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ON THE METAMORPHIC MODIFICATION OF CR-SPINEL COMPOSITIONS FROM THE ULTRABASIC ROCKS OF THE PINDOS OPHIOLITE COMPLEX (NW GREECE)

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Abstract

Serpentinites and serpentinised ultramafic rocks from the Pindos ophiolite complex, northwestern Greece, contain Cr-spinel grains that are usually altered. The extent of alteration differs among Cr-spinels and two alteration trends can be distinguished. The most dominant is characterised by Cr-spinel overgrown by Cr-magnetite, while the second shows gradual replacement of Cr-spinel by ferrian chromite locally combined with Cr-magnetite development. Compared to cores, the altered rims are enriched in Fe and show elevated Cr# in both types of alteration, while they are impoverished in Mg and Al only at the second one. The common association of Cr-magnetite with serpentine and ferrian chromite with chlorite provides insights to the metamorphic context of their formation through processes that include metasomatism by cation diffusion exchange.

Key words: *hydrothermal alteration, spinel, magnetite, ferrian chromite, peridotite, Greece.*

Περίληψη

Οι σερπεντινίτες και τα σερπεντινιωμένα υπερβασικά πετρώματα του οφιολιθικού συμπλέγματος της Πίνδου, Βορειοδυτική Ελλάδα, περιέχουν κόκκους χρωμιούχων σπινελίων που είναι συνήθως εξαλλοιωμένοι. Το εύρος της εξαλλοίωσης διαφέρει από κόκκο σε κόκκο και δύο τύποι εξαλλοίωσης μπορούν να διακριθούν. Συμφύσεις χρωμιούχου σπινελίου και χρωμιούχου μαγνητίτη είναι ο κυρίαρχος τύπος εξαλλοίωσης, ενώ προοδευτική εξαλλοίωση χρωμιούχου σπινελίου από σιδηρο-χρωμίτη σε συνδιασμό/ή όχι με την ανάπτυξη χρωμιούχου μαγνητίτη μπορεί να απαντά επίσης. Συγκριτικά με τους πυρήνες, τα περιθώρια αλλοίωσης είναι εμπλουτισμένα σε Fe και δείχνουν αυξημένα επίπεδα Cr# και στους δύο τύπους εξαλλοίωσης, αλλά είναι αποπτωχευμένα σε Mg και Al στο δεύτερο από αυτούς. Η κοινή συσχέτιση χρωμιούχου μαγνητίτη με σερπεντίνη και σιδηρο-χρωμίτη με χλωρίτη παρέχει πληροφορίες για το μεταμορφικό πλαίσιο σχηματισμού τους μέσω διαδικασιών που περιλαμβάνουν μετασωματικές διεργασίες που περιλαμβάνουν μηχανισμούς διάχυσης κατιόντων.

Λέξεις κλειδιά: *υδροθερμική εξαλλοίωση, σπινέλιος, μαγνητίτης, σιδηρο-χρωμίτης, περιδοτίτης, Ελλάδα.*

1. Introduction

Chromian spinels commonly occur as accessory minerals in ultramafic rocks that constitute the ophiolitic upper mantle. Their composition has been used as a petrogenetic indicator due to their sensitivity to melt differentiation, crystallisation pressure and the degree of melting of the mantle source region (Irvine 1965a, b, Dick and Bullen 1984, Hellebrand *et al.* 2001). Spinels are highly resistant minerals and tend to preserve their primary magmatic composition. However, they commonly change when they are subjected to alteration processes, like serpentinisation and regional metamorphism (Burkhard 1993).

Spinel alteration trends have been thoroughly described by several workers (e.g. Kimball 1990, Burkhard 1993, Fleet 1993, Christofides 1994, Abzalov 1998, Barnes 2000, Bidyananda and Mitra 2004, Mellini *et al.* 2005, Farahat 2006). Pure spinel compositions become unstable under post-magmatic processes and thus start to develop alteration products, which can be recognized by their high reflectance. Depending on the alteration extent, Cr-magnetite and/or ferrian chromite (previously known as ferritchromit/ferrichromite) will start to form. These two secondary phases are usually attributed to the effects of low to medium grade metamorphism up to lower amphibolite facies (Thalhammer *et al.* 1990, McEdulff and Stumpfl 1991, Farahat 2006).

The purpose of this paper is to discuss the extend and mechanisms of alteration of Cr-spinels from the serpentinised ultramafic rocks of the Pindos ophiolite complex in Northwestern Greece. Additionally, on the basis of spinel textures and compositions, the present study provides important information on the range of the metamorphic conditions that affected the host peridotites.

