

Small-scale mobility of platinum-group elements during serpentinization: evidence from the distribution of platinum-group minerals in chromitites from the Sagua de Tánamo district (Mayarí-Baracoa Ophiolite Belt, eastern Cuba)

J.M. González-Jiménez

Departamento de Mineralogía y Petrología, Facultad de Ciencias, and Instituto Andaluz de Ciencias de la Tierra (CSIC)-Universidad de Granada; Avda. Fuentenueva s/n, 18002 Granada, Spain.

J.A. Proenza

Departament de Cristal·lografia, Mineralogia i Dipòsits Minerals, Facultat de Geologia, Universitat de Barcelona, Martí i Franquès s/n, 08028 Barcelona, Spain

F. Gervilla

Departamento de Mineralogía y Petrología, Facultad de Ciencias, and Instituto Andaluz de Ciencias de la Tierra (CSIC)-Universidad de Granada; Avda. Fuentenueva s/n, 18002 Granada, Spain.

J.A. Blanco-Moreno

Departamento de Geología. Instituto Superior Minero-Metalúrgico de Moa, Las Coloradas s/n, 83320 Moa, Holguín, Cuba.

R. Ruiz-Sánchez

Empresa Geominera de Oriente, Carretera de Siboney s/n, Santiago de Cuba, Cuba

Abstract. We present a detailed statistical study of the distribution of platinum-group minerals in a set of strongly serpentinized chromitites from the Sagua de Tánamo mining district (Mayarí-Baracoa Ophiolite Belt, eastern Cuba). On the basis of the distribution, textures and chemical nature of the platinum-group minerals we show how platinum-group elements firstly concentrate as primary platinum-group minerals during the magmatic stage, then were mobilized during serpentinization in an ocean-floor scenario when these primary platinum-group minerals became unstable.

Keywords. Chromitites, platinum-group elements, mobility, ocean-floor serpentinization, Sagua de Tánamo.

1 Introduction

The platinum-group elements (PGE) have been classically considered as immobile elements during low-temperature alteration. However, many evidences suggest that such noble metals could be mobilized when pre-existing PGMs (usually magmatic) become unstable as result of their interaction with both reduced and/or oxidized altering fluids. Secondary re-mobilization and later re-deposition of PGE is not an extended process, but very limited or restricted to the proximities to their precursor PGMs (e.g. Thalhammer et al., 1990; Proenza et al., 2006). In this work, we provide evidence of mobility of PGE by low-temperature hydrothermal fluids, through a detailed mineralogical study of PGM. Our study is focussed on a set of chromite deposits from the Sagua de Tánamo chromite mining district (Mayarí-Baracoa Ophiolite Belt, eastern Cuba) (Figure 1). The chromite deposits are hosted by mantle tectonites (harzburgite and minor dunite) which are associated

with volcanic rocks typical of ocean island arc tholeiites, as well as chaotic and breccia rocks of a melange zone. D, O and C isotopes (Proenza et al., 2003) suggest that chromitites and host peridotites were serpentinized and partly chloritized by low-temperature fluids generated as a consequence of peridotite-seawater interaction, in a subocean-floor scenario.

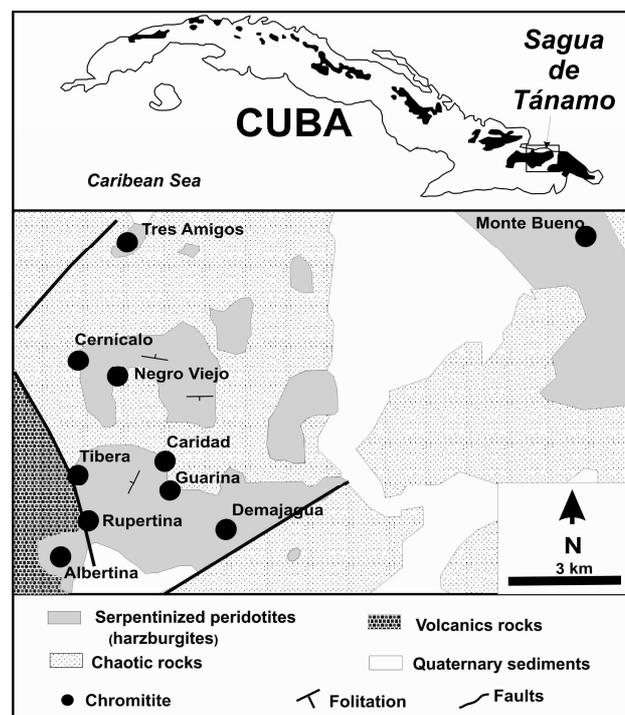


Figure 1. Geographical location and simplified geological map of the Sagua de Tánamo chromite mining district.

