Origin of Ferrian Chromite in Metamorphosed Podiform Chromitites: a Two-Stage Process

Fernando Gervilla
University of Granada, Dpt. Mineralogy & Petrology & IACT (UGR-CSIC), Avda. Fuentenueva s/n, 18002 Granada, Spain

Isabel Fanlo
University of Zaragoza, Dpt. of Earth Sciences, Pedro Cerbuna 12, 50009 Zaragoza, Spain.

Thomas Kerestedjian
Bulgarian Academy of Sciences, Geological Institute, 24 Georgi Bonchev Str., 1113 Sofia, Bulgaria.

Ricardo Castroviejo
Universidad Politécnica de Madrid, E.T.S.I.M., Rios Rosas 21, 28003 Madrid, Spain

José Alberto Padrón
University of Granada, Dpt. Mineralogy & Petrology, Avda. Fuentenueva s/n, 18002 Granada, Spain

José Feliciano Rodrigues
Dep. de Engenharia de Minas, Faculdade de Engenharia da Universidade do Porto, & LNEG, Laboratório Nacional de Energia e Geologia, Portugal

José María González-Jiménez
GEMOC ARC National Key Centre, Dpt. Earth and Planetary Sciences, Macquarie Univ., Sydney, NSW 2109, Australia

Abstract. The patterns of zoning in chromite from two highly metamorphosed ophiolite massifs (Golyamo Kamenyane, Bulgaria, and Tapo, Peru) reveal that such patterns were the result of two stages of alteration during their metamorphic evolution. The first one caused mass loss in chromite by removal of Al_2O_3 and some MgO (creating a porous texture) under reducing conditions. Alteration of chromite is associated with the formation of chlorite. The second stage took place under oxidizing conditions by the supply of Fe^{2+} and Fe^{3+} to the porous chromite. This process tends to overprint the porous texture giving rise to magnetite-rich, homogeneous ferritchromite. During this stage chlorite is partly replaced by antigorite.

Keywords. Ferrian chromite, zoning, metamorphic alteration, Rhodope massif, Tapo massif.

1 Introduction

The term ferrian chromite (or ferritchromite) is used to name the alteration product of chromite (e.g. Bliss and MacLean 1975; Barnes 2000). Its composition can be expressed as $(Fe^{2+}, Fe^{3+}, Mg)[Cr, Fe^{3+}, Fe^{2+}, Al]_2O_4$ and is characterized by significant to high Fe^{3+} contents and variable Cr/Al and Mg/Fe^{2+} ratios. Chromite replacement by ferrian chromite usually takes place from grain boundaries or micro-craks inwards giving rise to zoned grains consisting of mostly unaltered chromite cores enveloped by variably thick, ferrian chromite rims. These patterns of zoning are better preserved in chromite grains from chromitite bodies than in accessory chromite in peridotite at a given degree of alteration (e.g. Proenza et al. 2004). Thus, we have selected two portions of dismembered, highly metamorphosed ophiolite complexes, the Golyamo Kamenyane serpentinite massif (SE Bulgaria) and the Tapo ultramafic body (Peru), to study the mechanism of ferrian chromite formation in chromitite bodies.

2 Geological setting of chromitite bodies.

2.1 The Golyamo Kamenyane massif

The Golyamo Kamenyane Sepentinite Massif is located in the Avren Complex in SE Bulgaria. This complex forms part of the upper high-grade metamorphic unit (Bonev, 2006) of the metamorphic basement of the Rhodope crystalline massif (Variegated complex of Kozhoukharova (1984) or Kimi complex of Mposkos and Krohe (2000) on Greek territory). The Golyamo Kamenyane Serpentinite is made up of metaharzburgite containing lenses of metadunite and chromitite pods, as well as metagabbro sills in the uppermost part of the ultramafic section. The latter is topped by amphibolitized gabbros. Although the metamorphic conditions of the Golyamo Kamenyane Serpentinite have not been calculated yet, amphibolitized eclogites from the Avren Complex reached 12-17kb and 750-811ºC (Kozhoukharova 1998). Mogessie et al. (2008) calculated lower P-T conditions (8-12kb and 650-700ºC) in similar rocks.

2.1 The Tapo massif

The Tapo ultramafic massif is a 680 Ma old, NW-SE elongated body, located in the Eastern Cordillera, Perú (Castroviejo et al., 2010; Tassinari et al., 2010). It occurs tectonically emplaced upon Lower Carboniferous sedimentary rocks (the Ambo Group). The latter consist of conglomerates, sandstones and pelites interbedded with volcanic tuffs. The overall structure of the massif corresponds to a NW-SE trending, thrust bounded synform (Rodrigues et al. 2010).

The Tapo massif is made up of highly tectonized and metamorphosed, serpentinized peridotites with only scarce relics of the ultramafic protoliths, and of subordinate amphibolite bands, rodingites, listvenites, etc. The serpentinites contain disseminated chromite and several small (few tens of metres long) bodies of podiform chromitites. Metamorphic conditions reached ~12.5±1kb and 535±20ºC (Willner et al. 2010).

