

Podiform chromitites from the Calzadilla de los Barros serpentinite, Iberian Massif, SW Spain

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Abstract. Podiform chromitites occur as in situ and removed bodies in the Calzadilla de los Barros Serpentinite (Iberian Massif, SW Spain), a set of ultramafic massifs made up of partly serpentinized harzburgite with minor dunite and gabbros. They consist of massive to semi-massive chromitites, frequently with nodular texture. Chromite chemistry is characterized by high Al_2O_3 contents and up to 0.4 wt.% TiO_2 , in agreement with a MORB affinity of the parental melt. Platinum-group element abundances are similar to most Al-chromitites reported in the literature except for an unusual enrichment in Pt and Pd. High Pt and Pd values were probably caused by late metamorphic alteration.

Keywords. podiform chromitites, platinum-group elements, Iberian Massif

1 Introduction

The variety of chromite textures exhibited by podiform chromitites located in the mantle section of ophiolite complexes compared to those occurring in stratiform igneous intrusions as well as their chemical composition, trends and platinum-group element contents allow identifying isolated ultramafic massifs as portions of dismembered ophiolite sections. Thus, we have study different, in situ and removed chromitite bodies in the Calzadilla de los Barros Serpentinite, a set of partly serpentinized peridotite massifs located in the Iberian Massif, SW Spain, to confirm their supposed ophiolitic nature (Monterrubio 1991) and to understand their magmatic and metamorphic features.

2 Geological context

The Calzadilla de los Barros serpentinite massifs are located in the NE flank of the Olivenza-Monesterio antiform, a major WNW-ESE-trending Variscan structure occupying a central position within the Ossa-Morena zone of the Iberian Massif. These massifs mainly consist of two serpentinite bodies named Cerro Cabrera and Sierra Cabeza Gorda, as well as a narrow band of highly deformed serpentinites occurring along a NW-SE shear zone located to the SW of the major serpentinite bodies, close to the contact with Cambrian sediments (Fig. 1). The serpentinite massifs underlay the precambrian tuffaceous materials of the Malcocinado Formation and occur in tectonic contact with the schists

and shales of the Serie Negra Formation (Jiménez-Díaz et al. 2010; Fig. 1).

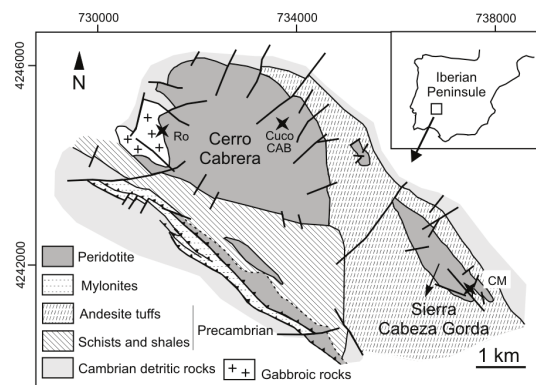


Figure 1. Schematic map showing the geology of the Calzadilla de los Barros serpentinite massifs (modified from Jiménez-Díaz et al. 2010) and the location of the sampled areas.

The different massifs are made up of strongly serpentinized harzburgite and dunite with minor chromitite. Some gabbroic rocks occur at the NW contact of the Cerro Cabrera massif. The tectonite foliation is poorly preserved but when visible it is oriented from N130°E to N160°W dipping to the NE and NW at high angles.

3 Chromitite deposits

3.1 Mineralogy and texture

Chromitites form variable sized, layers and lenses (pods) hosted by serpentinized dunites. They mainly show semi-massive (60-85% chromite) to massive texture (>85% chromite) although few centimetre-thick layers of disseminated chromitite (20-60% chromite) were drilled in the SW zone of Cerro Cabrera. Semi-massive chromitites often show nodular texture consisting of rounded to euhedral grains (up to 1 cm across) with interstitial Mg-chlorite. Single chromite nodules are not homogeneous crystals but aggregates of rounded grains (1-3 mm across) arranged in cubic packing. Disseminated chromitite layers are made up of subhedral, partly corroded chromite crystals associated

with interstitial Mg-chlorite and antigorite. Chromite grains are fractured and show variable thick (<250µm), alterations rims progressing from grain boundaries and fractures inward.

