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AN OVERVIEW OF THE PGE DISTRIBUTION IN THE BULQIZA OPHIOLITE COMPLEX, ALBANIA

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ABSTRACT

Platinum, Pd and Au were determined in peridotite samples, covering the mantle sequence of the Bulqiza complex, along with mineral phase analysis. Chromite samples from relatively small chromite bodies (Ceruja, Ajazaj, Shkolla and Thekna) were analyzed for precious metals (Os, Ir, Ru, Rh, Pt, Pd plus Au) and other trace elements.The compositional variation of Cr-spinel and coexisting orthopyroxene of the mantle sequence, indicate that the Eastern and Central parts of the Bulqiza complex are characterized by highly depleted harzburgite, whereas the Western part by less depleted harzburgite. The compilation of PGE, Ni, Co, V, Zn and Mn data in chromite ores provide evidence for the discrimination between ores derived from primitive magmas and those derived from partially fractionated magmas, despite their similar major element composition. The limited compositional variation in the large chromite deposit of the Bulqiza complex may reflect a formation directly above a supra subduction zone spreading center, whereas fractionated to some extent parent magmas in the areas of Ajazaj, Ceruja and Thekna may represent a distance from the spreading center and/or more shallow conditions.

KEY WORDS: Bulqiza, ophiolite, chromite, exploration, mineralization, platinum-group elements, trace elements

1. INTRODUCTION

The ophiolites in Albania occur in the Mirdita tectonic zone as two NNW-SSE trending elongated belts. Although various ophiolite- ophiolite sequences may appear to define continuous belts, their structural, petrological and geochemical characteristics may vary indicating changes in the geotectonic environment during their formation, which may affect the chromite potential and distribution. In the present study, bulk rock analyses of representative samples of ultramafic rocks and chromite ores from the Bulqiza complex for platinum-group elements (PGE) plus gold and other trace elements, and mineral phase analyses by electron microbrobe are given. These new and published data from previous studies are compiled and their implication on chromite mineralization and exploration is discussed.

2. GEOTECTONIC SETTING

Geological, petrological and geochemical data of the ophiolites in Albania have been given by many investigators and they are reviewed, and completed by Shallo (1994), Tashko (1996) and others. The Western Belt is composed of harzburgite-lherzolite tectonites and the magmatic sequence, which contains plagioclase-dunites, troctolites, plagioclase-pyroxenites, gabbros, plagiogranites and basaltic pillow lavas. The Eastern Belt is composed of harzburgitic mantle tectonite and the magmatic sequence, consisting of dunites, pyroxenites, gabbronorites, gabbros, quartz-diorites, plagiogranites, the sheeted dyke complex

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and a volcanic suite ranging in composition from basalts to rhyolites. The wide range of lavas, from MORB basalts to island arc tholeiites (IAT) and boninites, in combination with the mantle tectonites, reflect changes in the geotectonic environment. With respect to the western belt, the original setting is considered to be an oceanic spreading system, during Middle Jurassic, without any influence of subduction-related processes, whereas the the Eastern Belt is considered to be a supra-subduction zone (SSZ) ophiolite, during Late Jurassic (Shallo, 1994). In addition, in the northern part the ophiolites of Tropoja, Kukesi and Krrabi,among other particular features are condidered to be 28 Ma older than other ophiolites in Albania (Tashko, 1996). In a comparison of the Albanian to Hellenic ophiolites related with the sub-Pelagonian zone, it has been suggested that ophiolites of Kastoria, Pindos, Vourinos, Othrys, Euboea, Attica and Argolis derived from the Pindos ocean resulted from oceanic spreading above a westward-dipping subduction zone, and that spreading decreased southwards from Albania (Robertson et al., 1991).

