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CR-RICH-SPINEL CHEMISTRY OF THE SERPENTINITES FROM THE ISLAND OF ELBA, TUSCANY, ITALY: NOTE I

Riassunto — Chimismo degli spinelli cromiferi delle peridotiti serpentinizzate dell'Isola d'Elba.

Sono stati analizzati gli spinelli cromiferi contenuti in più di cento campioni di serpentiniti appartenenti alla serie ofiolitifera dell'Isola d'Elba. I campioni investigati, suddivisi in tre settori di campionamento (occidentale, centrale ed orientale), mostrano ampia variabilità composizionale correlabile sia al chimismo della roccia ospite che al tipo di metamorfismo subìto dalla roccia stessa. Le serpentiniti ricristallizzate del settore occidentale sono caratterizzate da spinelli molto zonati con nuclei ricchi in Mg, Al e bordi arricchiti in Fe_{tot}. Nel settore centrale gli spinelli hanno composizione meno variabile dei precedenti e presentano omogeneità chimica nell'ambito dello stesso cristallo. In questo settore si rinvengono anche granuli di spinelli con forti caratteri di primitività: valori molto bassi del rapporto $Cr x 100/(Cr+Al)$(12) contro valori relativamente alti di $Mg x 100/(Mg+Fe^{2+})$ (80). Gli spinelli del settore orientale hanno generalmente composizione intermedia rispetto ai primi due. Sono sovrapponibili a una parte delle composizioni degli spinelli del settore centrale per quanto riguarda i rapporti $Fe^{3+} \times 100/Fe^{3+}+Cr+Al$, mentre mostrano valori leggermente più alti per il rapporto $Cr x 100/(Cr+A1)$.

Globalmente vengono evidenziati due gruppi conposizionali ben distinti:
I tipo, rappresentato prevalentemente da spinelli del settore occidentale, caratterizzati generalmente da termini ferro-cromitici di generazione tardiva;
II tipo, rappresentato prevalentemente dagli spinelli degli altri due settori, caratterizzati da termini alluminiferi con forti caratteri di primitività, quelli centrali, e da alti contenuti in Cr, quelli orientali.

Nelle serpentiniti del settore orientale si rinvengono frequentemente spinelli microcristallini (1-2 μ) intimamente frammisti a clorite. La loro composizione è notevolmente diversa da quelli finora trattati in quanto caratterizzata, oltre che da tenori elevati in Fe e Cr, anche da altri contenuti di Mn.

Il diverso comportamento composizionale degli spinelli dei tre settori investigati riflette i vari eventi dinamotermici che hanno interessato il complesso ofiolitico elbano, procedendo da ovest verso est.

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Abstract — Chrome-bearing spinels contained in over a hundred samples of serpentinites of the ophiolite suite of Elba Island were analysed. The examined samples, divided into three sampling sectors (western, central and eastern), widely varied in their composition, due to serpentinite chemistry and metamorphism of the rock itself. The recrystallized serpentinites of the west sector are characterised by highly zoned spinels with Mg, Al and Cr rich cores and Fe_{tot} rich rims. The spinels from the central sector showed a less variable composition and are chemically homogeneous in the crystal itself. This sector also revealed spinel grains with strongly primitive characteristics: very low Crx100/(Cr+Al) ratios (12) against relatively high Mgx100/(Mg+Fe^{2+}) values (80). East sector spinels generally have a composition in between the former two. They are similar in part to central sector spinels as regards Fe^{3+}x100/(Fe^{3+}+Cr+Al) ratios, whilst showing slightly higher values for Crx100(Cr+Al).

On the whole, the spinels have been grouped from textural and chemical standpoint into two types:

Type I, mainly represented by western sector spinels, generally characterised by high Fe-Cr contents and therefore of later generation;

Type II, mainly represented by spinels from the other two sector, characterised by high A1 contents with strong primitivity in central sector spinels and high Cr contents in eastern sector ones.

Microcrystalline spinels (1-2μ) were frequently found in east sector serpentinites, closely intergrown with chlorite. Their composition was markedly different from those treated so far, being characterised by high Mn content as well as high levels of Fe and Cr.

The differences in spinel composition of the three sectors examined reflects the various dynamothermic events that have influenced Elban ophiolitic complex, going from west to east.

Key words — Cr-spinels, chemistry, serpentinites, Elba Island, Italy.

INTRODUCTION

The first Geologic Map of the Island of Elba was published by LOTTI (1885), but it was TREVISAN (1950) who established a turning point in our geological knowledge of the Island by suggesting a tectonic evolutionary pattern based on five distinct overlapping complexes. Several later works by BONATTI and MARINELLI (1953), BARBERI *et al.* (1965-69), CORTESOGNO *et al.* (1975) and PERRIN (1975), and more recently REUTTER and SPHON (1982) and BORTOLOTTI *et al.* (1991), show different and contrasting opinions on the Island's tectonic evolution. This is particularly evident for the events involving the ophiolitic complex, which are still not altogether clear. Finally, KELLER and PIALLI (1991), in a study that also involved the analysis of ophiolitic complex layout, highlight evolutionary processes involving the Sardinian-Corsican Block and the Apula Platform during Appennine orogeny.

The ophiolites, mostly in Complex IV, are largely distributed in the various lithotypes of the Mount Capanne thermometamorphic ring, in the central and north-eastern parts of Elba.

This preliminary note aims at characterising the composition of spinels contained in serpentinites of the ophiolitic suite in order to cerrelate mineral chemistry with the host rock, also as a function of type and degree of metamorphism characterising the rock itself. The data reported in this paper will then successively be related to data on ophiolites of the Tuscan southern peninsula (in progress), which are considered to be strictly related to the above.

Sampling

The examined spinels come from a hundred samples taken from various serpentinites in Complex IV. The sampled areas were in fact divided into three overall sector: *western* (Mt. Capanne metamorphic ring), *central* and *eastern*.

