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Spinels of Variscan olivine hornblendites related to the Montnegre granitoids revisited (NE Spain): petrogenetic evidence of mafic magma mixing

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ABSTRACT

Olivine hornblendites (cortlandtites) form part of the Montnegre mafic complex related to late-Variscan I-type granitoids in the Catalan Coastal Ranges. Two generations of spinel are present in these hornblendites: Spl1 forms euhedral crystals included in both olivine and Spl2. Spl2 forms euhedral to anhedral crystals associated with phlogopite and fibrous colourless amphibole forming pseudomorphs after olivine. Compositions of Spl1 are picotite-Al chromite (Fe#: 77.78-66.60; Cr#: 30.12-52.22; Fe³⁺/R³⁺: 6.99-21.89; 0.10 < TiO₂% < 0.62). Compositions of Spl2 are pleonaste (Fe#: 37.86-52.12; Cr#: 1.00-15.45; Fe³⁺/R³⁺: 0.31-5.21; TiO₂% < 0.10). The two types of spinel follow a CrAl trend, mainly due to the substitution (Fe²⁺)⁻¹Cr¹⁺ = MgAl, which is interpreted as the result of mixing between two different mantle-derived melts. The compositions of early Spl1 crystals included in olivine are characteristic of Al-rich basalts. More aluminous Spl2 would result from reaction of olivine with a less evolved, Al and K-rich mantle-derived melt after new refilling of the magma chamber or channel. As a whole, spinels from similar examples of Variscan olivine hornblendites also follow a CrAl trend with high Fe# and starting at higher Cr# than other trends of this type. Cr# heterogeneity in the early spinels from these Variscan hornblendites would be inherited from the variable Al content of the mafic melts involved in their genesis.

KEYWORDS Catalan Coastal Ranges. Olivine hornblendites. Spinel compositions. Mantle-derived melts.

INTRODUCTION

Hornblendites and olivine hornblendites (cortlandtites) have been frequently mentioned as part of the ultramafic-mafic rock associations, called “appinites” by some authors (Castro *et al.*, 2003; Molina *et al.*, 2009, 2012; Scarrow *et al.*, 2009; Murphy, 2013), which are related to granitoids and/or migmatites. Although olivine hornblendites are not the most abundant rock within the appinite suite, they are the most striking ones since the presence of olivine implies

the intrusion of mantle-derived magmas during the genesis of granitoids, if not involved in their formation. Frequent examples of these hornblendites are found related to granitoids and/or migmatites of the Iberian Massif (Galán, 1987a, b; Galán and Suárez, 1989; Moreno-Ventas *et al.*, 1995; Bea *et al.*, 1999, 2006; Castro *et al.*, 2003; Bea, 2004; Montero *et al.*, 2004; Molina *et al.*, 2009; Scarrow *et al.*, 2009) and other Variscan terranes, mostly in the Pyrenees (Leterrier, 1972; Fourcade and Allegre, 1981; Enrique, 1983; Roberts *et al.*, 2000; Vilà *et al.*, 2005).

Most of the previously mentioned studies deal with mineral and whole-rock geochemistry (major, trace element and isotope compositions) of olivine hornblendites, as part of the “appinites”, in order to assess their petrogenesis and relationships with coeval granitoids. In most studies, these peculiar ultramafic rocks were interpreted as early cumulates (Fourcade and Allegre, 1981; Galán, 1987a, b; Galán and Suárez, 1989; Moreno-Ventas *et al.*, 1995; Galán *et al.*, 1997; Bea *et al.*, 1999; Castro *et al.*, 2003; Vilà *et al.*, 2005; Molina *et al.*, 2009; Scarrow *et al.*, 2009) derived from hydrous basalt-type or more evolved magmas (*viz.* trachyte-andesite; Molina *et al.*, 2009), which can be severely hybridized with deep crustal melts (Fourcade and Allegre, 1981; Bea *et al.*, 1999). In the Montnegre case, the parental basalt-type melt would have been more Al-enriched than in other examples (Enrique and Galán, 1989). However, more recently, it has been also suggested that the Montnegre hornblendites could represent differentiated melts resulting from fractional crystallization of komatiite-type magmas evolving at high P_{H_2O} (Enrique, 2016).

Olivine hornblendites are characterized by a poikilitic texture with large amphibole oikocrystals including olivine, orthopyroxene and/or clinopyroxene. Minor phlogopite is usually present and spinel is frequent as an accessory mineral, but this phase has not been the focus of special attention so far; most available analytic data are of silicates. Spinel was mentioned in most hornblendites from the Iberian Massif and the Pyrenees. Compositions of hornblendite spinel from the Iberian Massif are chromian spinel-picotite and rarely pleonaste, whereas in examples from the Pyrenees, spinel compositions correspond to chromite, for example in the Quérigut complex (Galán, 1987b).

This study is focused on the textural relationships and compositions of spinel in the olivine hornblendites from the Montnegre Mafic Complex (MMC). For such a purpose, Secondary Electronic Microscope (SEM) backscattered images and new analytic data are used. They provide insight into magma mixing processes involved in the genesis of the MMC. In addition, comparison with spinel compositions in other olivine hornblendites reveals a characteristic CrAl trend for spinels of these ultramafic rocks.

GEOLOGICAL SETTING, RELATED GRANITOIDS AND FIELD RELATIONSHIPS

The olivine hornblendites of the MMC appear as metric enclaves in hornblende (mela) gabbros. These along with leucogabbros and quartz diorites (Enrique, 1983; Butjosa *et al.*, 2013) crop out scattered over an

area that is 4km long by 2.5km wide near the locality of Hortsavinyà (Enrique, 1983; Fig. 1), in the Catalan Coastal Ranges. All these rocks are located at the contact between the biotite granite of the Montnegre massif and the Siluro-Devonian country rocks formed by calc-silicate and pelitic metasediments. These metasediments were affected by an intense contact metamorphism that transformed them into marbles, calc-silicates and pelitic hornfels during the intrusion of the postectonic Variscan Montnegre granitoids.

The Montnegre granitoids are hornblende-biotite tonalites, biotite granodiorites and monzonitic granites and leucogranites intruded at shallow levels (Enrique, 1990). Along with the MMC, they define a calc-alkaline trend, similar to that of other coeval associations of ultramafic-mafic rocks and granitoids in the Pyrenees (*e.g.* Roberts *et al.*, 2000; Vilà *et al.*, 2005). Although the geodynamic setting is not well constrained, trace element compositions (*viz.* Rb, Y, Nb) of the granitoids are comparable to those formed in volcanic arc settings (Enrique and Solé, 2004). In the K_2O vs. SiO_2 diagram (Fig. 2), the MMC rocks and granitoids define a trend that straddles the boundary between medium- and high-K calc-alkaline series. Specifically, the olivine hornblendites are within the medium-K field.

