ON THE ORIGIN OF Ti- MAGNETITE FROM THE PUKA OPHIOLITIC MASSIF, ALBANIA

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ABSTRACT

In Albania, Fe-Ti oxide mineralization (Ti-magnetite,ilmenite) is mainly located in the magmatic sequence of the western ophiolite belt (MORB -type) of the Mirdita zone. Representative magnetite - bearing samples from the areas of Plani Kcires and Lufaj (Puka massif) were analyzed for major and trace elements, and mineral phases by electron microprobe. On the basis of the mineralogical and geochemical data, the degree of fractional crystallization and the conditions of temperature and oxygen fugacity are considered to have played an essential role to the composition of the Ti-bearing mineralization related to ophiolite complexes.

KEY WORDS: magnetite, ilmenite, ophiolite, Puka, Albania,

1. INTRODUCTION

It is well known that apart from a considerable amount of Ti which can enter the magnetite structure forming a continuous relationship between magnetite and the ulvospinel molecule, Fe_2TiO_4, other replacements which may occur in magnetite are in the trivalent group, V and Cr substituting for Fe^{3+}, and in the divalent group , Mg and Mn replacing Fe^{2+}.

Fe-Ti oxide mineralization (Ti-magnetite, ilmenite) is mainly located in the magmatic sequence of the western ophiolite belt (MORB -type) of the Mirdita zone, Albania (Cina et al., 1987; Tashko, 1996). Representative magnetite - bearing samples from the areas of Plani Kcires and Lufaj, in northern Albania (Puka massif) were analyzed for major, and trace elements, and mineral phases by electron microprobe.

The pronounced differences in the composition of Fe-Ti oxides from the studied areas, in comparison to those from the Vourinos and Pindos ophiolites complexes of Greece may be significant to the magnetite formation.

2. METHODS OF INVESTIGATION

Thin polished sections were investigated by optical microscopy and electron microprobe. Microprobe analyses were carried out at the Institute of Geology and Mineral Exploration (I.G.M.E), Athens, using the Camera Superprobe wavelength - dispersive automated system.

Bulk rock analyses for major and trace elements were carried out by Atomic absorption (University of Athens) and for platinum, palladium and gold at the XRAL Laboratories, Ontario, Canada, by lead fire-assay technique.

On the basis of the electron microprobe analyses temperature, and oxygen fugacity were calculated, using the QUILF, Version 4.1 software, based on the models : proposed by Andersen (1988).

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3. PETROGRAPHIC FEATURES

The Fe-Ti mineralization is mainly located in the magmatic sequence of the Gomsiqe (western part)-Terbuni (eastern part) ophiolite massif, which is located in the northeastern part of the Mirdita zone , Albania (Fig. 1).It is composed by a relatively fertile mantle sequence (lherzolites, harzburgites),with minor dunite bodies, accompanied by small chromite occurrences, and an iron rich magmatic sequence, (Cina et al. 1987). The magmatic sequence is comprised by the lowermost part, 0.4 - 0.7 Km thick, consisting of peridotite-troctolite-magnesian gabbro, the upper cumulate unit, 0.1-0.2 km thick, consisting of gabbros, gabbro-norites, ferro-gabbros, amphibole bearing gabbros, and MORB type pillow lavas (Tershana 1982, Tashko 1996).

More specifically, the Fe-Ti oxide mineralization is located in the lower part of the magmatic sequence, the ultramafic-mafic cumulate unit which crop out in the Puka region. The main mineralized zone (6 km long and 0.2-2 km thick) occurs in the gabbro-peridotite transition zone. Within the Fe-Ti bearing horizons, magnetite occurs as disseminated grains in a proportion ranging between 5 and 20 vol% whereas as high as 40 vol% magnetite proportion is rare. A small amounts (1-6 vol%) of sulfides (chalcopyrite, pyrrhotite, pyrite) are also present (Tershana, 1982).

