Osmium Isotope Characteristics of Primary and Secondary PGM in Ni-Laterites

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INTRODUCTION

Osmium-isotope compositions of Os-rich platinum-group minerals (PGM) provide critical insights about timing of melting/infiltration of melts that may produce PGM in the upper mantle (e.g. González-Jiménez et al. 2012). Earlier studies have used the $^{187}Os/^{186}Os$ ratios of PGM recovered from sediments in the supergene environment to elucidate whether PGM are supergene or hypogene in origin (Hattori and Cabri 1992). These authors concluded that PGM nuggets from placers around the world were all formed in the mantle and transferred to the supergene environment only by mechanical processes without modifying their original Os isotopic compositions.
However, a different view on the origin of PGM in supergene environments appears to suggest that PGM can effectively grow in supergene settings from low-T fluids (Augustithis 1965; Stumpfl 1974; Bowles 1986).

Our recent work on the Ni-laterites from the Dominican Republic provides textural and chemical evidence for the neo-formation of PGM at low-T in these type of soils, with an important biogenic contribution (for details see Aiglsperger et al. 2014; 2015 a, b).
Here we present the first Os-isotope data from PGM grains found in different horizons of Ni-laterites from the Falcondo mining camp. The aim of this work is to investigate the characteristics of the Re-Os system in PGM found in Ni-laterites and believed to be of either primary or secondary in origin.

SAMPLES AND ANALYTICAL METHODS

Chromitite samples as well as soil samples were collected from different levels in Ni-laterites (limonite and saprolite) from the Falcondo mining camp located in the central part of the Dominican Republic. The Falcondo mining camp is the largest Mg-silicate type Ni-laterite deposit in the Greater Antilles. The weathering profile is developed on 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 (Lewis et al. 2006; Villanova de Benavent et al. 2014; Aiglsperger et al. 2015a).
Recently, small-scale chromitite pods (2 - 5 m in diameter), included either in saprolite or in the highest levels of the limonite ("floating chromitites") were discovered during mining activities (Proenza et al. 2007; Baurier-Aymat et al. 2015). According to these authors these chromitites are systematically enriched in total PGE (up to 17 ppm) and show Ru-dominated PGM mineralogy (e.g. laurite – erlichmanite and Ru-Os-Fe compounds). In addition to PGM in chromitites, PGM also occur to a much lesser extent, within the limonite and saprolite (Aiglsperger et al. 2015a).
Numerous PGM grains were discovered in polished and thin sections as well as in heavy mineral concentrates after applying innovative hydro-separation techniques (www.hslab-barcelona.com). 40 Os-rich PGM from different horizons of the Ni-laterite profiles were selected for this study. Different occurrences of PGM were considered (e.g. PGM included in chromian spinel and primary in origin, or PGM occurring as free grains, believed to be secondary in origin) (Fig. 1).
PGM grains were investigated on a SEM microscope Quanta 200 FEI XTE 325/D8395 and a FE-SEM Jeol JSM-7100 at the Serveis Científics i Tecnòlogics, University of Barcelona, Spain.
In situ Re-Os isotope analyses were carried out at GEMOC (Australia) using a LA-MC-ICPMS following the analytical routine described by González-Jiménez et al. (2012).

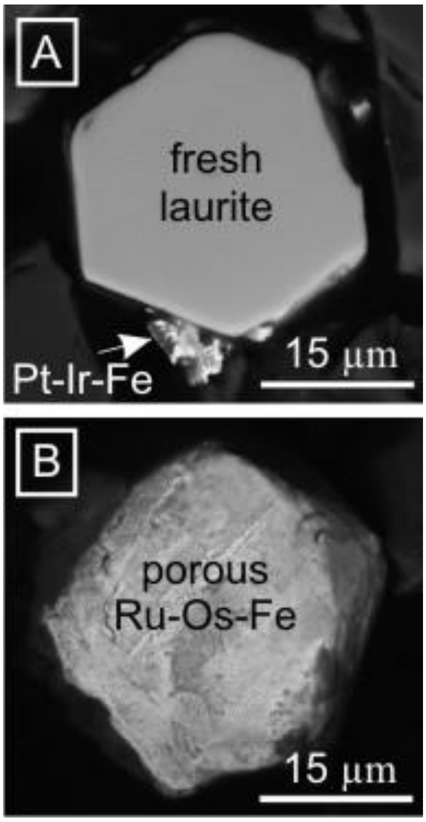

fig 1. Examples of BSE images of analyzed primary PGM (A) and secondary PGM (B).

RESULTS

$^{187}Os/^{188}Os$ ratios of investigated primary PGM, included within chromian spinel or as free grains of euhedral fresh

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laurite crystals, vary from 0.1197 to 0.1222, whereas PGM, considered secondary in origin, show systematically higher ratios up to 0.1265 (Fig. 2). $^{187}Re/^{188}Os$ values are very low in both primary and secondary PGM (<0.001) (Fig. 2). Two clusters can be observed for the calculated Rhenium-depleted (T_{RD}) model ages: primary PGM cluster around ~0.9 Ga while secondary PGM cluster around ~0.5 Ga (Fig. 3).