3 Petrography and texture of chromitites

Chromitites at Golyamo Kamenyane show massive (>85% chromite) to semi-massive (60-85% chromite) texture. In addition, chromite from chromitites can be classified into four textural groups: i) zoned chromite; ii) porous chromite, iii) homogeneous chromite and iv) homogeneous-zoned chromite. ***Zoned chromite*** shows homogeneous, unaltered cores surrounded by porous chromite containing abundant chlorite (clinochlore) in the pores (Fig. 1A). Clinochlore is the only intergranular silicate. ***Porous chromite*** does not contain cores. Grains contain abundant pores and clinochlore inclusions (Fig. 1B). Clinochlore is the most abundant intergranular silicate, but it becomes associated with some antigorite. ***Homogeneous chromite*** does not contain pores, but few inclusions of antigorite and shows mosaic-like, polygonal texture (Fig. 1C). Antigorite is the only intergranular silicate here. The term ***homogeneous-zoned chromites*** (Fig.1D), applies tosome coarse grains of homogeneous chromite showing compositionally different, but homogeneous cores, sharply separated from the homogeneous rim. .

The studied chromitites at Tapo also display massive and semi-massive textures. They consist of coarse-grained, fractured aggregates of rounded to sub-rounded, zoned crystals of chromite. Zoning is irregular consisting of two or three distinct optical zones, arranged concentrically from rims and, at lesser extent, fractures inward (Fig.1E). Irregular and patchy patterns of zoning are also present, developing a texture similar to porous chromite in Golyamo Kamenyane (Fig. 1F). The external bands in all zoned chromites contain variable amounts of clinochlore inclusions; nevertheless the outermost band contains some antigorite.

4 Chemical composition of chromite

Zoned chromite at Golyamo Kamenyane shows unaltered, Al-rich cores having Cr#[Cr/(Cr+Al)]=0.50-0.60, Mg#[Mg/(Mg+Fe^{2+})]=0.60-0.70 and Fe^{3+}/(Fe^{3+}+Fe^{2+})=0.20-0.30, surrounded irregularly by porous chromite with values of the Cr#, Mg# and Fe^{3+}/(Fe^{3+}+Fe^{2+}) evolving from 0.60 to 0.90, 0.60 to 0.47 and 0.2 to 0 from core to rim, respectively (Fig. 2A). Porous chromite has a relatively homogeneous composition varying within the following ranges: Fe^{3+}/(Fe^{3+}+Fe^{2+})=0.20-0.52, Cr#=0.92-0.97 and Mg#=0.35-0.48 (Fig. 2A). Homogeneous chromite has Fe^{3+}/(Fe^{3+}+Fe^{2+})=0.55-0.65, Cr#>0.96 and Mg#=0.32-0 (Fig. 2A). The core of homogeneous-zoned chromite has the same composition than that of zoned chromite whereas the rim shows the composition of homogeneous chromite (Fig. 2A).
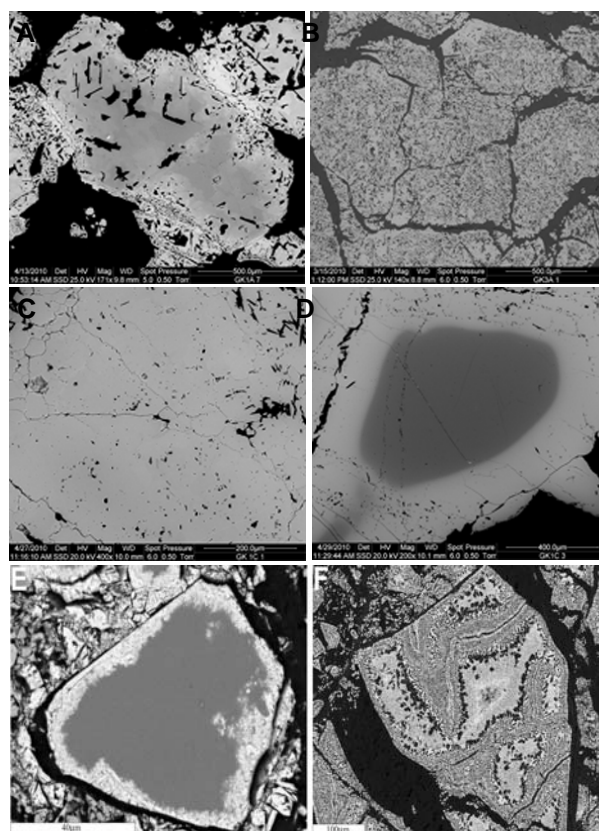

Figure 1. A to D: Different patterns of zoning of chromite from Golyamo Kamenyane. A: zoned chromite; B: porous chromite; C: homogeneous chromite, and D; homogeneous-zoned chromite. **E and F**: alteration patterns of chromite chrystals at Tapo.