3. GENERAL CHARECTERISTICS OF CHROMITE ORES

The mantle sequence of Bulqiza, which is the major source of chromite ore in Albania, forms about 82 percent of the complex and consists of deformed harzburgite and irregular dunite bodies enclosing chromite ores (Cina et al., 1986). More than 40 million tons of chromite ores are located in the uppermost part of the tectonized harzburgite, either within dunite bodies or enclosed in narrow dunite envelopes (Cina et al., 1986). Massive, disseminated, nodular, banded or schlieren types of chromite are all present. High temperature-low stress deformation, superimposed on primary magmatic textures, is dominant in the west and south-east parts, while in all other parts the low temperature-high stress deformation is present (Tashko, 1990). In the cumulate sequence only small chromite deposits are found in the dunites. Chromite bodies from the studied areas are mostly of massive and nodular type. Large chromite bodies of the Bulqiza mine are of metallurgical type (Cina et al., 1986). With the exception of the area of Thekna, the analyzed samples were collected from exploitation galaries with smaller chromite pods, which estimated to contain only a few thousand tons of ore, such as in the areas of Ceruja (Ceruja 1 and Ceruja 2), Ajazaj and Shkolla, covering the Western, Central and Eastern parts of the complex (Fig. 1). They are hosted in the series of dunite-harzburgite, which in the area of Ceruja are found in a close proximity to the magmatic sequence, including dunites, lherzolites and gabbros.

4. ANALYTICAL METHODS

Chromite and silicate analyses were carried out with a Cameca Camebax Microbeam wavelength-dispersive electron microprobe, at the Institute of Geology and Mineral Exploration (IGME).

Platinum group elements (PGE) were determined at X-Ray Assay Laboratories (XRAL), Canada, by Plasma Mass Spectrometry (ICP/MS) method, after preconcentration from large (30g) samples, using the nickel fire assay technique.

5. CHEMICAL COMPOSITION OF CHROMITE ORES AND HOST ROCKS

Platinum, palladiun and gold were determined in peridotite samples, covering the mantle sequence of the Bulqiza complex, along with mineral phase analysis, by electron microprobe (Table 1). The harzburgites have Pt plus Pd content ranging from <10 to 23 ppb, while in dunites it ranges between <10 and 46 ppb. The compositional variarion of Cr-spinel and coexisting orthopyroxene of the mantle sequence, which reflects the degree of partial melting in the upper mantle (Jaques and Green, 1980; Dick and Bullen, 1984) indicate that the Easten and Central parts of the Bulqiza complex are characterized by highly depleted harzburgite (which are comparable to the Vourinos complex), whereas the Western part is characterized by less depleted harzburgite (Table 1; Figure 2).

It is well known that the large chromite bodies of the Bulqiza mine are of metallurgical type [average rario of Cr/(Cr+Al) = 0.80] (Cina et al., 1986). Electron microprobe analyses and the compositional variation of chromite from the studied areas of Ceruja, Ajazaj, Shkolla and Thekna completed for the present study are given in the Table 2 and Figure 3, respectively. They exhibit a wide variation, the Cr/(Cr+Al) ratio ranging between 0.43 and 0.86, while the Mg/(Mg+Fe^{2+}) ratio ranges from 0.46 and 0.69. Although this compositional variation falls within the compositional field given by previous investigators (Cina et al., 1986), it is remarkable that samples with similar major element compositions may exhibit a wide variation in their trace element contents (Tables 2 and 3).

