



Fingerprints of metamorphism in chromite: New insights from minor and trace elements



Vanessa Colás^{a,b,*}, José M. González-Jiménez^{b,c}, William L. Griffin^b, Isabel Fanlo^a, Fernando Gervilla^d, Suzanne Y. O'Reilly^b, Norman J. Pearson^b, Thomas Kerestedjian^e, Joaquín A. Proenza^f

^a Universidad de Zaragoza, Departamento de Ciencias de la Tierra, Pedro Cerbuna 12, 50009 Zaragoza, Spain

^b Australian Research Council Centre of Excellence for Core to Crust Fluid Systems/GEMOC, Department of Earth and Planetary Sciences, Macquarie University, Sydney, NSW 2109, Australia

^c Departamento de Geología, Andean Geothermal Center of Excellence (CEGA), Universidad de Chile, Santiago, Chile

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

^e Geological Institute, Bulgarian Academy of Sciences, 24 Georgi Bonchev Str., 1113 Sofia, Bulgaria

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

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ABSTRACT

A suite of minor and trace elements (Ga, Ti, Ni, Zn, Co, Mn, V, Sc) in chromite grains from ophiolitic chromitites subjected to high-pressure metamorphism defines a metamorphic signature. A two-stage process associated with the infiltration of fluids during retrograde metamorphism from eclogite- to amphibolite-facies has produced four types of chromites: (1) *porous chromite* strongly enriched in Cr and Fe²⁺ but depleted in Al and Mg, with abundant chlorite filling the pores; (2) *non-porous chromite* strongly enriched in Fe³⁺ (i.e., ferrian chromite); (3) *partly altered chromite* with primary cores surrounded by chlorite-bearing porous chromite; and (4) *zoned chromite* made up of primary cores surrounded by non-porous rims of ferrian chromite.

Compared to spinels from unmetamorphosed chromitites the cores of partly altered chromites after primary high-Cr chromite are enriched in Zn, Co and Mn but strongly depleted in Ga, Ni and Sc. This distribution of minor- and trace-elements is related to a decrease in Mg# [Mg/(Mg + Fe²⁺)] and Al, produced by the crystallization of chlorite in the pores of porous chromite. Non-porous chromite is enriched in Ti, Ni, Zn, Co, Mn and Sc but depleted in Ga, suggesting that fluid-assisted processes have obliterated the primary magmatic signature. Zoned chromites have cores depleted in Ga, Ni and Sc but are progressively enriched in Zn, Co and Mn as Mg# and Al decrease toward the rims; they have overall lower concentrations in Ga, Ni and Sc and higher Zn and Co than the non-porous rims of ferrian chromite. The complex variation of the minor- and trace-elements vs Fe³⁺/(Fe³⁺ + Fe²⁺) in the different types of chromite suggests a complex interplay of substitutions, linked with the ability of fluids to infiltrate the chromite and the extent of the re-equilibration between pre-existing cores and newly-formed rims.

The results demonstrate that metamorphism can seriously disturb the original magmatic distribution of minor and trace elements in chromite. The abundances of these elements, and by inference the major elements, can be strongly modified even in the cores of grains that appear “unaltered” in terms of major elements. The use of the major elements as indicators of magmatic processes therefore must be linked to careful evaluation of metamorphic effects, using LA-ICP-MS analysis of minor and trace elements.

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1. Introduction

Chromite is an oxide with a spinel-type structure that might be expressed using the general formula AB₂O₄. The A site is occupied by Mg and Fe²⁺ in tetrahedral coordination and the B site is usually

occupied by Cr and Al in octahedral coordination; Cr and Al may be substituted by Fe³⁺ giving rise to *ferrian chromite*. Elements like Zn²⁺, Co²⁺, Mn²⁺ and Ni²⁺ can substitute Mg and Fe²⁺ in A and V³⁺, Sc³⁺, Ga³⁺ and Ti⁴⁺ can substitute Al and Cr in B (Table 1). These variations in the composition of chromite are commonly used to interpret the petrogenesis and the geodynamic setting of the host ultramafic rocks (Irvine, 1967; Dick and Bullen, 1984; Arai, 1992; Stowe, 1994; Zhou and Robinson, 1994; Barnes and Roeder, 2001; Kamenetsky et al., 2001; Ahmed et al., 2005; Rollinson, 2008; Pagé and Barnes, 2009). The high resistance of chromite to alteration (compared to the primary silicates) has made this oxide particularly useful as a petrogenetic indicator in ultramafic rocks in which metamorphic alteration has

* Corresponding author at: Universidad de Zaragoza, Departamento de Ciencias de la Tierra, Pedro Cerbuna 12, 50009 Zaragoza, Spain. Tel.: +34 976 84 10 98.