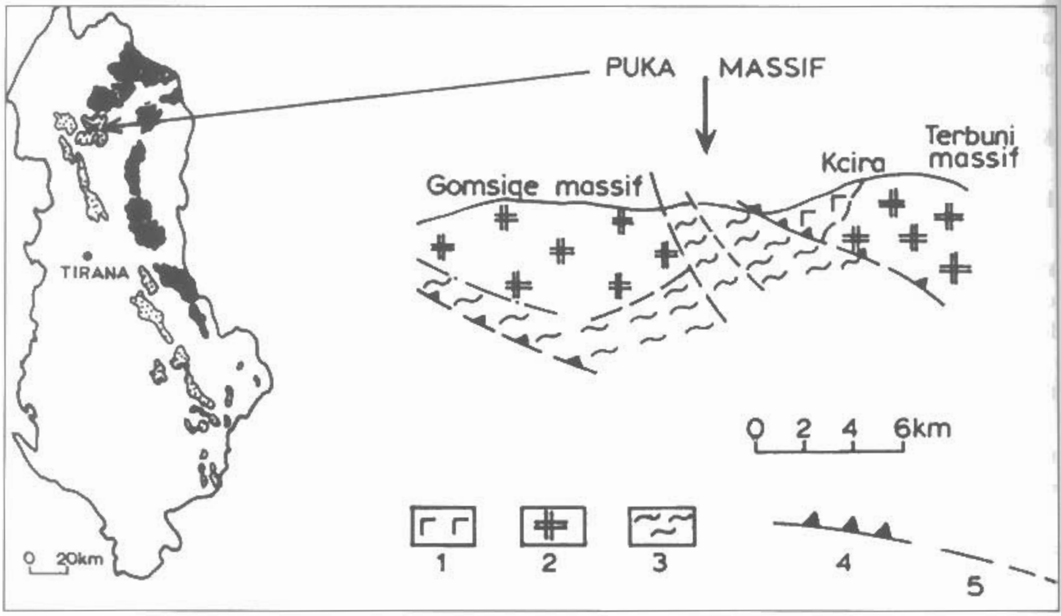

Fig. 1: Sketch map showing the distribution of ophiolites in Albania and the location of the studied magnetite mineralization.
Gomsiqe - Terbuni massif cross-section (after Kodra and Gjata, 1989).
Symbols: 1 = basic rocks; 2 =ultrabasic rocks; 3 = Triassic-Jurassic Formations; 4 = overthrust; 5 = fault.

4. MINERALOGICAL AND GEOCHEMICAL CHARACTERISTICS

The studied samples which are characterized by extensive serpentinization, are mainly composed of olivine, while Ti-magnetite occurs as interstitial to the major phases as small disseminated euhedral and occasionally irregular grains. Ilmenite is found in the contact with magnetite and/or between olivine crystals. Very fine secondary magnetite associated with serpentinized olivine is common. In the area of Lufaj, olivine is found in a proportion about 50 vol%, clinopyroxene in a proportion about 30 vol% and plagioclase in a proportion <10 vol%, while amphibole is also present. The proportion of Fe-Ti oxides is small, about 5 vol%. The studied samples from the area of Plani Kcires are strongly serpentinized. Olivine and Fe-Ti oxides are found in a higher proportion, 60-70 vol% and 12 vol%, respectively, compared to the area of Lufaj.

Although the bulk rock composition of the studied samples is similar, the Ti, Al, Fe, Ca and Cr content is higher, and Mg and Ni content lower in the area of Lufaj than in the area of Plani Kcires (Table 1). Also, the iron content of olivine is higher in the former than in the latter, the average values of the $FeO_t/(FeO_t+MgO)$ ratios being 0.44 and 0.37, respectively.

Besides secondary magnetite, which is pure magnetite, Ti-bearing magnetite exhibit a variable chromium and aluminum content. Cr_2O_3 ranges between 4.40 and 6.5 wt % in the magnetite from the area of Lufaj and from 9.60 to 15.20 in that from the area of Plani Kcires, while the average aluminum content of magnetites is 2.50 wt % Al_2O_3 in the former and 4.40 wt % Al_2O_3 in the latter. The vanadium content is in a comparable level in both areas (average 2.20 wt % V_2O_5) (Table 3, Fig. 2).