Field relationships indicate that the intrusion of the MMC and granitoids are broadly coeval and result in a complex mingled zone between dioritic rocks and the biotite granodiorite (Fig. 1). A whole-rock Rb-Sr isochrone for the granitoids provided 269 ± 4 Ma (Enrique and Debon, 1987) and an initial $^{87}Sr/^{86}Sr$ ratio of 0.71068 ± 6 (2s), typical of crustal rocks. Similar ages were estimated with a mineral-rock Rb-Sr isochrone for a hornblende-biotite tonalite (284 ± 7 Ma; Del Moro and Enrique, 1996) and with K-Ar (284 ± 4 Ma; Solé *et al.*, 1998) and Ar-Ar (286 ± 1 Ma, Solé, 1993) data of biotite.

ANALYTICAL METHODS

Five samples of olivine hornblendites were examined with the petrographic microscope, of which two were selected for analysing with SEM and with the electron microprobe analyser. The SEM is an EVO Zeiss of the Microscopy Service of the Universitat Autònoma de Barcelona provided with an energy dispersive spectrometer for semi-quantitative analyses. Quantitative chemical analyses of spinel were performed with a CAMECA SX50 in the Centres Científics i Tecnològics (CCiTUB) of the Universitat de Barcelona. The working conditions were: beam current of 15.0nA, acceleration voltage of 20.00kV and counting time of 10s. Standards were both natural and synthetic. Formula unit of spinel is

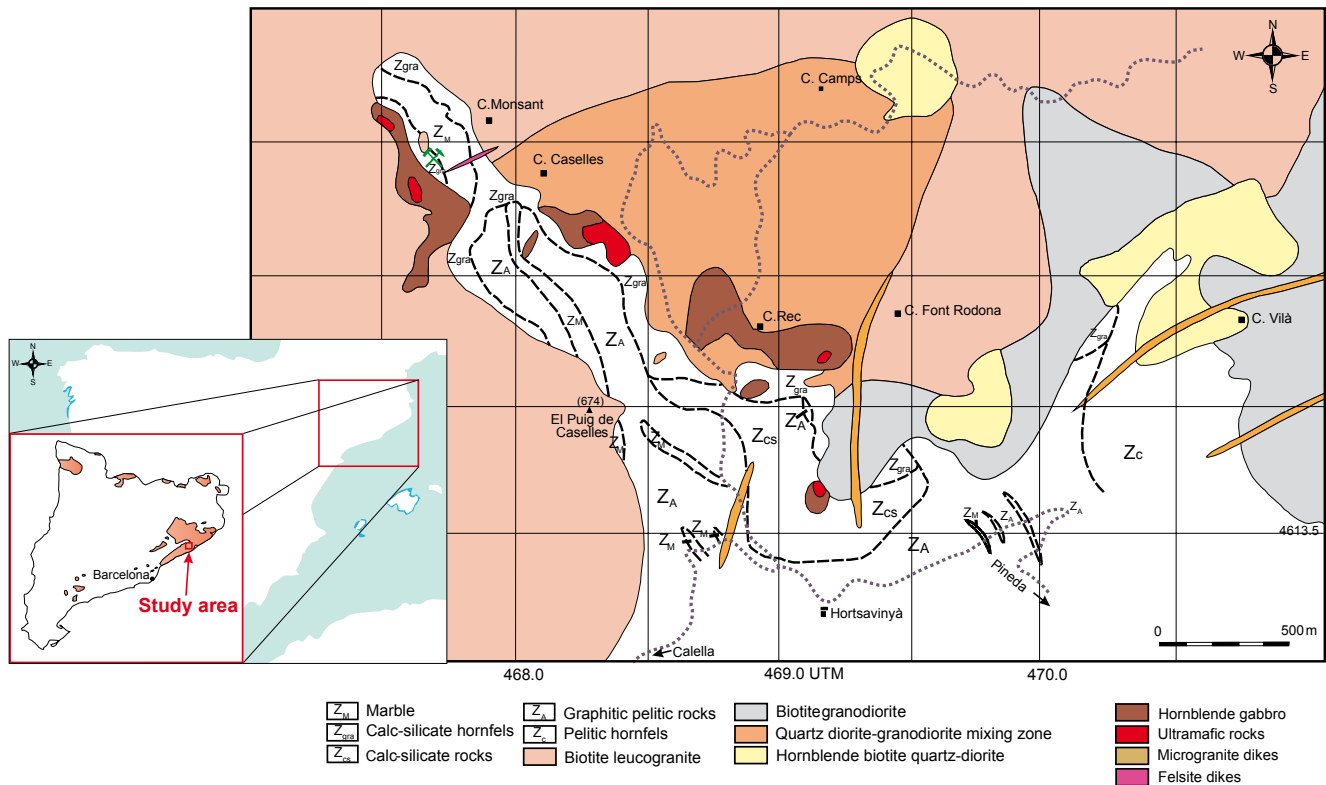


FIGURE 1. Location of the Montnegre mafic complex (MMC) within the Montnegre massif in the Catalan Coastal Ranges, based on Enrique (1983).

based on 32 oxygens and Fe^{3+} was estimated on charge balance (Table 1).

PETROGRAPHY

The olivine hornblendites show poikilitic texture defined by amphibole oikocrystals (1-2cm at their short axis) including olivine (Fig. 3A) and less frequently clinopyroxene and orthopyroxene. The oikocrystals of amphibole are brown to green in colour at the core (Amp1) and green to colourless displaying fibrous habit, towards the rim and around the inclusions (Fig. 3A; B). Crystals with fibrous habit (Amp2), with 100 μm at the short axis, also form pseudomorphs after earlier anhydrous mafic silicates. These pseudomorphs can be enclosed by Amp1 crystals or located between them. The brown cores of Amp1 often show angular forms and sharp edges, against the green and colourless rims (Fig. 3A), and frequent ilmenite lamellae following the cleavage (Fig. 3C). Compositions of brown-green Amp1, in oikocrystal cores, are of tschermakite and Mg-hornblende, respectively. They differ from compositions of Amp2, which are actinolite, tremolite, cummingtonite or anthophyllite. Olivine, with forsterite (Fo) range from 80 to 73%, appears as millimetric (up to 2mm) somewhat skeleton or amoeboid crystals (Fig. 3C), partially altered to serpentine+magnetite filling

cracks. It can be partially or totally replaced by Amp2-phlogopite-spinel clusters. Clinopyroxene composition is chromian diopside or augite close to diopside. It forms anhedral crystals (200 μm in size), which can enclose olivine (Fig. 3C), and is always transformed to amphibole (Amp2) which forms patches within the clinopyroxene crystals. This is also the case of orthopyroxene (enstatite) that is only present as relics within Amp2 pseudomorphs. Phlogopite mode is abundant (up to 7.6% in volume; Butjosa *et al.*, 2013) forming i) isolated subhedral crystals (200 μm at their long axis) with ilmenite lamellae at the core (Fig. 3D); ii) intergrown anhedral crystals (or corroded crystals?) with brown-green Amp1 (Fig. 3E); and iii), clusters together with spinel $\pm$ Amp2 (Fig. 3F) pseudomorphing olivine (Enrique and Galán, 1989). Phlogopite can be partially or totally altered to chlorite. More detailed petrographic description and compositional data of previously mentioned silicates were provided by Galán (1987b), Enrique and Galán (1989).