3.2 Mineral chemistry

The analysed samples come from removed pods in the SE (Cuco 7, 8 & 9 and CAB 2 & 10) and NW (RO 8 and 9) zones of Cerro Cabrera, as well as from a in situ, 4 m long and 1 m thick pod (CM-4), located in the SE end of Sierra Cabeza Gorda (Fig. 1). Only unaltered nuclei have been analysed to obtain the primary composition of chromite. This composition is similar in all samples but RO-8 and RO-9, and is characterized by small variations in Mg# [$Mg\# = Mg/(Mg+Fe^{2+}) = 0.52-0.69$] and Cr# [$Cr\# = Cr/(Cr+Al) = 0.49-0.55$] (Fig. 2A).

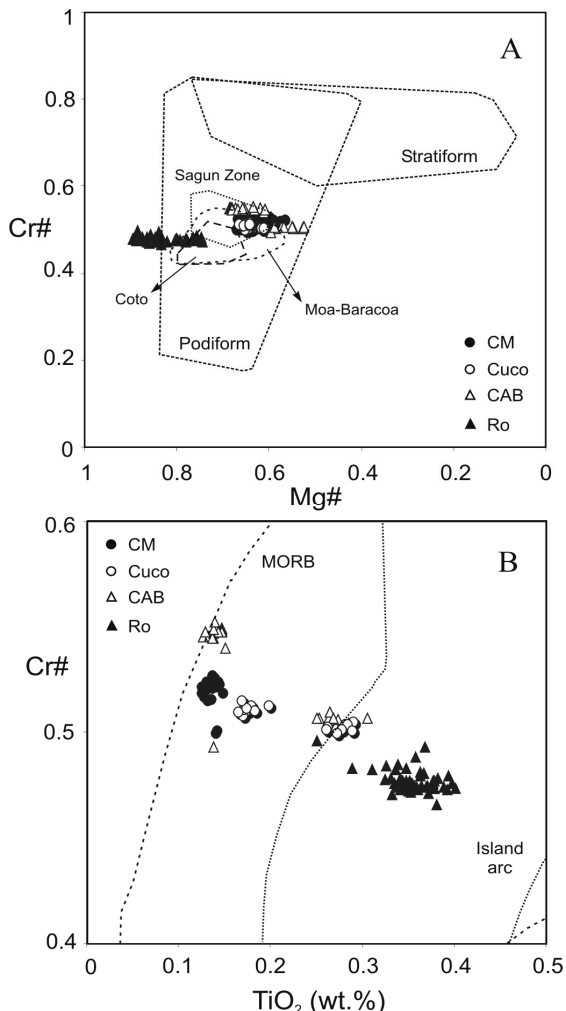


Figure 2. Cr# [$Cr/(Cr+Al)$] versus Mg# [$Mg/(Mg+Fe^{2+})$] (A) and TiO_2 (wt.%) (B), binary diagrams for individual analyses of chromite nuclei from Calzadilla de los Barros chromitites. The compositional fields of Al-rich chromite from Moa-Baracoa (Proenza et al. 1999), Coto (Leblanc and Violette 1983; Zhou et al. 2000) and Sagun Zone (Matsumoto et al. 1997) as well as chromian spinel in lavas of different geochemical affinities and tectonic settings (Arai 1992) are shown for comparison. MORB: dashed lines. Island arc: solid lines.

Chromite in RO-8 and RO-9 has almost identical composition with higher Mg# (0.74-0.89) and lower Cr# (0.46-0.49) than those from the other studied samples (Fig. 2A). TiO_2 content varies from 0.1 to 0.5wt.% and correlates negatively with Cr# (Fig. 2B). This diagram also shows that chromite from Calzadilla de los Barros serpentinite plots on a field where the composition of chromite from MORB- and Island Arc-type lavas overlap. MnO varies from 0.2 to 0.9 wt.%, V_2O_5 is <0.28 wt.%, NiO is <0.23wt.% and ZnO is <0.39wt.%. These compositions mostly overlap with those of Al-rich chromitites from Coto (Philippines), Sangun Zone (Japan) and Moa-Baracoa (eastern Cuba) ophiolites (Fig. 2A).