Fig. 1 schematically shows Elba ophiolitic complex distribution

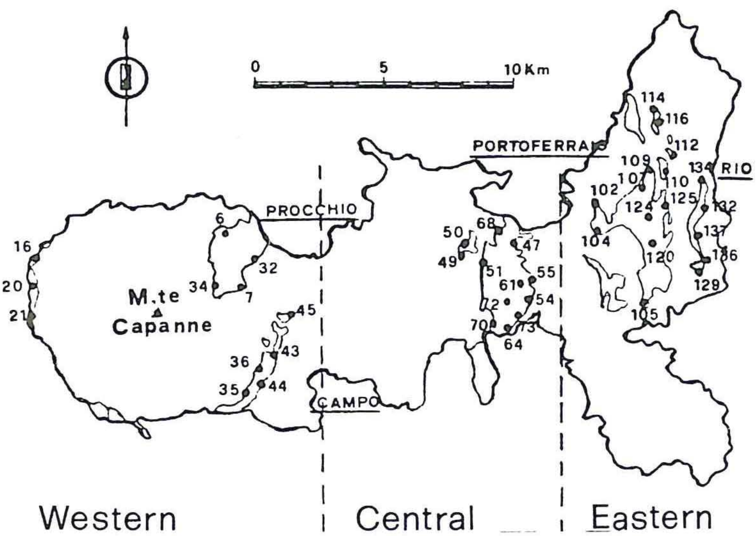

Fig. 1 - Elban ophiolitic complex schematic distribution and some sampling points of the investigated rocks.

together with some of the relative sampling points of serpentinites investigated in this paper.

Some western serpentinites, between S. Ilario and S. Piero, found in old magnesite quarries appear to have undergone prograde metamorphism and are strongly recrystallized with olivine and anthophyllitic amphibole. No recrystallized serpentinites were found in the central and eastern, but the rocks still show various stages of serpentinization according to the type and the degree of metamorphism.

Analytical procedures

Chemical analyses of the rocks were performed with a Philips PW1480 X-ray fluorescence spectrometer using lithium tetraborate (1:7) pearls. FeO content was determined by potassium permanganate titration. H_2O^- was determined at 110°C, while H_2O^+ by calcination at 900°C and by differential thermogravimetric analyses (TG, DTG, DTA). The spinels were analysed on double polished thin sections (D.P.T.S.) using a JOEL JXA-5A electron microprobe with an 860 Link system, ZAF 4- FLS correction at 15 Kv and 2nA, and a 5 spectrometer WDS CAMECA SX50, advanced PAP program, ZAF 4-FLS at 15 Kv and 15nA. Standards used were: synthetic diopside for Si, Ca and Mg, Norway olivine for Fe, corundum for A1, rutile for Ti, pure elements for Fe, Mn, Cr, V, Ni and Zn.

Mineralogical associations

Elba serpentinized peridotites are markedly fractured and weathered. In the western sector, thermometamorphic action has given the rocks a strongly lithoid appearance with a reduction in hydrated minerals.

Table 1 shows the more frequent mineralogical associations seen in the sampled rocks. From optical observations of petrographic sections, the following characteristics were found:

Spinel: always present in Elba serpentinites as a typical accessory phase of the original peridotitic paragenesis. The grains with different size, never exceeding 2.5 mm, show an irregular and slightly lobate shape; in many sections the spinel appears fractured and

TABLE 1 - *The more frequent mineralogical associations in serpentinite rocks.*

	VESTERN SECTOR					CENTRAL SECTOR					EASTERN SECTOR				
	6	34	36	43	44	47	51	64	68	73	109	110	112	129	136
Serpentine	*****	***	**	**	**	*****	****	*****	*****	*****	*****	****	*****	***	***
Olivine		***		***	****		**	**						***	
Opx	***					***	***	***	***	***	***	**	***	***	**
Cpx							**		**						*
Tremolite	**	**	*****				**								
Anthoph.		**		*****	***					**				***	
Talc	*	*	***				**				**	**		**	***
Chlorite		*										*		*	*
Spinel	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*

crossed by veins of magnetite, serpentine and/or chlorite (Fig. 2a, b, c and d). In the central and eastern sector sample grains vary in colour from reddish brown to dark and, at times, have a darked magnetite alteration rim. In the western sector, the spinels have a more regular roundish shape and systematically show a well-defined magnetitic rim. The serpentinites in the eastern sector frequently show dark opaque clusters of spinel (of μ size) intergrown with microcrystalline chlorite.

Magnetite: generally present in microcrystalline aggregates or in veins. It is easily distinguished from spinel by its more compact appearance and darker colour. At times, in prograde olivine of the western sector, it is found as euhedral inclusions.

Serpentine: is the main component in most of the rocks examined, except in those strongly recrystallized where prograde olivine is dominant. Serpentine is mainly present in the lizardite variety with its typical network structure and as a chrysotile variety in veins associated with epigenetic phases.

Orthopyroxene: is mainly present in central and eastern sector samples. Serpentinization has obliterated the original optic characteristics. It is found as a thick prismatic structure in which there are evident traces of cleavage sometimes marked by oxide exolutions and sometimes curved due to tectonic stress. Observable characteristics are, however, attributable to enstatitic components.

Clinopyroxene: with respect to orthopyroxene is much less present in both western and eastern sectors. This phase preserves the typical characteristics of diopside. Clinopyroxene relics often show tremolite alteration rims. In thermometamorphosed rocks of the western sector it is possible to observe small neoblastic diopside crystals.

Olivine: is seen in two distinct conditions:
1) as a relic mineral, showing strong fracturing which rarely preserves its optic characteristics. Colroureless and non-pleochroic, with average to high values of 2V corresponding to forsteritic components;
2) recrystallized olivine from serpetine (Fo95), in clear and well-shaped neoblastic grains frequently containing euhedral inclusions of magnetite. The olivine crystals are isooriented and are separated by a thin layer of residual serpentine, chlorite and sometimes talc.

Tremolite: pratically absent in the eastern sector, it appears in fibrous structures and in bunches, sometimes as an alteration rim