Spinel is the most abundant accessory mineral (up to 2.8% in volume; Enrique and Galán, 1989). Two types have been differentiated: Spl1 as small euhedral to anhedral black crystals of 10-2 μm (Spl1), usually included in olivine and in other green spinel (Spl2) (Fig. 4A; B); Spl2 as green euhedral to anhedral crystals up to 10 μm in size. The latter is the most abundant spinel, often forming

TABLE 1. Representative analyses of Sp11 and Sp12 in olivine hornblendites from the Montnegre Massif. The two samples are from Hortsaenyà area (UTM coordinates in Fig. 1)

Sample analyse	Sp11 (o) 12LB-1#6	Sp11(o) 12LB-1#14	Sp11(o) 12LB-1#66	Sp11(s) 12LB-1#33	Sp12 12LB-1#32	Sp12 rim 12LB-1#24	Sp12(p) 12LB-1#38	Sp11(s) A-92#8	Sp11(s) A-92#57	Sp11(s) A-92#11	Sp12 A-92#6	Sp12 A-92#1	Sp12 A-92#6b	Sp12 A-92#3
SiO ₂	0.10	0.04	0.24	0.07	0.03	0.11	0.02	0.06	0.08	0.46	0.42	0.09	0.2	0.03
TiO ₂	0.60	1.06	0.49	0.27	0.04	0.02	0.06	0.57	0.32	0.3	0.04	0.05	0.01	0.04
Al ₂ O ₃	23.29	21.08	24.59	24.37	63.4	61.23	61.79	23.23	31.57	29.8	63.73	61.87	61.75	52.58
Cr ₂ O ₃	33.58	34.34	31.81	34.59	0.32	2.02	1.61	33.86	27.39	26.85	0.88	2.17	1.59	10.3
Fe ₂ O ₃	8.87	10.12	7.68	7.17	2.37	2.77	2.34	8.22	6.31	7.27	0.31	2.09	2.71	3.11
FeO	27.82	28.03	27.1	26.44	16.75	17.29	17.64	28.18	26.4	27.21	18.96	18.17	17.33	21.4
MnO	0.30	0.40	0.35	0.35	0.05	0.15	0.07	0.28	0.26	0.3	0.1	0.12	0.08	0.1
MgO	5.29	5.14	5.5	5.92	16.35	15.77	15.54	4.93	6.78	6.2	15.38	15.42	15.95	12.3
NiO	0.05	0.04	0.01	0.04	0.12	0.09	0.1	0.00	0.07	0.03	0.06	0.08	0.15	0.03
Sum Ox wt. %	99.9	100.23	97.78	99.22	99.43	99.44	99.17	99.32	99.18	98.41	99.9	100.06	99.77	98.89
Si	0.003	0.001	0.008	0.002	0.001	0.003	0.001	0.002	0.003	0.014	0.011	0.002	0.005	0.001
Ti	0.015	0.026	0.012	0.006	0.001	0.000	0.001	0.014	0.008	0.007	0.001	0.001	0.0	0.001
Al	0.889	0.811	0.948	0.927	1.944	1.897	1.917	0.893	1.158	1.112	1.952	1.908	1.903	1.708
Cr	0.86	0.886	0.823	0.882	0.007	0.042	0.034	0.873	0.674	0.672	0.018	0.045	0.033	0.224
Fe ³⁺	0.216	0.249	0.189	0.174	0.046	0.055	0.046	0.202	0.148	0.173	0.006	0.041	0.053	0.065
Fe ²⁺	0.753	0.765	0.742	0.713	0.364	0.38	0.388	0.769	0.687	0.72	0.412	0.398	0.379	0.493
Mn ²⁺	0.008	0.011	0.01	0.009	0.001	0.003	0.002	0.008	0.007	0.008	0.002	0.003	0.002	0.002
Mg	0.255	0.25	0.268	0.285	0.634	0.618	0.61	0.24	0.314	0.292	0.596	0.601	0.622	0.505
Ni	0.001	0.001	0.000	0.001	0.002	0.002	0.002	0.0	0.002	0.001	0.001	0.002	0.003	0.001
Σ cations	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Cr#	49.2	52.2	46.5	48.8	0.4	2.2	1.7	49.4	36.8	37.7	0.9	2.3	1.7	11.6
Fe#	74.7	75.4	73.5	71.4	36.5	38.1	38.9	76.2	38.6	71.1	40.9	39.8	37.9	49.4
Mg#	25.3	24.6	26.5	28.6	63.5	61.9	61.1	23.8	31.4	28.9	59.1	60.2	62.1	50.6
Fe ³⁺ /R ³⁺	11.0	12.8	9.6	8.8	2.3	2.8	2.3	10.3	7.5	8.8	0.3	2.1	2.7	3.3

(o), inclusion in olivine; (s), inclusion in Sp12; (p), inclusion in phlogopite.

clusters or pseudomorphs along with phlogopite and Amp2 (Fig. 4D) after olivine. Less frequently, Spl2 follows the cleave of phlogopite included in Amp1 (Fig. 3E). Contacts between the two types of spinel are either sharp or gradual (Fig. 4A; C). Ilmenite is also an accessory mineral, either as isolated inclusions in Amp1, and more rarely in olivine, or as lamellae in brown Amp1 and phlogopite.

SPINEL COMPOSITIONS

Here, we only refer to compositions of the spinel and chromite series, not to those of magnetite series which appears together with serpentine as olivine alteration products. Spl1 and Spl2 show compositions of picotite-Al chromite and pleonaste, respectively (Table 1). Fe# $[100 \cdot \text{Fe}/(\text{Mg} + \text{Fe}^{2+})]$ in Spl1 ranges from 77.78 to 66.60, Cr# $[100 \cdot \text{Cr}/(\text{Cr} + \text{Al})]$ from 30.12 to 52.22 and $\text{Fe}^{3+}/\text{R}^{3+}$ $[100 \cdot \text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Al} + \text{Cr})]$ from 6.99 to 21.89, all numbers in atoms per formula unit. Spl2 pleonaste has Fe#: 37.87–52.12; Cr#: 1.00–15.45 and $\text{Fe}^{3+}/\text{R}^{3+}$: 1.98–5.21. Ti abundance is higher in Spl1 ($0.10 < \text{TiO}_2\% < 0.62$) than in Spl2 ($\text{TiO}_2\% < 0.10$). There is a compositional gap between the two types of Montnegre spinel, which is different from the spinel gap of Barnes and Roeder (2001) (Fig. 5A; B): the latter is observed between chromite and Fe^{3+} -rich spinels approaching magnetite. Finally, it is worth noting that Al concentration in Spl2 is as high as in spinels from high-grade metasedimentary rocks (Fig. 5A).

