



# Major and minor element geochemistry of chromite from the Xerolivado–Skoumtsa mine, Southern Vourinos: Implications for chrome ore exploration



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## ABSTRACT

The concentration of major (Cr, Al, Mg, Fe) and minor (Ti, V, Mn, Ni, Zn) elements was studied in chromitite ores and accessory chrome spinels within serpentinite host rocks from the Xerolivado–Skoumtsa mine (Southern Vourinos, Western Macedonia, Greece) by means of electron microprobe techniques. Chrome ores in the mine occur in seven extensive ore bodies. Chromite was analyzed with respect to its position within or between ore bodies, including the following classifications: chromitite (schlieren ore) band, accessory chromite in intercalated serpentinite within the ore bodies, disseminated chromite in non-ore bearing host rocks, and chromite within serpentinites intermediately adjacent to ore bodies. Chrome spinel originally forms at temperatures of around 1300 °C, but their hosts undergo ductile deformation to temperatures down to around 700 °C, thus facilitating solid state re-equilibration. Results showed that Mg in chromite was found to be substituted during re-equilibration mainly by Fe and, to a minor extent, by Mn and Zn. Cr is mainly substituted by Al and, to a minor extent, V. Compositions were found to vary in accessory chromite crystals as a function of their distance from chromitite bands. Specifically, the average concentrations of Cr and Mg are higher in spinels within chromitite ores than for the disseminated spinels in serpentinite gangue layers within chromitites. Chrome spinels in schlieren ore layers have higher Mg and Cr concentrations compared to the disseminated chromites in the serpentinites immediately adjacent to the chromite ore bodies and also slightly higher concentrations of Mg and Cr than the disseminated chromites in the host serpentinites. Fe<sup>2+</sup>, Mn, Zn, Al and V cations show exactly the opposite trend. We attribute these variations in the spinel chemistry to subsolidus reactions between chromite, silicate mineral phases and fluids. Geochemical maps presenting the spatial variation of these elements in disseminated Cr spinels of the Xerolivado mine can serve to delineate the precise position of the chrome ore bodies.

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## 1. Introduction

Chromite chemistry within ophiolitic suites has long been used as a petrogenetic indicator for establishing their geotectonic environment, the composition of the parental magma(s) and the genesis of

chromitites of various types (e.g., Irvine, 1967, 1977; Pearce et al., 1984; Roeder and Reynolds, 1991; Arai, 1992; Arai, 1997; Malpas et al., 1997; Zhou and Robinson, 1997; Arai and Matsukage, 1998; Barnes and Roeder, 2001; Kamenetsky et al., 2001; Ahmed and Economou-Eliopoulos, 2008; Pagé and Barnes, 2009; Kapsiotis et al., 2011; Kapsiotis, 2013; Grieco et al., 2014; Rollinson and Adetunji, 2015; Uysal et al., 2015; Zhou et al., 2015). Chromite chemistry can be affected during subsolidus reactions by re-equilibration processes with silicate mineral phases and fluids (Irvine, 1967; Arai, 1980; Ozawa, 1985; Roeder and Campbell, 1985; Auge, 1987; Christodoulou and Michailidis, 1990; Rassios and Kostopoulos, 1990; Van der Veen and Maaskant, 1995; Peltonen, 1995; Filippidis, 1997). In general, Mg and Cr in chromite may be substituted by other bivalent (e.g. Fe<sup>2+</sup>, Ni) and trivalent (e.g. Fe<sup>3+</sup>, Al) cations, respectively (e.g., Irvine, 1967;

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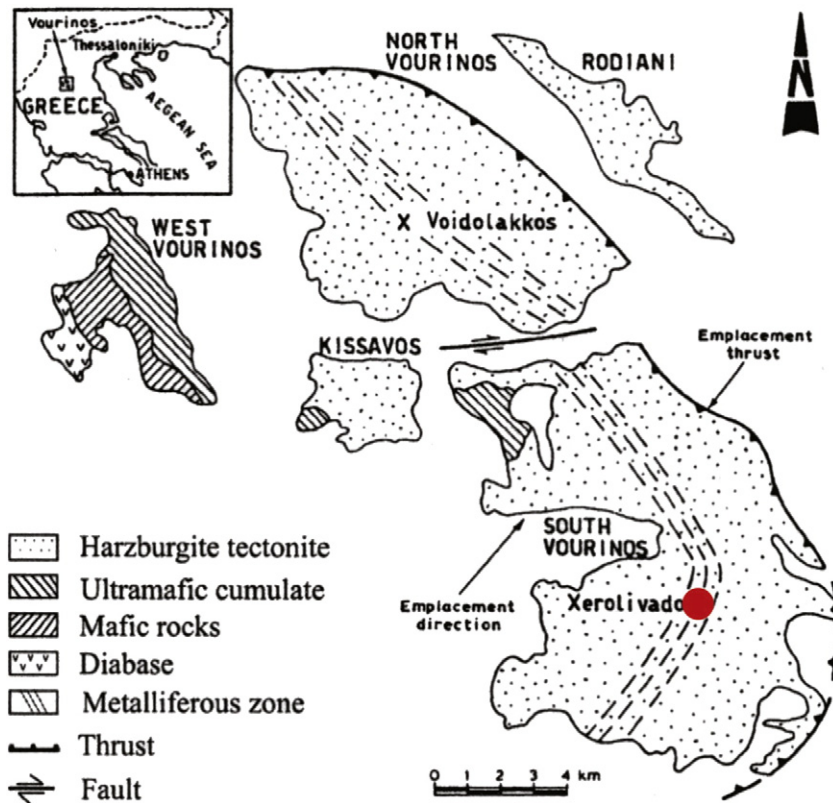


Fig. 1. Major units of the Vourinos ophiolite complex and location of the Xerolivado–Skoumtsas mine (red circle) (after Grivas et al., 1993).

Roeder and Campbell, 1985; Roeder and Reynolds, 1991; Michailidis, 1993, 1995; Peltonen, 1995; Filippidis, 1997; Kapsiotis, 2013). The purpose of the present investigation was the study of the substitution relations between bivalent and trivalent cations –with special emphasis on substitution of minor elements– in chromite from chromitite (ore) bands (spinel–spinel re-equilibration) and accessory chromite of host serpentinites (spinel–olivine re-equilibration) of the Xerolivado–Skoumtsas mine in the southern part of the Vourinos ophiolitic complex (Western Macedonia, Greece) (Fig. 1). We also examine whether these substitutions and the spatial distribution of the elements show any kind of pattern which could be useful for the implementation of a geochemical tool for chrome ore exploration. Geochemical anomaly maps of the major and minor element concentrations in chromite (following the

suggestions of Rassios and Kostopoulos, 1990) were constructed in effort to investigate their spatial distribution as an aid in chrome ore exploration. We propose that geochemical mapping could provide an added prospecting methodology that could significantly reduce the cost of exploratory drilling.

## 2. Geologic setting

### 2.1. The Vourinos ophiolite complex

The Vourinos Complex in northern Greece (Fig. 1) is a mid-Jurassic ophiolitic slab emplaced onto the Pelagonian continental margin during the upper Jurassic: its emplacement, long considered