TABLE 2 - *Representative rock analyses for the three sectors investigated.*

	VESTERN SECTOR					CENTRAL SECTOR					EASTERN SECTOR				
	6	34	36	43	44	47	51	64	68	73	109	110	112	129	136
SiO_2	44.77	41.46	46.69	40.77	48.01	40.76	45.96	42.69	41.18	40.64	40.83	41.60	40.93	44.25	46.53
TiO_2	0.06	0.03	0.14	0.05	0.12	0.02	0.07	0.03	0.03	0.05	0.04	0.03	0.03	0.07	0.06
Al_2O_3	1.65	1.62	2.98	1.65	5.12	1.13	2.57	1.63	1.16	2.03	1.78	1.79	1.61	1.41	1.71
Fe_2O_3	7.65	2.01	3.76	2.16	3.48	5.63	5.28	5.12	6.90	3.27	5.61	5.13	4.76	6.42	7.94
FeO	5.65	5.10	1.68	8.05	2.26	2.81	3.16	2.60	1.80	2.90	2.21	2.04	2.37	2.00	2.72
MnO	0.13	0.12	0.11	0.16	0.08	0.09	0.13	0.12	0.10	0.09	0.10	0.12	0.11	0.12	0.13
MgO	35.24	44.20	29.47	41.30	25.38	37.23	29.02	35.76	37.05	34.90	35.54	35.46	36.11	33.32	28.49
CaO	1.05	0.46	7.14	0.54	9.50	0.08	1.94	0.56	0.09	3.97	0.85	0.16	0.50	0.31	1.62
Na_2O	0.04	0.00	0.07	0.26	0.25	0.02	0.15	0.03	0.00	0.04	0.23	0.10	0.19	0.13	0.09
K_2O	0.00	0.00	0.01	0.13	0.05	0.00	0.02	0.00	0.00	0.00	0.03	0.01	0.02	0.01	0.01
P_2O_5	0.01	0.01	0.01	0.02	0.09	0.01	0.02	0.00	0.00	0.02	0.01	0.02	0.01	0.01	0.00
L.O.I.	4.42	4.40	6.79	3.57	4.75	12.68	11.59	11.38	12.00	11.81	12.73	13.54	13.34	11.95	10.68
Sum	100.67	99.41	98.85	98.66	99.09	100.46	99.91	99.92	100.31	99.72	98.18	98.21	99.98	100.00	99.98
Dio	2.19	0.91	14.76	1.05	19.00	0.17	4.12	1.21	0.20	8.44	1.79	0.30	1.05	0.64	3.49
En	1.80	0.84	13.62	0.94	17.20	0.15	3.63	1.10	0.18	7.80	1.63	0.27	0.96	0.58	2.98
Fs	7.36	1.54	4.50	1.95	5.75	3.95	9.06	4.70	4.22	2.64	4.13	4.33	3.61	6.65	11.64
Hyp	40.04	18.97	40.20	15.20	38.12	36.61	63.40	45.91	39.29	23.43	39.31	46.12	38.47	57.09	64.88
Jad	0.30	0.00	0.52	1.94	1.83	1.08	1.17	0.23	0.00	2.00	1.81	0.80	1.52	1.02	0.70
Acm	0.00	0.00	0.00	0.00	0.00	0.71	0.00	0.00	0.00	0.33	0.00	0.00	0.00	0.00	0.00
Crd	0.89	1.29	2.84	0.49	4.76	1.12	2.10	1.30	0.76	1.88	1.05	1.41	1.00	0.80	1.08
Fos	38.28	69.61	20.42	66.97	10.27	49.32	12.77	39.96	48.44	48.12	43.86	41.26	47.30	28.10	11.11
Fay	6.73	5.40	1.71	8.11	1.07	5.26	1.72	4.00	5.17	4.03	4.43	3.85	4.33	3.24	1.98
Phl	0.00	0.00	0.10	1.27	0.48	0.00	0.21	0.00	0.00	0.00	0.31	0.14	0.21	0.10	0.10
Apt	0.02	0.02	0.02	0.05	0.21	0.03	0.05	0.00	0.00	0.05	0.05	0.05	0.05	0.02	0.00
Spl	1.19	0.70	0.55	0.98	0.56	0.84	0.83	0.77	0.85	0.65	0.78	0.73	0.74	0.82	1.01
Crm	0.10	0.10	0.10	0.10	0.10	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11
Mgt	1.09	0.60	0.45	0.88	0.46	0.74	0.73	0.66	0.75	0.54	0.67	0.63	0.63	0.78	0.91
Ilm	0.09	0.04	0.20	0.07	0.17	0.03	0.11	0.05	0.05	0.08	0.06	0.05	0.05	0.8	0.09
Sum	100.08	100.02	99.99	100.00	99.98	100.12	100.01	100.00	100.02	100.10	99.99	100.05	100.03	100.03	100.08

on clinpyroxene. The 18° c$\wedge$z angle and positive elongation confirm the characteristics of the tremolitic amphibole.

Anthophyllite: is only found in the western sector in those rock samples that are strongly recrystallized by thermometamophism. It appears in large fanned bunches trapping prograde olivine and the strongly zoned spinel.

Talc: is subordinated with respect to the phases appears in aggregates or in viens of minute isooriented scales, easily distinguished from chrysotile owing to a higher birefringence.

Chlorite: also subordinated, shows a fibrous, colourless or pale brown appearance. Frequently found around corroded spinel grains or across spinel fractures.

Rock chemistry

Table 2 describes the chemistry and the relative CIPW norms, calculated according to a specific P.C. program for ultrabasic rocks, of the sepentinites considered to be more representative fot their texture and structure as well as for mineralogical composition.

Normally the serpentinites examined had an average SiO_2 content ranging from 40 to 46% in weight, but the serpentinites recrystallized through thermometamorphism of the western sector gave even higher silica values (up to 48%). These samples also showed high Ca and A1 contents (up to 9.5% of CaO and 5.12% of $A1_20_3$). The loss on ignition (L.O.I.) was instead relarively low, ranging from 3.6 to 6.8% in weight, to compare as for the higher values (10.7-13.5%) found in serpentinites of the central and eastern sectors. In the latter sectors the rocks generally appeared enriched in Fe_20_3 as compared with those of the western sector, while FeO seemed to present an inverse trend. Finally, it was interesting to note that MgO varied strongly in the western sector (25.4 to 44.2 weight %), while it remained fairly constant on average values of 35-36 weight % in the other sectors.

