

Inverse Zoning in Poly-Metamorphosed Chromite from the Calzadilla de los Barros Ultramafic Bodies (SW Iberian Peninsula)

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INTRODUCTION

Chromites in chromitites and ultramafic rocks are commonly zoned, reflecting mineralogical, textural and chemical changes induced by post-magmatic processes (e.g. González-Jiménez et al., 2009). Despite the large number of studies published on zoned chromite, little is known on how multiple metamorphic episodes or high-temperature contact metamorphism impact on the formation of zoned chromite.

Here, we report a detailed study of zoned chromite in chromitites and dunites from the ultramafic bodies of Calzadilla de los Barros (Ossa-Morena zone, SW Iberian Peninsula). This zone experienced a complex tectono-metamorphic evolution from the Neoproterozoic to late Carboniferous (Quesada 2006).

GEOLOGICAL SETTING

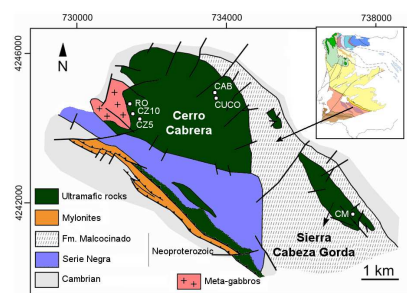


fig 1. Simplified geologic map of the Calzadilla de los Barros ultramafic bodies (modified from Merinero et al., 2013) with the locations of studied chromitites (RO, CAB, CUCC and CM sites) and dunites (CZ5 and CZ10 drill cores).

The ultramafic bodies of Calzadilla de los Barros are located on the NE flank of the Olivenza-Monesterio antiform, in the Ossa-Morena zone (Fig. 1). This zone of the Iberian Massif records a complex tectonic evolution with two major

episodes of regional metamorphism: the Cadomian (Neoproterozoic) and Variscan (Late Palaeozoic) orogenies, and the intrusion of abundant plutons during Cambrian and Variscan times.

There are two main ultramafic bodies cropping out in the Calzadilla de los Barros area: Cerro Cabrera and Sierra Cabeza Gorda. The rocks that constitute both massifs are highly serpentinised harzburgite and dunite hosting several chromitite bodies (Merinero et al., 2013). Strongly mylonitised meta-gabbros crop-out in contact with the western part of the Cerro Cabrera body (Jiménez-Díaz et al., 2009).

CHROMITE IN CHROMITITES

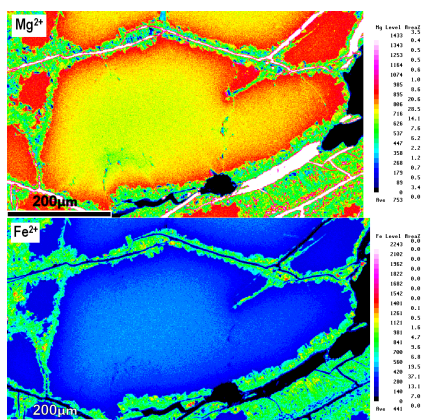


fig 2. Electron microprobe element maps (Mg^{2+} and Fe^{2+}) showing the compositional zoning of the second type of zoned chromite: Mg^{2+} increase whereas Fe^{2+} decrease from inner to outer core.

Chromite grains in massive and semi-massive chromitites of the Calzadilla de los Barros ultramafic bodies are commonly fractured and show complex patterns of zoning. These patterns are characterised by composite cores surrounded by thin rims of porous chromite. Inner cores of chromite present homogeneous high-Al

composition: $Cr\# [(Cr/(Cr+Al))]$ varies from 0.47 to 0.51 and $Mg\# [(Mg/(Mg+Fe^{2+}))]$ varies from 0.64 to 0.77. Two types of zoned chromite are observed: (1) chromite with zoned cores characterised by $Mg\#$ decrease from inner to outer core with constant $Cr\#$, surrounded by Fe^{3+} -poor, porous rims and (2) grains with the opposite chemical trend ($Mg\#$ increase from inner to outer core) surrounded by Fe^{3+} -rich porous rims (Fig. 2). The second type of zoned chromite is only observed in chromitites sampled in a pod located in the western part of the Cerro Cabrera body (RO in Fig. 1). Clinocllore is the only silicate mineral surrounding chromite grains and filling rims pores in all chromitites.

ACCESSORY CHROMITE IN DUNITES

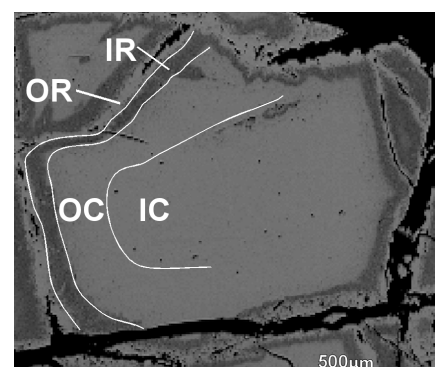


fig 3. Backscattered-electron image of accessory chromite in dunite showing complex textural and compositional zoning. IC = inner core, OC = outer core, IR = inner rim, OR = outer rim.

The grains of accessory chromite in dunites of the Calzadilla de los Barros ultramafic bodies are subhedral to anhedral with thick corroded margins; they are enveloped by clinocllore. Most of them are of very small size (< 1 mm) and show high degree of alteration and almost complete transformation to Cr-magnetite. However, some larger grains

(> 1 mm) exhibit complex mineralogical, textural and chemical zoning with three concentric zones (from inner core to outer core and to inner rim) characterised by progressive Mg# increase and Cr# decrease, surrounded by an outer rim with almost the same Cr-magnetite composition as the inner core (Fig. 3). This type of zoned chromite only occurs in dunites sampled in the drill core CZ10 (see location in Fig. 1).