E-mail addresses: vcolas@unizar.es (V. Colás), jose.gonzalez@mq.edu.au, jmgonzj@ing.uchile.cl (J.M. González-Jiménez), bill.griffin@mq.edu.au (W.L. Griffin), fanlo@unizar.es (I. Fanlo), gervilla@ugr.es (F. Gervilla), sue.oreilly@mq.edu.au (S.Y. O'Reilly), norman.pearson@mq.edu.au (N.J. Pearson), thomas@geology.bas.bg (T. Kerestedjian), japroenza@ub.edu (J.A. Proenza).

Table 1
Major-, minor- and trace element distribution in the different mineral structures.

	Chromite		Olivine	Chlorite
Formula	AB ₂ O ₄		A ₂ SiO ₄	(A ₅ Al)(Si ₃ Al)O ₁₀ (OH) ₈
Position	A ^(IV)	B ^(VI)	A ^(VI)	Al ^(VI)
Major elements	Mg ²⁺ , Fe ²⁺	Cr ³⁺ , Al ³⁺ , Fe ³⁺	Mg ²⁺ , Fe ²⁺	Mg ²⁺ , Fe ²⁺
Minor- and trace elements	Zn ²⁺ , Co ²⁺ , Mn ²⁺ , Ni ²⁺	V ³⁺ , Sc ³⁺ , Ga ³⁺ , Ti ⁴⁺	Zn ²⁺ , Co ²⁺ , Mn ²⁺ , Ni ²⁺	Ni ²⁺

obliterated other primary fingerprints (e.g. Proenza et al., 2004; Ahmed et al., 2005; González Jiménez et al., 2009). However, a growing body of work, based on the study of chromite-rich rocks from ophiolites, layered complexes and komatiites, has shown that the chemistry and structure of chromite can be also significantly modified during both prograde (Bliss and MacLean, 1975; Evans and Frost, 1975; Wylie et al., 1987; Frost, 1991; Burkhard, 1993; Abzalov, 1998; Barnes, 2000; González Jiménez et al., 2009; Merlini et al., 2009; Olobaniyi and Mücke, 2011) and retrograde metamorphism (Loferski, 1986; Proenza et al., 2004, 2008; Mellini et al., 2005; Mukherjee et al., 2010; Gervilla et al., 2012; Grieco and Merlini, 2012).

Metamorphism typically imposes an optical and chemical zoning on the primary chromite. In general, a zone enriched in FeO and Cr₂O₃ and depleted in MgO and Al₂O₃ surrounds the apparently pristine (or primary) core, which grades outwards to chromite strongly enriched in Fe³⁺ (ferrian chromite) (Bliss and MacLean, 1975; Evans and Frost, 1975; Wylie et al., 1987; Kimball, 1990; Barnes, 2000; Mellini et al., 2005; González Jiménez et al., 2009; Merlini et al., 2009; Mukherjee et al., 2010; Gervilla et al., 2012; Grieco and Merlini, 2012). Occasionally magnetite rims surround the cores and/or the ferrian chromite rims.

Evans and Frost (1975), Bliss and MacLean (1975) and Barnes (2000) have suggested that the ferrian chromite is produced by the reaction of pristine cores with magnetite rims during prograde metamorphism of serpentinised ultramafic rocks. In contrast, Gervilla et al. (2012) proposed that the formation of ferrian chromite is a two-stage process occurring during the retrograde evolution of chromitites from eclogite-facies conditions. During the first stage, magmatic chromite reacts with olivine in the presence of reducing fluids to produce a porous chromite enriched in FeO and Cr₂O₃ (hereafter *Fe²⁺-rich chromite*), which is in equilibrium with chlorite. In the second stage, oxidizing solutions circulate through the network of pores in the porous chromite, dissolving chlorite and adding Fe³⁺, which diffuses into the chromite lattice and converts it to ferrian chromite (i.e., *Fe³⁺-rich chromite*).

Both models implicitly assume that the cores of chromite grains represent relict primary chromite that remained unaffected by the alteration. However, the selective enrichment of a suite of minor elements including Mn, Ni, Co, Zn and Ti in such “pristine cores”, in metamorphosed chromites from the Tidding Suture Zone in the eastern Himalaya (Singh and Singh, 2013) and the Nuggihalli schist belt in India (Mukherjee et al., 2010) led us to investigate whether their compositions are perturbed and do not represent original pristine compositions. If so, important information about the metamorphic evolution of chromite might be lost by analyzing only microstructures and the abundances of major elements, and deductions about the original magmatic-tectonic situation of the chromitites and their host peridotites might be incorrect.

