CHEMICAL COMPOSITION OF CR-SPINELS IN DEFORMED AND METAMORPHOSED ULTRAMAFIC/MAFIC COMPLEXES FROM PORTUGAL; CAN IT BE USED AS AN ORE-GUIDE FOR NI-CU SULPHIDE MINERALISATIONS?

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Abstract

A set of 376 electron microprobe analyses of Cr-spinels included either in peridotites/chromitites belonging to the Continental Allochthonous Terrane (CAT) of the Bragança Nappe Complex or in peridotites/wehrlites/troctolites from the Beja-Acebuches Ophiolite Complex (BAOC) is examined. A common chemical feature displayed by these oxides is their relative iron enrichment, probably achieved by *subsolidus* re-equilibration under very high-temperature conditions (800-900ºC) accomplished in the course of the complex metamorphic P-T-t path experienced by CAT and during the anisotropic recrystallisation correlative of BAOC hot obduction. The use of Cr-spinels composition as an ore guide for Ni-Cu sulphide mineralisations is also discussed, using the discriminant chemical function proposed by Johan (1979).

Key-words: Cr-spinel chemistry; Bragança Nappe Complex; Beja-Acebuches Ophiolite Complex; Ore-guides for Ni-Cu sulphide mineralisation.

1. Introduction

In Portugal mainland, the most extensive outcrops of high-strained and metamorphosed peridotites can be found in the Bragança and Morais Nappe Complexes (NE Trás-os-Montes), the most important of which belong to the Continental Allochthonous Terrane (CAT - *e.g.* Marques *et al.*, 1996, and references therein) of the Bragança Complex and host massive chromitite bodies, some of them exploited in the past (*e.g.* Cotelo Neiva, 1948). Underlining the southern border of the Iberian Terrane, another tectonically dismembered ultramafic-mafic complex exists forming a narrow belt known as the Beja-Acebuches Ophiolite Complex (BAOC – *e.g.* Quesada *et al.*, 1994); peridotites are particularly well exposed between Beja and Ferreira do Alentejo.

The peridotites of CAT, together with gabbros and pyroxenites, are layered igneous bodies that have crystallised and reequilibrated in conditions typical of the lower continental crust, intruding earlier deformed granulites/paragneisses (for details see Marques, 1994, Marques *et al.*, 1996, and references therein); they record a clockwise metamorphic P-T-t path (680-700ºC, 10-12 kbar   750ºC, 15 kbar   800-850ºC, 10-12 kbar), followed by an isobaric cooling (until near 700ºC), and were subsequently retrogressed in amphibolite facies conditions during later Variscan blastomylonitisation events (*e.g.*, Marques, 1994, and references therein). In CAT, Cr-spinel bearing harzburgites comprise abundant relics of enstatite and Fo_{91-94} olivine (with average NiO contents around 0.4 wt% - *e.g.* Bridges, 1992; Figueiredo, 1998). A former lherzolitic nature can also be put in evidence for many outcropping peridotites, wherein variably amphibolitised diopside grains coexist with relatively well-preserved enstatite, Fo_{89-90} olivine (with average NiO contents near 0.3 wt%) and Cr-spinels. Samples representing earlier dunites (see also Prichard *et al.*, 1991; Figueiredo, 1998) show usually relics of Cr-spinels and of strongly serpentinised Fo_{93-95} olivine (with average NiO contents near 0.5 wt%). In this Terrane, chromitites are commonly hosted by harzburgitic and/or dunitic rocks (*e.g.* Cotelo Neiva, 1948; Bridges *et al.*, 1995; Figueiredo, 1998).

Peridotites and gabbroic rocks (both massive and layered varieties, locally intruded by pods and dykes of plagiogranites) are part of the lower and intermediate sections of the reconstructed ophiolite sequence of BAOC (*e.g.* Quesada *et al.*, 1994). Widespread mineral and textural evidence for early recrystallisation of gabbroic rocks under an anisotropic stress field, strongly suggest that BAOC has been emplaced before its final consolidation; this event took place under temperatures of 800-900ºC and pressure conditions below 5 kbar (*e.g.* Quesada *et al.*, 1994). The later evolution of these rocks reflects mainly the Variscan metamorphism, that peaked at amphibolite facies (initially under average 600-620ºC and pressures not exceeding 2-3 kbar), and its subsequent waning stages (for details see, *e.g.*, Quesada *et al.*, 1994; Figueiras *et al.*, 1998). In BAOC, Cr-spinel represents an important accessory phase in all of the peridotites and wehrlites/troctolites, sometimes being the only primary mineral (often badly preserved) in dunite-derived serpentinites. Harzburgites comprise Fo_{83-86} olivine (with average NiO contents near 0.24 wt%), enstatite and, sometimes, diopside, besides relatively abundant Cr-spinel. Dunites, now corresponding to serpentinites with relics of Cr-spinels only, occur mainly within the harzburgitic bodies. Wehrlite/troctolite rocks are apparently uncommon, and their primary mineral assemblage can be best characterised at the Palmeira sector (*e.g.* Mateus *et al.*, 1998a): Fo_{85} olivine (with NiO contents

