

Is Microbial Activity Causing PGM Neof ormation in Ni-Laterites? Evidence from Falcondo (Dominican Republic)

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INTRODUCTION

In a recent study Reith et al. (2014) reviewed our current knowledge of Pt dispersion and concentration mechanisms in supergene environments. These authors concluded that Pt is mobile under surface conditions and can become bioavailable. However, origin and (trans-)formation of Platinum Group Minerals (PGM) found in surface environments (e.g. placer deposits, gossans, laterites) is an ongoing subject of scientific debate. While one group believes that weathering of PGM bearing rocks is the sole factor for PGM accumulation in surface environments (e.g. Koen, 1964; Cabri and Harris, 1975; Hattori and Cabri, 1992), others propose *in-situ* neof ormation of PGM by secondary processes such as PGE remobilization and continual accretion in addition (e.g. Stumpfl, 1974; Bowles, 1986).

Recently botryoidal Pt bearing grains with strong biophilic element concentrations were found in tropical soils from Brazil and the Dominican Republic and were interpreted to have been formed by biogenic precious-metal fixation (Cabral et al., 2011; Aiglsperger et al., 2014, respectively).

Likely because of limited descriptions from natural sites, Platinum Group Elements (PGE) are still considered mostly immobile, inert and not biologically active at surface conditions. Further investigation might change our understanding about PGE and PGM in surface environments as it has been shown in the case of gold (Reith et al., 2007). Therefore the aim of this study is to present morphological and chemical evidence of biomineralization of PGM found in Ni-laterites from Falcondo (Dominican Republic), thus trying to fill the constantly growing gap between experimental laboratory data and extremely rare observations from natural sites. This is probably explained

by the difficulty to detect trace amounts of μm sized PGM in soils. In this study innovative hydroseparation (HS) technology at the University of Barcelona (www.hslab-barcelona.com) was successfully applied to master this challenge.

STUDY AREA

Located in the central part of the Dominican Republic, the Falcondo Ni-laterite deposit is known as the largest Mg-silicate type Ni-laterite deposit of the Greater Antilles. The weathering profile developed from underlying serpentinized ophiolite-related ultramafic rocks (harzburgite>dunite>lherzolite) and consists of a Fe-oxide/hydroxide dominated limonitic cover at the top and a thick silicate saprolite horizon beneath (Aiglsperger et al. 2014; Villanova de Benavent et al. 2014; Lewis et al. 2006).

PGE AND PGM AT FALCONDO

PGE contents determined at the Genalysis Ltd. (Maddington, Western Australia) reveal PGE enrichment trends from parent rocks (~30 ppb) to saprolite (~50 ppb) and limonite (up to 640 ppb) (Aiglsperger et al. 2014). This enrichment is mainly explained by residual accumulation of PGM bearing minerals (e.g. Cr-spinel) but also secondary PGE compounds and one botryoidal Pt-Ni-Fe grain are observed at highest levels of the profile (Aiglsperger et al. 2014).

METHODOLOGY

PGE enriched (up to 640 ppb) Ni-laterite samples from the limonitic horizon close to the surface were processed by HS following the method described by Aiglsperger et al. (2014). Detected PGM grains were subsequently investigated for microbially mediated neof ormation of PGM on a FE-SEM Jeol JSM-7100 at the Serveis Científicotècnics, University of Barcelona, Spain. Element

distribution maps were obtained on a JEOL JXA-8230 EMP at the same survey (for details see Aiglsperger et al. 2014).

RESULTS

One Pt bearing Fe-Ni nugget (40 μm) with oxidation rim shows rather heterogeneous Pt distribution. Highest Pt concentrations were detected in the center of the grain and lowest at its rim (Fig. 1). However, detailed FE-SEM investigation of the rim led to the discovery of a large number of nanometer sized Pt particles with spherical shapes. (Fig. 1).