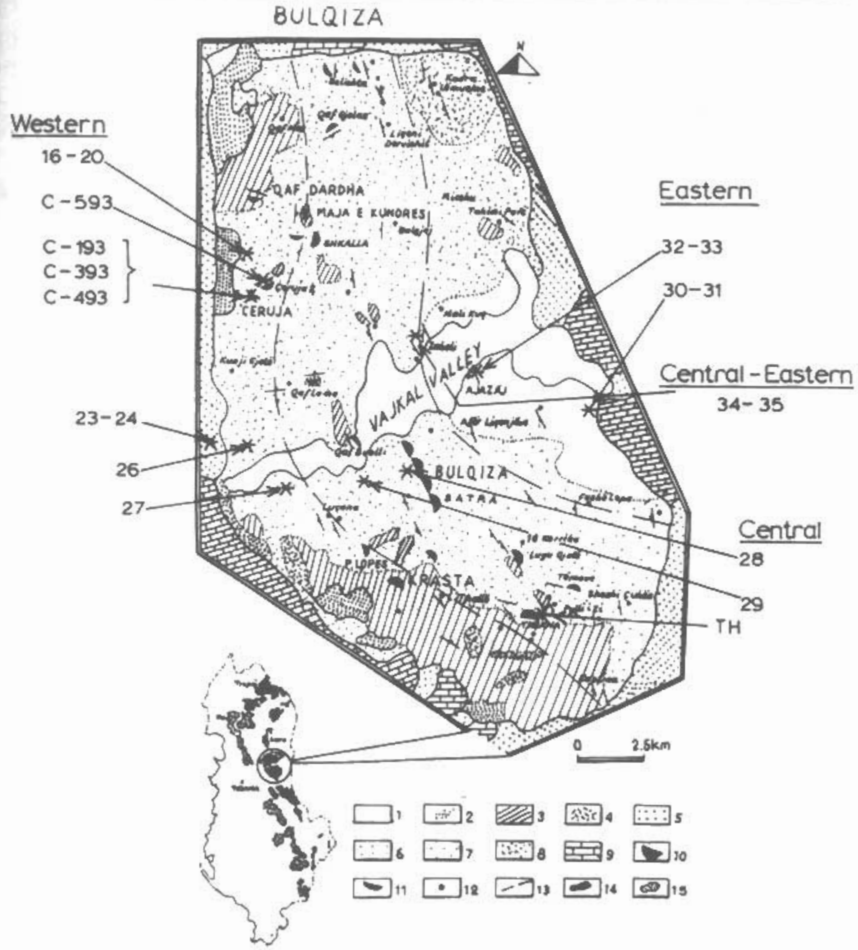

Fig. 1: Distribution of ophiolites in Albania and simplified geological map of the Bulqiza ophiolite complex (after Karaj, 1992), showing the location of the studied chromite ores and rocks.

Symbols: 1= tectonite harzburgite, 2= "fresh" harzburgite, 3= dunite within tectonite harzburgite, 4= pyroxenite, 5= gabbros, 6= supra-Moho dunite, 7= Quaternary, 8= Neogene mollase, 9=T3-J1 limestone, 10= chromite deposits with > 1 Mt reserves, 11=chromite deposits with < 1Mt reserves, 12= chromite deposits with < 0.5 Mt reserves, 13= boundary between eastern, central and western parts ofthe complex, 14= ophiolites of the western belt of Albania, and 15= ophiolites of the eastern belt.

Table 1. Platinum, Pd and Au concentrations in ultramafic rocks, and the composition of accessory chromite from the Bulqiza ophiolite complex

			ppb			spinel composition		Reference
Location	Rocks	Sample	Pd	Pt	Au	Mg/ (Mg+Fe2+	Cr/ (Cr+Al)	
Cerruja	Harzburgite	9516	23	5	0.5	0.56	0.47	This study
Cerruja	Harzburgite	9517	0.5	5	0.5	0.42	0.58	This study
Cerruja	Dunite	9518	0.5	5	0.5	0.57	0.76	This study
Cerruja	Harzburgite	9519	0.5	5	0.5	0.57	0.47	This study
Cerruja	Harzburgite	9520	0.5	5	0.5	0.47	0.57	This study
Klosi	Serpentinite	9523	0.5	15	0.5	0.51	0.65	This study
Klosi	Harzburgite	9524	3	5	0.5	0.54	0.59	This study
Veri Planit	Harzburgite	9526	6	5	0.5	0.57	0.56	This study
Plan I bardhe	Harzburgite	9527	17	5	0.5	0.42	0.57	This study
Bulqize	Harzburgite	9528	6	5	0.5	0.47	0.71	This study
Bulqize	Harzburgite	9529	17	5	3	0.48	0.78	This study
Pran Bulqizes	Dunite	9533	20	26	12	0.5	0.72	This study
Shkolla	Harzburgite	9534	3	5	0.5	0.51	0.68	This study
Fush Bulqiz	Harzburgite	9530	3	5	0.5	0.61	0.66	This study
Fush Bulqiz	Harzburgite	9531	0.5	5	0.5	0.53	0.63	This study
Ternove	Dunite	9154	1	11	1	0.62	0.75	Karaj, 1992
Ternove	cumul dunite	9151	3	5	3	0.39	0.77	Karaj, 1992
Ternove	Wehrlite	9152	4	16	2	0.34	0.78	Karaj, 1992
Cerruja	Troctolite	9521	0.5	5	0.5	0.21	0.65	This study