2 Distribution and assemblages of platinum-group minerals

A total of 70 PGM grains were identified in the chromitites. They occur within chromite crystals (69% in unaltered cores and 7% in ferritchromite rims) and along fractures (14%) or in the interstitial silicate matrix between chromite grains (10%).

2.1 PGM in chromite

The PGM assemblage in unaltered chromite consists of members of laurite (RuS_2)-erlichmanite (OsS_2) solid solution series (54%), followed by members of the irarsite (IrAsS)-hollingworthite (RhAsS) solid solution series (26%), iridium (7%), cuproiridsite (CuIr_2S_4) (4%) and kashinite (Ir_2S_3) (<1%) (Figure 2). Only laurite, erlichmanite, and iridium form single grains. Biphase grains consist of laurite with irarsite, hollingworthite or millerite; irarsite with hollingworthite, or iridium with kashinite. Polyphase aggregates consist of laurite and/or cuproiridsite with clinopyroxene. Crystal morphologies are predominantly idiomorphic and the grain size does not surpass 20 μm across.

In ferritchromite, Ru-Fe-Os-Ir-Ni-(Rh) oxides are the most abundant PGMs (57%), followed by laurite (28%), and iridium (14%) (Figure 2). Both Ru-Fe-Os-Ir-Ni-(Rh) oxides and laurite occur as single isolated grains. Whereas the unique identified biphasic grain is made up of laurite with pentlandite, the recognized polyphase inclusion is composed by iridium associated with pentlandite and chalcopyrite. These PGM show idiomorphic to subidiomorphic morphologies with corroded outlines. The PGE oxides show inner porosity as well as radial cracks. Grain size is less than 25 μm .

2.2 PGM in fractures and in the silicate matrix

Like in ferritchromite, the PGM assemblage in fractures is dominated by Ru-Fe-Os-Ir-Ni-(Rh) oxides (46%) and laurite (36%) whereas irarsite (9%) and cuproiridsite (9%) are less abundant (Figure 2). Ru-Fe-Os-Ir-Ni-(Rh) oxides and laurite are also the only PGM found as single grains. Composite grains are constituted by laurite or cuproiridsite with pentlandite, as well as Ru-Fe-Os-Ir-Ni-(Rh) oxides associated with irarsite. PGM shapes vary from idiomorphic to subidiomorphic with partly corroded external grain boundaries. Grain size rarely surpass 15 μm ; nevertheless, some PGE oxides reach 80 μm across.

The PGM mineralogy in the silicate matrix consists of members of the irarsite-hollingworthite (RhAsS)-ruarsite (RuAsS) solid solution series (34%), an unnamed RhNiAs phase (32%), Ru-Fe-Os-Ir-Ni-(Rh) oxides (17%) and laurite (17%) (Figure 2). Morphologies are the same than in altered chromite and fractures. In this textural position PGM grains show corroded borders too. Irarsite, Ru-Fe-Os-Ir-Ni-(Rh) oxides and laurite form single isolated grains. Biphasic grains are made up of Ru-Fe-Os-Ir-Ni-(Rh) oxides with unnamed RhNiAs. Polyphase grains are made up of an aggregate of hollingworthite and ruarsite associated with the unnamed RhNiAs. Grain size is less than 20 μm .