Andersen (1988) proposed that the calculation of the crystallization temperature and oxygen fugacity is possible on the basis of the microprobe analyses of coexisting magnetite and ilmenite in the host rocks. In an attempt to determine T and fO_2 conditions in the studied areas and to compare to these of the magnetite mineralization in the Vourinos and Pindos ophiolite complexes of Greece, representative analyses of magnetite-ilmenite from these complexes are given in the Table 4. Thus, using the QUILF calculation as it is described by Andersen (1988), the temperature ranges from 340 to 620 °C and the oxygen fugacity from -10.6 to 0.07 bars for this type of mineralization (Table 5). More specifically, the calculated values (average) of temperature for the area of Lufaj are higher (620 °C) than the range concerning the Vourinos (340-560 °C) and the Pindos complexes (510 °C). The oxygen fugacity exhibits the highest values 0.42 and 0.07 ΔfO_2 from FMQ buffer (log base 10 value) in the areas Kyra Kali (Pindos) and Lufaj, respectively. The calculated values of T and fO_2 for the area of Plani Kcires are unreasonable, probably due to the relatively high Cr content (Table 3) and are not included in the Table 5.

5. DISCUSSION

Assuming that the trace element contents in the disseminated magnetite from the studied areas reflect the composition of magnetite in equilibrium with the parent magmas, their compositional variation may reflect difference in the composition of parent magmas, different degree of fractional crystallization or difference in the conditions of temperature and oxygen fugacity. Although a small variation in the chromium content of magnetite may be caused by postcumulus alteration, the higher Cr_2O_3 content of magnetite from the area of Plani Kcires than that in the area of Lufaj, in combination with the lower iron content in olivine in the former than in latter area (Tables 2 & 3) and the presence of plagioclase in the area of Lufaj, is consistent with a less fractionated type in the case of Plani Kcires than in Lufaj. Also, considering the bulk rock composition, the relatively high Cr and Ni content in the studied samples from both areas of the Puka ophiolitic massif (Table 1) are comparable to those in magnetite bearing wehrlite - troctolite rather than gabbros (Rassios, 1981; Tershana, 1982). In addition, although chromium can be accommodated by silicates (Klemm et al., 1985) present data suggest that magnetite is the main collector of Cr (Tables 2 & 3).

Using the QUILF calculation, as it is described by Andersen (1988), on the basis of the composition of coexisting magnetite-ilmenite, an approach of the temperature and oxygen fugacity (Table 5) may provide evidence for the role of T and fO_2 on the Ti-magnetite mineralization in the Puka massif and that hosted in gabbronorites of the Vourinos (Krapa Hills area) and (Kyra Kali area) (Rassios, 1981; Dimou and Vacondios, 1993). The calculated values of temperature for the area of Lufaj is higher (620 °C) than that of the Vourinos mineralization (340 - 560 °C) and Pindos (510 °C), while the oxygen fugacity exhibits the highest values in the areas Kyra Kali (Pindos) and Lufaj. A decrease of the TiO_2 content in magnetite with increasing ΔfO_2 (Buddington and Lindsley, 1964) is not obvious in the studied samples, while a strong good

Table 1. Chemical composition of the studied rocks hosted Fe-Ti oxides

Plani Kcires						Lufaj					
wt%		ppm		ppb		wt%		ppm		ppb	
SiO2	39.40	Ni	1130	Au	12	SiO2	38.50	Ni	770	Au	<1
TiO2	0.12	Cr	1060	Pt	55	TiO2	0.37	Cr	1370	Pt	<10
Al2O3	2.55	Co	150	Pd	3	Al2O3	2.98	Co	160	Pd	<1
FeOt	18.52	Cu	160			FeOt	20.78	Cu	150		
MgO	28.52	Zn	130			MgO	25.70	Zn	150		
CaO	1.06	V	54			CaO	2.86	V	100		
MnO	0.24	Y	<5			MnO	0.30	Y	9		
K2O	0.06					K2O	0.05				
Na2O	0.20					Na2O	0.20				

Table 2. Electron microprobe analyses of clinopyr(cpx), amph(ab), oliv(ol) and plag(pl) from the Puka massif.