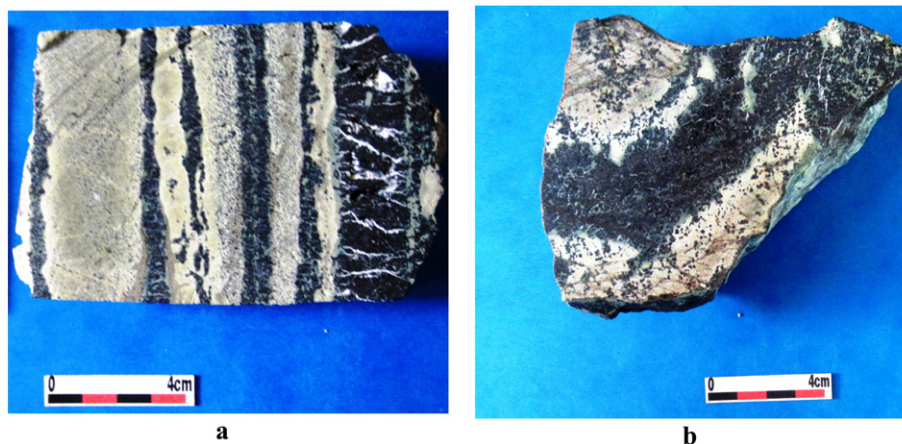
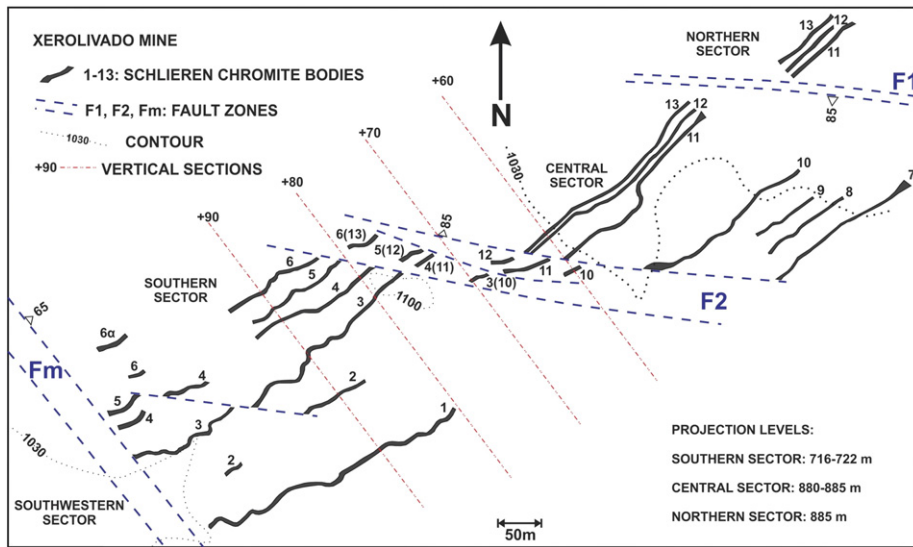
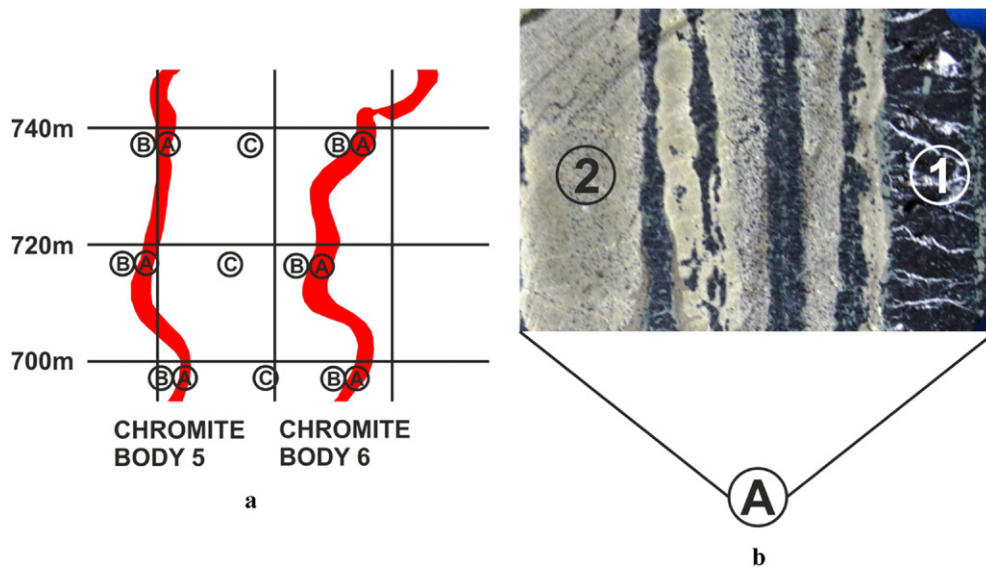


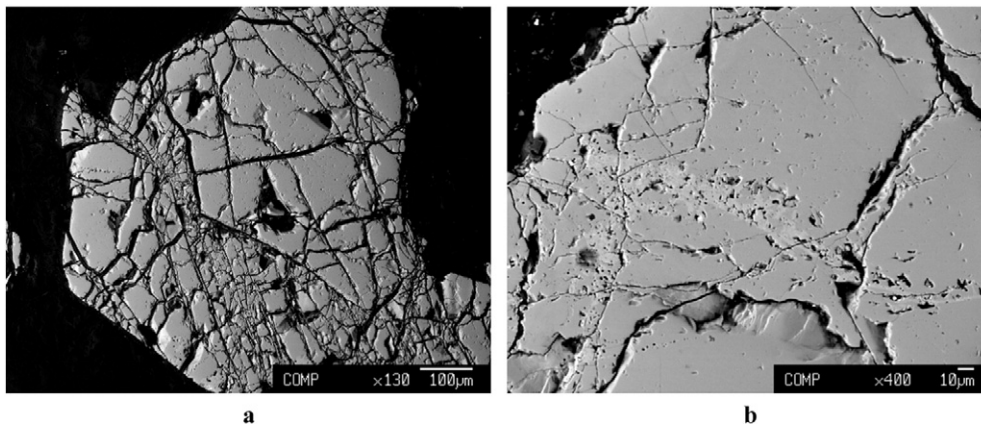
Fig. 2. Chrome ore samples from the Xerolivado–Skoumtsas mine showing (a) typical schlieren form (parallel dark-gray to black chromitite and serpentinitized dunite, oily bands) and (b) folded chromitite band.



**Fig. 3.** Distribution and form of the schlieren chromite ore bodies of the Vourinos Xerolivado–Skoumtsá mine (modified after Filippidis, 1996). Samples studied were collected from vertical section +90.



**Fig. 4.** Sampling methodology: (a) samples from chromitites (A), serpentinites near the chrome ore bodies (B) and between the chromitites (C). (b) Samples from chromitites: chromite band samples (1) and serpentine band samples (2).



**Fig. 5.** Back scattered electron images of chromite grains (gray) from the Xerolivado–Skoumtsá mine chromitite. (a) Pull apart texture, (b) pull apart texture, porous texture and alteration to Fe-chromite (light gray).



**Table 1**  
Representative microprobe analyses of chrome spinels from the Xerolivado Skoumtsa mine (wt.%).

Sample	C3/692	C3/717A	C4/765	C4/800	C5/692	C6/741	C3/750	C3/800	C4/692	C4/717A	C5/738	C6/692
Type <sup>a</sup>	1	1	1	1	1	1	2	2	2	2	2	2
SiO <sub>2</sub>	0.03	0.04	0.01	0.02	0.01	0.02	0.08	0.02	0.00	0.03	0.02	0.01
TiO <sub>2</sub>	0.12	0.15	0.13	0.15	0.14	0.14	0.16	0.17	0.14	0.14	0.16	0.14
Al <sub>2</sub> O <sub>3</sub>	8.67	9.05	9.29	9.69	8.86	9.85	11.83	11.39	8.61	8.14	9.94	8.24
Cr <sub>2</sub> O <sub>3</sub>	61.03	60.74	61.13	60.88	61.19	61.64	59.19	59.70	60.78	59.62	60.57	60.70
V <sub>2</sub> O <sub>3</sub>	0.09	0.12	0.09	0.10	0.07	0.09	0.11	0.09	0.11	0.09	0.10	0.11
Fe <sub>2</sub> O <sub>3</sub> <sup>b</sup>	4.20	3.87	3.61	3.09	4.19	2.90	2.77	2.92	4.42	4.63	3.55	4.09
FeO	11.45	11.65	12.49	13.57	11.62	12.20	13.27	13.57	14.09	16.04	12.99	15.39
MnO	0.03	0.06	0.09	0.03	0.04	0.04	0.06	0.07	0.09	0.12	0.08	0.14
MgO	14.25	14.16	13.75	13.15	14.26	14.11	13.60	13.41	12.74	11.14	13.58	11.70
NiO	0.07	0.04	0.05	0.05	0.04	0.06	0.11	0.08	0.01	0.05	0.06	0.05
CaO	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.00	0.00	0.01	0.00
ZnO	0.01	0.00	0.03	0.02	0.03	0.03	0.07	0.06	0.00	0.06	0.02	0.02
Total	99.96	99.87	100.68	100.75	100.45	101.09	101.23	101.47	100.98	100.06	101.08	100.60
<i>Structural formulae based on 32 (O)</i>												
Si	0.008	0.010	0.003	0.004	0.002	0.004	0.020	0.004	0.000	0.007	0.006	0.004
Ti	0.024	0.029	0.024	0.028	0.027	0.027	0.031	0.032	0.027	0.027	0.031	0.027
Al	2.645	2.759	2.817	2.942	2.689	2.961	3.535	3.406	2.631	2.541	2.999	2.547
Cr	12.487	12.424	12.436	12.405	12.455	12.434	11.864	11.982	12.457	12.483	12.260	12.592
V	0.019	0.025	0.020	0.022	0.015	0.019	0.022	0.018	0.022	0.019	0.021	0.024
Fe <sup>3+</sup>	0.818	0.753	0.700	0.599	0.812	0.556	0.528	0.558	0.863	0.923	0.683	0.807
Fe <sup>2+</sup>	2.478	2.520	2.688	2.924	2.502	2.604	2.813	2.882	3.055	3.552	2.781	3.376
Mn	0.007	0.012	0.020	0.007	0.009	0.010	0.012	0.015	0.019	0.028	0.017	0.031
Mg	5.498	5.459	5.275	5.053	5.474	5.367	5.139	5.075	4.924	4.397	5.184	4.577
Ni	0.015	0.008	0.010	0.010	0.007	0.013	0.023	0.016	0.002	0.010	0.013	0.011
Ca	0.001	0.001	0.000	0.002	0.002	0.000	0.001	0.003	0.000	0.001	0.001	0.001
Zn	0.001	0.000	0.006	0.005	0.006	0.006	0.012	0.010	0.000	0.013	0.004	0.003
<i>Cation ratios<sup>c</sup></i>												
Cr#	0.825	0.818	0.815	0.808	0.822	0.808	0.770	0.779	0.826	0.831	0.803	0.832
Mg#	0.689	0.684	0.662	0.633	0.686	0.673	0.646	0.638	0.617	0.553	0.651	0.576
Fe <sup>2+</sup> #	0.311	0.316	0.338	0.367	0.314	0.327	0.354	0.362	0.383	0.447	0.349	0.424
Fe <sup>3+</sup> #	0.051	0.047	0.044	0.038	0.051	0.035	0.033	0.035	0.054	0.058	0.043	0.051

<sup>a</sup> 1 = chrome spinel in chromitite ore layers, 2 = disseminated chrome spinel in serpentinized dunite within the ore bodies, 3 = disseminated chrome spinel in serpentinized dunite hosting the ore deposit, 4 = disseminated chrome spinel in serpentinized dunite lenses separating individual ore bodies within metalliferous zone (see Fig. 3).

