

CHROMITITE IN OPHIOLITE COMPLEXES: GENESIS AND ALTERATION

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World chromite supply has come under severe pressure over the past years driven by the robust demand for ferrochrome used in ferroalloy production, ultimately used to make stainless steel. The growing difference between supply and demand is driving prices up (Fig. 1).

The renewed interest in chromite ore deposits leads to the need of detailed knowledge of chemical features of chromitite ore bodies and aims new projects focused on the understanding of chemical composition variability of such deposits.

The present study, divided in two parts, has been focused on the understanding of the genesis and of the post-depositional alteration processes related to podiform chromitite ore bodies.

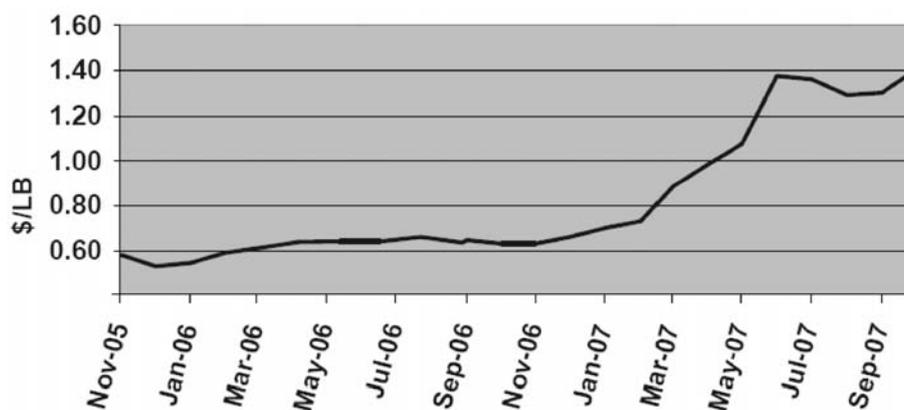


Fig. 1 – Chrome price history of last two years (data from U.S. Geological Survey).

1. GENESIS OF PODIFORM CHROMITITE: EXAMPLE OF TROODOS COMPLEX, CYPRUS

Troodos is a Mid Cretaceous ophiolite complex, overlain by *in situ*, upper Cretaceous to mid Tertiary deep sea deposits, and Neogene shallow-marine to continental sediments.

In this study we focus our attention on chromitite occurrences outcropping close to the English military base located close to Mt. Olympus area. These chromitites, already reported from other authors (*e.g.*, Greenbaum, 1977; Buchl *et al.*, 2004), have never been carefully investigated and have been here studied in order to understand the parental magma composition from which chromitite crystallized and to propose a genetic model for supra-subduction chromitite formation.

The studied chromitite (Fig. 2) grades toward external country rock represented by a fresh lherzolite (L) mainly composed of clinopyroxene, olivine and rare orthopyroxene occurring as exsolution lamellae of clinopyroxene. Lherzolite grades in a fresh dunite (Dunite 2 = D2) composed of rounded olivine of few mm (1-2 mm) and scattered spinel. D2 is in sharp contact with a completely serpentinized dunite (Dunite 1 = D1) that envelops irregular chromitite lenses and schlierens (CHR) of different sizes.