DISCUSSION

The decrease of Mg# at constant Cr# from inner to outer core observed in most studied zoned chromite from chromitites can be interpreted as a consequence of the sub-solidus re-equilibrium commonly described in unaltered chromite of ophiolites by cooling (e.g. Barnes, 1998). However, the chemical trend recorded in cores of zoned chromite from RO site requires a different explanation. According to Sack & Ghiorso (1991), the observed increase of Mg# from inner to outer core at constant Cr# requires strong increase in temperature (> 1200 °C). Fig. 2 shows that Mg# increase from inner to outer core takes place toward fracture edges (zoning post-date fracturing) discarding a magmatic origin for this zoning and suggesting that ultra-heated fluids migrating along fractures promoted Mg²⁺ partitioning towards chromite and Fe²⁺ towards associated silicates. The emplacement of small Mg-rich gabbroic plutons in the Ossa-Morena zone during Cambrian or Early Carboniferous times (Tornos et al., 2005; Sánchez-García et al., 2008) could be the source of the high-temperature required for this event.

The outer core to rim chemical and textural variations in both types of zoned chromite are similar evidencing that all chromitites of the Calzadilla de los Barros ultramafic bodies experienced the same late retrograde alteration. The development of the porous rims of chromite can be explained by the reaction between chromite and olivine producing clinocllore at high water-to-rock ratio and high silica activity during the retrograde metamorphic evolution of the host ultramafic rocks. Moreover, the Fe³⁺ enrichment in rims of RO chromites is caused by the late precipitation of magnetite in the pores followed by partial re-equilibrium (see Gervilla et al., 2012).

The complex chemical zoning observed in some, large accessory chromite in

dunites sampled in the CZ10 drill core reveals the superimposition of various alteration episodes. The slightly porous texture of the inner core as well as its Cr-magnetite composition suggests that it form by magnetite precipitation within highly porous chromite (as occurred in the rims of RO chromite) followed by extensive re-equilibrium between magnetite and host chromite. The low chromite/silicate ratio in dunites favours extensive percolation of metamorphic fluids promoting almost complete transformation of primary chromite into porous chromite and later, the precipitation of magnetite. The Mg# increase and the Cr# decrease from inner core to outer core and to inner rim involve the existence of a new alteration event. This trend can be only explained assuming a heating event that promoted a reaction between Cr-magnetite and the chlorite envelope, thus giving rise to slightly Al-richer chromite and minute olivine grains. The proximity of the CZ10 drill core and RO chromitites (Fig. 1) allows to correlate this heating event with that invoked to explain the zoning of the second type of zoned chromite in chromitites. The development of the outermost rim requires further reaction between the newly formed Al-rich inner rim and olivine to produce chromite with the same composition as that of the inner core and clinocllore. This reaction must take place during the retrograde evolution postdating the heating event.

CONCLUSIONS

The chemical and textural variations in zoned chromite from chromitites and dunites from Calzadilla de los Barros ultramafic bodies can be interpreted in terms of a multistage process characterised by two episodes of retrograde alteration separated by a high-temperature heating event. This interpretation correlates well with the tectono-metamorphic evolution of the Neoproterozoic basement of the Ossa-Morena zone (Quesada, 2006).

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REFERENCES

Barnes, S.J. (1998): *Chromite in komatiites, 1. Magmatic controls on crystallization and composition. J. Petrol.*, **39**, 1689-1720.
Gervilla, F., Padrón-Navarta, J.A.,

Kerestedjian, T., Sergeeva, I., González-Jiménez, J.M., Fanlo, I. (2012): *Formation of ferrian chromite in podiform chromitites from the Golyamo Kamenyane serpentinite, Eastern Rhodopes, SE Bulgaria: a two-stage process. Contrib. Mineral. Petr.*, **162**, 643-657.
González-Jiménez, J.M., Kerestedjian, T., Proenza, J.A., Gervilla, F. (2009): *Metamorphism on chromite ores from the Dobromirski ultramafic massif, Rhodope mountains (SE Bulgaria). Geol. Acta*, **7**, 413-429.
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.
Merinero, R., Lunar, R., Ortega, L., Piña, R., Monterrubio, S., Gervilla, F. (2013): *Hydrothermal palladium enrichment in podiform chromitites of Calzadilla de los Barros (SW Iberian Peninsula). Can. Mineral.*, **51**, 387-404.
Quesada, C. (2006): *The Ossa-Morena zone of the Iberian Massif: a tectonostratigraphic approach to its evolution. Z. Deut. G. Geowiss.*, **157**, 585-595.
Sack, R.O. & Ghiorso, M.S. (1991): *Chromian spinels as petrogenetic indicators: thermodynamic and petrological applications. Am. Mineral.*, **76**, 827-847.
Sánchez-García, T., Quesada, C., Bellido, F., Dunning, G., González de Tanago, J. (2008): *Two-step magma flooding of the upper crust during rifting: the Early Paleozoic of the Ossa-Morena zone (SW Iberia). Tectonophysics*, **461**, 72-90.
Tornos, F., Casquet, C., Relvas, J. (2005): *Transpressional tectonics, lower crust decoupling and intrusion of deep mafic sills: a model for the unusual metallogenesis of SW Iberia. Ore Geol. Rev.*, **27**, 133-163.