<sup>b</sup> Measured as FeO and assumed based on stoichiometry.

<sup>c</sup> Cr# = Cr/(Cr + Al), Mg# = Mg/(Mg + Fe<sup>2+</sup>), Fe<sup>2+</sup># = Fe<sup>2+</sup>/(Fe<sup>2+</sup> + Mg) and Fe<sup>3+</sup># = Fe<sup>3+</sup>/(Fe<sup>3+</sup> + Cr + Al).

a “type” obduction process (Zimmerman, 1968, 1969), was toward the east (Smith and Rassios, 2003), over the Pelagonian Margin, creating a sedimentary-tectonic mélange (Agiou Nikolaos or Zavordas mélange, Rassios et al., 2008; Ghikas et al., 2010). The Vourinos ophiolite covers an area of ~400 km<sup>2</sup> and constitutes a complete ophiolite sequence dominated by mantle rocks and including a well-exposed “petrologic Moho” (Jackson et al., 1975). Even though the Vourinos ophiolite complex is separated from the nearby Pindos ophiolite by the Eocene–Miocene Mesohellenic Trough, both ophiolitic belts are considered to be outcropping parts of a huge unique ophiolitic nappe known as the Pindos Basin Ophiolites (Bortolotti et al., 2004; Rassios and Moores, 2006; Rassios et al., 2008; Grieco and Merlini, 2012).

The dominating petrological unit of Vourinos is its mantle section consisting of highly depleted harzburgite that has been variably serpentinized, grading from non-serpentinized to totally serpentinized (Moores and Vine, 1971; Ross et al., 1980). This harzburgite hosts abundant irregularly shaped dunite bodies. Some of the dunite bodies host chromitite ore bodies (Saccani et al., 2004; Bortolotti et al., 2004; Grieco and Merlini, 2012). All economically interesting chrome ore bodies at Vourinos are hosted by dunite within harzburgite (Grivas et al., 1993; Filippidis, 1996; Economou-Eliopoulos, 1996; Kapsiotis, 2014).

The crustal sequence of Vourinos consists of ultramafic and mafic cumulates, dykes of plagiogranite and pillow lavas that are overlain by Jurassic radiolarian cherts and Cretaceous carbonate sediments (Moores, 1969; Rassios and Moores, 2006).

The existence of multiple magma chambers was documented by Moores (1974), Rassios (1981) and Rassios et al. (1983): the consensus interpretation is that the Vourinos harzburgite represents mantle

residue remaining after a high degree of partial melting (Moores, 1969; Jackson et al., 1975; Harkins et al., 1980; Beccaluva et al., 1984; Paraskevopoulos and Economou, 1986; Konstantopoulou and Economou-Eliopoulos, 1991).

The initial precipitation of chrome spinel in dunite occurred at about 1300 °C with re-equilibration between spinel and silicate phases (primarily olivine) continuing down to temperatures as low as 600 °C (Rassios and Kostopoulos, 1990). The predominant processes of the structural evolution and deformation that affected chrome ore-bearing dunite bodies were: a) dunite and chromite formation within the upper mantle, b) high-temperature plastic deformation resulting from mantle flow, c) low-temperature plastic to semi-brittle deformation during incipient obduction that resulted in folding of dunite and ore bodies and d) brittle deformation (faults and thrusts) displacing the dunitic and chromite ore bodies as the ophiolite passed from ductile to brittle conditions, and e) late (Tertiary to present) tectonism (Ross et al., 1980; Roberts et al., 1988; Konstantopoulou, 1993; Filippidis, 1996, 1997; Smith and Rassios, 2003; Grieco and Merlini, 2012).

The chrome ore deposits found at Vourinos were exploited in the post WWII era, and the mines were closed in 1991 due to economic fluctuation in the world price of chrome. The geologic ore reserves at Vourinos are estimated to be about 12.5 million tons (Stamoulis, 1990). Verified (via back-up drilling) chrome ore reserves are over 2,500,000 tons and are mainly found in the following localities: Xerolivado–Skoumtsa (1,000,000 tons), Aetoraches (500,000 tons), Rizo (400,000 tons), Koursoumia (250,000 tons), Voidolakkas (200,000 tons) and Kerasitsa (500,000 tons). The location of geologically predicted ore continuations at Xerolivado would raise tonnage estimates to 5 million tons.

D3/739	D3/800	D4/717A	D4/765	D5/766	D6/717	D2-3/692	D2-3/800	D3-4/717	D3-4/754	D4-5/765	D5-6/738
3	3	3	3	3	3	4	4	4	4	4	4
0.03	0.04	0.03	0.03	0.02	0.02	0.03	0.07	0.03	0.03	0.02	0.04
0.13	0.13	0.14	0.15	0.14	0.12	0.15	0.13	0.16	0.15	0.15	0.18
9.69	11.00	9.90	11.01	10.42	8.32	12.11	10.97	9.11	12.18	11.17	10.53
59.33	57.18	57.11	57.53	58.09	58.76	56.26	57.53	59.07	57.90	57.74	58.06
0.12	0.14	0.18	0.16	0.13	0.17	0.18	0.21	0.11	0.15	0.15	0.13
3.88	3.60	4.55	3.65	4.00	4.73	2.84	3.36	3.84	2.27	3.09	3.35
15.64	17.23	16.84	16.86	16.59	16.31	17.16	17.87	16.22	16.70	17.81	17.16
0.13	0.17	0.16	0.14	0.13	0.19	0.17	0.17	0.19	0.16	0.15	0.16
11.68	10.63	10.62	10.97	11.14	10.81	10.71	10.31	11.03	11.26	10.42	10.67
0.06	0.08	0.05	0.07	0.06	0.04	0.02	0.07	0.07	0.05	0.05	0.04
0.01	0.02	0.02	0.00	0.01	0.00	0.02	0.01	0.00	0.01	0.01	0.01
0.10	0.10	0.21	0.16	0.10	0.12	0.13	0.17	0.08	0.16	0.12	0.16
100.79	100.31	99.80	100.72	100.84	99.60	99.78	100.86	99.89	101.02	100.89	100.48
0.008	0.011	0.007	0.009	0.006	0.007	0.007	0.019	0.007	0.009	0.006	0.010
0.025	0.026	0.027	0.029	0.028	0.024	0.030	0.025	0.031	0.029	0.030	0.035
2.973	3.392	3.086	3.378	3.197	2.612	3.733	3.375	2.836	3.698	3.431	3.248
12.211	11.833	11.937	11.837	11.958	12.372	11.633	11.876	12.340	11.794	11.897	12.019
0.024	0.029	0.038	0.033	0.027	0.037	0.037	0.044	0.023	0.030	0.032	0.028
0.759	0.709	0.906	0.715	0.783	0.947	0.560	0.661	0.763	0.440	0.605	0.660
3.405	3.772	3.722	3.669	3.613	3.632	3.754	3.902	3.583	3.597	3.882	3.757
0.029	0.037	0.035	0.031	0.028	0.043	0.039	0.038	0.042	0.035	0.034	0.036
4.533	4.149	4.185	4.256	4.325	4.292	4.174	4.012	4.345	4.324	4.048	4.166
0.012	0.018	0.010	0.014	0.013	0.009	0.003	0.015	0.014	0.011	0.011	0.009
0.002	0.004	0.006	0.001	0.002	0.001	0.006	0.001	0.001	0.002	0.002	0.002
0.020	0.020	0.042	0.030	0.019	0.024	0.024	0.032	0.015	0.030	0.022	0.030
0.804	0.777	0.795	0.778	0.789	0.826	0.757	0.779	0.813	0.761	0.776	0.787
0.571	0.524	0.529	0.537	0.545	0.542	0.527	0.507	0.548	0.546	0.511	0.526
0.429	0.476	0.471	0.463	0.455	0.458	0.473	0.493	0.452	0.454	0.489	0.474
0.048	0.044	0.057	0.045	0.049	0.059	0.035	0.042	0.048	0.028	0.038	0.041

## 2.2. The Xerolivado–Skoumtsa Chrome Mine

The largest chromitiferous dunite body of the Vourinos Complex occurs at the Xerolivado locality (Fig. 1). The dunite body has an approximate surface exposure of 3 km<sup>2</sup> (3 × 1 km), and extends at least 400 m into the subsurface. The dunite is hosted by harzburgite tectonite interfolded with the dunite body during ductile phases of deformation. Harzburgite lenses within these folds have lengths up to 300 m, striking NE–SW (Apostolidis et al., 1980; Roberts et al., 1988; Stamoulis, 1990; Filippidis, 1996, 1997). The Xerolivado–Skoumtsa mine is one of the world's largest “ophiolite-hosted” chrome deposits with a potential of 6 million tons of ore assaying at ~22 wt.% Cr<sub>2</sub>O<sub>3</sub> (Stamoulis, 1990; Filippidis, 1997). Even so, chrome ore bodies compose less than 1% of the volume of the dunite, and their exploration consisted chiefly of expensive drilling programs.