2. Geology

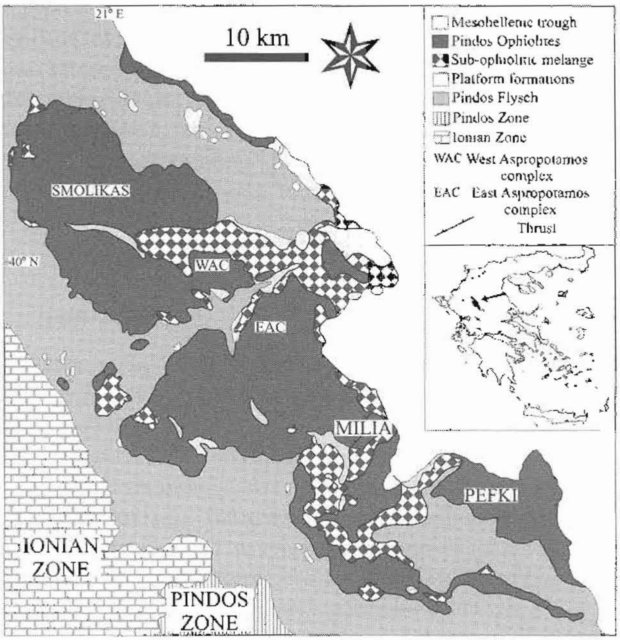

Figure 1 - Geological map of Pindos Ophiolite complex, NW Greece (after Jones and Robertson 1991)

The Pindos ophiolite complex is located in the western part of Northern Greece (Fig. 1) and corresponds to a piece of Middle-Upper Jurassic oceanic crust (Rassios and Smith 2000), which tectonically lies over the autochthonous Maastrichtian-Eocene Pindos flysch. It can be subdivided into three principal tectonic units: the Dramala Complex, the Loumnitsa Unit and the Aspropotamos Complex, all structurally overlying the Avdella mélange (Jones and Robertson 1991). The Dramala unit is comprised of large, variably depleted harzburgite-dunite masses (> 1000 km^2) (Economou-Eliopoulos and Vacondios 1995), which may host small chromitite bodies (Pefki, Milia, Korydallos etc.) (Rassios 1990) of massive, disseminated, schlieren and less commonly leopard texture (Economou-Eliopoulos *et al.* 1999). The crustal rocks of the Aspropotamos Complex cover a wide spectrum of geochemical affinities, ranging from MORB through MORB/IAT to IAT and finally boninitic series volcanics (BSV) (Pearce *et al.* 1984b, Pe-Piper *et al.* 2004). The Loumnitsa Unit represents the basal metamorphic sole of both the Dramala and Aspropotamos complexes, comprising lower amphibolite and greenschist facies meta-igneous and meta-sedimentary rocks that have yielded Ar-Ar ages of 169 ± 5 and 165 ± 3 Ma (Whitechurch and Parrot 1978, Spray and Roddick 1980). The Avdella mélange is about 1 km thick and comprises blocks of various rock types in tectonised matrix and mappable thrust sheets (Jones and Robertson 1991).

3. Petrography

The ultramafic samples were collected from the areas of Milia and Pefki, of the southern Pindos ophiolite complex. The samples consist of two distinct textural types of harzburgites and dunites that show variable degrees of serpentinisation. The two harzburgite types show different textural features.

The first type of harzburgite is clinopyroxene bearing. It displays medium grained (or subordinately framed porphyroclastic) texture and is composed of olivine (70-85 vol%), orthopyroxene (10-24 vol%), clinopyroxene (3-5 vol%) and reddish brown spinel (1-2 vol%) in apparent textural equlibrium. It displays typical features of plastic deformation, such as undulatory extinction, strain lamellae, kink-bands, shearing and recrystallisation, commonly observed in Alpine-type upper mantle peridotites. Olivine is medium grained (up to 2 mm in size) and shows undulose extinction, tectonic twinning and strain lamellae, but also forms smaller undeformed polygonal neoblasts (0.1-0.2 mm), which surround pyroxene porphyroclasts (< 2 mm). Orthopyroxene occurs as porhyroclastic crystals with lobate boundaries surrounded by a thin rim of recrystallised matrix, comprised of olivine and orthopyroxene neoblasts. Coronas and mm-scale patches of undeformed orthopyroxene surrounding exsolved porphyroclasts of mantle olivine have been recognised. Clinopyroxene exsolution lamellae parallel to (100) and replacement by olivine neoblasts are also commonly observed. Cr-spinel (np to 0.3 mm) forms anhedral to holly-leaf shaped grains. Locally mineral pairs consisting of lobate Cr-spinel and clinopyroxene occur, a textural feature which has been interpreted as a remnant of partial melting process (Menzies and Nicolas 1975).