DISCUSSION

Spl1 and Spl2 compositions of this study are comparable to those provided by Enrique and Galán (1989) for another olivine hornblendite from the MMC. However, previous interpretation was the reverse: pleonaste, or Spl2 of this study, was considered the early magmatic spinel, whereas chromian spinel (Spl1 of this study) was interpreted as a later spinel resulting from the transformation of pleonaste during the upwelling of these rocks, from 0.7–0.8 GPa pressure (transit of spinel to plagioclase lherzolites) towards the final intrusion depth (*ca.* 0.1–0.2 GPa) (Enrique and Galán, 1989). Chromian spinel inclusions in pleonaste (Fig. 4B) and spinel zoning in Figure 4C are definitely in conflict with this interpretation.

Both types of spinel follow a CrAl trend, similar to the Rum trend (Fig. 5A; B) but at higher Fe# than most CrAl trends (Barnes and Roeder, 2001) (Fig. 5B). This trend implies an increase in Al mainly at the expense of Cr and with a moderate Fe^{3+} increase (Fig. 5C). Therefore, it is inferred that the main operating substitution was $(\text{Fe}^{2+})^{-1}\text{Cr}^{-1} = \text{MgAl}$, with subordinate contribution of the magnetite substitution: $\text{Fe}^{2+}\text{Fe}^{3+} = \text{Mg}^{-1}\text{Cr}^{-1}(\text{Al}^{-1})$.

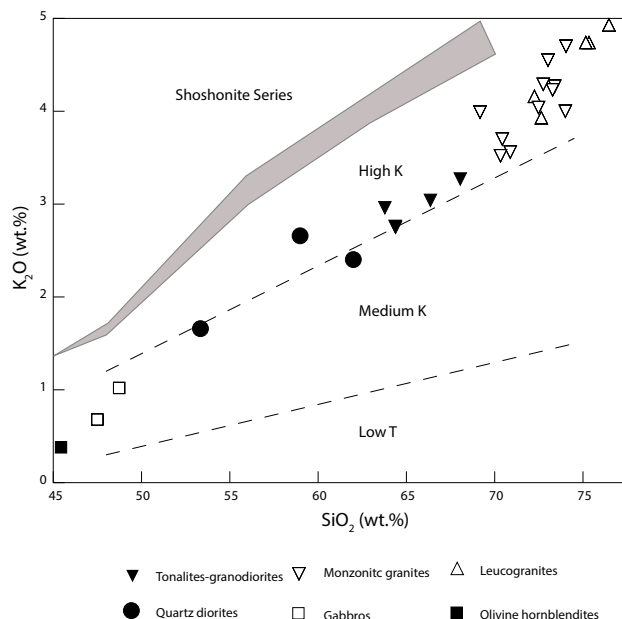


FIGURE 2. Evolution of the MMC and Montnegre granitoids in the K_2O vs. SiO_2 diagram of Le Maitre *et al.* (1989) (broken line limits). The limit between the high-K series and the shoshonite series is by Rickwood (1989). Data of the MMC by Butjosa *et al.* (2013), and of the Montnegre granitoids by Enrique (1985).

In the following paragraphs, we will discuss the origin of Spl1 and Spl2 and compare them with spinels in similar hornblendites from the Iberian Massif and the Pyrenees.

Spinel 1

Chromian spinel is frequent in ultramafic and mafic rocks and serves as proxy for the geochemical characteristics of the involved melts (Irvine, 1965, 1967; Dick and Bullen, 1984; Roeder, 1994; Kamenetsky *et al.*, 2001) and for their tectonic settings (Arai, 1992, 1994; Kamenetsky *et al.*, 2001; Arai *et al.*, 2011). However, spinel composition in these rocks also depends on other variables, (Kamenetsky *et al.*, 2001 and references therein): i) $f\text{O}_2$ during crystallization; ii) crystallization temperature and cooling rates, and iii) perhaps pressure. Moreover, subsolidus re-equilibration of spinel with silicates can deeply modify early magmatic compositions, especially in plutonic rocks (Arai *et al.*, 2011). This type of re-equilibration affects mainly the Mg# of spinel (Kamenetsky *et al.*, 2001; Arai *et al.*, 2011), but also the Cr#, especially in mantle peridotites (Voigt and Handt, 2011).

In spite of the previous drawbacks, Al_2O_3 (therefore Cr#) and TiO_2 components are less susceptible to experiment subsolidus re-equilibration, if spinel is trapped by olivine: this phase has low diffusivity for



FIGURE 3. A) Amp1-type crystal with a brown core passing to green zones and to a colourless fibrous rim. The olivine inclusion is being transformed to fibrous colourless Amp2 crystals. B) Olivine (Ol) inclusion partially pseudomorphed by fibrous colourless Amp2 and Spl2 crystals. The Amp1 rim is also fibrous. C) Amoeboid olivine crystals included in clinopyroxene which is itself included in Amp1. Ilmenite (Ilm) lamellae follow the Amp1 cleavage. D) Phlogopite (Phl) crystal with an olivine inclusion and ilmenite lamellae following the phlogopite cleavage. E) Anhedral phlogopite crystal intergrown with brown Amp1; anhedral crystals of Spl2 follow the phlogopite cleavage. F) Cluster of phlogopite, Amp2 and Spl2 crystals with olivine relic crystals. Mineral abbreviations after Whitney and Evans (2010).