The chromite ore itself is a type called “schlieren” ore, consisting of highly intra-deformed bands of serpentine-rich and chromite-rich rock (Fig. 2). Each spinel-rich band varies from one to fifteen cm in thickness (Stamoulis, 1990; Filippidis, 1996).

Three Tertiary-aged normal fault zones (F1, F2 and Fm) divide the Xerolivado mine into four sectors: the northern, the central, the southern and the southwestern (Fig. 3). These fault-bordered zones demonstrate dislocation and down-throw of the ultramafic body and ore bodies to the SW with horizontal and vertical offset (Stamoulis, 1990; Filippidis, 1996, 1997):

Chrome ores occur in seven extensive ore bodies located in the southern sector and continue in the central sector. Three of the schlieren ore bodies also continue in the northern sector; because of structural evidence, the southern ore bodies are predicted to continue into the

southwestern sector at a greater depth, with a possible future for renewed exploitation.

Within the Xerolivado dunite body, serpentinization is so pervasive that only relict grains of olivine can be found within the ore bodies.

## 3. Materials and methods

Samples used in the present study come from a well-documented suite collected during the final years of operation of the Xerolivado–Skoumtsa mine (1987–1988). The collection includes seventy-one (71) samples of: chromitite (20 from chromite ores and 20 from serpentine bands, gangue within the ore bodies) and serpentinite (31 samples). Most samples were taken on (or near) the same vertical section of the southern sector of the mine (Fig. 3) and the sampling scheme presented in Fig. 4 includes:

1. Chromitite, the chief constituent of the schlieren-type chrome ore bodies (A1).
2. Serpentinite: altered primary dunite tectonically included within the schlieren ore body zones (A2).
3. Serpentinite from the hosting dunite body adjacent to and surrounding the chrome ore bodies (B).
4. Serpentinite lenses from the hosting dunite body interfolded with the ore bodies, which appear as “layers” between the chrome rich ore bodies (C).

For each sample, a thin-polished section was mounted and studied under optical microscopes using both transmitted and reflected light. Back scattered electron images (BSI) were then taken (Fig. 5) and major and minor oxides were analyzed from all samples with a JEOL

**Table 2**  
Average and standard deviation (STDEV) data for the parameters examined for chromites of the Xerolivado–Skoumtsa mine.

Type <sup>a</sup>	A1		A2		B		C	
	AVERAGE	STDEV	AVERAGE	STDEV	AVERAGE	STDEV	AVERAGE	STDEV
SiO <sub>2</sub>	0.05	0.08	0.03	0.02	0.03	0.01	0.03	0.01
TiO <sub>2</sub>	0.14	0.01	0.15	0.02	0.14	0.02	0.14	0.02
Al <sub>2</sub> O <sub>3</sub>	9.60	1.10	9.42	1.11	10.28	1.10	10.53	0.91
Cr <sub>2</sub> O <sub>3</sub>	60.66	0.71	60.30	0.65	57.81	0.93	57.95	1.00
V <sub>2</sub> O <sub>3</sub>	0.09	0.01	0.10	0.02	0.15	0.03	0.16	0.03
Fe <sub>2</sub> O <sub>3</sub>	3.61	0.70	3.67	0.70	4.04	0.60	3.41	0.61
FeO	12.52	1.08	14.10	1.10	16.72	0.79	16.94	0.82
MnO	0.06	0.02	0.09	0.03	0.16	0.02	0.16	0.02
MgO	13.75	0.72	12.69	0.80	10.93	0.48	10.79	0.49
NiO	0.07	0.03	0.07	0.03	0.06	0.01	0.04	0.02
CaO	0.02	0.04	0.01	0.01	0.01	0.01	0.01	0.02
ZnO	0.03	0.03	0.04	0.03	0.12	0.04	0.14	0.04
Si	0.012	0.020	0.007	0.005	0.008	0.003	0.009	0.004
Ti	0.028	0.003	0.028	0.003	0.027	0.004	0.028	0.004
Al	2.907	0.314	2.874	0.311	3.170	0.317	3.250	0.267
Cr	12.335	0.199	12.352	0.204	11.967	0.235	12.006	0.232
V	0.020	0.003	0.022	0.004	0.031	0.006	0.034	0.007
Fe <sup>3+</sup>	0.699	0.138	0.716	0.142	0.797	0.123	0.672	0.123
Fe <sup>2+</sup>	2.694	0.246	3.058	0.264	3.661	0.173	3.712	0.181
Mn	0.013	0.005	0.020	0.007	0.035	0.005	0.035	0.005
Mg	5.270	0.248	4.899	0.267	4.267	0.180	4.213	0.188
Ni	0.014	0.005	0.014	0.005	0.012	0.003	0.009	0.003
Ca	0.005	0.010	0.002	0.002	0.003	0.002	0.004	0.005
Zn	0.006	0.005	0.008	0.005	0.023	0.009	0.027	0.007
Cr#	0.809	0.019	0.811	0.019	0.791	0.020	0.787	0.017
Mg#	0.662	0.031	0.616	0.033	0.538	0.022	0.532	0.023
Fe <sup>2+</sup> #	0.338	0.031	0.384	0.033	0.462	0.022	0.468	0.023
Fe <sup>3+</sup> #	0.044	0.009	0.045	0.009	0.050	0.008	0.042	0.008

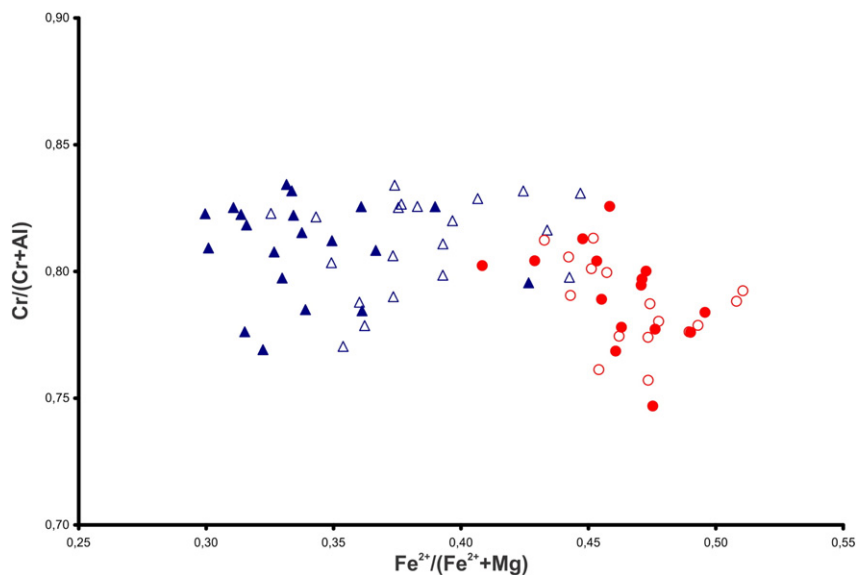
<sup>a</sup> A1 = chrome spinel in chromitite ore layers, A2 = disseminated chrome spinel in serpentinized dunite within the ore bodies, B = disseminated chrome spinel in serpentinized dunite hosting the ore deposit, C = disseminated chrome spinel in serpentinized dunite lenses separating individual ore bodies within metalliferous zone (see Fig. 3).

8200 electron microprobe equipped with a wavelength dispersive system (SEM-WDS) at the University of Milan. The system used an accelerating voltage of 15 kV, a sample current on brass of 15 nA, a counting time of 20 s on the peaks and 10 s on the background. A series of natural minerals was used as standards. For each sample, four to fifteen spots of unaltered chromite grains were analyzed and their compositions averaged to produce a statistically result.

Representative chemical analyses of chromites from twenty-four sampling sites are given in Table 1. The FeO and Fe<sub>2</sub>O<sub>3</sub> concentrations

were calculated from total iron assuming perfect spinel stoichiometry (RO:R<sub>2</sub>O<sub>3</sub> = 1:1). Table 2 presents the average and standard deviation data for the measured parameters. The database of these analyses was used for the construction of the diagrams in Figs. 6 to 13 which represent projections within the spinel prism after (Irvine, 1967).

