Evidence for the PGE Dispersion in the Aguablanca Gossan (Spain). A *LA-ICP-MS* Study

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INTRODUCTION.

Considerable evidence suggests that platinum-group elements (PGE) and particularly Pd and Pt, are mobile in surface environments (e.g. Fuchs & Rose, 1974; Travis et al., 1976; Wood & Vlassopoulos, 1990). However, the mobility of individual PGE and their distribution during weathering are poorly understood. This is especially the case in highly oxidizing supergene environments such as gossans, where few detailed studies of PGM and their alteration pathway during weathering have been reported.

The present study is focused on the gossan overlying the Aguablanca Ni-Cu-(PGE) sulfide deposit (Badajoz, Ossa Morena Zone). After the study of PGM and newly developed PGE-oxides within this gossan (Suárez et al., 2008), we have documented the total distribution of PGE at low concentrations throughout the Fe-oxides/oxyhydroxides to evaluate the PGE potential dispersion. This has been possible by using in situ techniques such as the laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS), which can detect PGE with concentrations as low as 10 ppm.

This study offers an example of PGE behaviour in a neutral but strongly oxidizing supergene environment, once Ni-Cu base-metal sulfides and platinum-group minerals (PGM) have been altered.

THE GOSSAN: PGE and PGM.

The Aguablanca gossan is a ~10m thick goethitic outcrop formed *in situ* over the gabbroic units that host the Ni-Cu semi-massive mineralization. From a mineralogical and geochemical point of view the gossan can be divided into the highly weathered *upper gossan* and the less leached *lower gossan*, where original ores and textures are much better preserved. Total PGE average values of 1723ppb in the upper gossan and 3418ppb in the lower gossan were recorded.

The detailed study of PGM in the gossan revealed that PGM are being fractured and oxidized in steps as the weathering progresses. The less altered PGM observed are sperrylite, moncheite, merenskyite, michenerite and an unknown (Pt, Pd)$_4$BiTe-mineral phase. Several generations of secondary partially oxidized Pt-Pd-PGM and more abundantly PGE-oxides, are formed. Almost 400 PGM grains were identified in the lower gossan, whereas only 24 grains were found in the upper one.

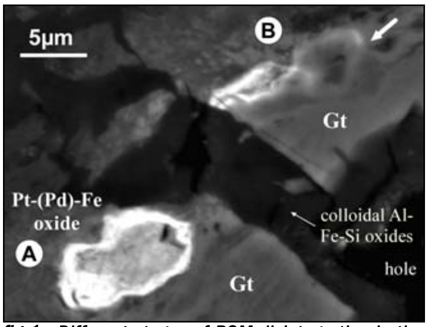

fig 1. *Different stages of PGM disintegration in the Aguablanca Gossan. **(A)** Pt-(Pd)-Fe oxide in goethite with increasing oxidation towards the core of the grain. **(B)** Ghost of a Pt-rich phase in goethite.*

PGE-oxides are in general Bi-, Te- and As-poor and can be either Pd±Pt-Cu-oxides or Pt±Pd-Fe-oxides. All appear to have formed from alteration of previous PGM to form pseudomorphs without PGE recrystallization in new sites.

However, Pt and Pd are later released into irregular masses of Fe- or Cu-rich Pt-Pd-bearing oxides. In highly weathered areas PGE-oxides have disintegrated dispersing PGE into the surrounding goethite, hematite and silicates (e.g. Fig 1). The character of this PGE dispersion has been measured by laser ablation.

MATERIALS AND METHODS.

Laser ablation was performed on two samples. One is from the *lower gossan*, where nine PGM were located including sperrylite, partially oxidised Pt-Pd PGM, Pt-Fe-Cu- and Pt-Pd-Fe-oxides. The other sample belongs to the *upper gossan*, with scarce sulfide relicts. Only one PGM, a Pd-Pt-Fe oxide was located in it. Both samples show cavities or fissures filled with hematite and limonite usually coated by later colloform goethite. In spite of their different mineralogical features, both samples contain very similar total PGE concentrations, each with more than 1700ppb Pt and more than 800ppb Pd.

LA-ICP-MS analyses were carried out using a New Wave Research UP213 UV laser system coupled to a Thermo X Series ICP-MS at the Cardiff University, UK. Ablations were carried out under He (flow rate ~0.7L/min) in the laser cell and the resulting vapour was combined with Ar (flow rate 0.56-0.65L/min) before delivery into the ICP-MS. All the analyses were performed using a 40µm laser spot (delivering 0.35mJ/pulse) at a frequency of 10Hz. The laser beam moved at 6µm/s along line traverses monitoring suitable isotopes. Elements were recorded in time-resolved analyses (TRA) mode in time slices of 250ms. Acquisitions lasted between 80 and 400s, and a gas blank was measured for 30-40s. More details of the analytical conditions and Ni sulfide standards used are described in McDonald (2005).

LASER ANALYSIS.