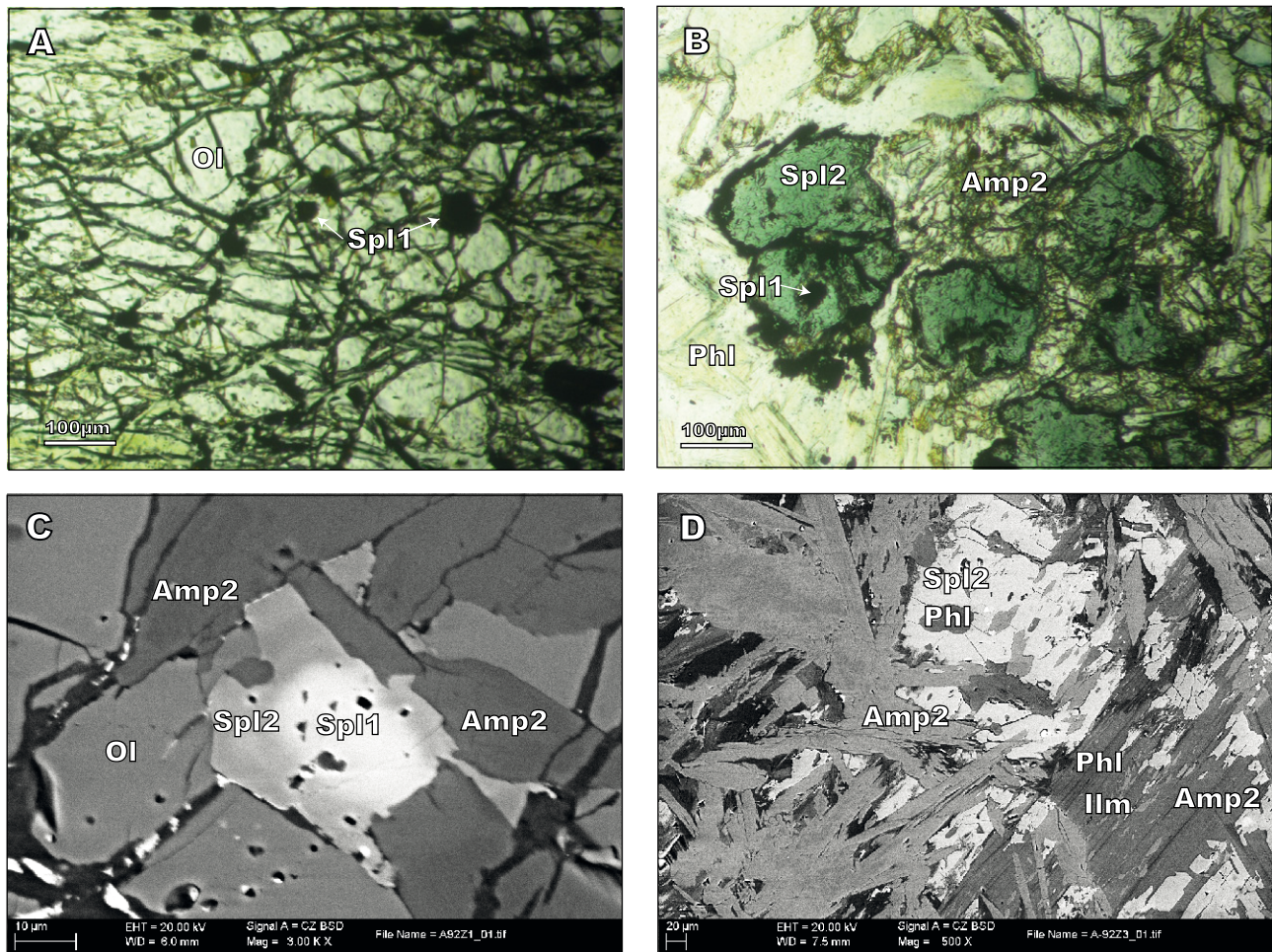


FIGURE 4. A) Spl1 crystals included in olivine (Ol). B) Spl1 inclusions in Spl2 crystals. C) Zoned spinel crystal with composition picotite-Al chromite (Spl1) at the core grading to pleonaste (Spl2) towards the rim. D) Pseudomorph of Spl2, Amp2 and phlogopite (Phl). Phlogopite crystals include Amp2, Spl2 and ilmenite (Ilm).

trivalent (Al, Cr) and tetravalent (Ti) cations (Scowen *et al.*, 1991; Barnes, 1998). Using Al and Ti contents of spinel as proxies for the co-existing melt composition also offers other advantages (Kamenetsky *et al.*, 2001): i) olivine is the first phase to crystallize from all virtually mantle-derived melts; ii) olivine remains on the liquidus at least during spinel crystallization; iii) Fo composition in olivine can be used as an index of fractional crystallization; and iv), olivine protects effectively enclosed spinel crystals from exchange reactions with other phases. Therefore, Al_2O_3 and TiO_2 of spinels were related to their abundance in co-existing melt over large compositional ranges of both phases (Kamenetsky *et al.*, 2001). In the case study, Al_2O_3 and TiO_2 of most Spl1 are within these compositional intervals (3.0–39 $\text{Al}_2\text{O}_3\%$ and 0.04–3.90 $\text{TiO}_2\%$) and four of these analyses are from Spl1 inclusions in olivine (Fig. 4A). Therefore, we

can assume that the concentrations of both components in these Spl1 inclusions were not much perturbed by subsolidus re-equilibration and use them to evaluate the nature of the co-existing melt. It is observed that most of these Spl1 inclusions would have been in equilibrium with MORB-type basalts (Fig. 6A), which does not fit the geological setting of the MMC. In spite of it, we can infer that the studied hornblendites would derive from Al-rich basalts than typical island arc tholeiites or melts from high-Ti calc-alkaline and high-K arc volcanic series (Fig. 6B; Kamenetsky *et al.*, 2001).

In summary, compositions of early magmatic spinel trapped by olivine can help to evaluate geochemical characteristics of the involved melt, but do not discriminate between most geodynamic settings (Fig. 6C; Arai *et al.*, 2011).

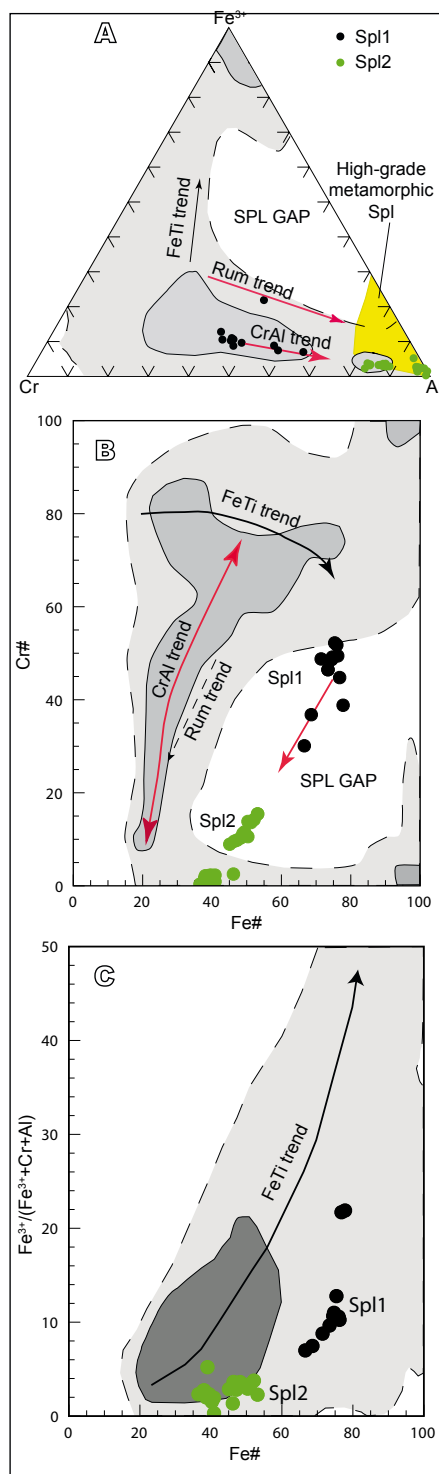


FIGURE 5. A) Spl1 and Spl2 of the Montnegre olivine hornblendites in the Fe³⁺-Cr-Al triangular diagram following a CrAl trend parallel to the Rum trend. The FeTi trend and spinel gap between Cr rich and magnetite compositions are also included (Barnes and Roeder, 2001). B) Spl1 and Spl2 in the Cr# vs. Fe# diagram. C) Idem in the Fe³⁺/R³⁺/(100*Fe³⁺/Al³⁺+Cr³⁺+Fe³⁺) vs. Fe# diagram. Contours in these diagrams include the most densely packed 50% (continuous line, dark grey field) and 90% (discontinuous line, lighter field) of spinel data compositions in ultramafic and mafic rocks. The field for high-grade metamorphic spinel is also illustrated. Contours and data from Barnes and Roeder (2001).