Table 2. **Representative analyses of chromite by electron microprobe from the Bulqiza ophiolite complex**

	Ceruja				Thekna	PranBul	Shkolla
	C-193 massive	C-393 massive	C-493 massive	C-593(*) dissemir	TH nodular	9532 massive	9535 nodular
SiO2	0.05	0.06	0.1	0.11	0.06	0.45	0
Al2O3	24.44	32.9	26.25	16.12	9.12	10.99	6.97
Cr2O3	46.23	37.6	42.8	47.38	59.99	62.21	65.04
Fe2O3	0.25	0.33	2.24	6.31	3.96	2.02	1.7
TiO2	0.1	0.2	0.1	0.11	0.06	0.1	0
MgO	14.18	15.6	15	9.35	14.18	11.34	13.52
FeO	13.68	12.71	12.63	19.91	11.28	12.12	12.01
MnO	0.52	0.62	0.44	0.4	0.52	0.3	0.44
NiO	0.13	0.1	0.38	0.1	0.19	0.1	0.26
Total	99.59	99.93	99.94	99.79	99.6	99.63	99.94
Cr/(Cr+Al)	0.56	0.43	0.52	0.66	0.82	0.79	0.86
Mg/(Mg+Fe2+	0.65	0.69	0.68	0.46	0.69	0.58	0.64

Symbols: (*) = disseminated (accessory) chromite
Fe2O3 and FeO were calculated from Fe total assuming that R2O3:RO = 1