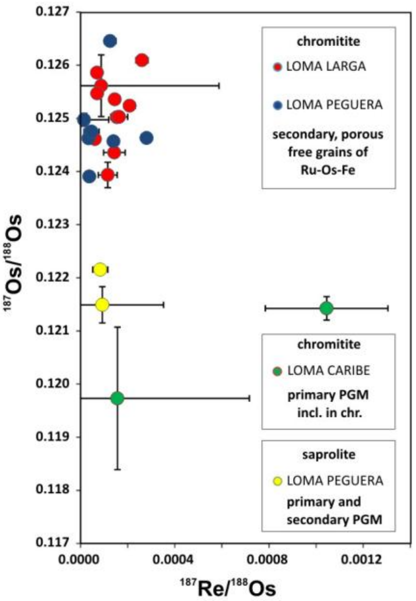

fig 2. *Plot of $^{187}Os/^{188}Os$ vs. $^{187}Re/^{188}Os$ of primary and secondary PGM from different sample locations within the Falcondo mining camp (see Baurier-Aymat et al. 2015). Uncertainties are 2σ; those not shown are smaller than the symbol.*

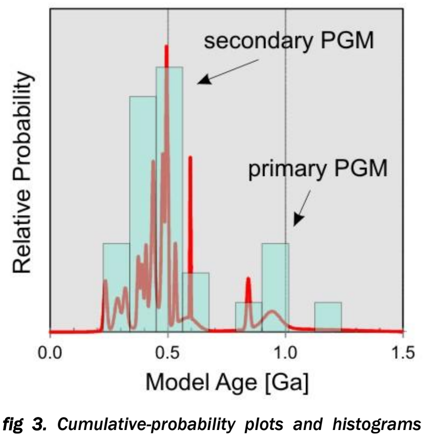

fig 3. *Cumulative-probability plots and histograms (shaded bars) of Os model ages (Ga) for investigated PGM.*

DISCUSSION AND FINAL REMARKS

Secondary PGM from the Falcondo Ni laterite yield low $^{187}Os/^{188}Os$ ratios typical of mantle PGM. This suggests that overall no significant addition of either crustal Os or Re to the PGM occurred. It is important to note that no PGM from highest levels in the limonite horizon with textural and chemical evidence suggesting neo-formation processes (e.g. Fig. 14 in Aiglsperger et al. 2015a) have been analyzed at this stage of investigation.

However, primary and secondary PGM of this study show very distinct Os-isotope compositions, suggesting that disturbance (i.e. opening) of the Re-Os system occurred during alteration of PGM.

This effect has been described for the first time in PGM from the metamorphosed chromitites of Bulgaria (González-Jiménez et al. (2012) and it is noted from PGM in the lateritic environment for the first time here.

In the case of the investigated Ni-laterites, it is believed that magmatic PGM lost S during serpentinisation, which subsequently led to the formation of highly porous, secondary Ru-Os-Fe compounds. Preliminary results, obtained using synchrotron micro-diffraction analysis at the ALBA Synchrotron (Barcelona), indicate that these secondary Ru-Os-Fe compounds most likely consist of intergrowths at the submicron scale of Ru-Os alloy and magnetite. Owing to the difference in the Os isotopic compositions between primary and secondary grains, we suggest that the fluids that altered the primary PGM while precipitating magnetite were also responsible for the disturbance of the $^{187}Os/^{188}Os$ ratios at the scale of a micron-sized PGM grain.

Our results demonstrate the importance of a detailed mineralogical study with up-to-date instruments prior to isotopic studies.

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REFERENCES

Aiglsperger T, Proenza J.A., Lewis J.F., Longo F. (2014): Is Microbial Activity Causing PGM Neoformation in Ni-Laterites? Evidence from Falcondo (Dominican Republic). Macla 19:aa-zz

*—, —, Zaccarini, F., Lewis, J.F., Garuti, G., Labrador, M., Longo, F. (2015a): Platinum group minerals (PGM) in the Falcondo Ni-laterite deposit, Loma Caribe peridotite (Dominican Republic). Miner. Deposita **50**, 105 – 123.*

—, —, —, Longo F (2015b): Multistage PGE nugget formation in Ni-Laterites: from hypogene to supergene, new insights from Falcondo (Dominican Republic). 13th SGA biennial meeting, 24-27, France.

*Augusthitis S.S. (1965): Mineralogical and geochemical studies of the platiniferous dunite – birbirite – pyroxenite complex of Yubdo, Birbir, W. Ethiopia. Chemie der Erde, **24**, 159-165.*

Baurier-Aymat S., Aiglsperger T., Proenza J.A., Lewis J.F., Longo F. (2015): Chromian spinel composition, PGE geochemistry and mineralogy of recently discovered chromitite bodies from the Loma Caribe peridotite, Dominican Republic. 13th SGA biennial meeting, 24-27, France.

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

*González-Jiménez, J.M., Gervilla, F., Griffin, W.L., Proenza, J.A., Augé, T., O´Reilly, S.Y., Pearson, N.J. (2012): Os-isotope variability within sulfides from podiform chromitites. Chem. Geol., **291**, 224 – 235.*

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

*Lewis, J.F., Draper G., Proenza J.A., Espaillat 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, Minerals. Sci. Engng., **6**, 120 – 141.*

*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.*