Spinel 2

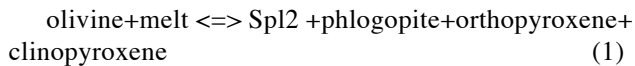
The other point in question is the origin of Spl2 compositions. Two hypotheses are envisaged: I) magmatic origin and II) hydrothermal subsolidus formation.

As regards the hypothesis I), zoned spinel crystals with increasing Al and Mg# and decreasing Cr# towards the rim are not very frequent in igneous rocks. Nevertheless, they have been previously mentioned in layered intrusions (*e.g.* Rhum and Mull; Henderson and Wood, 1981), in similar olivine hornblendites from Tapia (Galán and Suárez, 1989), in basalts (Allan *et al.*, 1988; Allan, 1992; Della-Pasqua *et al.*, 1995; Roeder *et al.*, 2001) and in kimberlites (Roeder and Schulze, 2008). From all these examples, one conclusion stands out: Al abundance in spinel of magmatic rocks does not depend necessarily on pressure (Kamenetsky *et al.*, 2001), as it was previously considered for the Montnegre hornblendites (Galán, 1987b; Enrique and Galán, 1989).

There are several magmatic hypotheses. The classical explanation for the Rum trend (Fig. 5) is attributed to reaction between cumulus chromite, trapped intercumulus melt, plagioclase and olivine (hypothesis Ia). A similar explanation was envisaged for the spinel zoning of Tapia hornblendites: crystallization of early Al-poor phases (*viz.* chromite, olivine, clinopyroxene) from an Al-rich melt would have increased enough this component to crystallize Al-enriched spinel (Galán and Suárez, 1989). In the case of basalts, Allan *et al.* (1988) and Allan (1992) suggested that crystallization of primitive chromite derived from an evolved melt, was followed by mixing with a more aluminous and less differentiated melt during the periodic refilling of a magma chamber, just prior to the eruption (hypothesis Ib). Finally, the varying rate of Cr diffusion in the melt ahead of a very fast growing crystals of spinel at near constant Fe in the melt, (*i.e.* diffusion-controlled crystallization) was posited for CrAl zoning in kimberlite spinel (Roeder *et al.*, 2001) (hypothesis Ic). Taken into account that the Spl2 dominates in the studied hornblendites and that along with phlogopite-Amp2 replaced olivine (Figs. 3F, 4B; D), we suggest that an origin similar to that of hypothesis Ib) would be the most likely. Neither hypothesis Ia) nor hypothesis Ic) do explain the Spl2-phlogopite-Amp2 clusters. Also, assimilation and breakdown of country-rock pelitic hornfels during the mafic magma injection could be an alternative explanation to increase both Al and K in the magmatic system. However, it would not fit the opposite tendency of Spl2 with respect to the metamorphic spinel composition in nearby undersaturated high-grade pelitic hornfels (Riesco *et al.*, 2004) (Fig. 7A; B). The CrAl trend from Montnegre Spl1 to Spl2 points to both increasing Al and Mg#, while

spinel from pelitic hornfels differs by showing higher Fe# than Spl2.

Assuming magma mixing (hypothesis Ib) between an earlier mafic magma, in equilibrium with olivine and Spl1, and a new Al- and K-rich and less differentiated melt refilling the magma chamber or conduit, an operative reaction could have been (Condamine and Médard, 2014) (Figs. 3B; F and 4D):



Subsequently, the resultant pyroxenes would have been replaced by Amp2 owing to increasing H₂O content during magmatic differentiation.

This model would be consistent with higher Mg# range in pyroxenes (orthopyroxene Mg#: 82-80; clinopyroxene Mg#: 89-86), Amp1 (Mg#: 99-77) and phlogopite (Mg#: 84-88) with respect to olivine in these hornblendites (Fo%: 79-73%); data from Galán (1987b), Enrique and Galán (1989) and Butjosa *et al.* (2013).

The Al- and K-rich mafic melt would have been most likely alkaline and resulted from partial melting of a metasomatized mantle, with variable amount of phlogopite and amphibole contributing to the melt. In a scenario of mafic magma mixing, without excluding subsequent assimilation of crustal melts (fluids) during the intrusion into the crust (Fourcade and Allegre, 1981; Moreno Ventas *et al.*, 1995; Galán *et al.*, 1997; Bea *et al.*, 1999), the nature of the parental mantle melts is difficult to evaluate. However, high Ti in Amp1-type crystals of hornblendites from Gredos was suggested as a proxy for the alkaline nature of co-existing melts (Molina *et al.*, 2009). In the Montnegre hornblendites, TiO₂ amount in Amp1 (up to 3.7%) and phlogopite (up to 0.74%) (Enrique and Galán, 1989; Butjosa *et al.*, 2013) is lower than in Gredos (amphibole: 2-5 TiO₂%; phlogopite: up to 3.8 TiO₂%; Molina *et al.*, 2009). However, the original amount of Ti in the Montnegre example would have been higher since Amp1 and phlogopite show exsolved ilmenite (Fig. 3D) and co-exist with this mineral. This further supports the alkaline nature of the melt co-existing with Spl2 and explains the early crystallization of phlogopite (Molina *et al.*, 2009), which appears as intergrown crystals or inclusions in Amp1 (Fig. 1E).

As regards the hydrothermal subsolidus formation of Spl2 (hypothesis II), green pleonaste spinel was found in drilled troctolites affected by hydrothermalism from the Mariana Trough (Natland *et al.*, 1982) and from the oceanic crust of the Hess Deep Rift, in the East Pacific Rise (Nozaka *et al.*, 2016). In both examples, spinel forms clusters along with fibrous amphibole

