The Use of in situ Os-isotopes in Understanding the Segregation of Immiscible Sulphide Melts in the Caridad Chromite Deposit, Cuba

/ JOSÉ MARÍA GONZÁLEZ JIMÉNEZ (1,*), FERNANDO GERVILLA (2), JOAQUÍN A. PROENZA (3), WILLIAM L. GRIFFIN (1), SUZANNE Y. O´REILLY (1), CLAUDIO MARCHESI (4), NORMAN J. PEARSON (1)

(1) GEMOC ARC National Key Centre, Department of Earth and Planetary Sciences, Macquarie University. NSW 2109, Sydney (Australia)
(2) Dpto. Mineralogía y Petrología e Instituto Andaluz de Ciencias de la Tierra. Universidad de Granada-CSIC. 18002, Granada (España)
(3) Departament de Cristal.lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, Martí i Franquès s/n. 08028, Barcelona (España)
(4) Géosciencies Montpellier, UMR 5243, CNRS-Université Montpellier II, Place E. Bataillon. 34095, Montpellier (France)

INTRODUCTION.

The in situ measurement of Re-Os in individual minerals by laser ablation multicollector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) has opened a new research line in the geosciences field. In particular, the use of in situ laser ablation analyses of platinum-group minerals (PGM) constitutes an important advance in understanding the origin of several ore deposits carrying these noble metals (Hattori et al., 2002). The application of this new technique to the analysis of PGM minerals usually found in podiform ophiolitic chromite ore deposits has revealed significant Os-isotope heterogeneities at the kilometric, hand sample and thin section scales in these ore deposits (Gervilla et al., 2009). New interpretations suggest that such variable Os isotopic compositions, also recognized in whole-rock analyses, are related to the origin of the chromitites (and their hosted PGM) as products of mixing of melts with different degrees of fractionation and Os-isotopic signatures. Individual PGM grains with distinct Ossignatures are now the records of these melts which were probably mixed within intramantle dunitc flow channels (e.g. Gervilla et al., 2005).

On the basis of the existing models, we have started a detailed study of the Osisotope distribution in a set of sulphides of platinum-group elements and basemetals found in the chromite ore deposit of Caridad (eastern Cuba). González-Jiménez et al. (2009) noted that such sulphide mineral assemblage was formed as product of the segregation of immiscible sulfide melts coeval with chromite crystallization. Here, by using the in situ analysis of Os-isotopes in these sulfides we show how this uncommon mechanism in ophiolite chromitites took place.

THE CARIDAD DEPOSIT.

The Caridad deposit is one of the ten Crrich (Cr/Cr+Al = 0.66) chromite ore deposits that crop out in the Sagua de Tánamo Chromite district, in the easternmost part of the Mavarí-Cristal Massif (eastern Cuba). This chromite deposit was historically mined at different stages with a total production of 100,000 tons of chromite ore. Like other chromite deposits of the Mayarí-Baracoa Ophiolitic Belt (Proenza et al., 1999), the Caridad chromite deposit is enclosed in thin dunite envelope hosted in tectonite harzburgite representative of the deeper mantle. The more frequent texture of chromitite is massive (> 85 % chromite), which preferentially vol. concentrates in the core of the body. Nevertheless, semi-massive, layered, chromite and disseminated-textured are also recognized in the ores peripheral parts towards the contact with the dunite envelope.

PRIMARY SULPHIDE MINERALOGY.

González-Jiménez et al. (2010) reported a great number of primary sulphide mineral grains in the unaltered chromite crystals of the Caridad chromite deposit. Laurite (RuS₂) is the most abundant sulphide. It is accompanied by basemetal sulphides (BM-sulphides): millerite (NiS), heazlewoodite (Ni₃S₂), pentlandite [(Ni,Fe)₉S₈], chalcocite (CuS₂), chalcopyrite bornite (CuFeS₂) and Other (Cu₅FeS₄). less abundant sulphides are cuproiridisite (CuPt₂S₄),

Ru-rich pentlandite $[Ru(Ni,Fe)_9S_8]$ and a mineral with a composition close to a monosulphide solid solution but rich in PGE (here after PGE-mss). Together with these sulphides there were found Ru-Os-Ir alloys and irarsite (IrAsS).

The sulphides and associated minerals usually form inclusions that are 50 μm in their larger dimension. Nevertheless some BM-sulphides reach up to 100 μm . Commonly these grains occur as single inclusions, although they may form composite aggregates. The composite inclusions made up exclusively of BM-sulphides consist of millerite with bornite, or large grains of pentlandite associate with bornite and/or millerite.

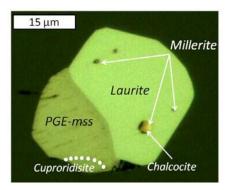


fig 1. Images (relflected light) of a composite grain containing PGM-sulphides and BM-sulphides within unaltered chromite.

The assemblages containing PGMsulphides and BM-sulphides include: 1) biphasic grains of laurite and chalcocite, 2)PGE-mss with pentlandite, millerite, bornite or chalcopyrite, and 3) Ru-Os-Ir alloys as blebs or laths at the margins of large grains of pentlandite or chalcopyrite. It is remarkable that some laurite grains carry small inclusions of

palabras clave: Isótopos de Os, Cromitita, Ofiolita.

key words: Os-istopes, Chromitite, Ophiolite.