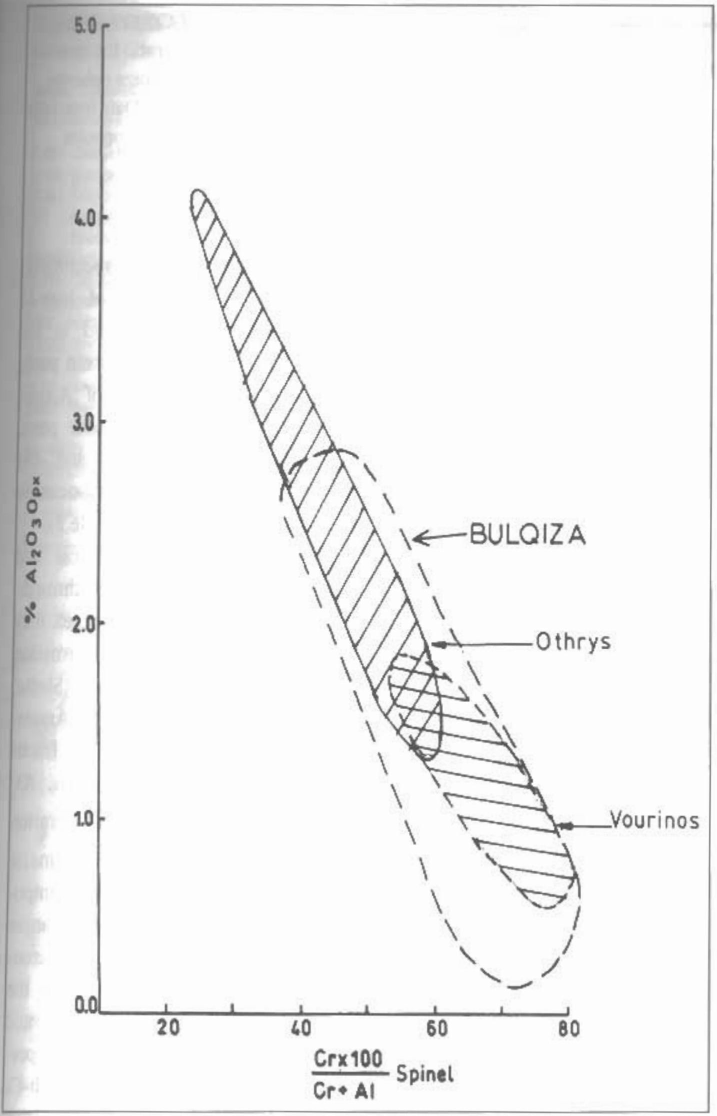

Fig. 2: Plot of %Al2O3 in orthopyroxene(opx) vs Cr/(Cr+Al) ratio in coexisting spinel from the mantle peridotites of Bulqiza, Vourinos and Othrys ophiolite complexes, showing the degree of depletion in harzburgite, plagioclase harzburgite and lherzolite. Data from Table 1 and Economou-Eliopoulos (1996).

Chromite samples from relatively small chromite bodies were chosen and analyzed for all PGE$_s$ (Os, Ir, Ru, Rh, Pt and Pd) plus Au and other trace elements (Table 3). The total PGE content in the studied samples is low, and the chondrite normalized PGE-patterns show a negative to smooth slope for chromite ores (Fig. 4a), and a positive slope for the sulfide-bearing dunites (Fig. 4b). The ratios of incompatible/compatible elements, like the (Pt+Pd)/(Os+Ir+Ru) ratio, which is considered to express a fractionation trend (Barnes et al., 1985) range between 0.04 and 1.48. The values of the latter ratio, and the average content of Ni, Co, V, Zn and Mn content are higher in the high-Al than in high-Cr type, although any correlation between major and trace element content is not obvious.

6. DISCUSSION

The Bulqiza complex in addition to the features of a supra-subduction zone (SSZ) geotectonic environment, exhibits a variation in the proportion of the dunite bodies and the composition of Cr-spinel and coexisting orthopyroxene of the mantle sequence (Karaj, 1992; Tashko, 1996; Table 1, Fig. 2), reflecting the degree of partial melting in the upper mantle (Jaques and Green, 1980; Dick and Bullen, 1984). More specifically, the Feasten part of the Bulqiza complex is characterized by fresh, highly depleted harzburgite, including small bodies of dunite, the Central part by fresh - highly depleted harzburgite also, and large dunite bodies and chromite deposits, whereas the Western part is characterized by less depleted harzburgite and the presence of the main magmatic sequence of the complex. The chromite and PGE mineralization in the Bulqiza ophiolite complex, is characterized by the presence of large chromite deposits of metallurgical chromite type, whereas the refractory type is present only in a small