The second type of harzburgite consists of olivine (75-85 vol%), orthopyroxene (15-23 vol%), clinopyroxene in traces and Cr-spinel (up to 2 vol%) and is characterized by porphyroclastic textures. Its constituent minerals display the same structures of plastic deformation with those mentioned for olivine and pyroxenes in clinopyroxene bearing harzburgites. The amount of olivine neoblasts increases in normal harzburgites, with frequent development of 120° triple junctions. Spinel (< 0.7 mm) becomes darker in colour and forms subhedral crystals. It occurs interstitially or as inclusions and exsolution lamellae (parallel to 100) in orthopyroxene porphyroclasts (< 3 mm). Both clinopyroxene bearing and normal harzburgites are characterized by the presence of subrounded intergrowths of orthopyroxene and Cr-spinel, which have been interpereted in peridotite occurrences worldwide as the breakdown product of a precursor garnet (Hoogerduijn-Strating *et al.* 1993, Vannucci *et al.* 1993b, Piccardo *et al.* 2004).

Dunite contains olivine (more than 90 vol%), orthopyroxene (5-8 vol%) and spinel (up to 2 vol%) and exhibits granular to porphyroclastic and mylonitic textures. Olivine grains (< 4 mm) can be widely elongated and deformed. In the most deformed samples, olivine is intensely sheared and displays mylonitic structures. In places, "tube-like" or vermicular structures made of orthopyroxene penetrate into the deformed and kinked mantle olivine. Locally, unstrained olivine grains are embodied inside the larger deformed olivine crystals, which indicates either recrystallisation of olivine porphyroclasts or initial crystallization of migrating melts within the dunites (i.e. Quick 1981a). Spinel crystals are euhedral and some times exhibit pull-apart textures. Rarely, orthopyroxene crystals can be found as remnants in the olivine matrix of dunites.

The silicate minerals are locally to intensively replaced by secondary phases due to serpentinisation process. Alteration of olivine and pyroxene has resulted in the development of serpentine and chlorite, while alteration of spinel led to the formation of Cr-magnetite, ferrian chromite and Cr-chlorite, as will be discussed below. Tremolite, talc and calcite replace orthopyroxene and iddingsite forms after olivine. Secondary sulfides, such as pentlandite, pyrite as well as native Cu, are likely part of the secondary assemblage.

Completely serpentinised peridotites exhibit pseudomorphic (mesh and bastite) textures, as well as non-pseudomorphic (interpenetrating and interlocking) textures, indicative of serpentine recrystallisation (O'Hanley 1996). The metamorphic mineral assemblage consists of serpentine, chlorite and rare calcite. Opaque minerals include syn-serpentinised and recrystallised (post-serpentinised) magnetites, relic Cr-spinels altered to Cr-magnetite and minor ferrian chromite, base metal sulfides (pentlandite, millerite) and alloys (awaruite, Cu-Zn alloys).

4. Methods of investigation

Eleven rock samples were collected from the two areas of investigation (Milia and Pefki) during field work. Polished sections were examined with optical and scanning electron microscopy using a Super Jeol-6300 SEM, equipped with EDS and WDS and a THETA software, at the Laboratory of Electron Microscopy and Microanalysis, University of Patras, Greece. Quantitative mineral analyses and BSE imaging were carried out. The microanalyses were done at operating conditions of 15 kV acceleration voltage and 3.3 nA beam current.

5. Microtextural features of Cr-spinels based on SEM images

Investigation of the Cr-spinel grains by using SEM has shown that most of them still retain their primary composition. The inner part of the grains usually is not modified by secondary processes. Strongly fractured grains display thin altered rims along fractures. At their margins, the grains are locally replaced by Cr-magnetite. The Cr-magnetite rims commonly exhibit partially porous structure, with rugged surfaces, probably due to the volume increase effect that accompanies serpentinisation. Spinel/Cr-magnetite boundary is well-defined without any kind of complex intergrowth between primary and secondary phases (Fig. 2A).