The exact location of all samples and the distance of the serpentinite samples are from the underground mining tunnels. GPS location was retro-fitted to the sample localities onto the underground database and the position of the chromite bodies were measured on the sampling



**Fig. 6.** Relation between Fe<sup>2+</sup># and Cr# values of the chromites from the Xerolivado–Skoumtsa mine. Closed triangles = chrome spinel in chromitite ore layers, open triangles = disseminated chrome spinel in serpentinized dunite within the ore bodies, closed circles = disseminated chrome spinel in serpentinized dunite hosting the ore deposit, open circles = disseminated chrome spinel in serpentinized dunite lenses separating individual ore bodies within metalliferous zone.

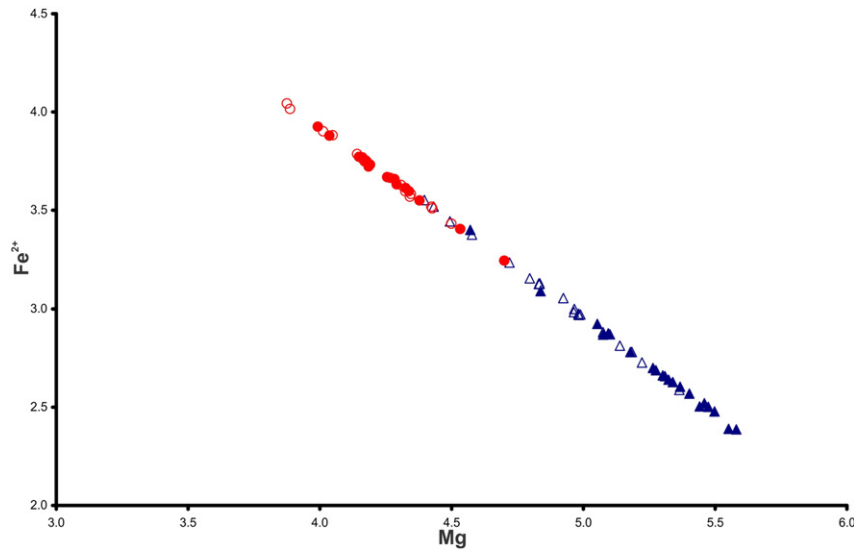


Fig. 7. Relation between Mg and  $\text{Fe}^{2+}$  cations of the chromites from the Xerolivado–Skoumtsa mine. Symbols as in Fig. 6.

maps by the use of CoreDRAW X5 software. Microprobe analysis data and spatial information data were entered in ORIGIN software for the creation of the geochemical maps which are presented in Figs. 14 to 17. The parameter “total points increase factor” was set at value 10,000 and parameter “Smoothing parameter” was set at value 0.0001.

## 4. Results

### 4.1. Petrography

The chromitite samples of the Xerolivado mine are typical of schlieren or banded type chrome ores: schlieren ore consists of irregular lense-shaped disseminations of chromite in a dunite (now serpentinite) matrix. These lensing structures were created by initial high-temperature ductile deformation. The chromite-rich bands (dark gray color) alternate with the serpentine bands (oily green color) (Fig. 2a). Each band is 1 to 15 cm thick and the lithologic alternations are, in most cases, parallel or sub-parallel on hand sample scale. In

many samples, banding displays folds, a continuation of deformation (Fig. 2b).

Microscopic examination of the schlieren chromitites shows that the chromitite bands of the samples are dominated (>70% modal) by interpenetrating chromite grains. Chromites display a much younger pull-apart texture imprinting the high-temperature tectonic events they have undergone (Fig. 5). Serpentine bands of the samples are dominated by the presence of serpentine having a typical mesh texture, a relict of the shapes of olivine grains in the original dunite. Disseminated chromite grains (~5–10% modal) are also found in the serpentine lenses within the ore bodies.

### 4.2. Chromite mineral chemistry

#### 4.2.1. Major elements

The cation number (based on 32 oxygens) of the major elements (Mg and  $\text{Fe}^{2+}$ ) occupying the tetrahedral sites in the chrome spinel lattice shows an opposite trend in the Xerolivado–Skoumtsa mine

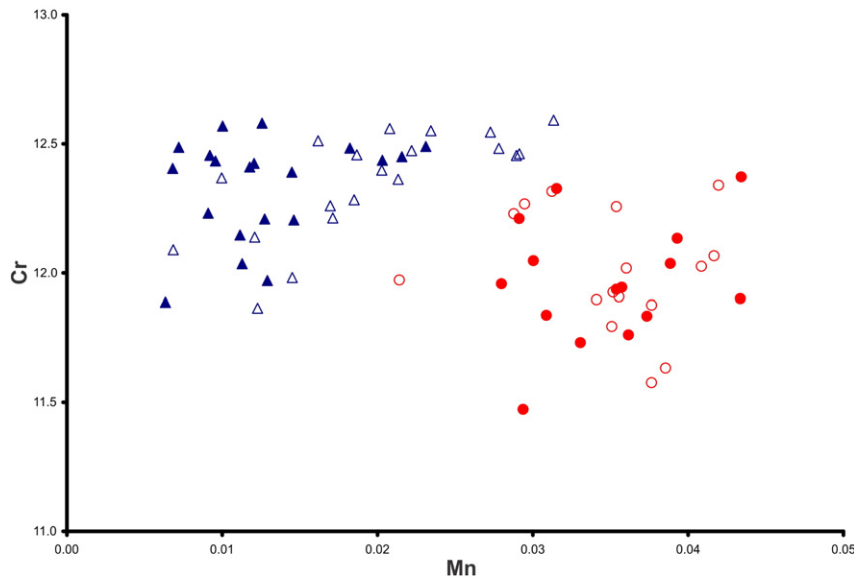


Fig. 8. Relation between Mn and Cr cations of the chromites from the Xerolivado–Skoumtsa mine. Symbols as in Fig. 6.

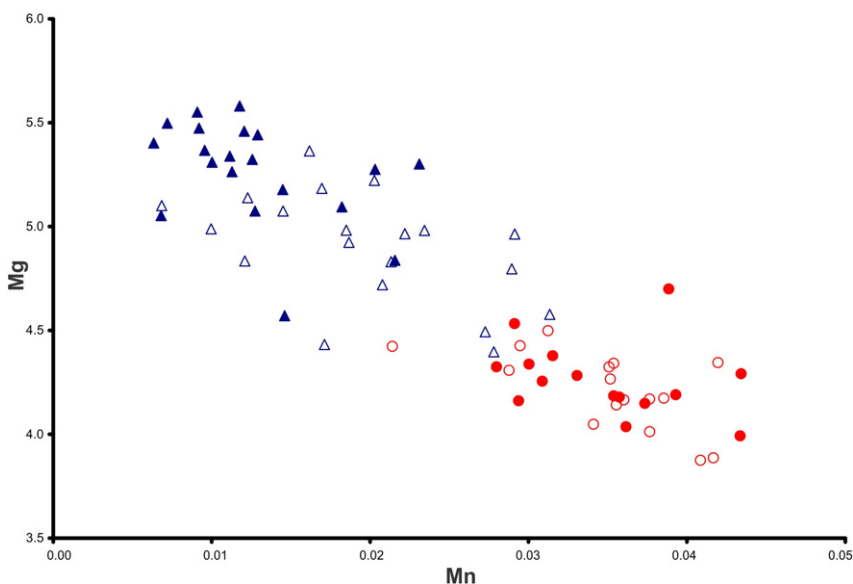


Fig. 9. Relation between Mn and Mg cations of the chromites from the Xerolivado–Skoumtsá mine. Symbols as in Fig. 6.

(also see Table 2). The average Mg cation number is  $5.270 \pm 0.248$  in the concentrated spinels (ore bands) and gradually decreases to an average of  $4.213 \pm 0.188$  among the disseminated chromites in the serpentine lenses that separate the ore bodies.  $\text{Fe}^{2+}$  is the lowest within the chrome ores ( $2.694 \pm 0.246$ ), and gradually increases to  $3.712 \pm 0.181$  among the disseminated chromites in the serpentinites between the ore bodies.

The cation number of the major elements (Cr, Al and  $\text{Fe}^{3+}$ ) occupying the octahedral sites in the lattice of chromites shows the following averages in the Xerolivado–Skoumtsá mine (also see Table 3):

- Cr decreases from  $12.335 \pm 0.199$  in the spinels concentrated within ore bodies, to  $11.967 \pm 0.235$  in disseminated chromites in the serpentine gangue within the ore bodies, and  $12.006 \pm 0.232$  in the disseminated chromites in the serpentinites that separate individual ore bodies.

- Al shows an average value of  $2.907 \pm 0.314$  in chromite within schlieren ore bodies, and gradually increases to an average of  $3.250 \pm 0.267$  in the serpentinites separating the ore bodies.
- $\text{Fe}^{3+}$  has an average of  $0.699 \pm 0.138$  in chromite in schlieren ores,  $0.716 \pm 0.142$  in the disseminated chromites in the serpentine bands within ore bodies,  $0.797 \pm 0.123$  in disseminated chromites in the serpentinites adjacent to the chromite ore bodies and  $0.672 \pm 0.123$  in disseminated chromites in the serpentine lenses separating the chromites.