The cores of chromite crystals from massive and semi-massive chromitites at Tapo show restricted composition, having Cr# [Cr/(Cr+Al)]=0.40-0.57, Mg# [Mg/(Mg+Fe)]=0.70-0.80 and Fe^{3+}#[Fe^{3+}/(Fe^{3+}+Cr+Al)] <0.16 (Fig. 2B). These cores evolve to a zone characterized by loss of Al$_2$O$_3$ increasing Cr# up to 0.74, and increasing Fe^{2+} (Mg# drops to 0.51) without changing Fe$_2$O$_3$ contents. This chemical trend continues in the first alteration zone (Mg# drops down to 0.2), but associated with significant enrinchment in Fe$_2$O$_3$ (up to 16 wt.%). The outermost zone has a composition, characterized by very small amounts of Al$_2$O$_3$, similar Cr$_2$O$_3$ and FeO contents (Cr#= 0.82-0.97 and Mg#=0.19-0.43), and higher Fe$_2$O$_3$ contents (20-36wt.%) than chromite from the first alteration zone (Fig. 2B).

5 Discussion

Texture and chemical variations of the studied chromitites from Golyamo Kamenyane show that alteration took place in two separate stages, probably during their retrograde metamorphic evolution.

During the first stage primary chromite is replaced by porous chromite under reducing conditions [Fe^{3+}/(Fe^{3+}+Fe^{2+}) decreases from core to rim of the grains]. Chromite loses Al$_2$O$_3$ and some MgO, and becomes enriched residually in Cr$_2$O$_3$ and, at lesser extent, FeO. This replacement involves mass loss in chromite without variations in the external volume of grains (resulting in the formation of pores), and is coeval

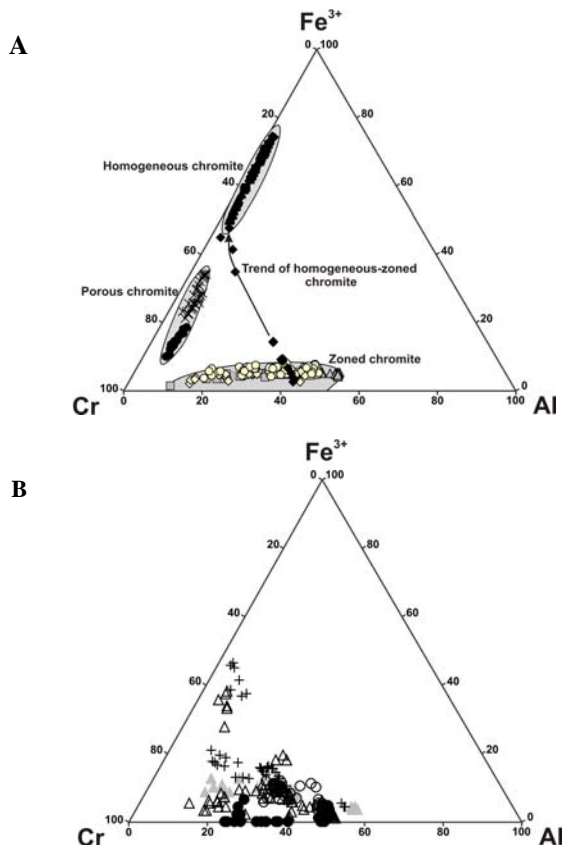with the alteration of the associated silicates to chlorite.

Figure 2. Chemical composition of altered chromite from Golyamo Kamenyane (A) and Tapo (B) chromitites.

The second stage took place under oxidizing conditions by the addition of magnetite to the Al-poor, porous chromite. These Fe-bearing fluids partly dissolve chlorite in the pores, promoting diffusion of Fe^{2+} and Fe^{3+} into chromite, overprinting the porous texture and forming the homogeneous chromite. Some chlorite is replaced by antigorite. Since during this process the volume of chromite grains does not change, the amount of magnetite component in homogeneous chromite is limited by the previous volume of pores; nevertheless, if the supply of Fe^{2+} and Fe^{3+} exceeds this limit, homogeneous chromite becomes coarser, promoting the development of mosaic-like, polygonal textures. Alteration of zoned chromite under the second-stage, oxidizing conditions allows diffusing Fe^{2+} and Fe^{3+} easily through the porous rim of chromite grains but becomes difficult in the unaltered, homogeneous core, giving rise to the homogeneous-zoned chromite. Phase relations in the system $(Fe^{2+},Mg)Cr_2O_4$ - $(Fe^{2+},Mg)Fe^{3+}_2O_4$ - $(Fe^{2+},Mg)Al_2O_4$ suggest that the studied homogeneous chromite could form at temperatures around 600ºC (Sack and Ghiorso 1991).

The alteration pattern of chromite in massive chromitites from Tapo can be interpreted in terms of the two-stage process described for Golyamo Kamenyane chromitites, but assuming that the oxidizing, second stage partly obliterated the first one. Evidences of the first stage remain preserved in the innermost alteration bands of some crystals. The second, oxidizing stage did not completely erase the porous texture, but only contributed to increase the magnetite component of

ferrian chromite. This process was very heterogeneous, resulting in samples with Fe^{3+}-poor, porous rims and samples with Fe^{3+}-rich, partly homogeneous rims. The volume of added magnetite never exceeded the previous volume of pores.

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