usually ranging from 0.13 to 0.23 wt%), diopside, An_{70} plagioclase, Na- and Ti-bearing brown hornblende, and accessory amounts of enstatite, Cr-spinel and sulphides (mainly pentlandite and pyrrhotite).

Finally, it should be emphasised that bulk-rock hydration leading to serpentinisation of variable intensity is a relatively late process in both Complexes that post-dates the mineral paragenesis established at amphibolite facies conditions and took place under temperatures below 500ºC.

2. Pertinent petrographic features concerning Cr-spinels of CAT and BAOC

Cr-spinel represent an important accessory phase in all of the peridotites belonging to both Complexes, sometimes being the only primary mineral (often badly preserved) in dunite-derived serpentinites of BAOC. It occurs usually as dispersed euhedral to subeuhedral grains of millimetric size, although in CAT it may form folded layers, irregular stringers or even discontinuous schlieren-type bodies of centimetric thickness. Frequently, fine serpentine and Mg-chlorite aggregates surround single spinel grains displaying more or less distinct reaction rims. Most of the grains are completely altered to ferritchromite (especially in serpentinites that do not preserve any other primary mineral), but the recognition of primary (unaltered) cores can easily be achieved under the reflected and/or transmitted light microscope: unaltered domains of Cr-spinel display an homogeneous shade of grey (sometimes slightly brownish) under reflected light, and are moderately translucent, transmitting a dark reddish-brown coloured light. Very often, completely and partially altered Cr-spinel grains retain their original habit, despite intense fracturation. In wehrlite/troctolite rocks of BAOC, Cr-spinel grains usually display a rounded morphology and do not have pronounced, optically visible, reaction rims. Chromitites found in CAT are often of limited size and of irregular morphology; very massive chromitites with coarse interlocking (somewhat fractured and altered) grains usually display interstitial (and variably serpentinised) forsteritic olivine and scarce enstatite.

3. Cr-spinels composition

Mineral chemical analyses were performed on polished sections using a three-channel wavelength dispersive JEOL-JCXA 733 electron microprobe routinely operated at an accelerating voltage of 18 kV and a beam current of 25 nA. Natural mineral and pure metal (V) standards were used before, during and after each analytical session; the estimated error of the values obtained is less than 2%. The ferric iron content of the spinels was estimated by an iterative procedure, assuming a stoichiometric composition on a basis of 32 oxygens. The complete set of analyses concerning BAOC spinels can be found in Mateus *et al.* (1998b). Electron microprobe analyses reported by Prichard *et al.* (1991) and by Figueiredo (1998) for peridotites and chromitites of CAT were also considered and the respective cation distribution per unit cell (*p.u.c*). was recalculated following the procedure referred to above.

The obtained cationic distributions *p.u.c.* are consistent with spinel compositions of almost ideal stoichiometry, being the chemically altered external rims of these oxides generally characterised by a relatively impoverishment in Mg and Al. In each Complex, the variability of Cr-spinel composition is not very large and, generally, these oxides can be thought of as solid solutions between chromite and spinel *s.s.*. This results in relatively high chromium concentrations (up to 13 cations *p..u.c.*) for spinels found in peridotites/chromitites of CAT, and in quite low, although not anomalous, chromium concentrations (usually corresponding to 4 to 6 Cr atoms *p.u.c.*) for spinels included in rocks of BAOC. In both cases, the remaining trivalent cations are made up mainly by aluminium and, to a much lesser extent, iron; divalent cations are essentially Fe and Mg and, on average, they occur in roughly equal amounts in the unit cell.