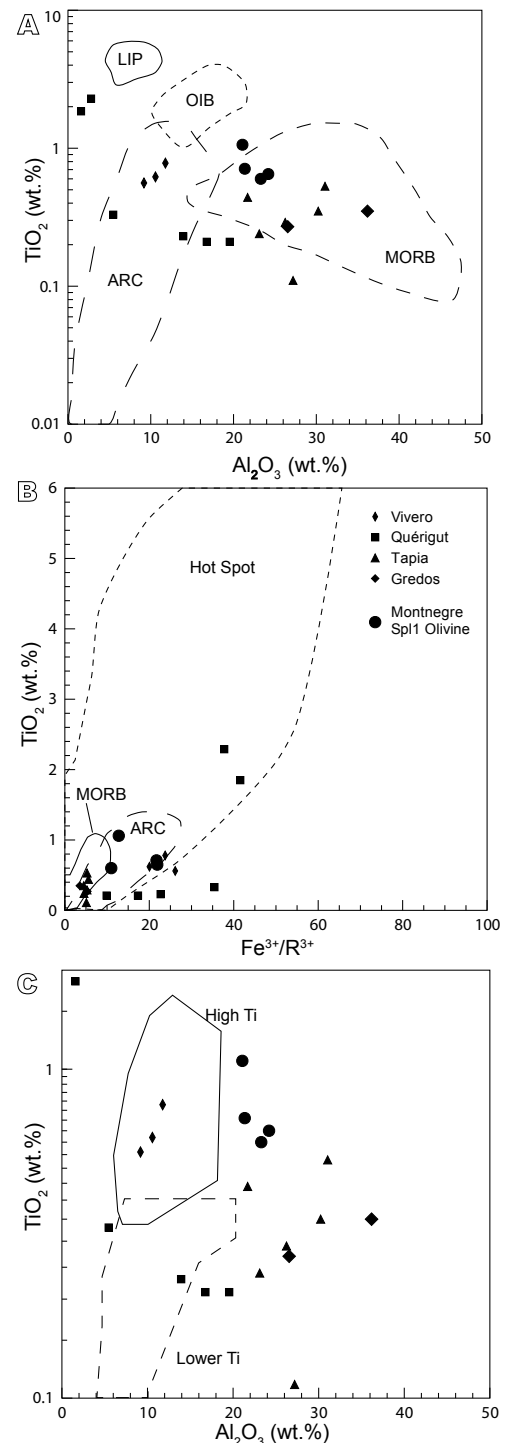


FIGURE 6. A) TiO₂ vs. Al₂O₃ compositions of Spl1 included in olivine from the Montnegre olivine hornblendites along with primitive spinel from other olivine hornblendites. Fields for island arc (ARC), MORB-type, OIB-type and large igneous province (LIP) type-basalts are from Kamenetsky *et al.* (2001). B) TiO₂ vs. Fe³⁺/R³⁺ diagram for Spl1 inclusions in olivine of the Montnegre hornblendites and for primitive spinel from other examples. Fields for ARC, MORB and Hot Spot-type basalts are from Arai *et al.* (2011). C) TiO₂ vs. Al₂O₃ diagram separating spinels of lower Ti boninites and tholeiites (dashed line) from those of high Ti (calc-alkaline and high-K) island-arc series (continuous line) (Kamenetsky *et al.*, 2001). Early Spl1 from Montnegre and from other Variscan examples are included.

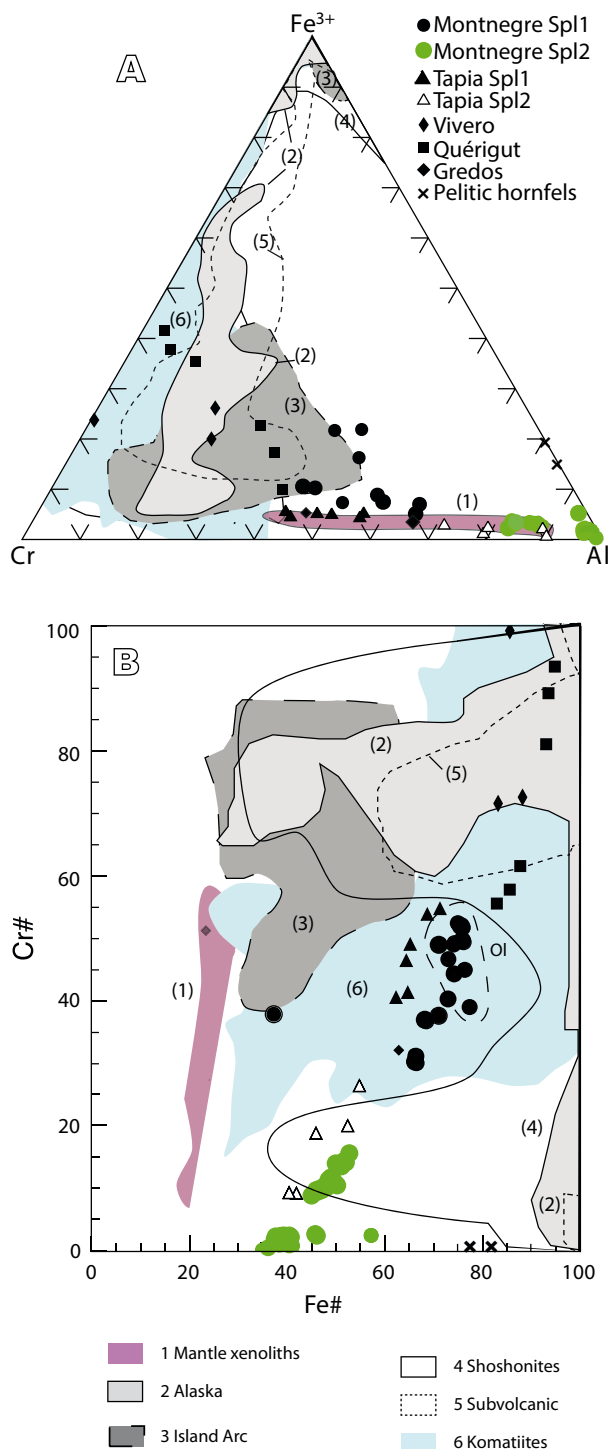


FIGURE 7. A) Fe^{3+} -Cr-Al triangular diagram for spinel of different olivine hornblendites related to granitoids (data from the present study and from Galán, 1987b, Galán and Suárez, 1989; Enrique and Galán, 1989; Molina *et al.*, 2009). Spinel from country-rock pelitic hornfels are also included (Riesco *et al.*, 2004). B) Spinel from different olivine hornblendites and pelitic hornfels in the Cr# vs. Fe# diagram. Spinel from hornblendites define a characteristic Cr# trend different from spinel trends in other plutonic or volcanic ultramafic and mafic rocks. Data as follows: spinel (1) mantle xenoliths in Neogene-Quaternary lavas of the Catalan Volcanic Zone (Galán *et al.*, 2008; 2011); (2) Alaskan zoned ultramafic complexes; (3) island arc basalts; (4) shoshonites; (5) subvolcanic continental mafic intrusions; (6) komatiites. All data are from Barnes and Roeder (2001).

(pargasite, Mg-hornblende, tremolite), which were formed by subsolidus reaction between olivine and An-rich plagioclase. The following arguments are against hypothesis II) in the case study: i) plagioclase is lacking in the Montnegre hornblendites and hydrothermalism is not significant; ii) Spl2 appears associated with earlier phlogopite crystals intergrown with or included in Amp1 (Fig. 4D); and iii) green hercynite-pleonaste spinel was also found in similar hornblendites from Tapia (see below), where it does not form clusters with hydrous silicates, but inclusions in orthopyroxene (Fig. 2D in Galán and Suárez, 1989).