Spinel overgrown by Cr-magnetite is the dominant textural feature caused by alteration in all the investigated rock types. In a few samples of serpentinites, ferrian chromite occurs as an intermediate rim between Cr-spinel and Cr-magnetite. However, ferrian chromite rim is not always accompanied by the development of Cr-magnetite at its margins. In the clinopyroxene bearing harzburgites, Cr-spinels are completely surrounded by well defined ferrian chromite grains. In that case the internal Cr-spinel/ferrian chromite rim is a sharp, but curved and lobate boundary between the two coexisting phases (Fig. 2B).

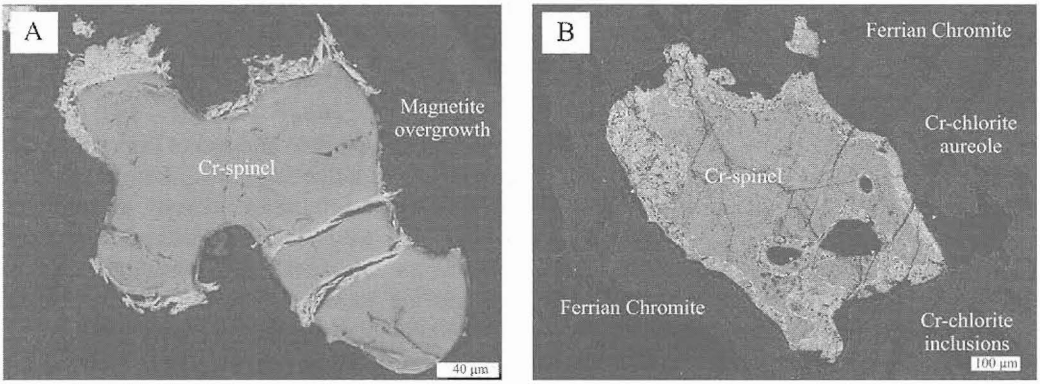

Figure 2 - A) Cr-spinel/Cr-Magnetite overgrowth, B) Cr-spinel replaced by ferrian chromite rims, and peripheral development of Cr-chlorite aureoles, also note the existence of Cr-chlorite inclusions

6. Mineral chemistry

6.1. Spinels

Table 1 shows representative primary Cr-spinel, ferrian chromite and Cr-magnetite compositions. Fe^{+3}/Fe^{+2} ratios were calculated on a stoichiometric basis. Spinel end-members include magnesiochromite and chromite based on the relative concentrations of Fe^{+2} and Mg (DEER *et al.* 1992). However, the term Cr-spinel is adopted for core compositions in order to avoid confusion.

The Cr# [(Cr/Cr+Al)] of chromian spinels ranges from 0.49 to 0.79. Cr# values are between 0.75 and 0.91 in ferrian chromite, while Cr-magnetite displays a wider compositional range of Cr# (0.65-1.00). Chromian spinels have Mg# $[(Mg/(Mg+Fe^{+2})]$ between 0.36 and 0.64. On the other hand, the metamorphic rims are strongly impoverished in Mg# (0-0.22) (Fig. 3). The Fe^{+3}# $[(Fe^{+3}/(Fe^{+3}+Cr+Al)]$ increases towards the rims, having the highest values in Cr-magnetite (0.97) (Fig. 4). The high Fe^{+3}# of the metamorphic spinels suggests that oxidizing conditions prevailed during hydrothermal metamorphism.