Figure 1 shows a compendium of the chemical variability of CAT and BAOC spinels, in the form of the classical $\#Cr=Cr/(Cr+Al)$ *versus* $\#Fe=Fe^{2+}/(Fe^{2+}+Mg)$ diagram. It should be noted that, irrespective of the Complex considered, spinels with *#Fe* higher than 0.65 are distinctively altered. Discarding these data, one may see that the plot of Cr-spinels of CAT define a relatively elongated and homogeneous cloud, limited by $0.62 \leq \#Cr \leq 0.85$ and $0.32 \leq \#Fe \leq 0.65$ values. The compositional variability displayed by non-altered Cr-spinels of BAOC is also relatively small, with all points of all locations clustering in a more or less circular dense cloud, except in the
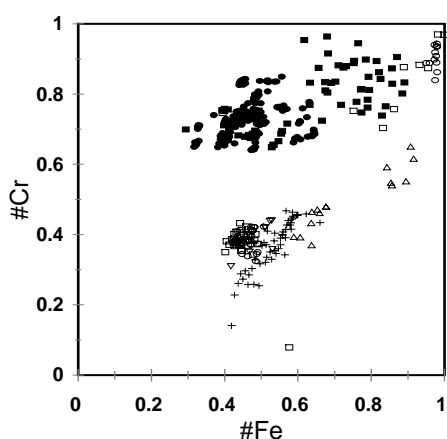

Fig.1 - *#Cr - #Fe* plot for spinels of CAT (black circles: peridotites; black squares: chromitites) and BAOC (cross-sign: wehrlites/troctolites; open square: peridotites of Sete Pés; open circle: peridotites of Azenha dos Machadinhos; triangles: peridotites of Ferreira do Alentejo; inverted triangles: diopside-rich peridotites of Ferreira do Alentejo).

case of disopside-bearing rocks. In other words: 1) spinels included in the prevailing harzburgites of BAOC, display relatively constant #Cr and #Fe values, ranging in the intervals [0.35, 0.45] and [0.40, 0.50], respectively; and 2) spinels within diopside-rich peridotites and wehrlites/troctolites of BAOC, record a positive *#Cr - #Fe* correlation, together with a wider variation of each of them individually.

Another remarkable point is that all the non-altered Cr-spinels plot to the right of the theoretical high-temperature isopleth estimated on the basis of the forsteritic content of the coexisting olivine, the deviation being larger for diopside-rich peridotites and for wehrlites/troctolites of BAOC. Moreover, one may emphasise that the spinel compositions of BAOC plot in all cases significantly to the right of the main trend shown in the unpublished large Cr-spinel database described in Roeder (1994). All these features seem to be independent of the late chemical transformations experienced by Cr-spinels, particularly those developed during serpentinisation, and so they probably record: 1) the compositional evolution of the magmatic melt during Cr-spinel growth; or 2) a relative Fe-enrichment attained during postdepositional processes, namely those due to chemical re-equilibrium of spinels during very-high temperature conditions.

4. Discussion

Following the empirical approach of Roeder (1994), one may conclude that natural Cr-bearing spinels form two different populations. The first one, *A*, occurs mainly in normal oceanic crust and can be found in all its rock types, from basalts to ultramafic cumulates other than pyroxenites (which, when spinel-bearing, seem to carry extremely Mg-impoverished spinels). In the diagram *#Cr-#Fe*, these spinels plot along an elongated trend which begins not far from the spinel corner and crosses the diagram diagonally towards the region of high *#Cr* and *#Fe* ratios close to 0.5. The second population, *B*, itself composed of several sub-populations very similar to each other, plots on a region corresponding to quite high *#Cr* ratios and horizontally spread over a wide range of *#Fe* ratios. The rocks bearing these spinels are very diverse in lithology and geological setting, since they include, among others, chromitites from all origins, ocean island basalts, boninites and continental stratified complexes. The detailed physical and chemical interpretation of these general trends of the natural spinel chemistry is not yet possible, but the database (available on request from Roeder) may be used to constrain the geological interpretation of any new natural spinels analysed.

Cr-spinels of BAOC belong clearly to population *A* and this is taken to mean, with a very high probability, that the rocks of BAOC have an oceanic origin, even considering the two different behaviours stated above. The composition shown by Cr-spinels of CAT demonstrates that they belong to population *B* and this prevents their use for any inference on any particular geological environment of crystallisation, which clearly contrasts with the interpretation given by Bridges *et al.* (1995).