	Lufaj													Plani Kcires		
wt%	cpx 1	cpx 3	cpx 13	cpx 15	ab 11	ab 12	ol 5	ol 6	ol 7	ol 8	pl 13	pl 14	pl 15	ol 10	ol 11	ol 12
SiO2	54.44	51.58	53.19	50.77	42.82	43.31	36.80	37.06	37.96	38.09	52.61	52.25	52.40	38.85	38.55	38.55
Al2O3	2.84	4.44	3.07	6.21	14.41	13.99	1.17	2.20	3.90	2.02	30.12	30.01	29.92	0.00	0.00	0.00
Cr2O3	0.00	0.49	0.00	0.00	0.42	0.74	0.00	0.00	0.00	0.00	-	-	-	0.37	0.36	0.32
V2O5	0.00	0.00	0.00	0.00	1.16	1.19	0.00	0.00	0.00	0.00	-	-	-	0.00	0.00	0.00
FeOt	6.39	6.68	6.64	7.29	9.14	8.97	27.50	26.70	25.92	25.87	0.00	0.00	0.00	22.01	22.21	22.29
MgO	16.65	17.84	15.23	15.64	14.88	14.96	33.83	33.87	32.20	32.77	0.00	0.00	0.00	38.14	38.34	38.44
TiO2	0.00	0.00	0.00	0.95	2.50	1.89	0.00	0.00	0.00	0.00	-	-	-	0.00	0.00	0.00
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.52	0.00	0.00	1.02	-	-	-	0.48	0.45	0.43
CaO	19.52	18.84	20.98	17.79	11.45	11.49	0.00	0.00	0.00	0.00	12.95	13.06	13.15	0.00	0.00	0.00
NiO	0.00	0.00	0.00	0.51	0.00	0.00	0.00	0.00	0.00	0.00	-	-	-	0.00	0.00	0.00
Na2O	-	-	-	-	-	-	-	-	-	-	3.75	3.98	3.86	-	-	-
K2O	-	-	-	-	-	-	-	-	-	-	0.30	0.36	0.35	-	-	-

Table 3. Electron microprobe analyses of magnetite (mt) and coexisting ilmenite (ilm), from the Puka ophiolitic massif.

	Lufaj				Plani Kcires						
	L. 9	L. 10	L. 3	L.6	P.K. 1	P.K. 2	P.K. 8	P.K.9	P.K. 4	P.K. 5	P.K. 6
wt%	mt	mt	ilm	ilm	mt	mt	mt	mt	ilm	ilm	ilm
SiO2	0.00	0.00	0.00	0.17	0.00	0.00	0.00	0.30	0.26	0.00	0.00
Al2O3	2.34	2.76	0.60	5.66	4.08	5.83	4.21	3.71	0.00	0.00	0.00
Cr2O3	6.54	4.39	0.00	0.00	14.94	15.19	9.63	9.94	0.00	0.00	0.00
V2O5	1.76	2.50	2.33	1.55	1.89	2.55	2.36	2.46	2.13	2.05	1.99
FeOt	78.23	79.31	44.90	40.89	69.56	67.23	73.19	72.32	42.74	41.38	41.56
MgO	0.69	0.59	2.60	2.78	0.00	0.00	0.00	1.10	0.86	1.97	1.77
TiO2	5.38	4.16	48.11	47.82	4.66	4.32	4.99	5.09	52.02	52.44	52.22
MnO	0.00	0.72	1.01	0.35	0.58	0.88	1.14	0.98	1.80	1.73	1.66
CaO	0.34	0.00	0.00	0.29	0.17	0.00	0.00	0.00	0.00	0.00	0.00
NiO	0.00	0.40	0.23	0.29	0.00	0.00	0.00	0.00	0.00	0.15	0.12

Table 4. Chemical composition of magnetite-ilmenite from Greece.