Streckeisen's classification chart (1976) for ultrafemic rocks (Ol-Hy-Di) was used to plot (Fig. 3) the composition of the examined rocks. It should be stressed that this representation is purely indicative, considering that the serpentinization process involves composition and volume variations from the original rock, so the normative compositions obtained should only be taken as indicators for

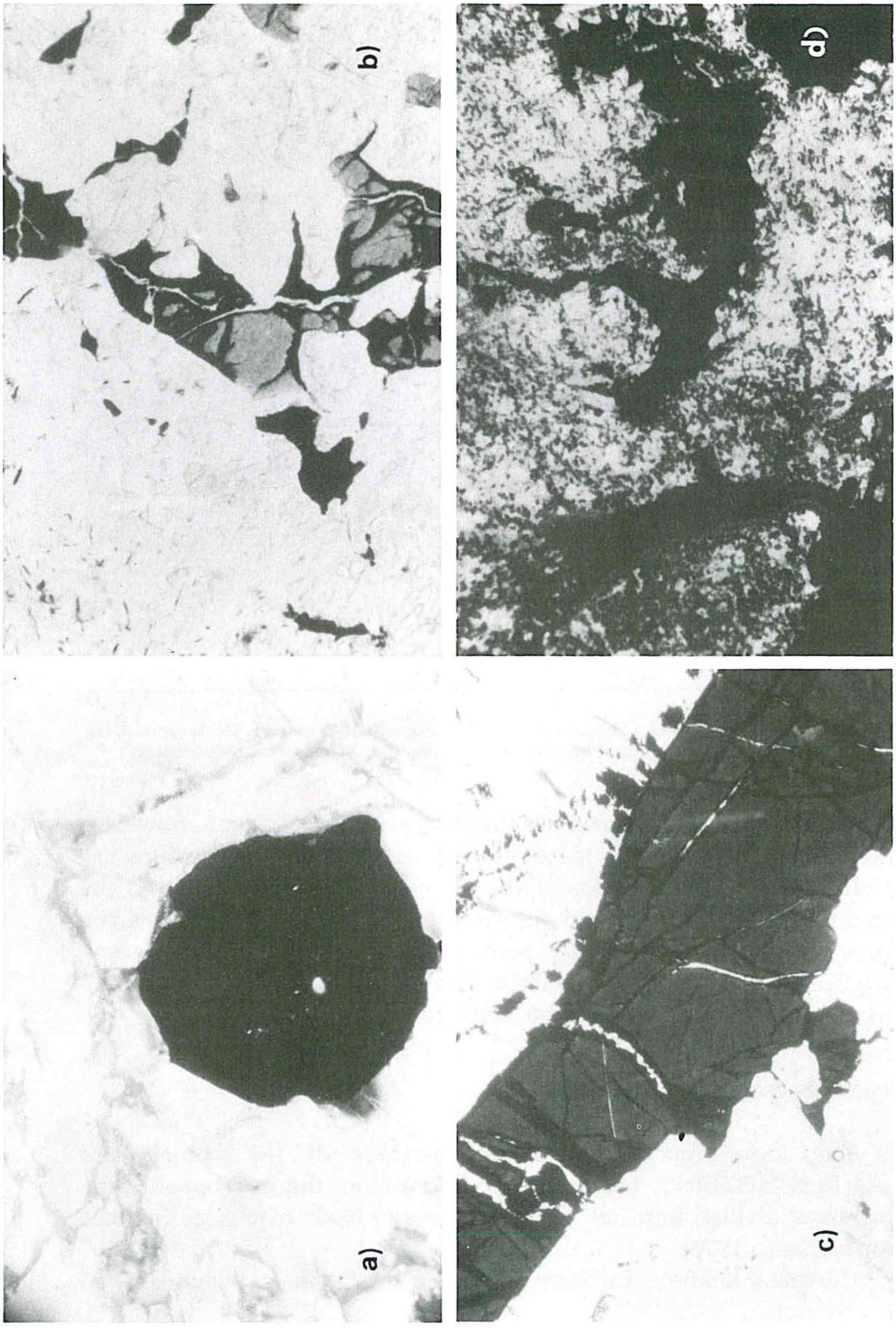

Fig. 2 - Photomicrographs of the chromium-spinel studied: a) rounded spinel of the recrystallized sperpentinite of the western sector, containing birefringent inclusions (reflected light, crossed polar, X 100); b) relic of Al-spinel (black) with chlorite (gray) of the central sector (one polar, X 100); c) a large crystal of fracturated Fe-Cr-spinel of the central sector, crossed by magnetite and serpentine veins (crossed polar, X 80); d) irregular and interstitial spinel grains of the eastern sector, with chiefly Cr-Al composition (crossed polar, X 70).

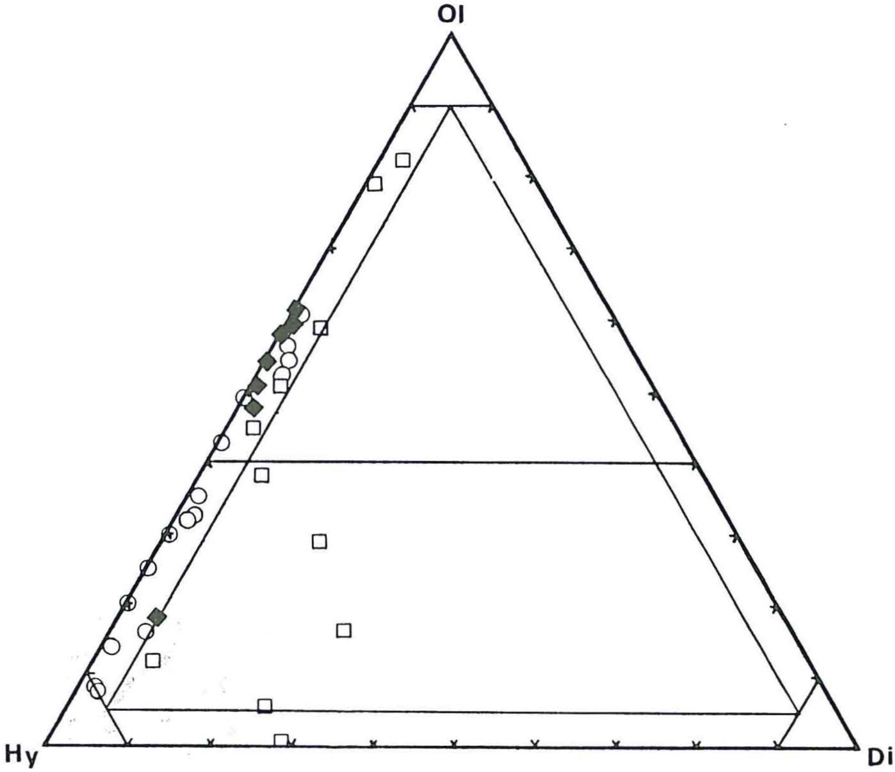

Fig. 3 - Ultramafic rock classification diagram (STREICKEISEN, 1976, modified). *Squares*=western sector, *rhombs*=central sector, *circles*=eastern sector.

the original peridotitic ones (GROHMANN *et al.*, 1982). Fig. 3, however, shows that the serpentinites of the central and eastern sectors are in alignment with the fields of the olivine orthopyroxenites and the harzburgites, while those of the western sector have greater variability noticeable by the wider point spread in the diagram, particularly in the olivine wesberite field. The latter's variability in composition is attribued to the high CaO content in these rocks.