Table 1 - Representative chromite-ferrian chromite-magnetite microanalyses

Sample	P13a	P13b	P21a	P21b	P2Aa	P2Ab	P4a	P4b	P5a	P5b
Location	Pefki	Pefki	Pefki	Pefki	Milia	Milia	Milia	Milia	Milia	Milia
Mineral	Frt*	Chr*	Frt	MgChr*	Frt	MgChr	Mgt*	Chr	Mgt	Chr
SiO_2	-	0.26	0.27	-	0.35	0.20	1.25	0.27	-	0.39
TiO_2	0.08	0.26	0.21	-	0.48	0.19	-	-	-	0.26
Al_2O_3	11.07	20.4	4.02	25.34	5.48	24.55	0.38	10.8	0.07	21.84
Cr_2O_3	52.77	47.95	57.10	45.58	34.10	41.83	1.6	57.99	1.42	46.12
FeO^t	31.65	19.36	34.46	17.32	56.04	20.74	95.11	20.33	98.54	21.14
MnO	0.52	1.14	0.73	-	1.14	-	-	0.60	-	-
MgO	3.82	10.27	2.94	11.42	2.27	11.53	1.36	9.02	-	10.74
CaO	-	-	-	-	-	-	-	-	-	-
Na_2O	-	-	-	-	-	-	-	-	-	-
K_2O	-	-	-	-	-	-	-	-	-	-
NiO	-	-	0.08	-	-	-	0.46	-	-	-
Total	99.91	99.64	99.81	99.66	99.86	99.04	100.16	99.01	100.03	100.49
Number of ions on the basis of 4O										
Si	-	0.008	0.010	-	0.012	0.006	0.044	0.009	-	0.012
Al	0.448	0.760	0.169	0.920	0.227	0.896	0.016	0.425	0.003	0.800
Cr	1.432	1.199	1.609	1.110	0.948	1.024	0.045	1.532	0.040	1.134
Fe^{+3}	0.117	0.012	0.192	-	0.775	0.059	1.851	0.025	1.957	0.029
Ti	0.002	0.006	0.006	-	0.013	0.004	-	-	-	0.006
Mg	0.195	0.484	0.156	0.524	0.119	0.532	0.072	0.449	-	0.498
Fe^{+2}	0.792	0.500	0.835	0.446	0.872	0.478	0.959	0.543	1.000	0.520
Mn	0.015	0.031	0.022	-	0.034	-	-	0.017	-	-
Ca	-	-	-	-	-	-	-	-	-	-
Ni	-	-	0.002	-	-	-	0.013	-	-	-
Cations	3.001	3.000	3.001	3.000	3.000	2.999	3.000	3.000	3.000	2.999
Cr#	0.76	0.61	0.91	0.55	0.81	0.53	0.74	0.78	0.93	0.59
Mg#	0.2	0.49	0.16	0.54	0.12	0.53	0.07	0.45	0	0.49
Fe^{+3}#	0.058	0.006	0.098	0	0.398	0.029	0.968	0.013	0.980	0.015

* Frt: Ferrian chromite, Chr: Chromite, MgChr: Magnesiochromite, Mgt: Cr-magnetite

The high amount of MnO in ferritchromit (up to 1.83 wt. %) compared to that of primary spinel suggests a possible preference of Mn for the structure of ferritchromit. Barnes (2000) interpreted the elevated Mn content in Cr-spinels as a result of the introduction of this element during low temperature alteration.

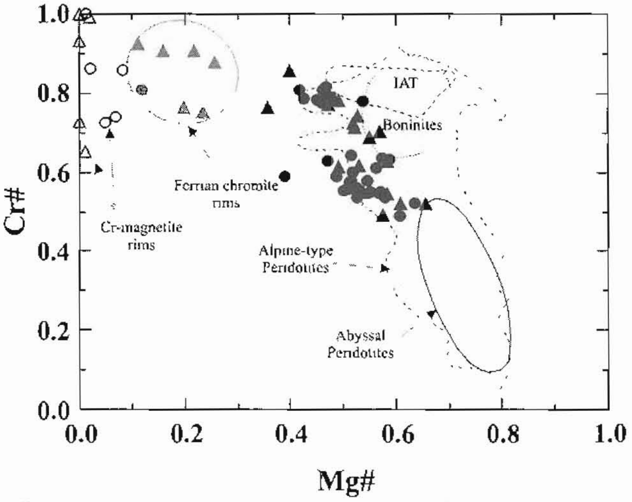

Figure 3 - Cr# vs. Mg# plot of the analysed Cr-spinels and their alteration products. Note the increase in Cr# and the decrease in Mg# from cores to rims (black, grey and open circles represent Cr-spinels, ferrian chromites and Cr-magnetites, respectively, from the area of Milia. Black, grey and open triangles represent Cr-spinels, ferrian chromites and Cr-magnetites, respectively, from the Pefki area). The fields of spinels from the abyssal and alpine-type peridotites, island arc tholeites and boninites are superimposed on the diagram. Sources: Dick and Bullen (1984), Dick and Brayan (1979), Cameron *et al.* (1979), Dietrich *et al.* (1987)