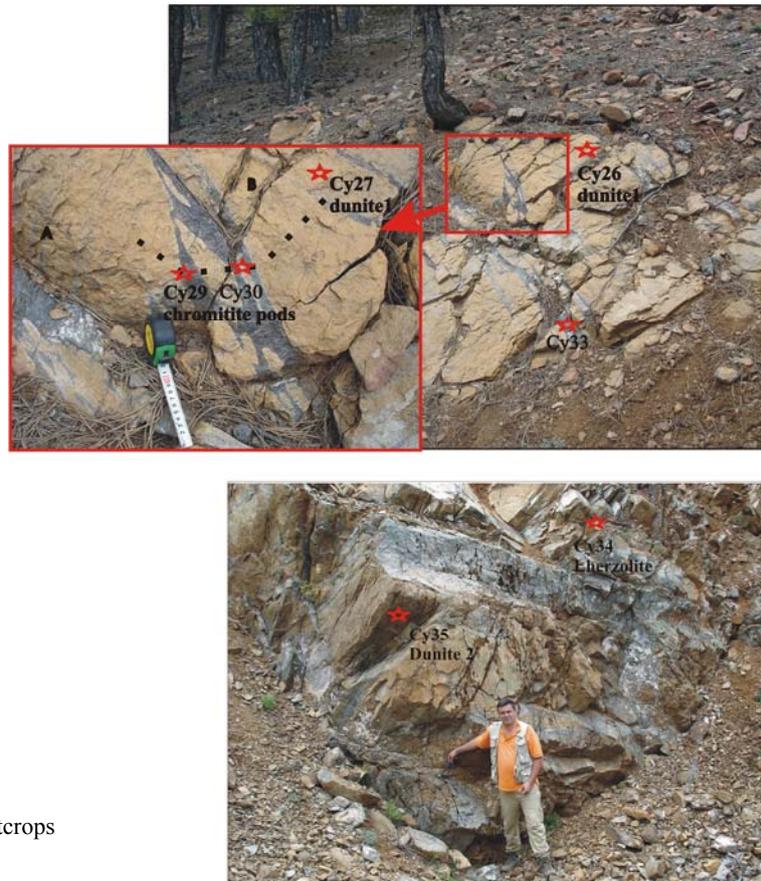


Fig. 2 – Picture from studied outcrops with location of the samples.

The primary composition of chromite allowed us to use it to compute the composition of basaltic melt from which chromitite crystallized.

The calculation is based on the equation proposed by Maurel & Maurel (1982) and recently used by Mondal (2006) that is constructed on inference that Al_2O_3 in spinel is only a function of Al_2O_3 in the parental melt (Mondal, 2006).

$$(Al_2O_3)_{spinel} = 0.035 \cdot (Al_2O_3)_{liquid}^{2.42} \quad [Al_2O_3 \text{ in wt.\%}]$$

Also the FeO/MgO ratio of the melt can be calculated using the equation of Maurel & Maurel (1982):

$$\ln (FeO/MgO)_{spinel} = 0.47 - 1.07 Y_{spinel}^{Al} + 0.64 Y_{spinel}^{Fe^{3+}} + \ln (FeO/MgO)_{liquid}$$

[MgO and FeO in wt.%, $Y_{spinel}^{Al} = Al/(Al+Cr+Fe^{3+})$ and $Y_{spinel}^{Fe^{3+}} = Fe^{3+}/(Al+Cr+Fe^{3+})$]

The results show that the parental magma from which chromitite crystallized is characterized by Al_2O_3 contents between 9.5 and 10.5 wt.%, and FeO/MgO between 0.27 and 0.65. The comparison of calculated parental magma composition with the composition of primitive magmas from different tectonic settings shows a good overlapping with boninite field melts.

Silicate inclusions

The detailed study of silicate inclusions, that may preserve important information on parental magma source from which chromitite crystallized, have been here used to investigate genetic processes. The compositional features of silicate inclusions have been compared in term of major and REE elements with those of mineral matrix of fresh host rocks (Fig. 3).

By the analysis of REE pattern is evident how L clinopyroxenes are similar to those of clinopyroxenes from a primitive mantle with LREE depletion respect to HREE.

These trends have been compared to those of clinopyroxene obtained by experiments performed by Gaetani *et al.* (2003) on hydrous partial melting of a lherzolitic peridotite at 1.2 and 1.6 GPa and at 1185 and 1370°C. Experimental results of Gaetani produced silicate melt saturated with a peridotite mineral assemblage of olivine + orthopyroxene + clinopyroxene + spinel or garnet. The comparison shows that clinopyroxene REE contents of Gaetani *et al.* (2003) are generally lower than those of included clinopyroxene from Troodos chromitites representing the lower limit of CHR cpx range and showing anyway similar trends especially in experiments performed at 1185°C and 1.2 GPa. This similarity can be due to a similar hydrated partial melting process of mantle peridotites in a temperature and pressure range comparable to that investigated by Gaetani *et al.* (2003) which produces a water-rich melt. On the other hand general higher values in LREE content could be related to metasomatic interaction of such melt with L that provides REE, Ca and Cr due to the assimilation of clinopyroxenes.

