Factors Controlling Chromite Alteration: Example from Kosturino, SE Bulgaria

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INTRODUCTION

It is widely accepted that chromite alters to ferrian chromite, $(Fe^{2+},Fe^{3+},Mg)(Cr,Fe^{3+},Fe^{2+},Al)_2O_4$, this latter being marked by Fe^{3+} enrichment, high Cr/Al and low Mg/Fe^{2+} ratios. Nevertheless, the timing of such a process, mainly prograde (Barnes, 2000; Merlini et al. 2009, among others) vs. retrograde (Proenza et al, 2004; Mellini et al. 2005, among others) metamorphism is still under debate. The aforementioned chromite alteration usually takes place from grain boundaries or fractures inwards, giving rise to zoned grains with unaltered cores mostly surrounded by ferrian chromite rims. Factors controlling the extent of ferrian chromite formation are: fluid (mainly H_2O) pressure (Candia & Gaspar 1997), chromite/silicate ratio (Proenza et al. 2004 and González-Jiménez et al. 2009) and size of the chromitite body. In this contribution we study the relationship between the alteration degree of chromite, the size of the chromitite body and the chromite/silicate ratio (assuming water-saturated conditions) of several chromitite bodies from Kosturino, in SE Bulgaria.

GEOLOGICAL SETTING

The Kosturino area is located in the north-eastern part of the Yakovitsa Massif which is one of the metamorphosed ultramafic massifs scattered in the Central and Eastern zones of the Rhodope Crystalline Massif in SE Bulgaria. The Yakovitsa ultramafic massif is 13 km long and 500-800 m wide and builds a part of the eastern-most outcrop of the Borovitsa lithotectonic unit, occupying the limbs of a large-scale synform. The core of the synform is represented by the volcanic and volcano-sedimentary rocks of the Kurdjali litho-tectonic unit. In the opposite direction (towards the limbs of the synform) ductile shear zones separate the Borovitsa unit from the outer-most shell of the synform limbs: Krumovitsa (on the east) and Startsevo (on the west) lithotectonic units. The Borovitsa unit comprises biotite gneisses, marbles, amphibolites, ultramafic bodies, porphyroblastic and aplitoid metagranites. The Yakovitsa shear zone, which separates Borovitsa and Krumovitsa units is also the eastern contact of the Yakovitsa massif, while its western contact is a normal fault. A number of smaller stack-faults displace parts of the body, giving its specific echelon shape with 3 separate tails at the south-western end (Sarov et al, 2007).

PETROGRAPHY OF THE CHROMITITES

Chromitites are represented by a chain of small bodies, up to several tens of meters long and few centimeters to few meters wide. They show massive (>85% chromite), semi-massive (60-85% chromite) and disseminated (<60% chromite) textures. The matrix consists of serpentine and chlorite. Chlorite crystals form either intergrowth aggregates with serpentine or aureoles surrounding chromite. The aureole width is proportional to the composition of chromite and to the chromite/silicate ratio.

Chromites are fractured at different extents and can be classified into two groups: i) zoned chromite and ii) porous chromite. **Zoned chromite** shows homogeneous cores surrounded by porous chromite (Type 1 rim; Fig. 1.A) containing variable amounts of chlorite in the pores or more reflective, nearly homogeneous rims (Type 2 rim; Fig. 1.B). Zoning is usually concentric, advancing inwards from rims, major fractures and, at lesser extent, micro-cracks. Furthermore, irregular and patchy patterns of zoning may be also present in Type 1 rim (Fig. 1.A), their development being controlled by the size of the chromitite body and by the chromite/silicate ratio. Type 2 rims are exclusive of very small chromitite bodies with low chromite/silicate ratio (66.6% chromite). **Porous chromite** does not contain unaltered core and shows abundant chlorite inclusions in the pores (Fig. 1.A). This chromite type only occurs in chromitite bodies with intermediate chromite/silicate ratio (70.4% chromite).

CHROMITE MINERAL CHEMISTRY

Cores in **zoned chromite** can be classified in three compositional groups (Fig. 2.A): C1) with Cr# and Mg# values

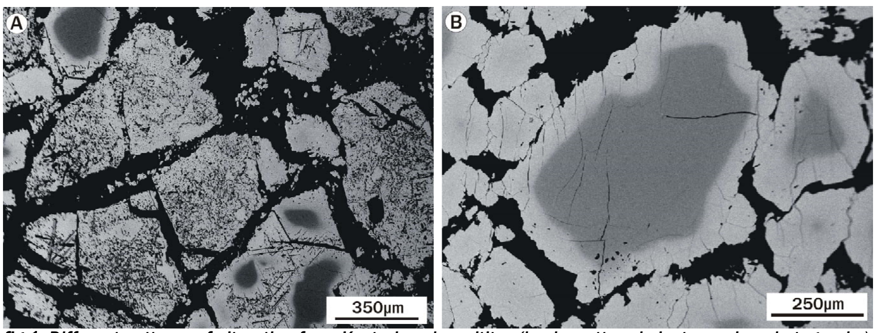

fig 1. Different patterns of alteration from Kosturino chromitites (back-scattered electron microphotographs). A. Type 1 rim to zoned chromite and porous chromite. B. Type 2 rim to zoned chromite.