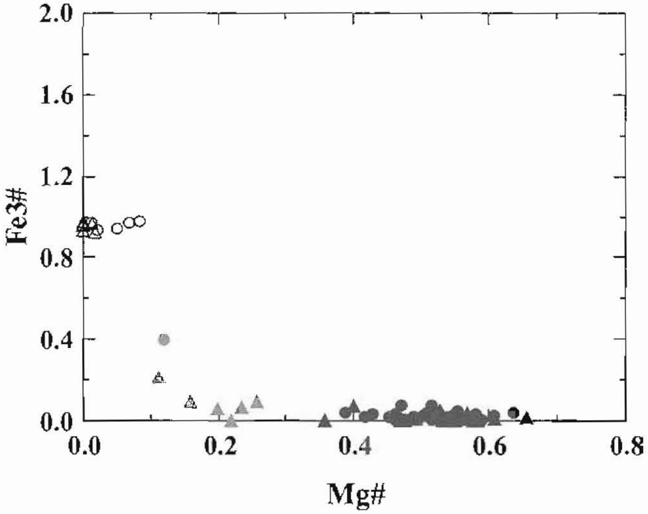

Figure 4 - Fe^{+3}# vs. Mg# plot of the analysed Cr-spinels and their alteration products. Note the rapid increase in Fe^{+3}# for ferrian chromite and Cr-magnetite (black, grey and open circles represent Cr-spinels, ferrian chromites and Cr-magnetites, respectively, from the area of Milia. Black, grey and open triangles represent Cr-spinels, ferrian chromites and Cr-magnetites, respectively, from the area of Pefki)

6.2. Associated silicates

Altered spinels are in close association with serpentine and scarcely with chlorite. Representative analyses of serpentine and chlorite are shown in Tables 2 and 3.

Serpentine has a broad SiO_2 content, varying between 34.74 and 46.23 %. It is enriched in FeO_t (up to 9.21 %), while some contain minor amounts of Cr_2O_3 (up to 0.71 %). The majority of the analysed serpentines have high Si/Mg ratio (between 0.7 and 0.95), suggesting the possible predominance of the high *T* polymorph, antigorite. X-ray data also confirm the predominance of antigorite against chrysotile and lizardite in the investigated serpentinised peridotites from both areas.

Table 2 - Representative serpentine electron microprobe analyses

Sample	**P13**	**P13**	**P15**	**P16**	**P22**	**PM11**	**PM5**
Location	**Pefki**	**Pefki**	**Pefki**	**Pefki**	**Pefki**	**Milia**	**Milia**
SiO_2	42.36	44.92	44.86	43.16	44.70	45.68	42.07
TiO_2	-	0.09	-	-	-	-	-
Al_2O_3	0.18	0.33	0.68	0.47	0.23	0.49	0.73
Cr_2O_3	-	0.13	0.22	0.05		0.13	
$Fe_2O_3^t$	3.48	4.83	4.70	4.05	4.59	3.11	3.97
MgO	38.36	36.2	33.86	36.88	36.89	39.46	36.13
NiO	-	0.15	0.24	0.25	0.03	0.04	0.1
MnO	-	-	-	-	-	0.19	0.08
CaO	-	-	-	-	0.02	0.15	0.17
Na_2O	-	-	-	-	-	-	-
K_2O	-	-	0.10	-	0.07	0.15	0.24
Total	84.38	86.65	84.66	84.86	86.53	89.4	83.49
Number of ions on the basis of 9 (O,OH)							
Si	2.029	2.093	2.133	2.056	2.085	2.000	2.000
Al^{IV}	-	-	-	-	-	-	-
	2.029	2.093	2.133	2.056	2.085	2.000	2.000
Al^{VI}	0.010	0.018	0.038	0.026	0.013	0.026	0.042
Ti	-	0.003	-	-	-	-	-
Cr	-	0.005	0.008	0.002	-	-	-
Fe^{3+}	0.130	0.170	0.170	0.150	0.160	-	-
Fe^{2+}	-	-	-	-	-	-	-
Ni	-	0.010	0.010	0.010	-	-	-
Mn	-	-	-	-	-	0.007	0.003
Mg	2.739	2.514	2.400	2.619	2.565	3.000	3.000
Ca	-	-	-	-	0.001	0.007	0.009
Na	-	-	-	-	-	-	-
K	-	-	0.006	-	0.004	0.009	0.015
Cations	4.908	4.813	4.765	4.863	4.828	5.049	5.069

Chlorites, mainly penninites and less frequently clinochlores (following the classification of Hey, 1954), contain variable amounts of Al_2O_3 (9.64-21.07 %) and high amounts of Cr_2O_3 (up to 3.33 %). It may be possible that the small deficiency in Al_2O_3 in some of the analysed chlorites (i.e. the majority of chlorites with Al_2O_3 content between 9.64 and 18.85 wt%), compared to chlorites from other parageneses, is compensated by the elevated content in Cr_2O_3.