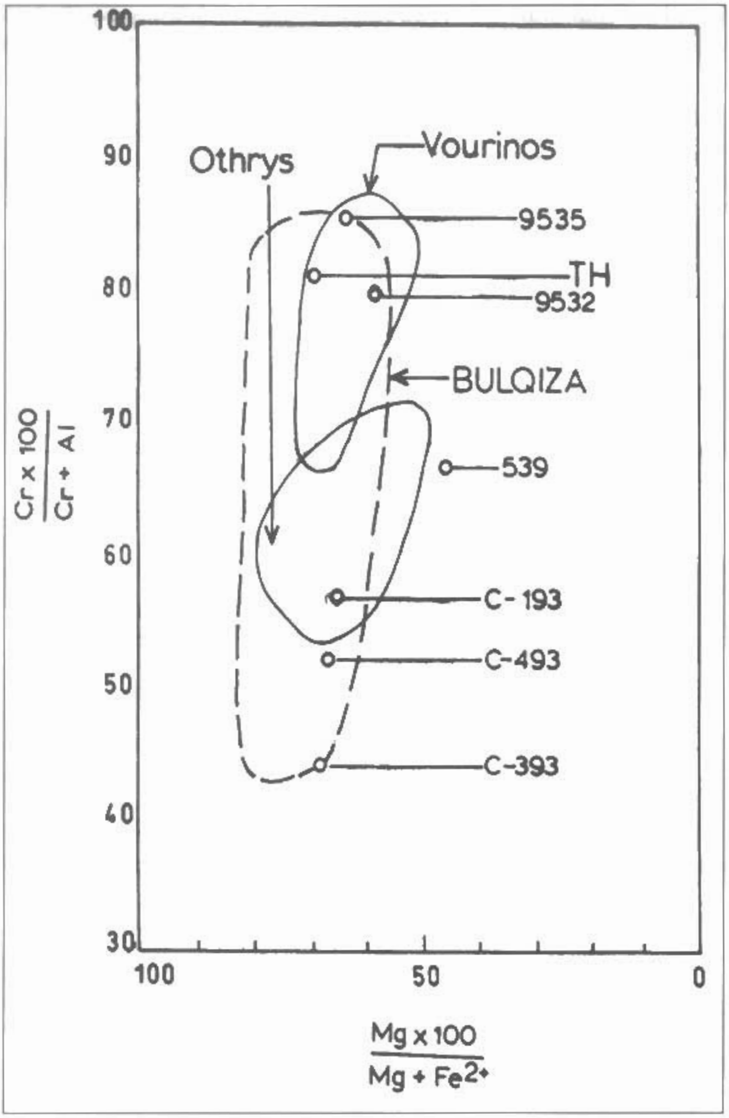

Fig. 3: Plot of Cr/(Cr+Al) vs Mg/(Mg+Fe2+) ratio for chromite ores from the Bulqiza ophiolite complex, Albania. Data from table 2 and Economou-Eliopoulos (1996)

proportion. More specifically, small occurrences of high-Al chromitite are found in the area of Ceruja (Western part), while in the area of Ajazaj-Pran Bulqiza (Eastern part), both types (high-Al and -Cr) occur in a spatial association (Cina et al., 1986; Table 2).

These petrological and geochemical features throughout the Bulqiza complex may reflect a multistage formation of ophiolite sequences (Shallo, 1994; Tashko, 1996). Assuming that partial melting, fractionational crystallization, fO_2 and fS_2, rather than alteration and metamorphism are major factors controlling the composition of chromite ore, changes in the geotectonic environment may be related to the chromite mineralization and exploration. Thus, the presence of large, high-Cr chromite deposits in the cental part of the complex, seems to be consistent with the SSZ setting of the complex and the highly depleted nature of the mantle sequence (Table 1; Fig. 2). This is due to high input of volatile components, derived from the subducted slab into the overlying mantle wedge and in turn high degree of partial melting (Pearce et al., 1984; Roberts, 1988; Economou-Eliopoulos, 1996). In addition, these large chromite deposits in Bulqiza are characterized by a remarkably homogeneous composition in their major and PGE distribution (Cina et al., 1986, 1995; Karaj, 1992). With respect to the high-Al chromite ores their composition may be the result of either lower degree of melting in the mantle source and/or the formation from more evolved magmas. The composition of large chromite deposits of refractoty-type in certain ophiolite complexes, like the Othrys complex in Greece, which are characterized by constant composition in both major and trace elements (PGE, Ni, Co, Cu, V, Zn) and low values of the incompatible /compatible ratios, has been attributed to the composition of parent magmas derived by a lower degree of partial melting in the mantle source than that of high-Cr ores, and uniform conditions over large areas (Economou-Eliopoulos et al., 1997). However, the studied high-Al chromite ores from the area of Ceruja, W. Bulqiza, exhibit a wide variation in the PGE, Ni, V, Zn and Mn content and the ratios of