SPINEL CHEMISTRY

The more representative compositions of the spinels are described in Table 3. The total Fe content from the microprobe analyses was divided into Fe^{2+} and Fe^{3+} on the basis of charge balance (CARMICHAEL, 1976).

Chemical analyses for most western sector spinels, which showed

TABLE 3 - *Representative spinel analyses of three sectors investigated.*

	WESTERN SECTOR												
	16 n=7	20 n=7			34 n=5		35 n=5			43 n=6		
		C	M	R	C	R	C	M	R	C	M	R
SiO_2	0.21	0.06	0.09	0.20	—	0.42	—	—	0.16	0.41	0.06	0.43
TiO_2	0.89	1.05	2.17	0.81	0.21	0.58	0.05	0.13	0.89	0.28	0.22	0.21
Al_2O_3	3.20	26.70	17.84	6.20	29.06	0.82	57.01	45.71	1.82	8.09	1.26	0.52
Cr_2O_3	26.83	35.76	41.19	29.15	35.17	27.04	5.25	16.41	9.30	7.06	7.67	6.54
Fe_2O_3*	36.19	4.67	5.56	31.56	4.80	37.63	6.69	6.95	56.19	54.23	60.86	61.84
FeO	25.71	18.71	21.19	24.47	16.22	28.64	8.59	14.21	27.34	21.60	25.40	26.23
MgO	3.95	11.64	8.96	4.82	12.48	2.02	20.00	15.97	2.68	6.87	3.73	3.45
MnO	0.48	0.11	0.65	0.78	—	0.11	0.04	0.17	0.11	0.31	0.29	0.35
NiO	0.66	—	—	0.57	0.19	0.56	0.66	0.39	0.78	0.48	0.58	0.64
CaO	—	—	—	—	—	—	0.32	—	—	0.08	0.08	0.03
ZnO	—	0.35	0.96	0.43	1.34	—	0.56	0.23	0.07	0.41	0.03	0.01
V_2O_5	—	—	—	—	—	—	0.11	0.22	0.30	—	0.08	—
Sum	98.18	99.05	98.61	98.89	99.47	97.82	99.28	100.40	99.64	100.12	99.95	100.25
Cations on the basis of 32 oxygens												
Si	.064	.016	.024	.056	—	.123	—	—	.048	.112	.016	.128
Ti	.200	.195	.424	.176	.038	.133	.008	.024	.200	.056	.048	.048
Al	1.112	7.749	5.496	2.056	8.297	.294	14.044	11.904	.640	2.656	.448	.184
Cr	6.248	6.965	8.508	6.584	6.733	6.502	.872	2.864	2.192	1.552	1.792	1.552
Fe^{3}*	8.024	867	1.088	6.808	.875	8.613	1.056	1.152	12.624	11.368	13.512	13.792
Fe	6.336	3.853	4.632	5.880	3.285	7.285	1.504	2.624	2.824	5.104	6.272	6.496
Mg	1.736	4.269	3.492	2.036	4.504	.916	6.228	5.256	1.192	2.856	1.640	1.520
Mn	.136	.24	.144	.188	—	.028	.008	.032	.028	.072	.072	.136
Ni	.152	—	—	.132	.037	.137	.112	.072	.188	.104	.144	.160
Ca	—	—	—	—	—	—	.072	—	—	.024	.024	.008
Zn	—	.064	.186	.088	.240	—	.088	.040	.016	.088	.008	.008
V	—	—	—	—	—	—	.016	.032	.060	—	.016	—
Sum	24.008	24.003	23.994	24.004	24.009	24.035	24.008	24.000	24.012	23.992	23.992	24.032

n = number of spot analyses averaged; C = Core; M = Mantle and R = Rim.
* Fe separated according to Carmichael (1967). ** recalculated analysis without chlorite component (see text).

TABLE 3 (Continued)

CENTRAL SECTOR							EASTERN SECTOR				
47 n=7	49 n=7	50 n=6	55 n=7 C	55 n=7 M	55 n=7 R	61 n=7	107 n=5	109** n=3	116 n=4	129 n=2	136 n=3
0.05	0.11	—	1.45	1.49	0.83	0.17	0.16	—	0.29	1.23	0.21
0.20	0.06	—	0.73	0.74	0.55	1.01	35.00	0.10	01.32	00.36	00.17
29.04	2.02	54.31	0.73	0.52	0.18	23.38	22.29	—	28.60	0.40	0.17
53.32	18.93	12.31	13.99	11.98	7.53	37.97	41.89	22.85	32.14	20.06	16.87
5.89	49.15	2.75	51.63	54.52	59.05	7.59	4.18	45.75	6.08	45.31	50.82
14.29	19.37	9.44	26.21	23.54	26.08	14.62	19.96	24.21	14.97	25.21	26.67
14.45	6.38	19.83	3.97	4.41	2.45	13.98	10.20	—	14.45	3.03	1.54
0.09	1.67	0.08	0.50	0.43	0.55	0.19	0.38	6.98	0.23	2.55	1.33
0.19	0.68	0.31	0.55	0.57	0.90	0.24	0.01	0.25	0.44	0.31	0.51
0.10	0.50	0.06	—	—	—	0.10	0.03	0.33	0.11	0.11	0.12
0.12	0.11	0.11	—	—	—	0.08	0.06	0.05	—	0.21	0.49
0.17	0.16	—	0.21	0.18	0.20	0.25	0.44	—	0.27	0.15	0.19
99.91	99.14	99.20	99.97	98.38	98.03	99.58	99.95	99.52	98.90	98.97	98.96
.112	.032	—	.425	.441	.253	.041	.040	—	.070	.370	.060
.036	.013	—	.161	.165	.126	.185	.070	.020	.240	.080	.040
8.151	.692	13.510	.252	.181	.064	6.719	7.300	—	8.100	.140	.060
6.648	4.342	2.053	3.243	2.844	1.870	7.318	7.540	5.410	6.100	4.740	4.050
1.055	10.731	.437	11.395	12.130	13.618	1.392	.570	10.480	1.100	10.180	11.620
2.845	4.700	1.666	6.428	5.822	6.612	2.981	3.220	6.030	3.000	6.300	6.780
5.127	2.758	6.236	1.735	1.942	1.112	5.079	4.930	—	5.170	1.350	.700
.018	.410	.014	.124	.108	.064	.039	.050	1.760	.050	.640	.340
.036	.158	.053	.129	.136	.221	.047	.030	.080	—	.070	.120
.026	.155	.014	—	—	—	.026	.010	.110	.030	.030	.040
.021	.023	.017	—	—	—	.014	.030	—	.090	.040	.110
.032	.037	—	.049	.043	.049	.049	.050	—	.050	.040	.040
24.009	24.050	24.000	23.941	23.859	23.992	23.890	23.990	23.890	23.990	23.990	23.970