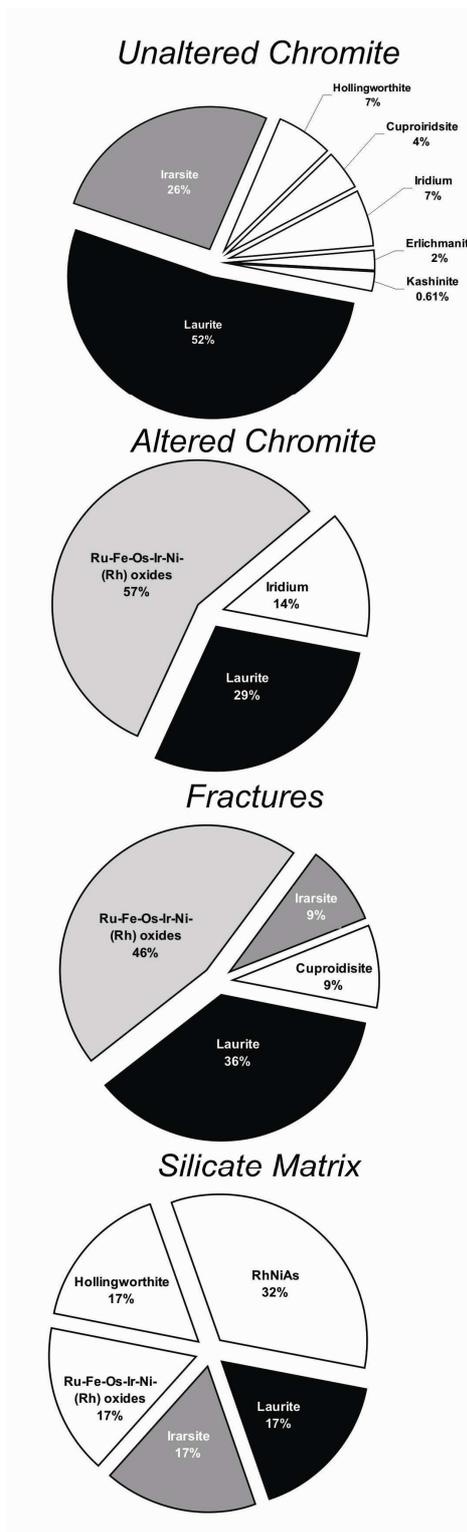


Figure 2. Sector diagrams showing the proportions of the platinum-group minerals identified in the different textural positions in the chromitites.

3 Chemical variations

Laurite shows a variable Ru/(Ru+Os) ratio (0.63 to 0.90 in unaltered chromite, 0.62 in ferritchromite, 0.82 to 0.94 in fractures, and 0.77 to 0.78 in silicate matrix) (Figure 3). This strong variation of the Ru/(Ru+Os) ratio in laurite is caused by its variable Os contents (0.10apfu to 0.36 in grains located within chromite, and 0.06 to 0.22 in grains outside of chromite).

The Ru/(Ru+Os) ratio shown by Ru-Fe-Os-Ir-Ni-(Rh) oxides (0.81 to 0.91 in fractures and 0.80 to 0.91 in silicate matrix) is practically the same than in laurites located in fractures and slightly higher than in the silicate matrix (Figure 3). Ru-Fe-Os-Ir-Ni-(Rh) oxides in fractures are richer in PGE (0.54 to 0.68, 0.11 to 0.16, 0.05 to 0.09 and up to 0.01apfu of Ru, Os, Ir and Rh respectively) and poorer in base metals (0.02 to 0.21, 0.01 to 0.07apfu of Fe and Ni respectively) than those located in the silicate matrix (0.29 to 0.58, 0.05 to 0.10, 0.03 to 0.10apfu of Ru, Os and Ir; and 0.28 to 0.53 and 0.02 to 0.04apfu of Fe and Ni, respectively). Some grains show residual As and S contents (up to 3.13 and 0.19 at.%).

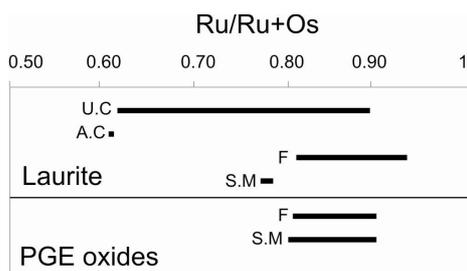


Figure 3. Variations of Ru/Ru+Os ratio in laurite and PGE oxides. U.C.(unaltered chromite), A.C. (altered chromite), F (fractures), S.M. (silicate matrix)..