Table 3. Trace element data of chromite ores and sulfide-bearing dunites from the Bulqiza ophiolite complex

			ppb							ppm					Cr/	(Pt+Pd)/	
Sample	Location	Description	Os	Ir	Ru	Rh	Pt	Pd	Au	Ni	Co	V	Zn	Mn	(Cr+Al)	(Os+Ir+Ru)	Reference
C-493	Cerruja1	Mass.Chromite	3	7	15	2	28	9	10	1640	160	1030	420	1210	0.52	1 48	This study
C-193	Cerruja 1	Mass.Chromite	3	6.9	18	3	25	7	3	2150	160	990	340	1100	0.56	1	This study
C-393	Cerruja 1	Mass.Chromite	3	7	18	3	25	7	3	2640	170	610	300	980	0.43	1.14	This study
K-7	Cerruja 1	Mass.Chromite	nd	nd	nd	nd	510	1300	nd								Karaj 1992
	Cerruja 1	Mass.Chromite	nd	nd	nd	nd	10	3	nd								Karaj 1992
K-106	Cerruja 2	Mass.Chromite	nd	nd	nd	nd	10	6	nd								Karaj 1992
K-274	Cerruja 2	Mass.Chromite	nd	nd	nd	nd	4	10	3								Karaj 1992
9532	PranBul	Mass.Chromite	nd	nd	nd	nd	5	3	0 5	1200	140	1130	300	1060	0.79		This study
9535	Shkolla	Nodular Chromite	nd	nd	nd	nd	14	0.5	0.5	1320	130	600	230	990	0.86		This study
LK-236	Ajazaj	Mass Chromite	13	33.7	59	9	35	11	4							0.43	Karaj 1992
K-156	Qafe Lame	Mass.Chromite	nd	700	nd	nd	490	330	14								Karaj 1992
K-159	Kunji gjate	Mass.Chromite	nd	1149	nd	nd	100	33	2								Karaj 1992
K-271	Rrasa Martinit	Mass.Chromite	356	461	1130	50	62	6	1							0.04	Karaj 1992
TH	Thekna	Nodular Chromite	3	9.6	41	5	28	4	13	2550	180	610	220	1000	0.82	0.6	This study
LK-195	Cerruja 2	Sulfides in dunites	614	234	1094	nd	3580	7540	2010							5.73	Karaj 1992
LK-279	Cerruja 2	Sulfides in dunites	381	253	958	nd	3461	5804	2097							5.82	Karaj 1992
C-593	Cerruja	Dunite with sulfides	3	3.3	4	1	25	27	12							5.01	This study
LK-220	Krasta	Dunite with sulfides	39	21	57	nd	690	1725	900							20.6	Karaj 1992