Table 3 - Representative chlorite electron microprobe analyses.

Sample	**P13**	**P21**	**P22**	**PM11**	**PM5**
Location	**Pefki**	**Pefki**	**Pefki**	**Milia**	**Milia**
SiO_2	33.53	33.27	37.15	34.85	34.16
TiO_2	0.02	-	-	-	-
Al_2O_3	17.36	17.01	9.64	13.06	11.11
Cr_2O_3	2.07	2.54	2.37	3.33	1.63
FeO^t	2.42	2.83	3.47	1.42	4.6
MgO	33.58	32.59	34.52	33.14	31.24
NiO	0.26	-	0.42	0.22	-
MnO	-	0.03	-	-	-
CaO	-	-	-	0.05	-
Na_2O	-	0.29	-	-	-
K_2O	-	-	-	-	-
Total	89.24	88.56	87.57	86.07	82.74
Number of ions on the basis of 28 O					
Si	6.155	6.174	6.988	6.613	6.817
AlIV	1.845	1.826	1.012	1.387	1.183
	8.000	8.000	8.000	8.000	8.000
Al^{VI}	1.908	1.891	1.123	1.531	1.428
Ti	0.003	-	-	-	-
Fe^{2+}	0.372	0.439	0.546	0.225	0.768
Cr	0.300	0.372	0.352	0.499	0.257
Mn	-	0.005	-	-	-
Mg	9.189	9.016	9.680	9.374	9.293
Ca	-	-	-	0.010	-
Na	-	0.104	-	-	-
K	-	-	-	-	-
Ni	0.040	-	0.060	0.030	-
Cations	19.812	19.827	19.761	19.669	19.746
Fe#	0.04	0.05	0.05	0.02	0.08
Mg#	0.96	0.95	0.95	0.98	0.92

7. Discussion

The data presented above provide insights on the textural and compositional modification of Cr-spinels hosted in the Pindos ophiolite complex peridotites during alteration processes.

Three different spinel compositions have been identified within the Pindos serpentinised ultramafic rocks.

These are:

- Primary Cr-spinels, occurring as anhedral to euhedral crystals.
- Hydrothermally altered spinels (ferrian chromite and Cr-magnetite rims).

- Syn-serpentinisation and post-serpentinisation magnetites, occurring in pseudomorphic and non-pseudomorphic serpentine textures.

Each of these compositional groups provides information about the extend and evolution of hydrothermal alteration history in both areas of investigation.

7.1. Magnetite formation

The preservation of both pseudomorphic and non pseudomorphic textures, particularly in the extremely serpentinised rock samples from both areas of investigation, accounts for the common occurrence of syn- and post-serpentinised magnetite, respectively. Therefore, magnetite forms contemporaneously with serpentine in both cases. Magnetite is a product of the oxidation of Fe^{+2} contained in olivine to Fe^{+3} (O'Hanley 1993), thus it forms before the re-equilibration of magmatic Cr-spinels to hydrothermally altered spinels.

7.2. Cr-magnetite formation

During hydrothermal alteration Cr-spinels re-equilibrate with the surrounding silicate minerals by releasing Al and Mg and capturing Cr, as well as Fe^{+2} and Fe^{+3}, thus promoting the formation of ferrian chromite. Although Cr behaves as an immobile element during the initial stages of the process, a small proportion of Cr is incorporated into the structure of syn- and post-serpentinised magnetites, which overgrow Cr-spinels, resulting in the formation of Cr-magnetites. Conclusively, Cr-magnetite rims are produced during low-grade hydrothermal alteration.

Moreover, the diffusive replacement of Mg^{+2} by Fe^{+2} in Cr-spinel structure during low grade hydrothermal metamorphism, results in the development of narrow alteration zones enriched in Fe^{+2}# [$Fe^{+2}/(Fe^{+2}+Mg)$] along the margins and fracture rims of Cr-spinel grains, especially were these are in contact with serpentine. Similar alteration zones have been identified by Barnes (2000) in modified Cr-spinels from komatiitic rocks. Additionally, Kimball (1990) attributes the slight increase in Fe^{+2}# towards the rims of Cr-spinels in contact with serpentine to a hydrothermal alteration process.

Cr-magnetite rimming apparently unaltered Cr-spinel grains occurs in all rock types from both studied areas. Especially in the area of Milia, Cr-magnetite overgrown is the exclusive alteration type of Cr-spinel.