Fig. 6 depicts the  $\text{Fe}^{2+}\#$  vs. Cr# relation for the Cr-spinels of the Xerolivado–Skoumtsá mine. Chromites from spinel-rich chromitite ores clearly show lower  $\text{Fe}^{2+}\#$  values than chromites in host serpentinite. This observation has also been shown in studies of the Rhum Intrusion (Scotland), Bushveld (S. Africa), Bird River Sill (Canada) (Henderson, 1975; Cameron, 1977; Henderson and Wood,

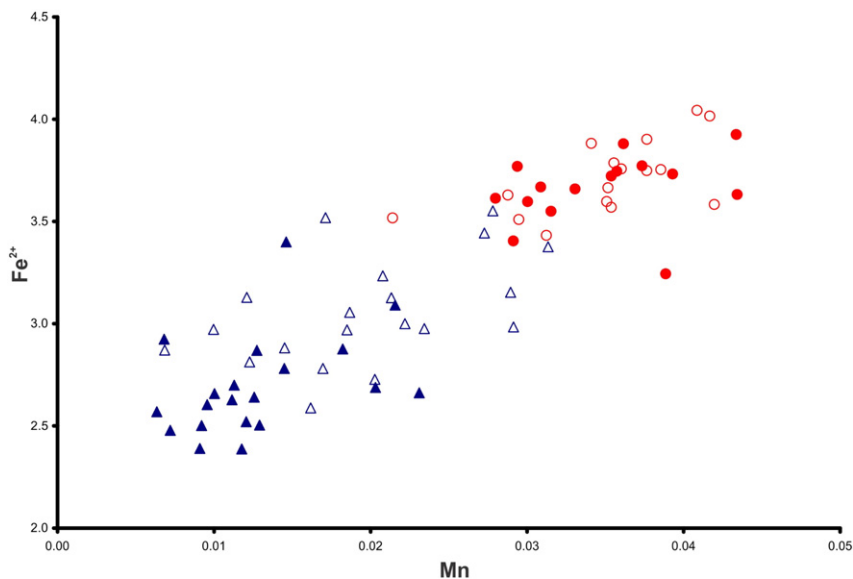


Fig. 10. Relation between Mn and  $\text{Fe}^{2+}$  cations of the chromites from the Xerolivado–Skoumtsá mine. Symbols as in Fig. 6.



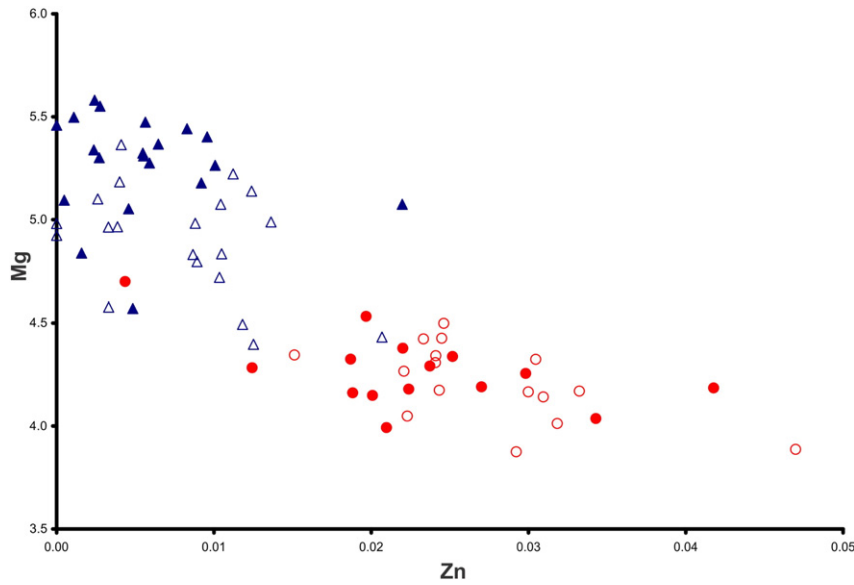


Fig. 11. Relation between Zn and Mg cations of the chromites from the Xerolivado–Skoumtsa mine. Symbols as in Fig. 6.

1981; Hatton and von Gruenewaldt, 1985; Ohnenstetter et al., 1986) and locally at the central sector of the Xerolivado mine (Filippidis, 1997). This result is also shown in Fig. 7, where the negative correlation between  $\text{Fe}^{2+}$  and Mg cations in chromite is presented.

#### 4.2.2. Minor elements

The cation number of some minor elements (V, Mn and Zn) shows significant variations between different categories of samples. Vanadium, manganese and zinc contents appear the lowest in spinels within the chrome ore schlieren bands:  $0.020 \pm 0.003$ ,  $0.013 \pm 0.005$  and  $0.006 \pm 0.005$  respectively. The average values are slightly higher in disseminated chromites in the serpentine bands within the ores,  $0.022 \pm 0.004$ ,  $0.020 \pm 0.007$  and  $0.008 \pm 0.005$  respectively. For the disseminated chromites in the host serpentinites adjacent to the ore layers the average values are  $0.031 \pm 0.006$ ,  $0.035 \pm 0.005$  and  $0.023 \pm 0.009$  respectively. The highest average contents of V, Mn, and Zn of the studied samples are in disseminated chrome spinels in serpentinite lenses separating

the ore bodies, with compositions of:  $0.034 \pm 0.007$ ,  $0.035 \pm 0.005$  and  $0.027 \pm 0.007$  respectively.

The correlations between minor and major elements of the samples are presented in Figs. 8 to 13; Mn cations do not show a clear correlation with Cr cations (Fig. 8) but show a negative correlation with Mg cations (Fig. 9) and a positive one with  $\text{Fe}^{2+}$  cations (Fig. 10). Zn cations also correlate positively with Mg cations (Fig. 11) and negatively with  $\text{Fe}^{2+}$  cations (Fig. 12) whereas, V cations correlate negatively with Cr cations (Fig. 13).

#### 4.3. Geochemical maps

The sampling scheme of this study provided an excellent coverage of some of the chief underground ore bodies: samples taken along the same vertical section of the mine were referenced on the topographic map. As Rassios and Kostopoulos (1990) demonstrated, chromite samples are dominated by chromite–chromite re-equilibration, while the disseminated spinels in what was originally dunite, owe their

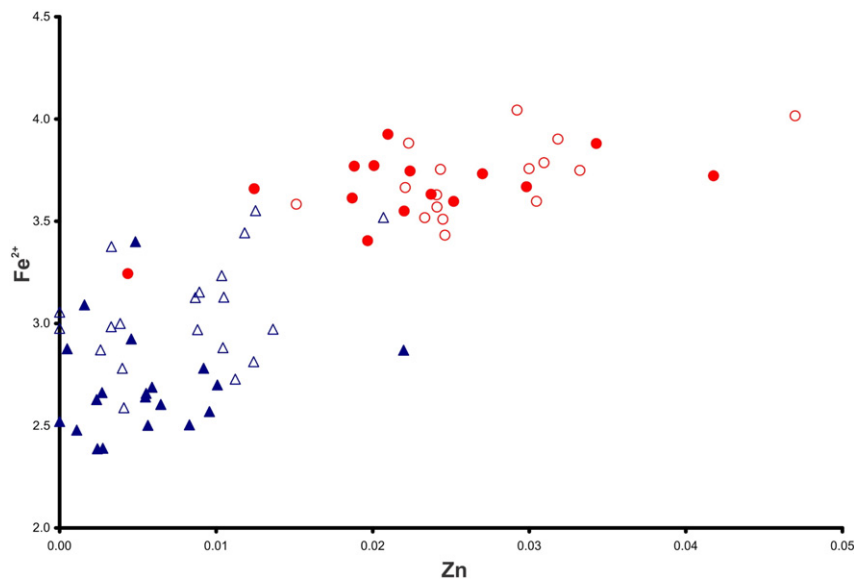


Fig. 12. Relation between Zn and  $\text{Fe}^{2+}$  cations of the chromites from the Xerolivado–Skoumtsa mine. Symbols as in Fig. 6.

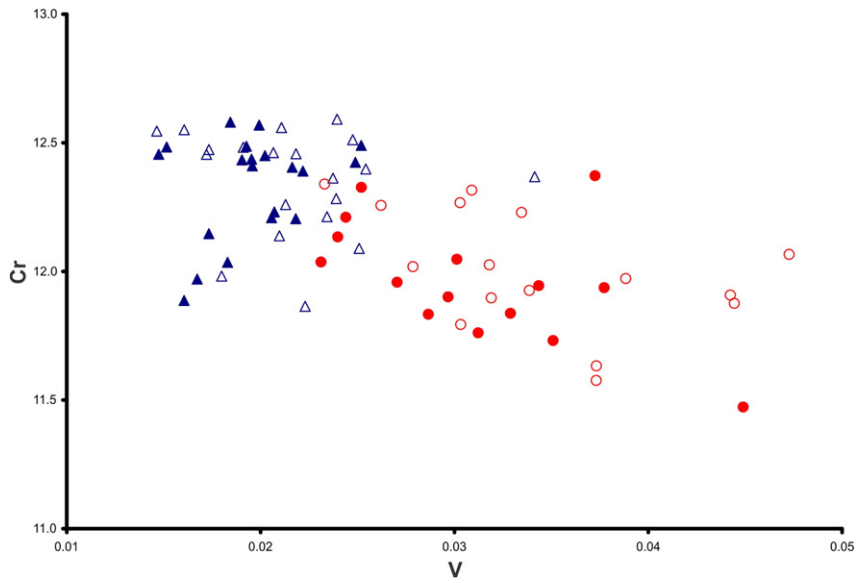


Fig. 13. Relation between V and Cr cations of the chromites from the Xerolivado–Skoumtsas mine. Symbols as in Fig. 6.