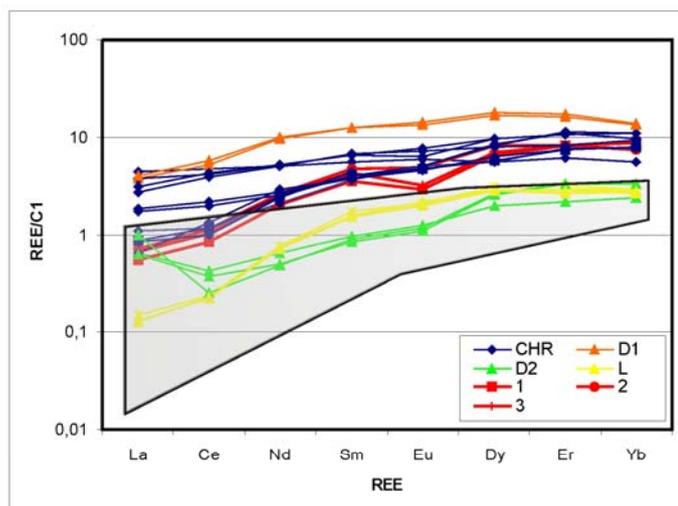


Fig. 3 – REE contents of Troodos clinopyroxene. Experiments of Gaetani *et al.* (2003), performed at 1) 1315°C and 1.2 GPa, 2) 1185°C and 1.2 GPa, 3) 1370°C and 1.6 GPa. Shaded region represents clinopyroxenes from primitive mantle (Dick & Johnson, 1995).

Concluding remarks

The analysis of Troodos chromitites associated to the study of silicate inclusions detected in chromitite pods as well as in host rock suggests a complex genesis probably related to the interaction between a hydrous melt, rich in incompatible elements with a mantle lherzolite host rock.

By textural and chemical evidences water played a fundamental role in metasomatism of host rock favoring also the increasing of Cr solubility in the melt itself.

The investigation of relationship between studied chromitite and its host-rock highlights the following evidences:

- The investigated chromite compositions are typical of supra-subduction geodynamic setting.

- Peridotite host rock (L) preserves the signs of partial melting with evident transformation of clinopyroxene into orthopyroxene. Moreover the metasomatic interaction with an ascending basaltic melt is testified by REE content of analyzed clinopyroxene.

- The two dunite bodies show different chemical composition related to their different genetic processes. D2 can be considered as the remnant of lherzolite after its metasomatic interaction with boninitic melt and consequent assimilation of clinopyroxene. D1 is the crystallization product of boninite saturated only in olivine due to metasomatic interaction with L.

- Such basaltic melt is boninitic, as calculated by chemical composition of chromite grains. It is enriched in Ca, REE and especially in Cr.

- Enrichment in Cr in boninitic melt is favored by water presence that has the main effects of:

1. To increase the Cr solubility through depolymerization of the melt itself.
2. To enlarge the chromite stability field favoring the stabilization of the chromite itself.

- The involvement of water in such metasomatic process is testified by the presence of numerous hydrous silicate inclusions and by REE content of clinopyroxene included in chromite grains.

- Later serpentinization processes did not affect chromite grains allowing to use them and their primary silicate inclusions as powerful tools for chromite genesis understanding.

On the basis of discussed data a genetic model for analyzed chromitite ore is here proposed (Fig. 4 and 5):

1. In a supra-subduction geodynamic setting, a primitive mantle begins to melt due to dehydration from subducting slab with production of a boninitic melt (stage 1).

2. Ascending hydrated boninitic melt interacts with lherzolitic host mantle to form a metasomatic dunite (D2, stage 2).

3. Such water-rich boninitic melt will be enriched in incompatible elements (REE), Cr, Ca.

4. The dissolution of pyroxene in L and the high content of water of ascending melt increase the Cr solubility of the boninitic melt itself.

5. As the interaction between host rock and boninitic Cr-enriched melt proceeds the melt will be saturated only in olivine favoring the formation of D1 (Stage 3).