palabras clave: Yakovitsa, Macizo Rhodope, Bulgaria, Cromitita, Alteración, Relación cromita/silicato	*key words:* Yakovitsa, Rhodope massif, Bulgary, Chromitite, Alteration, Chromite/silicate ratio

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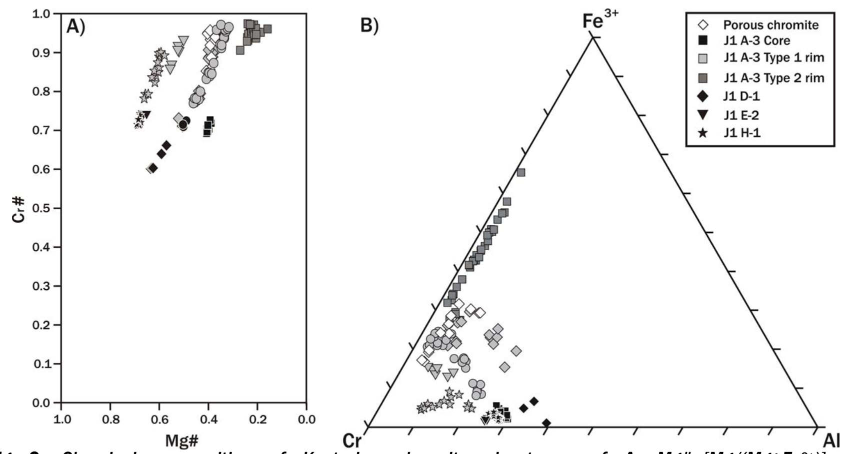

*fig 2. Chemical composition of Kosturino chromites in terms of **A.** Mg#=[Mg/(Mg+Fe²⁺)] vs Cr#=[Cr/(Cr+Al+Fe³⁺)], and **B.** Fe^{3+}, Cr^{3+} and Al^{3+} contents..*

from 0.71 to 0.75 and from 0.65 to 0.69, respectively; C2) with Cr# and Mg# from 0.60 to 0.73 and from 0.49 to 0.64, respectively; and C3) with Cr# and Mg# values from 0.68 to 0.74 and from 0.38 to 0.42, respectively. Fe^{3+} contents remains almost constant in the three groups [$Fe^{3+}/(Fe^{3+}+Fe^{2+})$=0.05-0.25] (Fig. 2.B). Whereas the overall Cr# varies within relatively narrow limits (from 0.60 to 0.75), the variation of Mg# is very pronounced (from 0.69 to 0.38). The latter variations depend on the size of the chromitite body and on its chromite/silicate ratio. In samples with low chromite/silicate ratio from small chromitite bodies chromite cores tend to be richer in Fe^{2+} than those from nearly massive, thick chromitite bodies (Fig. 2.A).

Type 1 rims are characterized by very small amounts of Al_2O_3, an increase in Cr# (from 0.71 to 0.97) and in $Fe^{3+}/(Fe^{3+}+Fe^{2+})$ (from 0.18 to 0.49), and a decrease of Mg# (from 0.66 to 0.32; Fig. 2). The alteration trends of rims depend on the composition of the cores (Fig. 2.B). Chromite from small chromitite bodies with low chromite/silicate ratio reach higher Cr# (up to 0.97) and lower Mg# (down to 0.32) in the outermost rims than those from nearly massive, thick chromitite bodies.

Type 2 rims display high Cr# and $Fe^{3+}/(Fe^{3+}+Fe^{2+})$ values (from 0.91 to 0.98 and from 0.42 to 0.61, respectively) and very low Mg# (0.16 to 0.27) (Fig. 2).

Porous chromite has a relatively homogeneous composition varying within the following ranges: Cr#=0.85-0.96, Mg#=0.37-0.41 and $Fe^{3+}/(Fe^{3+}+Fe^{2+})$=0.36-0.50 (Fig. 2).

DISCUSSION

Textures and chemical variations of the studied chromitites from Kosturino show that alteration took place in three separate stages, probably during retrograde metamorphism.

In the first stage, chromitites equilibrated with olivine during their subsolidus evolution in the eclogite-facies field. Whereas Cr# of chromite mostly did not change during such evolution, preserving the primary igneous values, subsolidus equilibration between chromite and olivine promoted Fe^{2+} and Mg exchange giving rise to chromite with low Mg#. Fe^{2+} enrichment in chromite was favoured by low chromite/silicate ratios. Chromite from massive-textured, thick chromitites preserved their cores almost unaltered (*e.g.*, J1-H-1).

Subsequent irregular and patchy replacement of primary chromite by porous chromite (second stage) took place at lower temperatures (in the amphibolite-green schist facies fields) under reducing conditions as deduced from the $Fe^{3+}/(Fe^{3+}+Fe^{2+})$ ratio. Chromite loses Al_2O_3, MgO and, to lesser extent Fe_2O_3, with coeval enrichment in Cr_2O_3 and FeO. This replacement took place during olivine alteration to chlorite under water-saturated conditions and decreasing SiO_2 activity.

The third stage was developed under moderately 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+} in chromite and forming homogeneous rims in pervasively altered chromite. The amount of magnetite component in chromite is mainly limited by the pore volume. 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 rims could form at temperatures around 600ºC (Sack & Ghiorso, 1991).

As a final statement, the different degrees of alteration evidenced at Kosturino chromitites allow us to conclude that alteration processes mainly depend on the chromite/silicate ratio, the size of chromitite bodies and fluid (water) pressure.

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