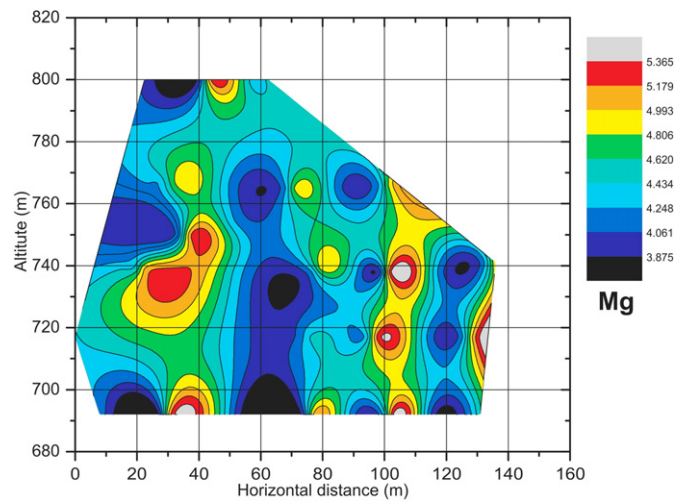
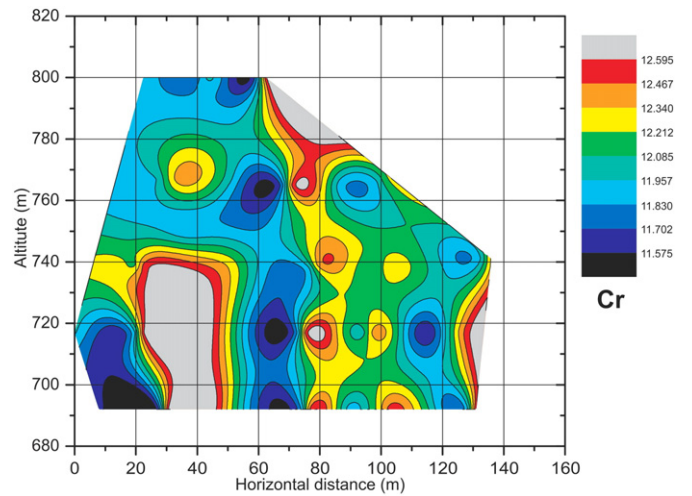
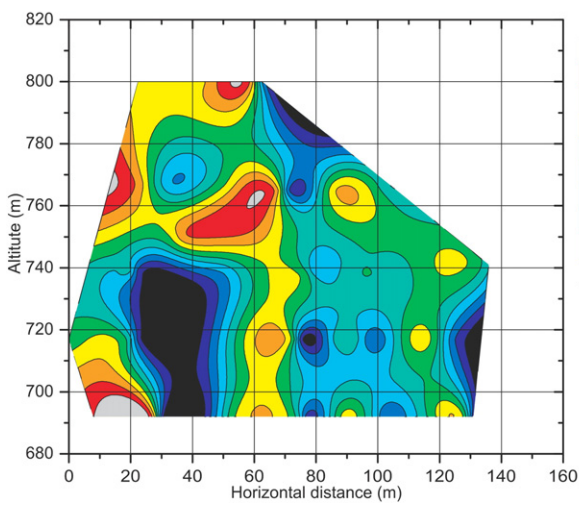
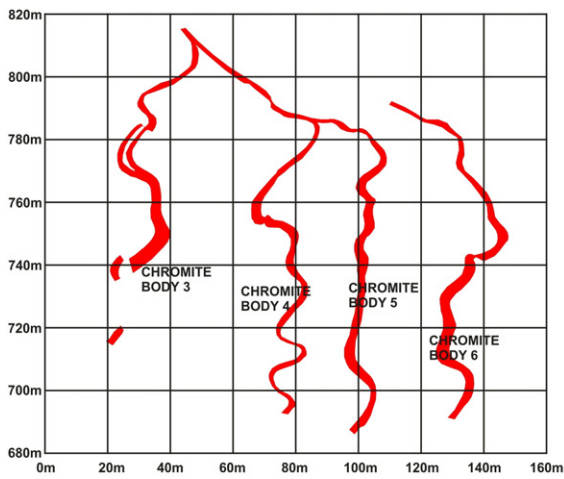
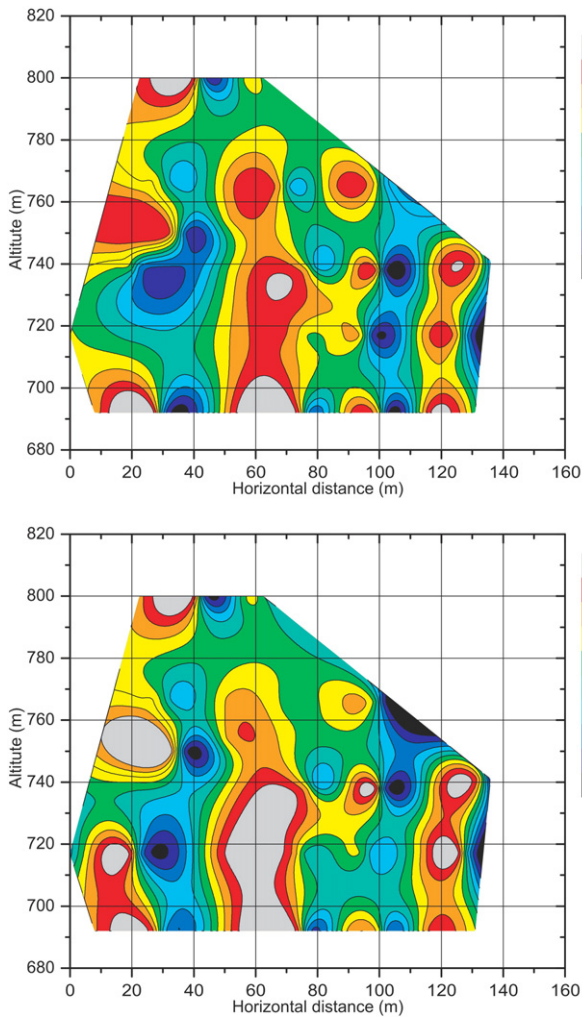


Fig. 14. Upper figure: Vertical section from which samples were collected showing the actual position of chrome ore bodies (digitized after Stamouliis, 1990). Lower figure: Geochemical map of the studied vertical section of the Xerolivado–Skoumtsas mine for Al cations.

Fig. 15. Geochemical maps of the studied vertical section of the Xerolivado–Skoumtsas mine for Cr (upper) and Mg (lower) cations.



**Fig. 16.** Geochemical maps of the studied vertical section of the Xerolivado–Skoumtsas mine for  $\text{Fe}^{2+}$  (upper) and Mn (lower) cations.

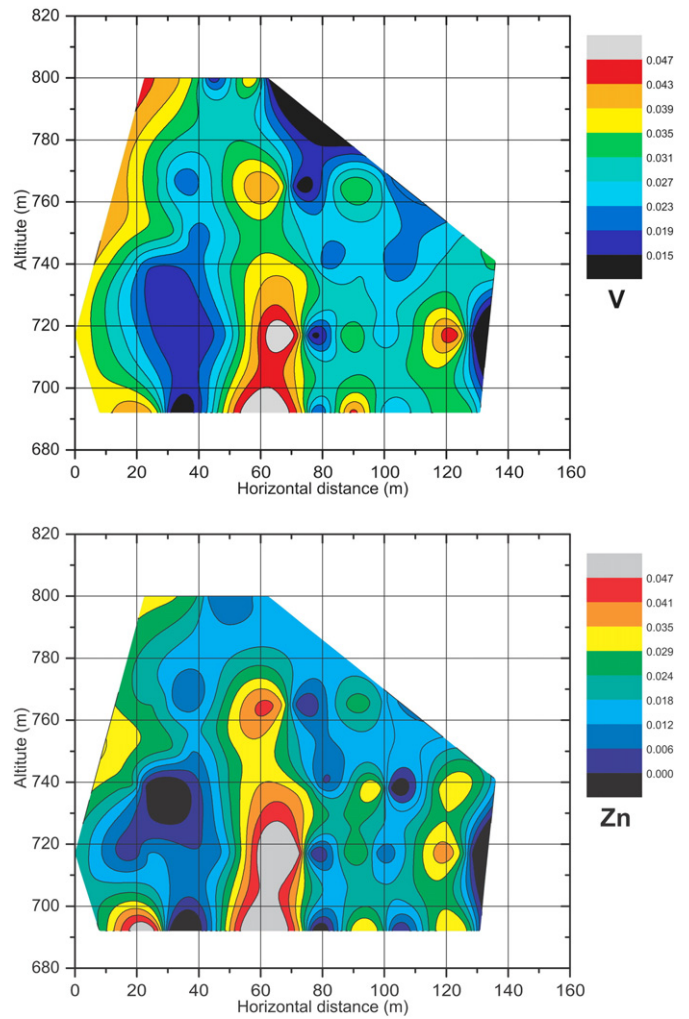
compositions to spinel–silicate (olivine) re-equilibration. By excluding the chromitite analyses and using only the disseminated chromite analyses found in the serpentine bands of the schlieren ore samples and accessory chromite in the serpentinite samples, we created geochemical maps of oxides of the elements and compared them with the spatial distribution of the chromite bodies.