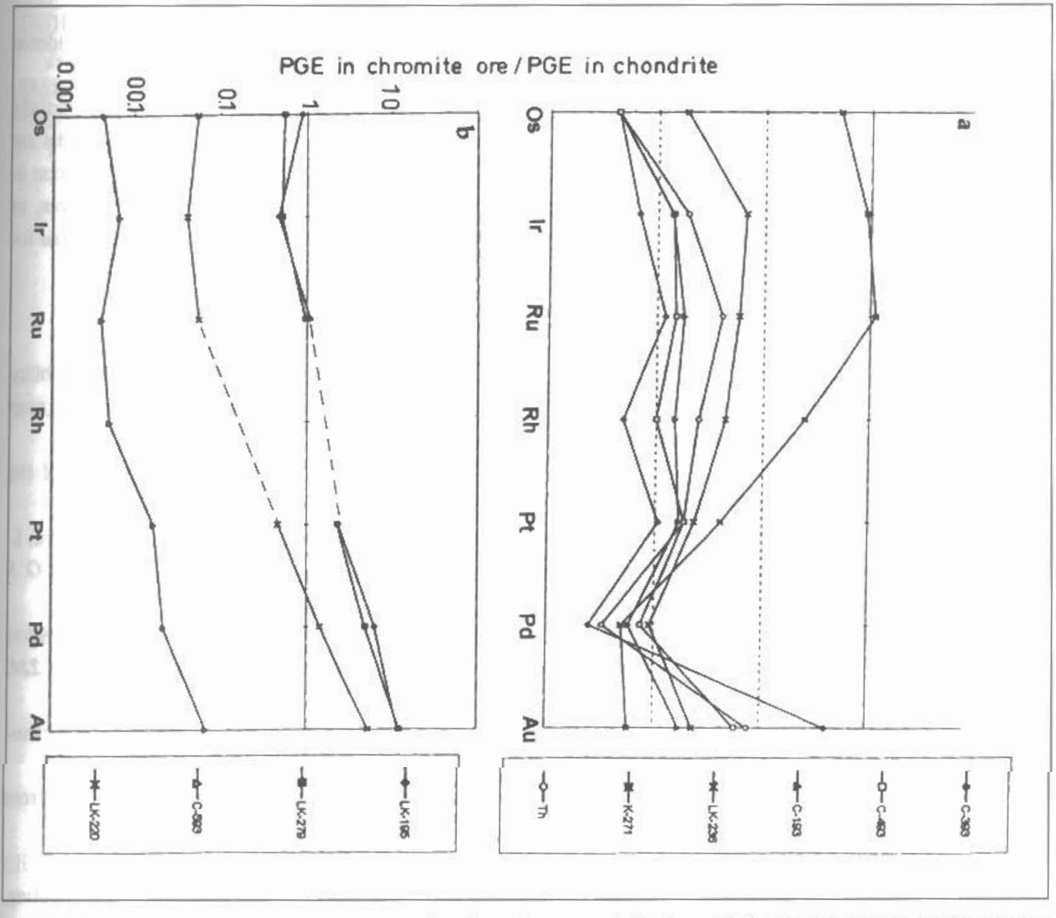

Fig. 4: Chondrite normalized PGE-patterns (a) for chromite ores and (b) for sulphide-bearing dunites of the Bulqiza ophiolite complex. Data from Table 3.

(Pt+Pd)/(Os+Ir+Ru), ranging from 1 to 1.5, and Ni/V ranging from 1.6 to 4.3 (Table 3). The wide variation of Ni, ranging from 1640 to 2640 ppm, may have been effected by the segregation of sulfides (pentlandite) in dunites close to the petrological Moho (Cina et al., 1995). The higher V, Zn and Mn contents, and the higher values of the (Pt+Pd)/(Os+Ir+Ru) ratio in the sample labelled as C-493 compared to other chromitite samples from the area of Ceruja 1 (Table 3) is consistent with a well pronounced fractionation trend of parent magmas (Ohnenstetter et al., 1991). Similarly, high-Cr ores from small chromite occurrences of the areã of Pran Bulqiza-Ajazag indicate a fractionation trend (Table 1). This fractionation trend obseved in chromite ores (of both high-Al and -Cr type) from Albania, is comparable to that in several small chromite occurrences of Greece (Konstantopoulou, 1990; Economou-eliopoulos, unpub.data). Such a PGE fractionation, which is well defined at different conditions of fO_2 and fS_2 (Amosse et al., 1990; Naldrett et al., 1990) has been suggested, and three stratigraphic levels of the Bulqiza complex have been distinguished (Ohnenstetter et al., 1991; Cina et al., 1995). Therefore, based on the incorporation of present and literature data (Karaj, 1992; Table 3; Fig.2) into models proposed for the ophiolite complexes (Nicolas, 1989) it is suggested that the limited compositional variation in the large chromite deposit of the Bulqiza complex, probably due to limited variability in fO_2, fS_2, and fractionation (Amosse et al., 1990; Naldrett et al., 1990) may reflects a formation directly above a supra subduction zone spreading center, whereas fractionated to some extent parent magmas in the areas of Ajazaj, Ceruja and Thekna may represent a distance from the spreading center and/or more shallow conditions.

In summary, the compilation of PGE, Ni, Co, V, Zn and Mn data in chromite ores provide evidence for the following:

a) discrimination between ores derived from primitive magmas and those derived from partially fractionated magmas, despite their similar major element composition b) large chromite deposits are characterized by uniform composition, in contrast a well pronounced fractionation trend is common in small chromite occurrences c) the chromite composition and variation in ophiolite sequences, in combination with the petrological and geochemical features may be informative for their potential for chromite.

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