6. Crystallization of dunite D1 increases Cr content of the melt till saturation.

7. High water and Cr contents of the boninitic melt favor the precipitation of chromite together with olivine and clinopyroxene (stage 4).

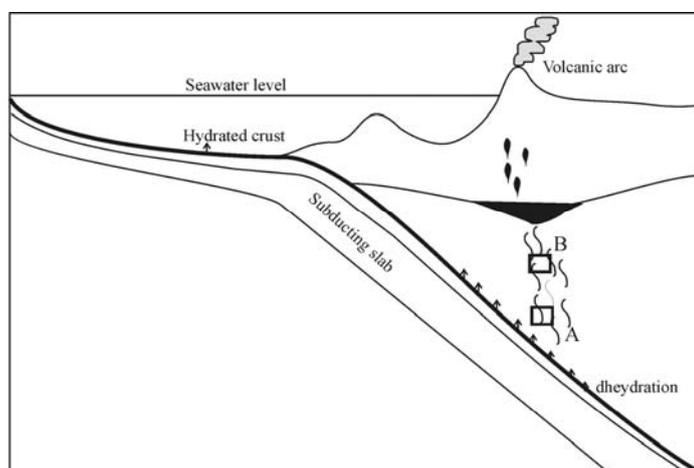


Fig. 4 - Suprasubduction geodynamic environment where chromitite formation takes place.

8. As the precipitation of chromite proceeds clinopyroxene and olivine are included in chromite grains. Primary olivine and clinopyroxene relics are preserved only as inclusions in chromite grains due to continue reaction between host rock and ascending boninitic melt (stage 5).