The technique of laser-ablation inductively-coupled plasma-mass spectrometry (LA-ICP-MS) has lower limits of detection than the electron microprobe and thus can analyze a more comprehensive suite of elements present in a chromite (Ga, Ti, Ni, Zn, Co, Mn, V and Sc), providing useful information about its petrogenesis (Dare et al., 2009; Pagé and Barnes, 2009; González Jiménez et al., 2011, 2013, 2014; Aldanmaz, 2012). In this work LA-ICP-MS was used to measure the minor- and trace elements in highly metamorphosed chromites, in order to define the fingerprints of metamorphism that are not revealed by conventional

approaches based on electron microprobe data. We have studied chromite from metamorphosed chromitites because they preserve zoning patterns better than accessory chromites in peridotite at a given degree of alteration (e.g. Proenza et al., 2004). The chromitites are enclosed in four ultramafic massifs (Golyamo Kamenyane, Chernichevo, Yakovitsa and Avren) representing portions of the dismembered ophiolites of the Rhodope Metamorphic Core Complex in southern Bulgaria. The chromitites and their host ultramafic rocks underwent metamorphism in eclogite facies with a later amphibolite-facies overprint (Mposkos and Krohe, 2000, 2006; Mposkos, 2002; Mposkos et al., 2012). In order to test the validity of our approach we have additionally compared our chromites with those from unaltered chromitites in unmetamorphosed ophiolites (Eastern Cuba and New Caledonia) with well-documented post-magmatic histories.

2. Sample background

The samples selected for this study are from Type I ophiolitic chromitites (i.e., enriched in IPGE relative to PPG; González Jiménez et al., 2014) in the metamorphosed ultramafic massifs of Golyamo Kamenyane, Chernichevo, Yakovitsa and Avren in the eastern part of the Rhodope Metamorphic Core Complex, of southern Bulgaria and northern Greece (Table 2 and Fig. 1).

The Rhodope Metamorphic Core Complex is a large domal structure formed mainly during the Alpine orogeny; it lies between the Balkan belt to the north and the Dinarides–Hellenides to the south-southwest (Fig. 1). The complex consists of (1) a lower unit corresponding to the *autochthonous core* and known as the Gneiss–Migmatite Complex (Kozhoukharov et al., 1988; Haydoutov et al., 2001), the lower High-Grade Unit (Bonev, 2006) or the Lower Allochthon (Janák et al., 2011), and (2) an upper unit with meta-ophiolites (Kolcheva and Eskenazy, 1988; Bazylev et al., 1999; Kolcheva et al., 2000; Haydoutov et al., 2001, 2004; Bonev et al., 2006; Daieva et al., 2007) which represents the *allochthonous rim* and is known as the Variegated Complex (Kozhoukharov et al., 1988; Haydoutov et al., 2001), the upper High-Grade Unit (Bonev, 2006) or the Upper Allochthon (Janák et al., 2011). In the eastern part of the Rhodope Metamorphic Core Complex, both the autochthonous core and the allochthonous rim crop out in two large-scale domal structures: the Kesebir–Kardamos Dome to the west and the Byala Reka–Kechros Dome to the east (Fig. 1; Georgiev, 2006).

The ultramafic massifs of Golyamo Kamenyane, Avren, and Chernichevo crop out in the western limb of the Byala Reka–Kechros Dome along the Avren synform (Fig. 1). The ultramafic massif of Yakovitsa crops out in the western limb of the Kesebir–Kardamos Dome (Fig. 1). These ultramafic massifs consist of partly serpentinised harzburgite and dunite, which are overlain by layers of amphibolites (i.e. formerly layered gabbros; Bazylev et al., 1999; Kolcheva et al., 2000; Haydoutov et al., 2004; Gervilla et al., 2012) in the massifs of Golyamo Kamenyane and Chernichevo. These lithologies, including chromitites, are cut by sub-vertical veins of asbestos, mainly anthophyllite and chrysotile, and talc in the massifs of Golyamo Kamenyane (Gervilla et al., 2012) and Avren (Kolkovski et al., 2003).

Mposkos and Krohe (2000, 2006) and Mposkos (2002) investigated spinel-garnet metaperidotites and garnet pyroxenites of the Kimi Complex (the Greek equivalent of the Avren synform in Bulgaria) and concluded that the mantle rocks of the allochthonous rim of the

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