	Vourinos						Pindos					
	mt	ilm	mt	ilm	mt	ilm	mt	mt	mt	ilm	ilm	ilm
wt%	22KH	22KH	27KH	27KH	77-2	77-2	Pi 1	Pi 3	Pi 4	Pi1	Pi 3	Pi 4
MgO	0.01	0.02	0.97	0.51	0.34	0.32	-	-	0.52	-	0.73	-
Al2O3	1.67	0.07	2.37	0.14	2.31	0.90	0.91	0.83	0.46	-	-	0.08
TiO2	6.87	51.54	4.29	49.9	3.54	50.51	1	0.7	1.49	49.48	52.2	51.39
Cr2O3	0.04	0.00	0.24	0.03	0.56	0.03	-	-	-	-	-	-
MnO	0.47	2.65	0.24	1.85	0.26	4.82	0.26	-	0.27	2.09	2.62	2.76
FeO	33.11	32.23	32.54	31.74	32.71	29.93	36.91	37.57	32.93	42.53	43.20	41.97
Fe2O3	55.11	13.27	57.75	14.96	56.39	14.74	59.92	57.63	62.00	5.44	0.77	2.71
NiO	0.13	0.08	ND	ND	0.15	0.06	-	-	-	-	-	-
V2O5	-	-	-	-	-	-	0.63	1.05	1.10	-	-	-

positive correlation between T and ΔfO_2 (r = 0.90; Fig. 3) is in agreement with the suggested correlation by Buddington and Lindsley (1964).

Therefore, on the basis of the mineralogical and geochemical data on magnetite bearing rocks from the Puka ophiolite massif and those published in previous studies (Rassios, 1981; Dimou and Vacondios, 1993), the degree of fractional crystallization, and the conditions of temperature and oxygen fugacity are considered to have played an essential role to the composition of the Ti-bearing mineralization related to ophiolite complexes.

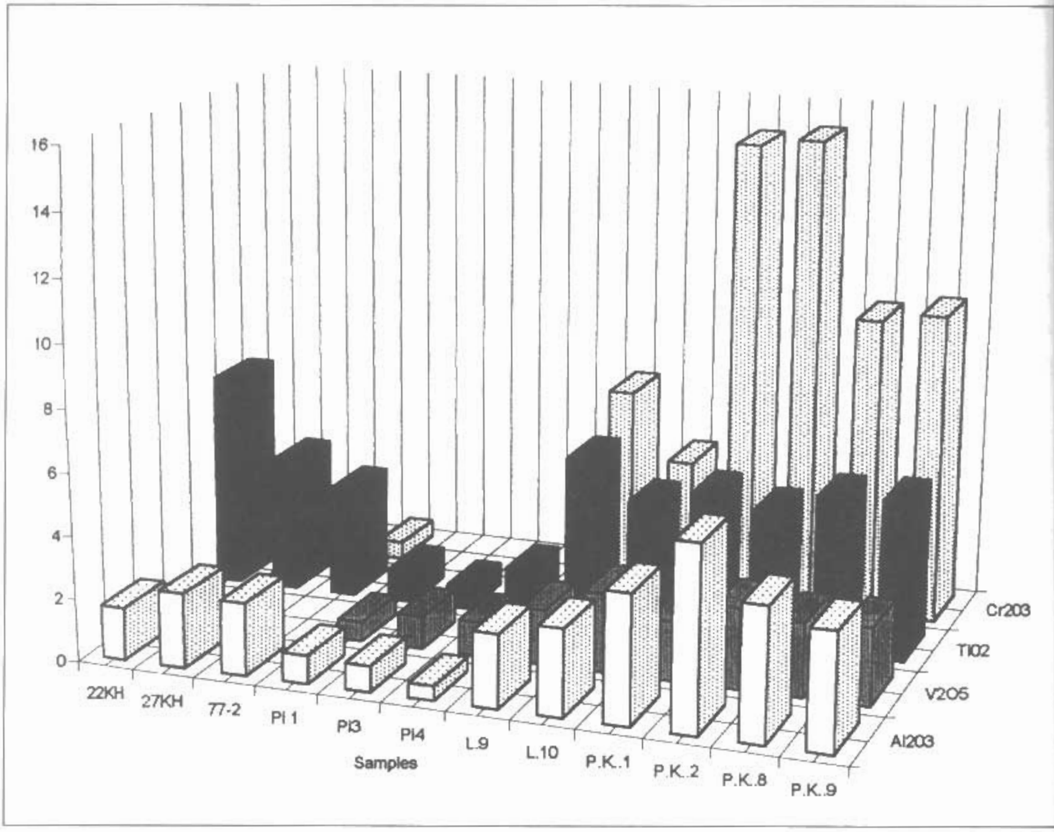

Fig. 2. Variation of selected elements in magnetites from the Puka, Vourinos and Pindos ophiolites