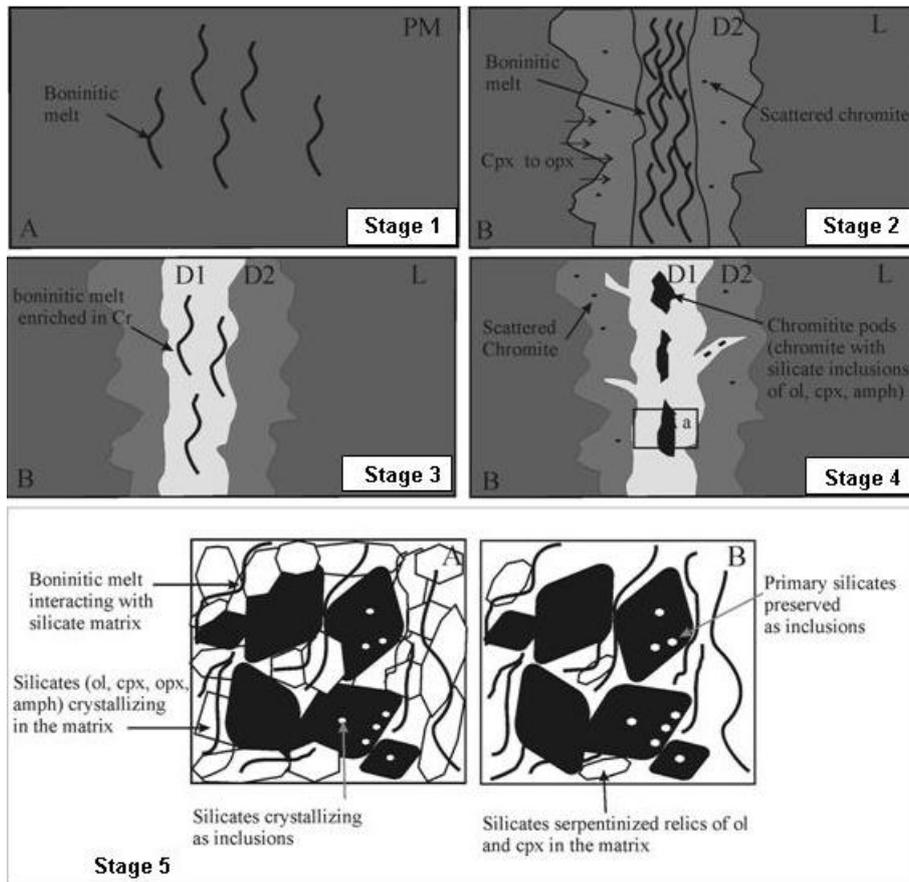


Fig. 5 – Schematic genetic model for Troodos chromitite formation. *Stage 1*) Production of boninitic melt rich in incompatible elements (REE), SiO₂ and H₂O due to dehydration of primitive mantle (PM). *Stage 2*) Reaction between lherzolite mantle and boninitic melt rich in incompatible elements (REE), SiO₂ and H₂O to form metasomatic dunite D2. Clinopyroxenes of L are transformed into orthopyroxenes. *Stage 3*) formation of dunite D1 from boninitic melt. *Stage 4*) Formation of chromitite pods (CHR) from Cr-saturated boninitic melt. *Stage 5*) Boninitic melt interacting with silicate matrix to form cpx-bearing dunite and primary silicates preserved as inclusions (serpentinized silicate relics of ol and cpx in the matrix).

9. Small amounts of hydrous basaltic melt, entrapped in chromite grains, evolve as a closed system with crystallization of hydrous silicate inclusions (mainly amphibole). On the contrary intergranular silicates, dominated by anhydrous mineral phases are products of an open system of the same melt where volatiles are transported away from the site of chromite crystallization. This is the main reason why no amphibole has been detected in the matrix.

10. Later serpentinization led to general obliteration of primary features of silicate matrix of chromitite pods.

2. CHROMITE ALTERATION PROCESSES: “FERRITCHROMITE” FORMATION (KALKAN COMPLEX, RUSSIA)

The second part of the study has been focused on post-depositional alteration processes that affected chromitite deposits of serpentinitic mélangé in Kalkan ophiolite complex (Southern Urals).

In Kalkan melange chromitite bodies mainly outcrop in prospecting trenches dug during a survey for chromitite ores between 2000 and 2002 and are here described for the first time.

Chromitites are always associated with serpentinitized dunites and show a wide variety of textures ranging from disseminated to massive. Fluidal textures are marked by iso-oriented serpentinite eyes that form irregular and elongated lenses and layers. In all studied samples millimetric to centimetric veins of serpentine have been detected.

Chromite grains are often fractured and dismembered with a habit varying from euhedral to anhedral. They are unzoned but chromite dissolution into highly porous “ferritchromite” changes wide portions of the grains.

Ferritchromite is associated to the growth of chlorite that substitutes serpentine, rarely detected in the matrix and only as relic (Fig. 6).

Relative volumes of phases have been evaluated collecting Back Scattered Electron (BSE) images of representative selected areas and processing such images with Image-Pro Plus software to perform modal analysis. The relative volumes among phases have been calculated using their grey scale intensity variation.

Since chromite forms equigranular grains, relative volumes are assumed equivalent to relative areas; modal volumes (MV%) have been calculated dividing area of each class by the image total area. Relics of serpentine have been ignored.

Chromite is one of the first minerals to crystallize from basaltic melts and its stability, under a range of geological conditions, allows to consider it as an useful indicator of magmatic conditions at the time of initial crystallization (Roeder, 1994). Chromite is often the only igneous phase that seems to have been not modified by alteration processes, however, as observed in Kalkan chromitites, geochemical features may change during later processes, giving secondary alteration products such as ferritchromite and Cr-rich chlorite (Shen *et al.*, 1988; O’Hanley & Dyar 1993; Proenza *et al.*, 1999; Nozaka 2003; Palandri & Reed 2004; Bach *et al.*, 2006; Caillaud *et al.*, 2006).