evident concentric zoning, have been reported as Core, Mantle, Rim; chemical analyses for some spinels from the central sector were similarly presented, although their zoning is limited. The cores of western sector spinels appear richer in Al, Mg and Cr compared with the rims, which instead are particularly rich in Fe tot. This may clearly be seen in Fig. 4 where Fe^{2+}, Mg, Al, Cr and Fe^{3+} content of this

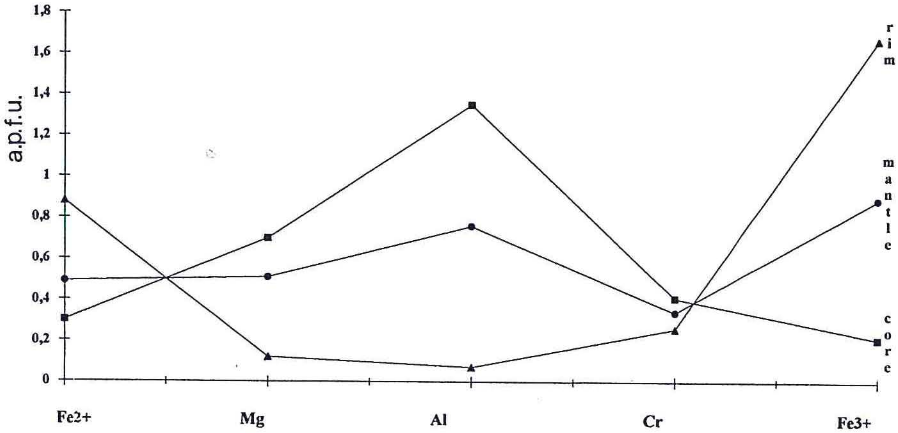

Fig. 4 - Compositional variability of western sector zoned spinels.

sector's zoned spinels is reported. Fig. 5 further highlights the wide compositional variabilly of spinels from the western sector. For example, while sample 35 has a core with the highest Al content, its rim is decidedly anomalous with relatively low Cr content, indicating a mainly magnetitic composition. Fig. 5 also shows how the area representing the central sector distributed along a well-defined trend in which Al (from 14 to 6.5 a.p.f.u.) negatively correlates diagram indicating very low Al content, with average to high Cr content, typical of Fe-Cr enriched spinels. Overlapping the latter, although slightly larger, is the area representing Fe-Cr spinels from the eastern sector; those spinels, however, are mainly represented in the lower part of the trend for the central sector, they present much narrower compositional range, with average Al and avegare to high Cr contents.

Analytical data on some microcrystalline spinels particularly widespread in the eastern sector are reported separately (Tab. 4). These spinels, around μ in size and finely intergrown with microcrystalline chlorite, have a composition characterised by considerable Mn content, ranging from 10 to 15 MnO in weight %, and

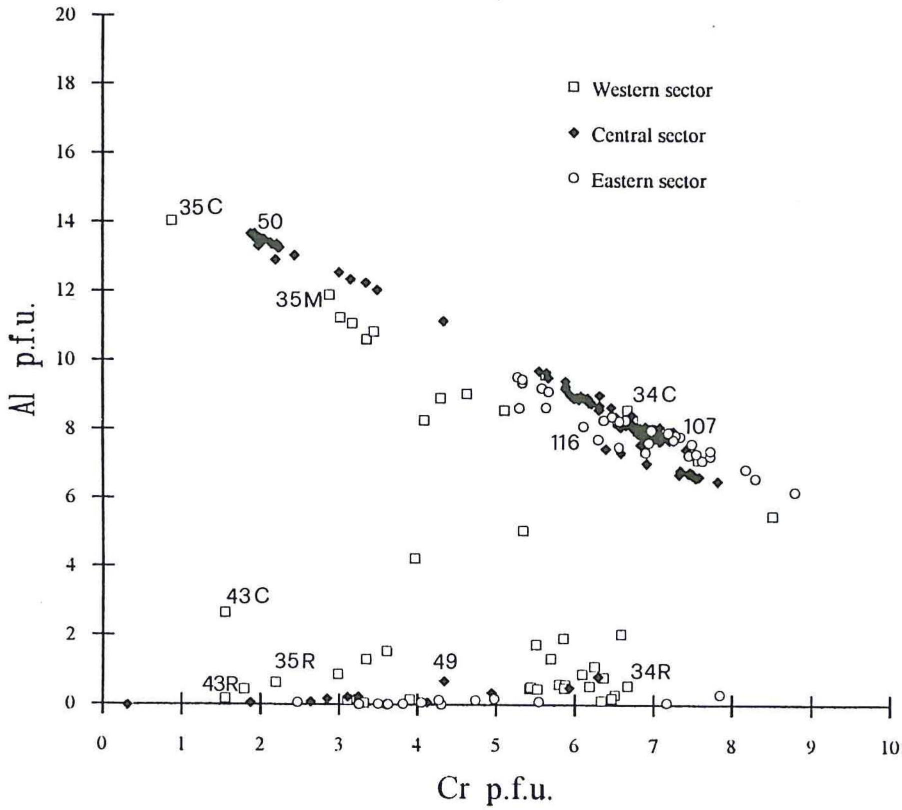

Fig. 5 - Cr vs Al cation contents per formula unit for the Elba spinels (Numbers as in Tab. 3).

dominant Fe and Cr contents. In this case the fine-scale intergrowth of the two phases spinel and chlorite prevented reliable analyses of spinels through microprobe equipment. A compositional qualitative test carried out through SEM equipped with an EDS system, confirmed the composition of the manganese spinel reported in Table 4. In the same table «mixed» analyses of spinel + chlorite are reported and the analytical late for two phases are recalculated from the bulk analysis. The composition of spinel obtained in this way appeared completely different from those discussed so far. The almost complete absence of Mg and Al together with high Mn contents correspond to a composition ranging between chromite ($FeCr_2O_4$) and jacobsite ($MnFe_2O_4$).