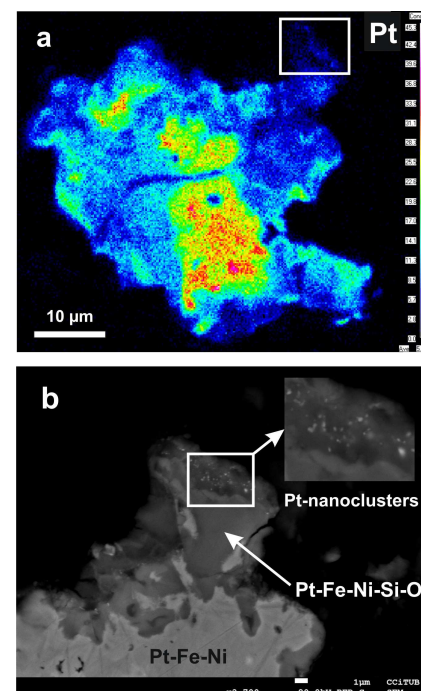


fig 1. Pt distribution map with indicated region of Pt-nanocluster formation; red: high content, blue: low content (a). BSE image and close up of the rim region; note the Si bearing Pt-Fe-Ni-O matrix (b).

High resolution FE-SEM images of one botryoidal Pt-Ni-Fe grain (20 μm) exhibit nano- and micro-particulate Pt clusters and rings, morphologies of microbially mediated accumulations (Fig. 2).

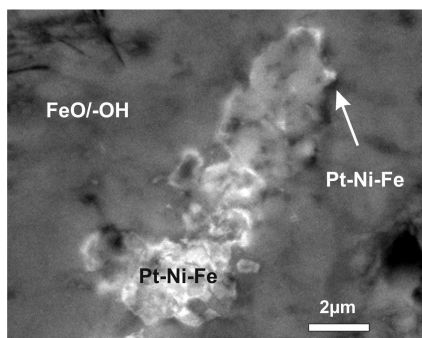


fig 2. BSE image close up of a Pt-Ni-Fe grain with botryoidal textures found in the surface environment at Falcondo (modified after Aiglsperger et al. 2014).

WDS spectra obtained by EMP confirmed the presence of iodine, a strong biophilic element, in the central part of the grain (Aiglsperger et al. 2014).

DISCUSSION AND FINAL REMARKS

Several laboratory studies have proven that Pt is mobile and bioavailable under surface conditions, subsequently leading to bio-neoformation of Pt nanoclusters in the presence of certain microorganisms (e.g. Lengke et al., 2006; Konishi et al., 2007). However, evidence from natural sites is lagging far behind. One reason could be the habitual use of not sufficiently sensitive standard heavy mineral concentration methods (e.g. panning) as microbially mediated PGM have to be considered extremely small in grain size (<20 µm).

The use of innovative hydroseparation technique applied in this investigation led to the discovery of several PGM in PGE enriched limonites of the Falcondo Ni-laterite deposit. Some of these PGM have or host delicate morphological features such as botryoidal textures or spherical nanoclusters, respectively. Their appearance suggests formation *in situ* by biogenic processes (e.g. biofilms) previously reported and widely accepted in the case of gold (e.g. Reith et al. 2012).

Chemical evidence for microbially mediated PGM at Falcondo is provided by iodine enrichment within one botryoidal Pt-Ni-Fe grain. Our findings are in good agreement with previous observations from Brazil (Cabral et al. 2011). These authors explained PGE nugget formation in soils by continuous bioreduction and/or electrochemical accretion.

However, Brugger et al. (2013)

investigated the contrasting behavior of platinum and gold in surface environments and found that Au has a higher cell-toxicity compared to Pt-complexes, thus resulting in Au-detoxifying biofilms and subsequent formation of spheroidal nanoparticulate. Such features were not observed for Pt and explained by its lower toxicity.

Assuming biofilms were responsible for the formation of described PGM at Falcondo and considering cell-toxicity as the main factor for their growth: what could be the reason for their formation in field but not in experiments? In a recent study Le et al. (2006) assessed bioleaching of weathered saprolite nickel ore by using heavy metal tolerant fungi (*Aspergillus foetidus*). One remarkable result of this research was that the presence of multi-metals (e.g. Ni, Fe, Co, Al, Cr, Cu, Mg, Mn, Zn) led to greater toxic response to the growth behavior of the microorganism in comparison to single metals. At Falcondo the presence of multi-metals in the limonitic horizon is verified by geochemical analyses and possibly explains a sufficient toxicity for the formation of Pt-detoxifying biofilms with subsequent neoformation of observed spheroidal nano-particulate and botryoidal Pt-Ni-Fe grains.