Sulpharsenides of the irarsite-hollingworthite series show a wide compositional range in unaltered chromite (from 0.52apfu Rh to 0.71apfu Ir). Ru and Pt contents reaches up to 0.20 and 0.01apfu respectively. Irarsite in fractures (0.66 to 0.50 apfu Ir and 0.20 to 0.15apfu Rh) is richer in Pt (up to 0.15apfu) and poorer in Ru (up to 0.13apfu). In contrast, irarsite in the silicate matrix (0.87 to 0.60apfu Ir and 0.28 to 0.03apfu Rh) is poorer in Ru (up to 0.09apfu) and Pt (not detected) than those located in unaltered chromite and fractures. Some irarsite-hollingworthite grains in alteration zones show partial desulphurization as well as loss of As.

4 Discussion

PGM in unaltered chromite are magmatic, crystallized before or contemporarily with chromite (González-Jiménez et al., 2009). In contrast, PGM located in ferritchromite, fractures and in the silicate matrix probably are secondary, formed, or at least affected, by alteration processes, after the magmatic stage (e.g. Stockman & Hlava 1984). The Os variation range in laurite within chromite is wider than in laurite outside of chromite. However, the lower (on average) Os content in the latter suggests certain re-mobilization of Os during alteration as suggested Tarkian & Prichard (1987) in chromitites from Shetland. The corroded borders shown by laurite outside of chromite crystal suggests that destabilization of the sulphide and the subsequent Os mobilization had take place during initial stages of serpentinization (Garuti y Zaccarini 1997; Proenza et al., 2003). Likewise, decreasing of Ru, Pt and Rh in irarsite-hollingworthite grains located in fractures and in silicate matrix also suggests their mobility during alteration

from sulpharsenides. However, the irregular distribution of Ir contents in these minerals does not allow establishing a clear trend of mobilization. Predominant, highly oxidizing conditions during low-temperature chloritization (< 190 °C; Proenza et al., 2003) resulted in oxidation of previously altered sulphides and sulpharsenides (e.g. laurite and irarsite) and their transformation to PGE oxides. The lower PGE contents shown by PGE oxides located in the silicate matrix compared with those located in fractures, suggest that major interaction with oxidizing fluids favoured mobilization of PGE. The close association of the unnamed RhNiAs phase with a PGE oxide suggests that some amounts of the re-mobilized PGE combined with base metals released during alteration.

All these facts suggest that mobilization of PGE by low-temperature fluids generated during serpentinization takes place at small-scale (grain by grain). Our observations agree with previous work suggesting a very limited mobility of PGE during alteration (Tarkian & Prichard 1987; Thalhammer et al., 1990).

Acknowledgements

This research has been financially supported by the Spanish project CGL2007-61205 of the MEC, the research group (RNM 131) of the Junta de Andalucía, and F.P.I grant BES-2005-8328 of the Spanish Ministry of Education and Sciences.

References

- Garuti G, Zaccarini F, (1997) In situ alteration of platinum-group minerals at low temperature: evidence from serpentinized and weathered chromitite of the Vourinos Complex, Greece. *The Canadian Mineralogist*. 35, 611-626.
- González-Jiménez JM, Gervilla F, Proenza JA, 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* (in press).
- Proenza JA, Alfonso P, Melgarejo JC, Gervilla F, Tritlla J, Fallick AE (2003) D, O and C isotopes in podiform chromitites as fluid tracer for hydrothermal alteration processes of the Mayarí-Baracoa Ophiolitic Belt, eastern Cuba. *Journal of Geochemical Exploration*. 78-79, 117-122.
- Proenza JA, Zaccarini F, Cábana C, Escayola M, Schalamuk A, Garuti G (2006). Chromite composition and platinum-group minerals in chromitites of the Western Ophiolite Belt from Pampeans Ranges of Córdoba, Argentina. *Ore Geology Review*. 33, 32-48.
- Stockman HW, Hlava P (1984) Platinum-Group Minerals in Alpine Chromitites from Southwestern Oregon; *Economic Geology* 79: 491-508.
- Tarkian M, Prichard HM (1987) Irarsite-hollingworthite Ru-, Os-, Ir- and Rh-Bearing PGM's from the Shetland Ophiolite Complex. *Mineralium Deposita*. 22, 178-184.
- Thalhammer OAR, Prochaska W, Mühlhans HW (1990) Solid inclusions in chrome-spinels and platinum group element concentrations from the Hochgrössen and Kraubath ultramafic massif (Austria). *Contributions to Mineralogy and Petrology*. 105, 66-80.