Figs. 14 to 17 present geochemical anomaly maps for the vertical section of the Xerolivado–Skoumtsas mine defined for the variations in Al, Cr, Mg,  $\text{Fe}^{2+}$ , Mn, V and Zn cations present in disseminated and accessory chromite.

## 5. Discussion

### 5.1. MgO and FeO

Microprobe analysis results show that chromites in different sample types show gradual differences in Mg and  $\text{Fe}^{2+}$  contents. Similar results were found by Filippidis (1997) in analyses of chromites of the central sector of the Xerolivado mine. The variations in Mg and Fe concentrations are attributed to subsolidus reactions between chromite and silicate mineral phases. Subsidiary reactions, mainly displayed by divalent cations, explain the compositional variations in chromite previously studied by Hamlyn and Keays (1979), Wilson (1982), Yang and Secombe (1993), Peltonen (1995), and Filippidis (1997). According to Irvine (1967), changes in the chromite composition due to subsolidus reactions depend on the amount of chromite present (Rassios and



**Fig. 17.** Geochemical maps of the studied vertical section of the Xerolivado–Skoumtsas mine for V (upper) and Zn (lower) cations.

Kostopoulos, 1990). This is clearly confirmed by the microprobe results since in serpentinites the mineral chemistry of chromites from the Xerolivado mine showed that the most intense substitution of Mg by  $\text{Fe}^{2+}$  during re-equilibration took place in the olivine phases (now serpentinitized) separating the chrome ore bodies. This substitution was slightly less intense in the dunite near the ore bodies, and clearly less intense in the chromitites themselves; the substitution of Mg by  $\text{Fe}^{2+}$  appears to be more efficient in dunite (now serpentinite bands with disseminated chromite) than the chromite bands of the schlieren ore. This result is graphically presented in Fig. 7, showing the competitive relation between Mg and  $\text{Fe}^{2+}$  cations.

**Table 3**

Average data for the major element parameters examined for chromites of the Xerolivado–Skoumtsas mine.

Type <sup>a</sup>	A1	A2	B	C
$\text{Fe}^{2+}$ cations	2.694	3.058	3.661	3.712
Mg cations	5.270	4.899	4.267	4.213
Cr#	0.809	0.811	0.791	0.787
Mg#	0.662	0.616	0.538	0.532
$\text{Fe}^{2+}$ #	0.338	0.384	0.462	0.468
$\text{Fe}^{3+}$ #	0.044	0.045	0.050	0.042

<sup>a</sup> A1 = chrome spinel in chromitite ore layers, A2 = disseminated chrome spinel in serpentinitized dunite within the ore bodies, B = disseminated chrome spinel in serpentinitized dunite hosting the ore deposit, C = disseminated chrome spinel in serpentinitized dunite lenses separating individual ore bodies within metalliferous zone (see Fig. 3).

## 5.2. Minor oxides

Concentration of MnO in chrome spinels of Alpine-type chrome ore deposits does not generally exceed 1.00 wt.% (Scarpelis and Economou, 1978; Economou, 1984; Migiros and Economou, 1988; Michailidis, 1993; Michailidis et al., 1995; Michailidis and Sklavounos, 1996). Higher concentrations of MnO in ophiolites have only been reported for altered chromites (i.e. Paraskevopoulos and Economou, 1980; Michailidis, 1990, 1993). In the Xerolivado–Skoumtsa mine, the concentration of MnO (wt.%) is lowest in the chrome spinels of the chrome ores (chromitites), and the highest average values are found in the disseminated chromites within the serpentinites. The disseminated chromites in the serpentine gangues within the schlieren layers show an intermediate value. These relations suggest the effectiveness of re-equilibration of MnO between olivine and spinel.

Figs. 8, 9 and 10 demonstrate the relations between Mn and Cr, Mg, Fe<sup>2+</sup> cations for the chromites of the Xerolivado mine. Fig. 8 shows a slight negative correlation between Mn and Cr cations, Fig. 9 shows a clear negative correlation between Mn and Mg cations and Fig. 10 shows a clear positive correlation between Mn and Fe<sup>2+</sup> cations. From these relations, we may assume that during re-equilibration between chromite and silicates, Mn mainly substitutes for Mg in the lattice of chromite but also possibly substitutes some Cr in the octahedral sites. Further verification of this assumption, however, can only be given by measuring the valence number of Mn.

Zn also shows particularly interesting variations in the Xerolivado mine chromites. Spinel in chromitites have the lowest average values of ZnO. Spinel in serpentinites have ~3 to 4 times higher average wt.% concentration in ZnO. Figs. 11 and 12 depict the relations between Zn and Mg, Fe<sup>2+</sup> cations in spinels of the Xerolivado mine. The negative correlation between Zn and Mg cations and the positive correlation between Zn and Fe<sup>2+</sup> cations show that Zn also behaves antagonistically, similar to Fe<sup>2+</sup>, and substitutes for Mg during re-equilibration.

The relation between V and Cr cations is presented in Fig. 13. A negative correlation between these two elements is verified. Chrome spinels in the ores of Xerolivado–Skoumtsa mine contain on average almost 2 times less V than spinels in hosting serpentinites. During re-equilibration processes, available V substitutes for Cr in the chromite lattice.

Thus, we have demonstrated that Cr-spinels in serpentinites contain more Mn, Zn and V than spinels in chrome ores (Figs. 8–13). There appears a slight variation in the presence of the latter elements within spinels in chromitite (schlieren ores) as follow; spinels in the chromitite ore layers contain less Mn, Zn and V than spinels in the serpentinitized dunite bands within the schlieren ore bodies. These differences in the concentrations of the elements can be explained by assuming that where the availability of silicates was higher and the amount of chromite lower, Cr and Mg substitution during re-equilibration was more effective, leading to a higher exchange of Mn, Zn and V into chromites.

## 5.3. Geochemical application of chromite chemistry

The chemical variations in major and minor oxides and consequently in cations found in the Xerolivado mine chromites could provide a useful tool for the exploration of ophiolite hosted chrome bodies, in particular those in which the morphology of ore bodies are a result of ductile tectonic conditions. We can demonstrate this by constructing geochemical anomaly maps of the ore-hosting areas.

Such maps were first applied in surficial exposures of chrome ore by Rassios and Kostopoulos (1990): a geochemical traverse of an exposed layer of chrome ore and host at an exposed ore site of Xerolivado (the Xerolivado Trench profile) demonstrated re-equilibration, but the geochemical anomalies were very narrow.

Comparing the topographic map with the geochemical maps indicates with a good precision the location of the chrome ore bodies in

the Xerolivado–Skoumtsa mine. The presence of ore bodies can be geochemically predicted at a scale of five to thirty meters. We thus believe that this geochemical tool could be applied for the exploration of the continuation of the chromite bodies at the southwestern sector of the Xerolivado–Skoumtsa mine. Analyses of disseminated spinels from a single exploratory borehole have been done (Rassios, unpub.), but more data is required to construct a suitable geochemical anomaly map. If so, such an exploration methodology could contribute to locating chrome ore bodies that have been predicted for the area based on structural analysis (Stamoulis, 1990).

## 6. Conclusions

Within the Xerolivado–Skoumtsa Chrome Mine, the contents of Cr, Al, Mg, Fe<sup>2+</sup>, Mn, Zn and V cations in spinels within schlieren chrome ore bodies and accessory chromite in host and gangue serpentinites demonstrate systematic variations due to subsolidus reactions between chromite and silicate mineral phases (now totally serpentinitized) during re-equilibration. Cr is substituted mainly by Al and to a minor extent by available V and –possibly– Mn. Mg is substituted mainly by Fe<sup>2+</sup> and to a minor extent by available Zn and Mn. Geochemical anomaly maps demonstrate the chemical variation of these elements in such a way as to designate the position of the chromite ore bodies. The use of this geochemical tool could prove useful for chrome ore exploration not only for the unexploited part of the Xerolivado mine but also for podiform schlieren-type chromitites in other ophiolitic hosts.

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