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REFERENCES

Aiglsperger, T., Proenza, J.A., Zaccarini, F., Lewis, J.F., Garuti, G., Labrador, M., Longo, F. (2014): Platinum group minerals (PGM) in the Falcondo Ni-laterite deposit, Loma Caribe peridotite (Dominican Republic). *Miner. Deposita* (DOI: 10.1007/s00126-014-0520-9).

Bowles, J.F.W. (1986): The development of platinum-group minerals in laterites. *Econ Geol.* **81**, 1278 - 1285.

Brugger, J., Etschmann, B., Grosse, C., Plumridge, C., Kaminski, J., Paterson, D., Shar, S.S., Ta, C., Howard, D.L., de Jonge, M.D., Ball, A.S., Reith, F. (2013): Can biological toxicity drive the contrasting behavior of platinum and gold in surface environments? *Chem. Geol.*, **343**, 99 - 110.

Cabral, A.R., Radtke, M., Munnik, F., Lehmann, B., Reinholz, U., Riesemeier, H., Tupinambá, M., Kwitko-Ribeiro, R. (2011): Iodine in alluvial platinum-palladium nuggets: Evidence for biogenic precious-metal fixation. *Chem Geol.* **281**, 152 - 132.

Cabri, L. J., Harris, D. C. (1975): Zoning in Os-Ir alloys and the relation of the geological and tectonic environment of the source rocks to the bulk Pt: Pt + Ir + Os ratio for placers. *Can Mineral.* **13**, 266 - 274.

Hattori, K.H., Cabri, L.J., (1992): Origin of platinum-group mineral nuggets inferred from an osmium-isotope study. *Can. Mineral.*, **30**, 289 - 301.

Koen, G.M. (1964): Rounded platinoid grains in the Witwatersrand blanket. *Trans. Geol. Soc. S. Afr.*, **67**, 139 - 147.

Konishi, Y., Ohno, K., Saitoh, N., Nomura, T., Nagamine, S., Hishida, H., Takahashi, Y., Uruga, T. (2007): Bioreductive deposition of platinum nanoparticles on the bacterium *Shewanella algae*. *J. of Biotech.*, **128**, 648 - 653.

Le, L., Tang, J., Ryan, D., Valix, M. (2006): Bioleaching nickel laterite ores using multi-metal tolerant *Aspergillus foetidus* organism. *Min. Eng.*, **19**, 1259 - 1265.

Lengke, M.F., Southam, G., (2006): Bioaccumulation of gold by sulfate-reducing bacteria cultured in the presence of gold(I)-thiosulfate complex. *Geochim. Cosmochim. Acta.* **70**, 3646 - 3661.

Lewis, J.F., Draper G., Proenza J.A., Espallat J., Jiménez J. (2006): Ophiolite-related ultramafic rocks (serpentinites) in the Caribbean region: a review of their occurrence, composition, origin, emplacement and nickel laterite soils. *Geol Acta*, **4**, 237 - 263.

Stumpfl, E.F., (1974): The genesis of platinum deposits. Further thoughts. *Min. Sci. Eng.* **6**, 120 - 141.

Reith, F., Lengke, M.F., Falconer, D., Craw, D., Southam, G. (2007): The geomicrobiology of Au. *ISME J.* **1**, 567 - 584.

Reith, F., Stewart, L., Wakelin, S. (2012): Supergene gold transformation: Secondary and nano-particulate gold from southern New Zealand. *Chem. Geol.*, **320-321**, 32 - 45.

Reith, F., Campbell, S.G., Ball, A.S., Pring, A., Southam, G. (2014): Platinum in Earth surface environments. *Earth-Sc. Rev.*, **131**, 1 - 21.

Villanova-de-Benavent C., Proenza J.A., Galí S., García-Casco A., Tauler E., Lewis J.F., Longo F. (2014): Garnierites and garnierites: Textures, mineralogy and geochemistry of garnierites in the Falcondo Ni-laterite deposit, Dominican Republic. *Ore Geol Rev.* **58**, 91 - 109.