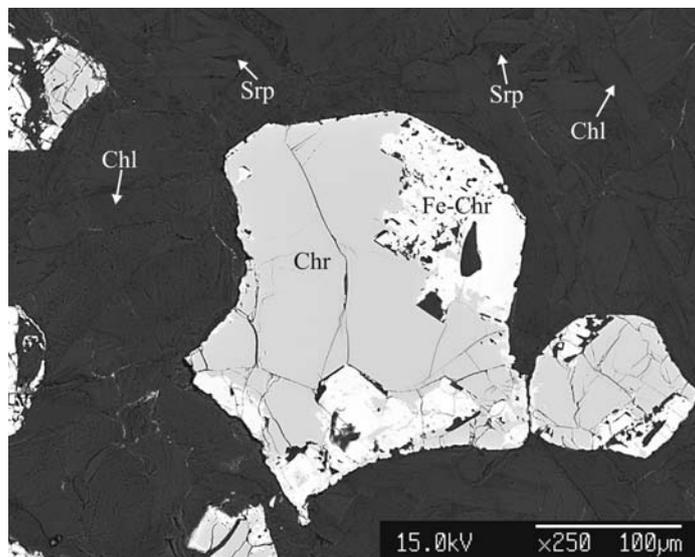
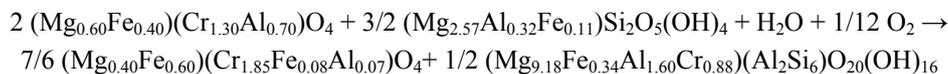


Fig. 6 – Highly porous ferritchromite replacing chromite grain surrounded by chlorite with serpentine relics. Fe-Chr = ferritchromite, Chl = chlorite, Srp = Serpentine.

At Kalkan chromite reacts with serpentine similarly to what suggested by Mellini *et al.* (2005) but the products are slightly different consisting of ferritchromite and Cr-bearing chlorite.

On the basis of chemical analyses and using the real stoichiometric data we suggest the following reaction:



In order to compare stoichiometry of reaction with modal analyses the stoichiometric ratios between phases have been transformed into normalized volumes RV_x assuming 100 the chromite volume:

$$\text{RV}_x = (n_x \cdot \text{MW}_x / \text{D}_x) \times 100 / (n_{\text{chr}} \cdot \text{MW}_{\text{chr}} / \text{D}_{\text{chr}})$$

where n_x is the stoichiometric coefficient, MW_x the molecular weight and D_x the density of phase x . Densities for each mineral are averages on the basis of bibliographic data (Duda & Rejl, 1990). Applied values together with normalized volumes for each phase are listed in Table 1.

Table 1 - Relative volumes.

Phase	Formula	n	MW	D	RV
Chr	$(\text{Mg}_{0.60}\text{Fe}_{0.40})(\text{Cr}_{1.30}\text{Al}_{0.70})\text{O}_4$	2	187.35	4.43	100
Srp	$(\text{Mg}_{2.57}\text{Al}_{0.32}\text{Fe}_{0.11})\text{Si}_2\text{O}_5(\text{OH})_4$	3/2	281.43	2.59	192.7
Fe-Chr	$(\text{Fe}_{0.60}\text{Mg}_{0.40})(\text{Cr}_{1.85}\text{Fe}_{0.08}\text{Al}_{0.07})\text{O}_4$	7/6	209.7	4.50	64.28
Chl	$(\text{Mg}_{9.18}\text{Fe}_{0.34}\text{Al}_{1.60}\text{Cr}_{0.88})(\text{Al}_2\text{Si}_6)\text{O}_{20}(\text{OH})_{16}$	1/2	1145.53	2.60	255.54

Chr = chromite, Srp = serpentine, Fe-Chr = ferritchromite, Chl = chlorite.
n = stoichiometric coefficient, MV = molecular weight, D = density, RV = relative volume.

In a second step chromite and serpentine volumes before reaction have been calculated from BSE images considering two classes of gray scale intensity: initial chromite (IV_{chr}) and initial serpentine (IV_{srp}).

Ferritchromite replaces chromite and this occurs with a volume decrease, testified by its typical porous texture. We assumed IV_{chr} to be the sum of chromite, ferritchromite and its porosity. In order to eliminate holes and fractures we applied morphological filters. Silicate matrix is assumed to be originally all serpentine as testified by the presence of serpentine relics and by the complete serpentinization of chromitite host rock. Therefore second class (IV_{srp}) is assumed to be all silicate matrix after subtraction of the silicates within chromite and ferritchromite porosity.

The phase that works as limiting agent depends on the initial ratios of phases; for

$$\text{IV}_{\text{chr}} < 100 \cdot \text{RV}_{\text{chr}} / (\text{RV}_{\text{srp}} + \text{RV}_{\text{chr}}) = 34.16$$

limiting agent is chromite, while for $\text{IV}_{\text{chr}} > 34.16$ limiting agent is serpentine. Since all studied chromitites have $\text{IV}_{\text{chr}} > 34.16$ limiting agent is always serpentine.