Table 5: Calculated values of T(°C), log fO_2 and ΔfO_2

Location	T (°C)	log fO_2 (bars)	ΔfO_2 from FMQ buffer (log base 10 value)
LUFAJ			
average	620	-17.01	0.07
VOURINOS			
77-2	360	-39.96	-10.6
27-KH	560	-21.21	-2.6
22-KH	430	-32.09	-7.8
PINDOS			
average	510	-20.13	0.42

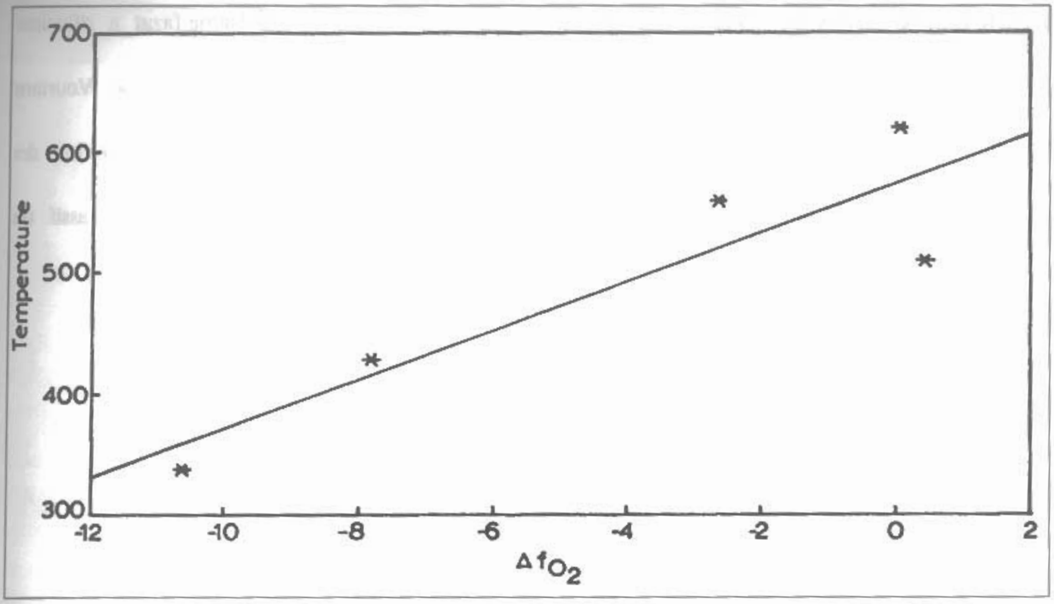

Fig. 3: Plot of the calculated values of ΔfO_2 vs T (°C)

Using the QUILF calculation, as it is described by Andersen (1988), on the basis of the composition of coexisting magnetite-ilmenite, an approach of the temperature and oxygen fugacity (Table 5) may provide evidence for the role of T and fO2 on the Ti-magnetite mineralization in the Puka massif and that hosted in gabbronorites of the Vourinos (Krapa Hills area) and (Kyra Kali area) (Rassios, 1981; Dimou and Vacondios, 1993). The calculated values of temperature for the area of Lufaj is higher (620 °C) than that of the Vourinos mineralization (340 - 560 °C) and Pindos (510 °C), while the oxygen fugacity exhibits the highest values in the areas Kyra Kali (Pindos) and Lufaj. A decrease of the TiO2 content in magnetite with increasing ΔfO2 (Buddington and Lindsley, 1964) is not obvious in the studied samples, while a strong good positive correlation between T and ΔfO_2 ($r = 0.90$; Fig. 3) is in agreement with the suggested correlation by Buddington and Lindsley (1964).

Therefore, on the basis of the mineralogical and geochemical data on magnetite bearing rocks from the Puka ophiolite massif and those published in previous studies (Rassios, 1981; Dimou and Vacondios, 1993), the degree of fractional crystallization, and the conditions of temperature and oxygen fugacity are considered to have played an essential role to the composition of the Ti-bearing mineralization related to ophiolite complexes.

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