3.3 Platinum-group elements

Thirty-six representative rock samples of the different chromitite pods were analysed for whole rock PGE geochemistry in Genalysis Laboratory Services Pty. Ltd., Maddington (Western Australia). Platinum-group elements were analysed by ICP-MS after nickel sulphide digest. Detection limits were 2 ppb for Ir, Os, Ru, Pd and Pt, and 1 ppb for Rh.

Chromitite samples show low PGE abundances. Total PGE contents range from 105 to 291 ppb but two samples show even lower PGE values: 29 and 52 ppb. Nevertheless, these chromites are unusually rich in Pt (up to 66 ppm) and, mainly, Pd (up to 172 ppm) compared with most ophiolite chromitites.

Chondrite-normalized PGE patterns plot between 0.4 and 0.002 times the chondritic values and are characterized by a variably slope (from positive to nearly flat) from Os to Ru followed by significant depletion in Rh and a positive-sloped segment from Rh to Pd. These patterns partly resemble those reported for Al-rich chromitites from Moa-Baracoa and Sagua de Tánamo ophiolite massifs (Proenza et al. 1999; Gervilla et al. 2005; González-Jiménez et al. 2011) but differ in the high Pt (up to 0.065 Pt_N) and Pd (up to 0.3 Pd_N) chondrite-normalized values.

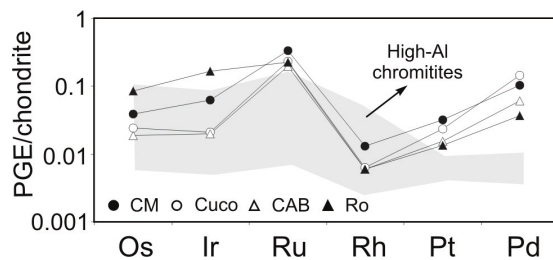


Figure 3. Chondrite-normalized, PGE patterns of chromitites from Calzadilla de los Barros serpentinite massifs. Drawn patterns represent the average values of each sampled pod. Gray field is compilation of data of high-Al chromitites from Proenza et al. (1999) and Gervilla et al. (2005).

4 Concluding remarks

The Podiform shape of the in situ chromitite body from Sierra Cabeza Gorda, the nodular texture of most samples from both in situ and removed chromitite



bodies, and the chemical composition of all studied chromite grains, similar to that of chromitites from Coto (Zambales ophiolite, Philippines; Leblanc and Violette, 1983; Zhou et al. 2000), Sangun Zone ophiolites (Matsumoto et al. 1997) and Moa Baracoa (Mayarí-Baracoa Ophiolitic Belt, Proenza et al. 1999) evidence the ophiolitic nature of the Calzadilla de los Barros chromitites and serpentinite (Monterrubio 1991). The Al-rich composition of chromite (Fig. 2) further suggest that these chromitites formed in the upper part of the ophiolite mantle section or in the mantle-crust transition zone, close to the overlying crustal gabbros, as occur in Mayarí-Baracoa (Proenza et al. 1999), Oman (Ahmed and Arai 2002) and Bay of Islands (Bédard and Hébert 1998) ophiolite complexes. In fact, the Al₂O₃-richest chromitite (samples RO) are those located close to the gabbro outcrop. The Al₂O₃ content of the melt in equilibrium with chromites [calculated from Maurel and Maurel's (1982) equation] varies from 15.98 to 16.45 wt.% in RO samples and from 14.97 to 15.96 wt.% in CM, Cuco and CAB samples, and agrees with a MORB affinity of such melt. TiO₂ contents also support such affinity, probably related with an Back Arc geodynamic setting (Fig. 2).