Assuming complete reaction of initial serpentine and using the stoichiometric coefficients of the reaction the relation between IV_{chr} and theoretical volumes (TVs) of all involved phases can be expressed by the following relations:

$$\begin{aligned}
 1) \quad TV_{chl} &= IV_{srp} \cdot RV_{chl} / RV_{srp} \\
 2) \quad TV_{fe-chr} &= IV_{srp} \cdot RV_{fe-chr} / RV_{srp} \\
 3) \quad TV_{chr} &= IV_{chr} - IV_{srp} \cdot RV_{chr} / RV_{srp}
 \end{aligned}$$

TVs are straight lines in an IV_{chr} vs. volumes % diagram. Comparison between TVs and modal volumes (MVs) shows a good fitting of data (Fig. 7), validating the stoichiometry of the reaction we proposed. The displacement between theoretical lines and MVs is low but constantly MVs are lower than TVs for products (chlorite and ferritchromite) and higher for reactants (chromite). This suggests that reaction, although close

to completion, never reaches it, leaving small unreacted areas, as testified by mineralogical evidences that show the presence of rare serpentine relics in the silicate matrix. We suggest that in the final stages of reaction distance between reactants is high enough to prevent completion of reaction itself. This is also suggested by the location of serpentine relics in the silicate matrix always far from chromite grains.

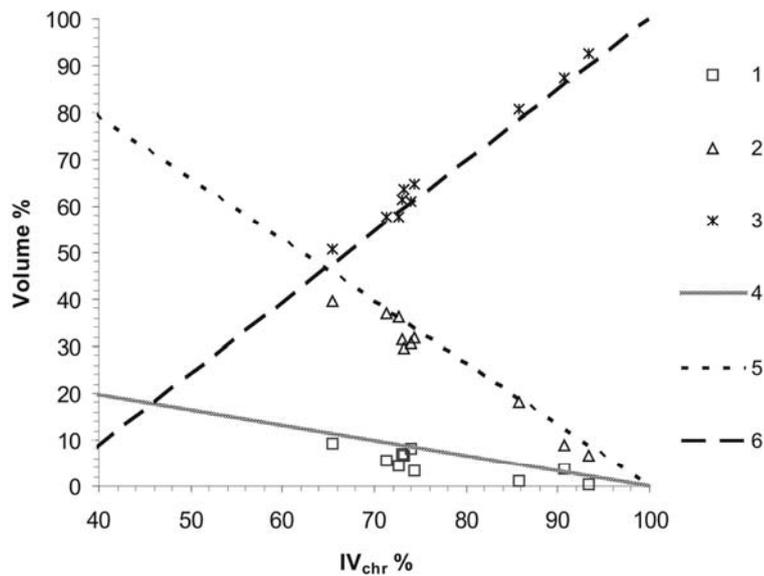


Fig. 7 – IV_{chr} vs. Volumes % of chlorite (chl), chromite (chr), and ferritchromite (Fe-Chr). 1) Ferritchromite modal volumes; 2) chlorite modal volumes; 3) chromite modal volumes; 4) ferritchromite theoretical volumes; 5) chlorite theoretical volumes; 6) chromite theoretical volumes.

Concluding remarks

The study performed on Kalkan ophiolite melange chromitites leads to the following conclusions:

- In Kalkan ophiolite melange ferritchromite formation is related to post-serpentinization processes that led to the alteration of original chromite that is preserved only in some areas. As a consequence of such alteration the use of chromite chemistry to infer magmatic processes can be misleading.
- Ferritchromite and chlorite form by reaction between chromite and serpentine in presence of aqueous fluids without any external contribution of metals.
- In chromitites serpentine works as the limiting agent of the reaction. The incomplete reaction between chromite and serpentine can explain the observed textures.
- Modal analyses results confirm the proposed reaction, suggesting that it usually progresses almost to completion.

- In altered chromitites development of ferritchromite is a function of the chromitite texture, being strongly limited for very massive chromitites.

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