The sulfide grains are almost completely barren of PGE or Au with only traces of Pt (maximum contents of 0.34ppm) associated with smaller quantities of Rh,

palabras clave: LA-ICP-MS, Elementos del grupo del platino, Fe-óxidos, Gossan, Aguablanca	***key words:*** LA- ICP-MS, Platinum-group elements, Fe-oxides, Gossan, Aguablanca

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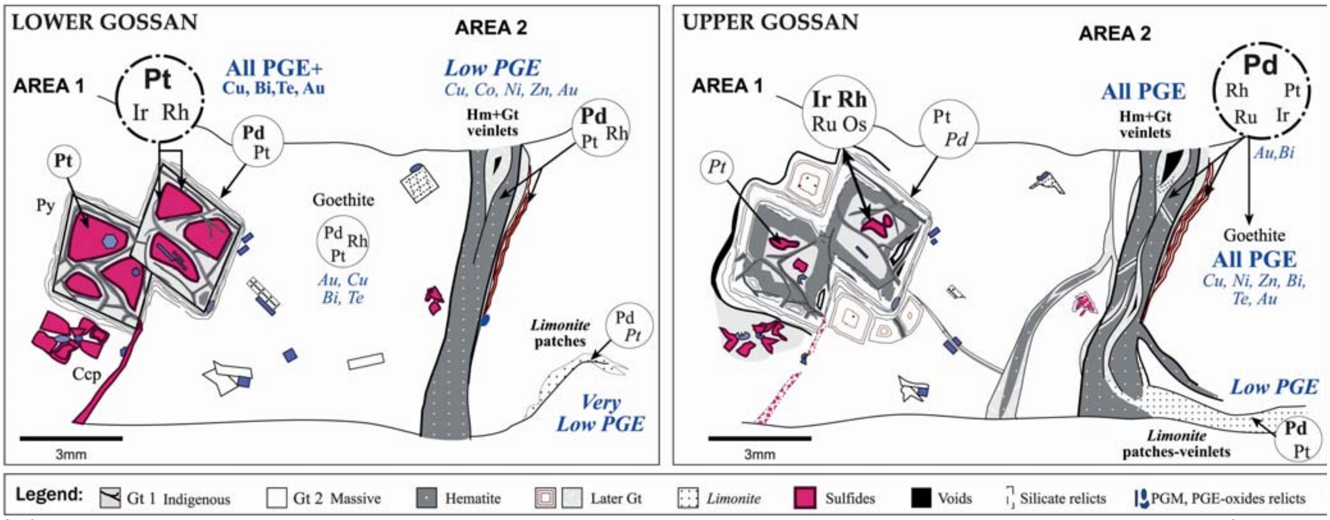

fig 2. *Sketches of the 2 gossan samples showing the relative distribution of PGE after disintegration of PGM, as obtained by LA-ICP-MS. The studied* ***Area 1*** *is close to sulfide relicts;* ***Area 2*** *represents goethitic/hematitic-rich zones of the samples. The dashed circles represent the major PGE concentration areas in each part of the gossan. Abbreviations:* Ccp *chalcopyrite,* Gt *goethite,* Hm *hematite.*

Ir or Ru. All six PGE were found concentrated at the junctions of pyrite/goethite and goethite/hematite and in cracks cross cutting goethite, often with Cu and Bi. PGE can also occur within late hematite filled veins or limonitic vughs. Pt, Pd and Rh ± Au with elevated Cu, Co, Ni and Zn are concentrated mainly at these veins edges. Away from junctions the massive goethite itself is sometimes variably enriched in Pt, Pd, Rh, Au, Cu and Bi. Main observations for each part of the gossan are summarized in Fig 2.

In the lower gossan PGE stay preferably in the first goethite generations and are rarely present in later oxides. Whereas Pt, Rh and Ir are the main PGE detected close to sulfides, in more oxidized areas with massive goethite, Pd is enriched.

In the upper gossan PGE are focused at junctions between minerals including vein edges but unlike the lower gossan all 6 PGE occur more dispersed and do not always occur together. Pt, Rh, Ir, Ru and Os are concentrated adjacent to the sulfide relicts. However Pd is no longer concentrated with the other PGE at pyrite/goethite junctions. Pd reaches its highest concentrations at the edge of goethite, further from sulfides, where it is adjacent to hematite. Here, Pd also may occur with Pt, Au and Bi.

CONCLUDING REMARKS.

It is well-known that Pd is more easily mobilized during weathering than Pt, at least in less acid conditions (e.g. Wood & Vlassopoulos, 1990). This is also the case in Aguablanca, with a greater dispersion of Pd than Pt.

LA-ICP-MS analysis showed that Pt, Ir, Os and Ru in oxides are located close to the sulfide relicts. In contrast, Pd accompanied by Cu, Ni, Bi or Te, occurs widely distributed within last generations of goethite. This PGE behaviour is more evident in the upper gossan, where alteration has been more intense.

Occasionally Pt goes into the massive goethite or/and into later veins, but this only occurs in the highly weathered upper gossan, where Pt is always scarce compared to Pd. In the same way, if Pd occurs within goethite near pyrite relicts in the lower gossan, it is always in a more distant position from sulfide relicts than Pt.

Extensive Pd mobilization is also supported by the mineralogy. Pt-bearing minerals better resist alteration during the gossan formation, indicating a poor mobilization of Pt. However, Pd always appears in PGE-oxides and no unoxidized Pd-rich PGM were observed (Suárez et al., 2008).

High level Eh-pH conditions typical of goethitic and hematitic Ni-Cu gossans (e.g. Thornber, 1985), should have favoured a greater remobilization of elements such as Pd, Cu and Ni compared to Pt. Under increasing oxidizing and moderate pH conditions, the PGE-oxides formed in the gossan could become unstable. Thus, Pt and Pd would be dispersed into the Fe oxides and finally retained as traces on the edges of goethite or later veins as has been corroborated by the LA-ICP-MS analysis.

This study in the Aguablanca gossan proves the different mobility of Pd and Pt during supergene alteration processes and contributes to the understanding of the PGE cycle in surface weathering environments.

ACKNOWLEDGEMENTS.

We thank Río Narcea Recursos S.A. Financial support was given by IT-446-07 (Basque Dept Edu Uni & Res) and AP-20034667 (MEC).

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