Comparison with other examples

Spinel compositions in olivine hornblendites from other Variscan associations of ultramafic-mafic rocks and granitoids (*viz.* the Vivero massif and Tapia plutons in the West-Asturianleonese Zone, the Gredos dome in the Central Iberian Zone, both zones of the Iberian Massif, and the Quérigut complex in the Pyrenean Axial Zone) are compared with the Montnegre case in Figures 6 and 7. All data are from Galán (1987b) and Galán and Suárez (1989), except spinel from Gredos (Molina *et al.*, 2009). Granitoids of all these examples are calc-alkaline or I-type (Chappel and White, 1974). The only exception is Gredos, where ultramafic-mafic rocks (appinites) define a calc-alkaline trend, but the related granitoids are mostly peraluminous (Bea *et al.*, 1999) or S-type. Spinel in these other hornblendites (Spl1 in the case of Tapia) has compositions from chromite to picotite. Quérigut and Vivero examples show higher Cr# than the Montnegre Spl1 trapped by olivine, whereas Tapia (Spl1) and Gredos have similar to or lower Cr# than Montnegre (Fig. 7B). Tapia and Montnegre examples are very much alike, both with two similar generations of spinel. Overall spinels from hornblendites in Figure 7A, B define a CrAl trend at higher Fe# than most trends of this type. This trend also differs by starting at much higher Cr#.

In Figure 7, we also include the compositional range of spinel from: (1) mantle xenoliths (lherzolites and harzburgites) from the Catalan Volcanic Zone, which represent the subcontinental lithospheric mantle beneath the Catalan Coastal Ranges; (2) Alaskan zoned ultramafic complexes, which are rich in amphibole as the studied olivine hornblendites; (3) island arc basalts; (4) shoshonites; (5) subvolcanic continental mafic intrusions; and (6) komatiites. Spinel from undersaturated hornfels and restites representing the high-grade metamorphic country rocks nearby the MMC are also included. Data (1) are from Galán *et al.* (2008; 2011), (2) to (6) from Barnes and Roeder (2001) and of spinel from hornfels after Riesco *et al.* (2004).

Mantle spinels in xenoliths (1 in Fig. 7A; B) define a CrAl trend which differs from that of the Montnegre spinels by displaying lower Fe and Fe³⁺ and narrower Cr and Al compositional range (Fig. 7A; B). Spinel trend from Alaskan zoned ultramafic complexes (2 in Fig. 7A; B) is not CrAl type. It can be classified as a CrFe³⁺ trend in Figure 7A, which also differs from a FeTi trend (Fig. 5A; B) because Ti is not strongly enriched (Barnes and Roeder, 2001). However, Alaskan type spinels can show very high Cr# and Fe# as the Vivero and Quérigut spinels (Fig. 7B). High Cr# spinels as those in Vivero and Quérigut hornblendites can also be found in a wide variety of mafic-ultramafic igneous rocks: island arc basalts (3 in Fig. 7B), shoshonites (4 in Fig. 7B), subvolcanic continental mafic inclusions (dot line 5 in Fig. 7B) and komatiites (6 in Fig. 7B). However, spinels from island arc basalts differ by showing lower Fe# (Fig. 7B); the wide compositional range in komatiite spinel is explained by effects of later metamorphism (Barnes and Roeder, 2001); and finally, spinel from most of these rocks define CrFe³⁺ trends instead of a CrAl trend (Fig. 7A). Hence, it is concluded that, as a whole, the spinel CrAl trend in olivine hornblendites related to granitoids is characteristic: it shows a wide compositional variation, from very high to very low Cr#, from high to moderate #Fe, with low to moderate Fe³⁺ (Fig. 7A; B) and with moderate to high TiO₂ (Fig. 6C).

The CrAl trend of spinels from different hornblendites suggests that the mafic melts involved in the formation of these rocks must have been heterogeneous, with variable Al₂O₃ and TiO₂ concentrations (Fig. 6A; C; Kamenetsky *et al.*, 2001). For instance, the melt in equilibrium with olivine and early spinel could have been less aluminous in Vivero and Quérigut than in the other examples (Fig. 6A). If the melts were primary, mantle sources would also be heterogeneous. Nevertheless, low Fo component in olivine from all these hornblendites (ranging from 83% in Gredos to 73% in Montnegre) suggests that the co-existing melt must have been differentiated. That is to say, Fo component is much lower in all these hornblendites than in olivine from melt in equilibrium with mantle peridotites (*e.g.* Fo in peridotitic xenoliths representing the lithospheric mantle beneath the Catalan Coastal Ranges varies from 88 to 92%; Galán and Oliveras, 2014; Fernández-Roig *et al.*, 2017). Alternatively, the mantle source of these mafic melts may have been more enriched in Fe than the mantle represented by the xenoliths. This enrichment in Fe is characteristic of some peridotites from active subduction zones that experienced melt-rock interaction (metasomatism) (Herzberg, 2004).

In summary, it is likely that the mantle sources were variable fertile and previously metasomatized, with

amphibole and phlogopite breakdown contributing to the mafic melts. These melts could have been initially alkaline, as in Gredos (Castro *et al.*, 2003; Scarrow *et al.*, 2009), or that new batches of mantle-derived alkaline melts were subsequently incorporated, during the refilling of the magma chamber, as in Montnegre. However, the differentiation of these melts under high H₂O content would have determined their calc-alkaline evolution by retarding the crystallization of plagioclase with respect to that of spinel and mafic silicates (Sisson and Grove, 1993). Thus, typical high H₂O content during the crystallization of hornblendites could be inherited from the breakdown of hydrated mafic silicates during the melting of a metasomatized mantle (Castro *et al.*, 2003) and increased later on, during the injection of the resulting magmas through the crust (Scarrow *et al.*, 2009). The H₂O effect would be enhanced if shear zones favouring fluid circulation acted as magma conduits (Galán *et al.*, 1997; Scarrow *et al.*, 2011).

CONCLUSIONS

The olivine hornblendites from the Montnegre mafic complex include two types of spinel: an early spinel of picotite-Al chromite composition and a second type of pleonaste composition associated with phlogopite and fibrous colourless amphibole. The early type co-existed with olivine and a melt enriched in Al and differentiated with respect to a normal residual mantle. The second spinel was the result of mixing between the earlier magmatic system and a new injection of mantle-derived melt more enriched in both Al and K than the previous one. This latter melt reacted with olivine to yield phlogopite-amphibole and the second spinel.

The two generations of Montnegre spinel follow a CrAl trend with high Fe#. Spinel from other olivine hornblendites related to Variscan granitoids also follow and enlarge this trend towards both higher Cr# and Fe# values. This CrAl trend with high Fe# is characteristic and differs from both the CrAl trend of spinel from mantle-peridotites and from the CrFe³⁺ trend of spinel in other ultramafic rocks, also rich in amphibole, as the Alaskan-type. The variable Cr# in early spinel from different hornblendites is related to variable amount of Al in the co-existing melt.

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