PGE abundances resemble those of ophiolitic chromitites; however, chondrite-normalized PGE patterns do not show the characteristic negative slope from Ru to Pd (e.g. Leblanc 1991) but an unusual Pt and Pd enrichment up to values close to those of Ru. These anomalous Pt and Pd contents could be either of primary origin or related with the metamorphic alteration that affected the chromitites and the host serpentinite. The low PGE contents of MORB melts hardly support the primary origin of such Pt and Pd enrichment but point to a secondary enrichment in these PGE during metamorphism. This interpretation agrees with the fact that Pd and, at lesser extent, Pt are the most soluble PGE in hydrothermal fluids.

Acknowledgements

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References

- Ahmed AH, Arai S (2002) Unexpectedly high-PGE chromitite from the deeper mantle section of the northern Oman ophiolite and its tectonics implications. *Contrib Mineral Petr* 143:263-278
- Arai S (1992) Chemistry of chromian spinel in volcanic rocks as a potential guide to magma chemistry. *Mineral Mag* 56:173-184
- Bédard JH, Hébert R (1998) Formation of Chromitites by assimilation of crustal pyroxenites and gabbros into peridotite intrusions: North Arm Mountain massif, Bay of Islands ophiolite, Newfoundland, Canada. *J Geophys Res* 103:5165-5184
- Jiménez-Díaz A, Capote R, Tejero R, Lunar R, Ortega L, Monterrubio S, Maldonado C, Rodríguez D (2009) La fábrica de las rocas miloníticas de la zona de cizalla de Los Llanos (Calzadilla de los Barros, Badajoz). *Geogaceta* 46:27-30
- Gervilla F, Proenza JA, Frei R, González-Jiménez JM, Garrido CJ, Melgarejo JC, Meibom A, Díaz-Martínez R, Lavaut W (2005). Distribution of platinum-group elements and Os isotopes in Chromite ores from Mayarí-Baracoa Ophiolitic Belt (Eastern Cuba). *Contrib Mineral Petr* 150:589-607
- González-Jiménez JM, Proenza JA, Gervilla F, Melgarejo JC, Blanco-Moreno JA, Ruiz-Sánchez R, Griffin WJ (2011) High-Cr and high-Al Chromitites from the Sagua de Tánamo district, Mayarí-Cristal ophiolitic massif (Eastern Cuba): Constraints on their origin from mineralogy and geochemistry of chromian spinel and platinum-group elements. *Lithos* DOI:10.1016/j.lithos.2011.01.016
- Leblanc M (1991) Platinum-group elements and gold in ophiolitic complexes: distribution and fractionation from mantle to oceanic floor. In: Peters TJ, Nicolas A, Coleman RG (eds) *Ophiolite genesis and evolution of oceanic lithosphere*. Kluwer, Dordrecht, 231-260
- Leblanc M and Violette JF (1983) Distribution of aluminium-rich and chromium-rich Chromite pods in ophiolite peridotites. *Econ Geol* 78:293-301
- Matsumoto I, Arai S, Yamauchi H (1997) High-Al Podiform Chromitites in dunite-harzburgite complexes of the Sangun zone, central Chugoku district, Southwest Japan. *J Asian Earth Sci* 15:295-302
- Maurel C, Maurel P (1982) Étude expérimentale de la distribution de l'aluminium entre bain silicaté basique et spinelle chromifère. Implications pétrogénétiques: tener en chromie des spinelles. *Bulletin de Minéralogie* 105:197-202
- Monterrubio S (1991) Las mineralizaciones de Cr-platinoides asociadas a las rocas ultrabásicas del macizo Hespérico. PhD dissertation Universidad Complutense de Madrid, 323 p
- Proenza JA, Gervilla F, Melgarejo JC, Bodinier JL (1999). Al- and Cr-rich Chromitites from the Mayarí-Baracoa Ophiolitic Belt (Eastern Cuba): consequence of interaction between volatile-rich melts and peridotites in suprasubduction mantle. *Econ Geol* 94:547-566
- Zhou MF, Yumul GP, Malpas J, Sun M (2000) Comparative study of platinum-group elements in the Coto and Acoje blocks of the Zambales Ophiolite Complex, Philippines. *Island Arc* 9:556-564