Te	[1 - 17]	20	1	21
		Pt-Pd-Fe	[1 - 31.1]	46	7	53
		Pd-Pt-Fe	[1.3 - 11.5]	0	11	11
		Pd-Pt-Cu	[1.5 - 27.7]	30	0	30
		→Clusters	[1.0-4.0]	187	0	187
		Pt oxide	[3.2 - 8.0]	2	0	2
4. Fe/Cu Ox. (± PGE)		Fe/Cu-O-(Pt-Pd)	[4.0 - 20.0]	(15)	(6)	21

Table 1. *Summary of the PGE-bearing minerals founded in the Aguablanca gossan. Abbreviations:* LG *Lower Gossan,* UG *Upper Gossan,* Ox. *Oxides,* Merens *merenskyit,* Mon *moncheite.*
** *Stoichiometric formulae*

they may retain very high Pd, Pt, Bi and Te contents even in sites reasonably far away from the PGM (~10-20 µm). In several cases, maximum values of 17.7% Pd, 17.2% Bi, 13.1% Te and 9.1% Pt have been recorded in these Fe-rich products.

On the other hand, Pd-Cu hydroxides have been detected at the edges of composite Pd-Bi-Te-Fe-Cu oxides that pseudomorph former PGM. Hydroxides occur as darker minerals than PGE oxides and display a porous texture. Although repeat analyses were performed, totals of only 74-91% were achieved, including the oxygen.

CONCLUSIONS
The gossan overlying the Aguablanca Ni-Cu-(PGE) deposit has preserved some of the same PGM as those reported in the underlying ores, but also hosts several generations of secondary PGM and PGE concentrations that have formed during the exogenic cycle.

This work describes how PGM break down from exsolution in pyrite to partial oxidation of PGM and then formation of PGE-oxides and PGE-hydroxides. This is followed by dispersion of Pt and Pd into Pt- and Pd-rich Fe-oxides and finally into traces of Pt and Pd on the edges of the goethite. In this situation of gossan formation the sequence of alteration is one of oxide formation from the precursor PGM and dispersion of the PGE into the iron oxides rather than formation of PGE-alloys as observed in placers. There-fore, this environment does not appear suitable for growth of nuggets of PGE but rather dispersal of PGE after disintegration of the PGE-oxides. This study adds to our understanding of the processes that affect PGE-oxide formation and mobility of PGE in the surface domain.

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