4.1. The iron-enrichment of Cr-spinels

If the *#Fe* increase in the examined spinels is taken to be of primary origin, then it may have arisen due to lower than normal crystallisation temperatures or to co-precipitation with a forsterite-poor olivine, which is not consistent with the available data for olivines, nor with the fact that some of the observed rocks have enstatite along with olivine and Cr-spinel (for details, see Sack & Ghiorso, 1991). Therefore, Cr-spinel compositions must have been modified after initial crystallisation, but obviously before the alteration pattern clearly related to late serpentinisation events. This means that the variable chemical resetting experienced by the examined spinels is ascribable to fast *subsolidus* re-equilibration reactions under very-high temperature (800-900ºC) and relatively oxidising conditions, easily achieved during the initial stages of the complex metamorphic P-T-t path recorded by CAT and in the course of the anisotropic recrystallisation correlative of BAOC hot obduction. It should be further noted that Cr-spinel compositions obtained for some rocks of BAOC may encompass the whole compositional range of population *A*, without any significant segregation within the igneous rock or readily observable zonation of the individual crystals. For some authors (*e.g.* Peltonen, 1995), a possible mechanism for this is a progressive contamination of the magma by an influx of melt which would alter the values of critical parameters without significantly altering the bulk composition of the rock. This explanation is favoured in the case of BAOC because the rocks where a compositional trend is observed in Cr-spinels are also characterised by the presence of Ni-depleted olivines, sulphides and/or of considerable amounts of diopside probably caused by the incoming new magma (Mateus *et al.*, 1998a, b).

4.2. The variability of Cr-spinel as an ore guide for Ni-Cu sulphide mineralisations

The investigation carried out by Johan (1979) in the compositional plane Fe_3O_4-$FeCr_2O_4$-$MgAl_2O_4$ led to a crystallochemical model from which the discriminant function $\mathbf{G} = [(0.711/\mathbf{X}) - 1.111\mathbf{X}]/(1 - \mathbf{X})$, with $\mathbf{X} \equiv \#Mg = Mg/(Mg+Fe^{2+})$, can be deduced. Since $\mathbf{G}$ is also equivalent to $[Cr(Al+Fe^{2+})]/(Fe^{2+}Al)$, the $\mathbf{G}$ - $\mathbf{X}$ diagram results in a graphical expression extremely sensitive to Fe^{3+} incorporation and to Mg- and Al- depletion. According to Johan (1979) this diagram enables also the distinction of spinels included in mineralised (sulphide-bearing) ultramafic complexes (always plotted below the theoretical curve) from those usually found in common (sulphide barren) ultramafic-suites.

Figures 2 and 3 display the projection of the available Cr-spinel data for CAT and BAOC. They show clearly that spinels included in chromitites, peridotites and in wehrlites /troctolites do plot in distinct graphical fields. Also clear and distinct shifts in **G** and/or **X** values are obtained: 1) for a limited range of **X**, the variation of **G** exhibited by spinels in chromitites reflect mainly differences in Al contents, the influence of Fe^{3+} being also perceptive (particularly significant if notable amounts of interstitial silicates are present); 2) wide variations in **X** for narrow ranges in **G**
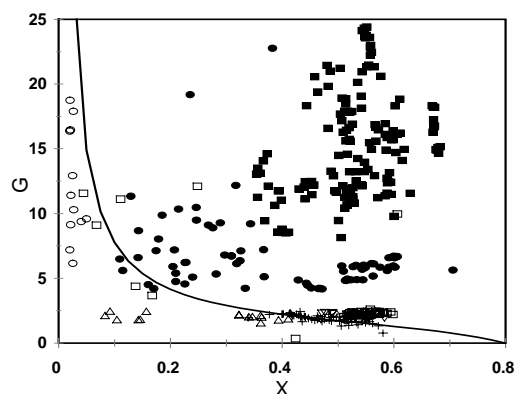

Fig.2 – Graphical expression of the function **G** (curve) and projection of the available data for Cr-spinels from CAT and BAOC (symbols as in fig.1).
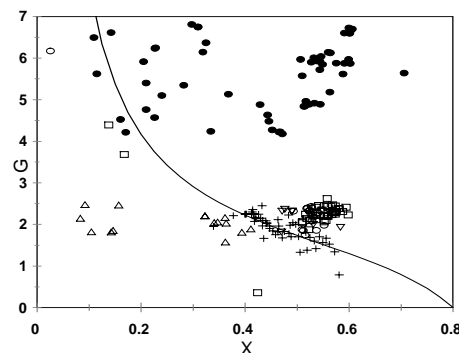

Fig.3 – Zoom of the **G** – **X** plot shown in figure 2.

characterise spinels included in peridotites, suggesting that the above mentioned *subsolidus* re-equilibration is, as expected, fostered by the inclusion of spinels within a silicate matrix; 3) the composition variability of spinels included in wehrlites/troctolites follows the one predicted by the theoretical discriminant function **G**; and 4) Cr-spinels in rocks that contain accessory amounts of Ni(-Cu) sulphides do plot at or below the curve that expresses the **G** function. According to the last statement, the existence of a sulphide phase in BAOC lithologies before Cr-spinel re-equilibration is strongly favoured, which is compatible with the metallogenetic model discussed in Mateus *et al.* (1998a).

Acknowledgments

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