BM-sulphides (millerite, chalcocite and/or pentlandite). Frequently, the laurite grains are zoned and these BMsulphide inclusions occur oriented along their growing planes (Fig. 1).

IN SITU OS-ISOTOPES.

A total of 25 grains of primary sulphides comprising laurite, PGE-mss and millerite were analyzed for this study, using a 213nm laser attached to a Nu Plasma MC-ICPMS; ion beams were collected in an array of Faraday cups. Each single grain was fully analyzed during ablation runs. As a whole in the Caridad deposit, initial 1870s/1880s cover a range from 0.11880 ± 0.0006 and 0.12740 ± 0.0003 (2 σ). γOs has subchondritic values ranging between -6.80 and -0.82 compared with the primitive mantle (Walker et al., 2004) at the time of the chromitite formation (90 Ma; Iturralde-Vinent et al., 2006). 1870s/1880s and 187Re/1880s correlate negatively, and there is a clear difference in the isotopic compositions of the different analyzed minerals. Laurite has 1870s/1880s that varies between 0.1263 \pm 0.0007 and 0.1243 ± 0.0001 (20) and 187Re/188Os that ranges between 0.0050 ± 0.0001 and 0.00140 ± 0.00002 (2 σ), with $\gamma Os_{(90 Ma)}$ varying between -0.9 and -2.8. The PGEmss analyzed show ¹⁸⁷Os/¹⁸⁸Os of 0.12242 ± 0.0003 (2 σ) and ¹⁸⁷Re/¹⁸⁸Os between 0.0025 \pm 0.0002 (2\sigma), with γOs_(90 Ma) of -3.96. Millerite has ¹⁸⁷0s/¹⁸⁸0s 0.12292±0.006-0.12191±0.0002 (2 σ) and ¹⁸⁷Re/¹⁸⁸Os $=0.0168\pm0.002-0.0023\pm0.001(2\sigma)$ with yOs(90 Ma) varying between -3.6 and -4.4.

DISCUSSION.

Primary sulphides in unaltered chromite are believed to be faithful records of the magmatic environment in which chromitite formed since they crystallized from the same parental melt (González-Jiménez et al., 2009). Furthermore, they preserve the isotopic composition of their parental melt, thereby inheriting the isotopic signature of the mantle source (Walker et al., 2004). The low ¹⁸⁷Re/¹⁸⁸Os and unradiogenic yOs values of the analyzed sulphide grains suggest that parental melts of the chromitites were derived from a strongly depleted mantle. Moreover, the strong variability in the isotopic composition shown by the different mineral species suggests that individual grains crystallized from melts with different

isotopic signatures. Thus chromite crystallized from a S-undersaturated melt with an Os isotopic composition slightly more radiogenic than that of the PGE-mss and millerite, which most probably derived from a more evolved, S-saturated melt with and lower yOs values. The association of laurite, PGEmss and millerite in the same aggregate suggests that these distinct melts coexisted in space and time when chromite formed. The formation of chromitites as a result of mingling of melts within intramantle melt channels. generated by reaction of mantle melts and peridotite is a feasible mechanism to explain such processes (Gervilla et al., 2005; González-Jiménez et al., 2009).

REFERENCES.

- Gervilla, F., Proenza, J.A. Frei, R., González-Jiménez, J.M., Garrido, C.J., Melgarejo, J.C., Meibom, A., Día-Martínez, R. Lavaut, W. (2005): Distribution of platinum-group elements and Os isotopes in chromite ores from Mayari-Baracoa Ophiolitic Belt (eastern Cuba). Contributions to Mineralogy and Petrology, **150**, 589-607.
- Gervilla, F., Marchesi, C., González-Jiménez, J.M., Proenza, J.A., Garrido, C.J., Griffin, W.L., O'Reilly, S.Y., Pearson, N. (2009): Different scales of Os isotopic heterogeneity in ophiolite chromitites from Sagua de Tánamo and Mayarí mining districts (eastern Cuba). Geophysical Research Abstracts, **11**, EGU2009-12876.
- González-Jiménez, J.M., Gervilla., F., Proenza, J.A., Kerestedjian, T., Augé, T., Bailly, L. (2009): Zoning in laurite (RuS₂)erlichmanite (OSS₂): implications for the origin of PGM in ophiolite chromitites. European Journal of Mineralogy, **21**, 419-432.
- Iturralde-Vinent, M.A., Díaz-Otero, C., Rodíguez-Vega, A., Díaz-Martínez, R. (2006): Tectonic implications of paleontologic dating of Cretaceous-Danian sections of Eastern Cuba. Geologica Acta, 4, 89-102.
- Hattori, K., Arai, S., Clarke, D.B. (2002): Selenium, Tellurium, Arsenic and Antimony contents of primary mantle sulphides. The Canadian Mineralogist 40, 637-650.
- Proenza, J., Gervilla, F., Melgarejo, J.C., Bodinier, J.L. (1999): AI- and Cr-rich chromitites from the Mayarí-Baracoa Ophiolitic Belt (Eastern Cuba): consequence of interaction between volatile-rich melts and peridotite in suprasubduction mantle. Economic Geology, **94**, 547-566.
- Walker, R.J. Brandon, A.D., Bird, J.M., Piccoli, P.M., McDonough, W.F., Ash, R.D. (2004): ¹⁸⁷Os-¹⁸⁶Os systematic of Os-Ir-Ru alloy grains from wouthwestern Oregon. Earth and Planetary Science Letters, **230**, 211-216.