Considering the particular composition of this spinel and the extremely small size of material we undertook a detailed study in electron microscopy (SEM and TEM) to better define genetic characteristics and crystal chemistry.

TABLE 4 - *Chemical analyses of Mn-bearing phases frequently found in the eastern sector (see text).*

	(a)	(b)	(c)	(d)
SiO_2	6.73	—	1.35	—
TiO_2	0.29	0.42	—	—
Al_2O_3	6.84	—	0.19	—
Cr_2O_3	25.21	36.08	21.72	20.90
MgO	8.05	—	0.27	—
MnO	9.89	14.15	13.16	19.00
FeO	31.07	44.47	58.96	55.10
CaO	0.28	0.39	0.25	—
Na_2O	1.53	—	—	—
K_2O	0.18	—	—	—
NiO	—	—	0.36	—
Sum	90.07	95.51	96.26	95.00
FeO	—	16.81	16.66	12.12
Fe_2O_3	—	30.74	47.01	47.77
Cations on the basis of 32 oxygens				
Si	2.07	—	.40	—
Ti	.06	.10	—	—
Al	2.48	—	.06	—
Cr	6.12	8.73	5.09	5.04
Fe^{3+}	—	7.08	10.49	10.96
Fe^{2+}	7.98	4.30	4.13	3.10
Mg	3.69	—	.12	—
Mn	2.57	3.67	3.30	4.90
Ca	.09	.13	.07	—
Na	.91	—	—	—
K	.07	—	—	—
Ni	—	—	.08	—

End-members (d):
Jacobsite ($MnFe_2O_4$) 61.3%
Chromite ($FeCr_2O_4$) 31.5%
Magnetite ($FeFe_2O_4$) 7.2%

a) «mixed» analysis (chlorite+Mn-rich spinel)
b) spinel analysis obtained subtracting the chlorite component
c) Mn-rich spinel analysis
d) EDS analysis of a pure Mn-rich spinel

DISCUSSION

The analytical data described in Table 3 and the diagrams in Figures 4 and 5 clearly evidenced the different composition of the spinels in the three sectors examined.

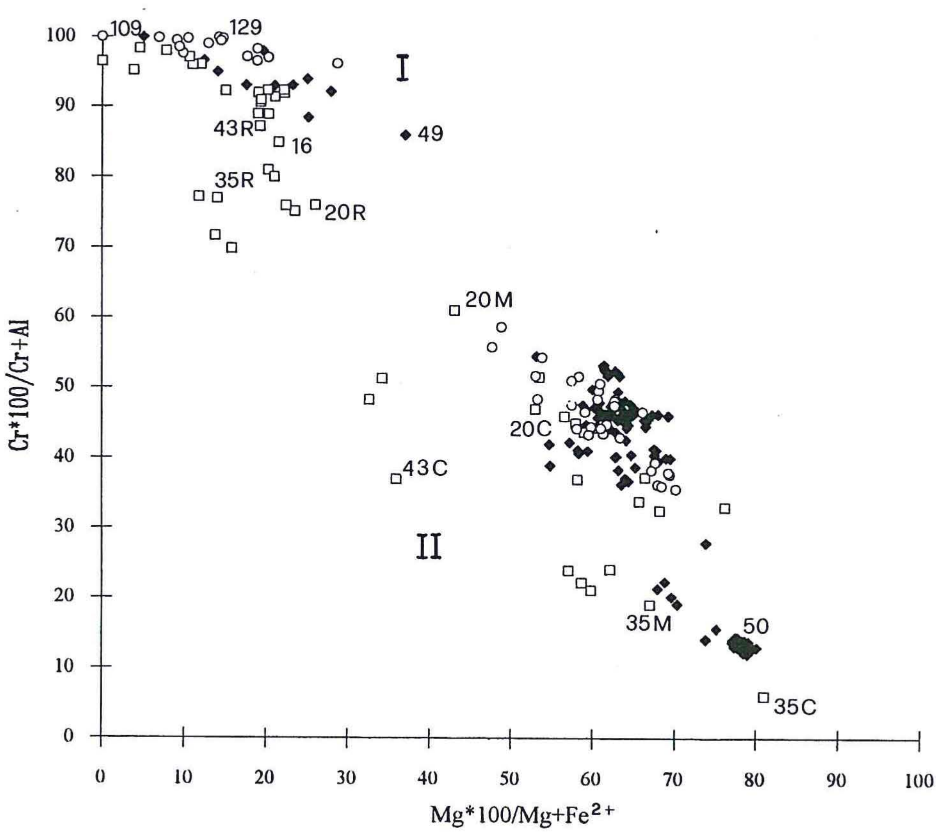

Fig. 6 - Mg*100/Mg+Fe^{2+} vs Cr*100/Cr+Al for the Elba spinels. (Symbols as in Fig. 5; numbers as in Tab. 3).

The Figures 6 and 7, Mgx100/(Mg+Fe^{2+}+Mg) vs. Cr×100/(Cr+Al) and Fe^{2+}×100/(Fe^{2+}+Mg) vs. Fe^{3+}×100/(Fe^{3+}+Cr+Al) respectively, give an overall view of the of the compositions of all the spinels examined. Both diagrams show two distinct spinel types:

Type I, mainly from the western sector, represented generally by Fe-Cr cores and/or magnetitic rims; with high (Fig. 6) and medium high (fig. 7) cationic ratios and a wider compositional range.

Type II, mainly from central and eaestern sectors, almost completely overlap (Fig. 7); very low Fe^{3+}x100/(Fe^{3+}+Cr+Al) ratios, but more homogeneous than the former.