7.3. Development of ferrian chromite-chromian chlorite association

Progressive exchange of Al^{+3}, Mg^{+2}, Cr^{+3} and Fe^{+3} between Cr-spinels and the surrounding silicates leads to the formation of thick rims of ferrian chromite. This process continues even when Cr-spinels are completely coated with Cr-magnetite, as shown by thin ferrian chromite rims replacing Cr-spinel grains, which are entirely surrounded by Cr-magnetite. Similar observations on the diffusive ability of Al^{+3}, Mg^{+2}, Cr^{+3} and Fe^{+3} through magnetire have been done by Barnes (2000).

Ferrian chromite rims are typically surrounded by Cr-chlorite aureoles. Cr-chlorite has higher Mg# than chlorite that forms as a result of olivine and pyroxene serpentinisation, during low grade hydrothermal alteration. Additionally, the former contain appreciable amounts of Cr_2O_3 (3.33 wt%) than the latter. The exclusive textural association of Cr-chlorite with ferrian chromite shows that these two phases are paragenetically related. The replacement of serpentine in mesh and bastite textures by Cr-chlorites indicates that the formation of Cr-chlorite took place at a more advanced stage of hydrothermal metamorphism than that for the formation of serpentine and its accompanying Cr-depleted chlorite. Cr-chlorite aureoles overgrowing mesh textures have been previously mentioned by Mellini *et al.* (2005).

Ferrian chromite rims with Cr-chlorite aureoles is the dominant alteration type of Cr-spinel from clinopyroxene bearing harzburgites from the area of Pefki.

7.4. Metamorphic evolution

The common textural associations: Cr-spinel+Cr-magnetite+(Al-Cr)-serpentine and Cr-spinel+ferrian chromite+Cr-chlorite, combined with compositional data, provide insights into the metamorphic history of the investigated peridotites from the areas of Milia and Pefki.

Initially thin magnetite rims formed during serpentinisation. Cation exchange between Cr-spinel and the surrounding serpentine took place during low grade hydrothermal metamorphism leading to the formation of Cr-magnetite and Al-Cr-serpentine. At this metamorphic stage Mg, Al and to a much lesser extent Cr diffuse from spinel towards serpentine and magnetite, during greenschist facies hydrothermal metamorphism. At the area of Milia the exclusive textural association of Cr-spinel with Cr-magnetite and (Al-Cr)-serpentine, is representative of a low hydrothermal alteration process.

At a more evolved stage, extensive release of Al, Mg and minor Cr from spinel structure cause spinel dissolution and ferrian chromite formation combined with serpentine transformation to Cr-chlorite, commonly observed in Cr-spinels from the area of Pefki. Ferrian chromite rims and Cr-chlorite aureoles have been interpreted to indicate the rise of the metamorphic conditions up to lower amphibolite facies (McLean 1975, Burkhard 1993, Farahat 2006). Thus, a metamorphic context between greenschist and low amphibolite facies, below temperatures of chlorite decomposition, is suggested for the modified Cr-spinels of the Pindos ophiolite complex.

8. Conclusions

Variably serpentinised ultramafic rocks from the Pindos massif in northwestern Greece contain Cr-spinels which are overgrown by thin rims of Cr-magnetite and/or ferrian chromite. Cr-magnetite rims are surrounded by serpentine, while ferrian chromite is always in apparent paragenetic relationship with Cr-chlorite. Textural and compositional data provide evidence that during low-temperature serpentinisation pure magnetite starts to overgrow Cr-spinels and fill their protoclastic fractures. More extensive fluid interaction involves Mg^{+2}, Fe^{+2} and Cr^{+3} exchange between chromite rims and surrounding silicates, thus promoting the formation of Cr-magnetite and zoned Cr-spinels in terms of Fe^{+2}#. Prolonged diffusion of Al^{+3}, Mg^{+2}, Cr^{+3} and Fe^{+3} at more elevated metamorphic conditions results to Cr-spinel transformation into ferrian chromite, accompanied by Cr-chlorite aureoles. The progressive modification of Cr-spinel composition marks the transition of the metamorphic conditions from the lower greenschist facies up to the lower amphibolite ones. The difference in the alteration type of Cr-spinels between the two investigated areas of the Pindos ophiolite complex, indicates that they have been affected by different metamorphic grades. The common occurrence of thin Cr-magnetite rims in the area of Milia suggests that lower greenschist facies conditions prevailed during hydrothermal metamorphism, while the coexistence of ferrian chromite with Cr-chlorite reflects the rise of the metamorphic conditions up to lower amphibolite phacies.

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