The area of Type I is characterised by high Crx100/(Cr+Al) and Fe^{3+}x100/(Fe^{3+}+Cr+Al) values, indicating a high f_{O2} during crystallization. The thermal effect of Mt. Capanne granodioritic intrusion led to the recrystallization of the surrounding serpentinites, substantially chaning the spinel chemistry. In fact, the more marked

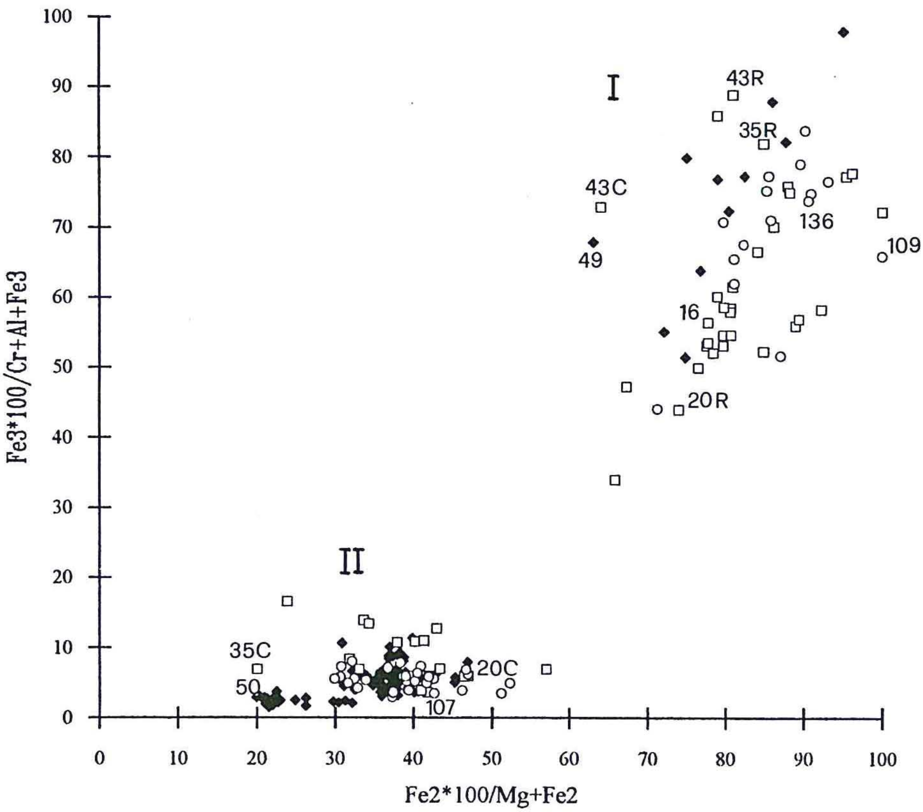

Fig. 7 - Fe^{3+}*100/Fe^{3+}+Cr+Al vs Fe^{2+}*100/Fe^{2+}+Mg for the Elba spinels. (Symbols as in Fig. 5; numbers as in Tab. 3).

zonation of western sector spinels indicates migration processes from core to rim of some elements (Al, Fe) with successive oxydation of Fe due to increases in f_{O2} (Evans and Frost, 1975).

Type II spinels appear less influenced by this phenomenon. Their chemical homogeneity and low Fe_{tot} content indicate an unchanged primary origin of the spinel, apart from the desultory presence of magnetite rims or veins attributable more to serpentinization processes than to thermal events. The low Crx100/(Cr+Al) values as against high Mgx100/(Mg+Fe^{2+}) values (Fig. 7), suggest high Al and Mg contents, normally typical indicators of primitiveness (Haggerty, 1976). The compositional characteristics of spinels of this seem to correlate well with those reported for spinels of ophiolites of Baldissero and Balmuccia, Western Alps (Lombardo and Pognante, 1982) and the ultrafemic xenoliths of S. Giovanni Ilarione, Lessini mountains (Morten *et al.*, 1989).

The frequent fracturing observed in grains of Type II indicates considerable tectonic activity involving the serpentinites without changing the chemical characteristics of the spinel.

Taking into account the bulk composition of the host rocks, a good correlation may be seen between spinel chemistry and the host rock. Western sector serpentinites show marked compositional heterogeneity, sometimes cheracterised by considerably high levels of normative diopside and orthopyroxene (Fig. 3). The spinels of these rocks in fact present high compositional variability and marked zonation (Tab. 3, Fig. 4).

Central sector serpentinites fall into the harzburgites field (Fig. 3). These rocks generally contain most primitive spinels with prevailing Al, Mg and Cr content.

Finally eastern sector seperntinites only partially overlap with some serpentinites from the central sector, but mainly in the olivine pyroxenite field; the spinels show a composition that lies between western and central sector values but with a much narrower range, as may easily be seen in Figs. 5, 6 and 7.

Conclusion

In this first part of our study it has been possible to establish compositional trends of spinels from serpentinites of the Elba ophiolitic complex.

The clear distinction into two types, I and II, highlighted by the compositional diagrams, indicates a different evolution for Elba serpentinites spinels:

Type I, mainly represented by Fe-Cr terms of presumably later generation.

Type II, represented by more Al terms with low Fe content and marked characteristics of primitivity.

Variation in spinel chemistry seems to well correlate with the bulk compositional examined host rock, taking into account also the serpentinization process that partly changed original peridotite composition.

Spinels from the western sector (thermometamorphosed serpentinites) in most cases show evident secondary processes, at different evolutive stages, observable in the more marked compositional zoning; the compositional variability of these spinels is characterised by high Mg and Cr contents, and sometimes Al, in the core, high Fe content in the rims.

The central sector spinels are fairly homogenous and show only slight chemical variation with high Al, Cr and Mg contents, also due to the type of original host rock, very probably corresponding to harzburgitic composition. This sector has most of the more primitive non-zoned Cr spinels found in Elba serpentinized rocks. Such homogeneity suggest a long period of relatively constant physical condition.

Finally, eastern sector spinels, in part comparable to those of the central sector, normally show a chemical homogeneity, with very narrow compositional range, characterised by an intermediate cationic ratios Crx100/(Cr+Al) and Mgx100/Mg+Fe^{2+}).

From the global chemical data of Cr-spinels in Elba serpentinites chemistry significant elements are obtained about the vaious dynamothermic events that characterised the evolution of the Island's ophiolitic complex. The thermal effect of granodioritic pluton intrusion of Mt. Capanne led to recrystallization of some serpentinized peridotites; spinel show the thermometamorphic effects in marked compositional zonation. Even if a bland metamorphism could still be seen in the spinel type of the central sector, they appear more primitive compared with those of the eastern sector, which suggests a vertical evolutionary trend, from the bottom up, of the original serpentinized peridotitic pack, indicating successive gravitational sliding of some ophiolitic plates eastwards.

The preliminary data reported in this paper, together with further detailed studies underway, will be compared with data still to be obtained for spinels of South Tuscan serpentinites; it will contribute to our understanding of the events involving the Tuscan insular and peninsular ophiolitic complex.

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