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COMPARATIVE STUDY OF THE GEOCHEMISTRY OF CHROMITE ORES FROM THE KEMPIRSAI (URALS) AND RHODOPE (BALKAN PENINSULA) OPHIOLITIC MASSIFS

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ABSTRACT

The Kempirsai ultramafic massif, Urals, Kazakhstan, is part of the old (Silurian) ophiolite complex. The southern part of the massif, which is related to a highly depleted mantle sequence (ophiolite complex with SSZ-features), is hosting exceptionally large high-Cr chromite reserves.The chromite ores of the XL Let Kazakh SSR - Molodezhnoe deposits, are characterized by a limited variation in the Pt, Pd, Au, Ni, Co, Zn, V, Mn and Ti content, in contrast to smaller ore bodies mainly from the northern part of the massif, the Batamshinskoe type (high-Al), and small chromite occurrences in the Rhodope massif. The remarkably homogeneous composition (both major and trace elements) in chromite ores of large deposits, may reflect uniform conditions over large areas (large volumes of magma), and provide evidence for chromite exploration.

KEY WORDS: Kempirsai, Rhodope ophiolite massifs, ophiolite, chromite, exploration, mineralization, trace elements, platinum, palladium

1. INTRODUCTION

The study of platinum-group element (PGE) distribution in ores and host rocks related with ophiolite complexes is a major research topic in the Athens Univesesiry in an attempt to establish a methodology for chromite exploration. Assuming that the magma composition is a major factor controlling the composition of chromite ores, it has been suggested that large chromite deposits are related to ophiolites with supra-subduction zone (SSZ) characteristic (Pearce et al., 1984; Robers, 1988) Based on the distribution of platinum-group elements (PGE), Ni, Co, Cu, V and Zn on chromite ore and host rocks from Greece (Economou-Eliopoulos and Vacondios, 1995; Economou-Eliopoulos (1996) and Economou-Eliopoulos et al., (1997), suggested that the most promising ophiolites are those which apart from the petrological and geochemical characteristics indicating extensive degree of partial melting in the mantle source, contain only one chromite type (the other being only in small proportion) of limited compositional variation in both major and trace elements, and low values of incompatible/compatible ratios. In the present study some geochemical characteristics of chromite ores from the Kempirsai chromite deposit, Urals, Kazakhstan, of podiform type, which is exceptionally large (> 300 million tons of ore), and from relatively small chromite deposits hosted in ophiolites of the Rhodope massif, Balkan peninsula are given and their implication to the chromite exploration is discussed.

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2. CHARACTERISTIC FEATURES

2A. Kimpersai massif, Urals

The Kempirsai ultramafic massif in the southern Ural, Kazakhstan, is part of the old (Silurian, 400 m.y) ophiolite/ophiolites sequences, which have been

obducted onto the Russian craton during Variscan orogeny (Pavlov et al., 1968; Kolotilov et al., 1968; Edwards and Wasserburg, 1985). It has been extensively studied concerning its geology, structure, petrology and geochemistry (Pavlov et al., 1968; Kolotilov et al., 1968; Kravchenko and Grigoreva 1986; Melcher et al., 1994, 1997). The chromite ore reserves of the Kimpersai massif are exceptionally large, more than 300 million tons and on the basis of textural and chemical features can be clasified into two types, a) the high-Cr type (metallurgical type) in the southeastern part of the massif, which contain the largest reserves, the ore bodies being up to 230 m thick and 2000 m long, and known as the Main Ore Field and b) the high-Al type, in the central and northern parts of the massif, which is known as Batamŝhinsk type and contain about 50 smaller chromite bodies.The ore bodies are relatively small (10-150 m length and 0.5-7(10) m width, the estimated reserves are only tens of thousands. Although both chromite types are hosted in dunite bodies and/or dunite envelopes, within serpentinized harzburgites, they exhibit some petrological and geochemical differences and are separated by a system of N-S faults (Kravchenko and Grigoryeva, 1986; Melcher et al., 1994, 1997).

2B. Rhodope massif

The ophiolites in the Rhodope massif are of uncertain age. They are traditionally regarded as Paleozoic or older, but recently it has been suggested that they are of probably Mesozoic age (Ivanov, 1989). Several dismembered meta-ophiolitic masses are scattered within central and eastern Rhodope massif, which is composed by amphibolites, mica gneisses and marbles. The largest, highly serpentinized ultramafic (harzburgite and dunite, and in lesser amounts lherzolites) outcrops are found in the south- eastern Rhodope massif of Bulgaria and Greece. The majority of chromite ores in the Rhodope massif are found in tectonized harzburgite, either within dunite bodies or enclosed in narrow dunite envelopes. Only a low potential for chromite (thousands to hundreds of tons) is known in the Rhodope massif, the largest reserves in the area of Dobromirci being about 230.000 tons, while a spatial association of high-Cr and -Al chromitite is common (Zhelyaskova-Panayotova and Milev, 1980). The majority of the studied chromitite samples are coarce grained, except the Pletena ore. Zhelyaskova-Panayotova and Economou-Eliopoulos (1993) based on petrological, mineralogical and geochemical data, including the distribution of platinum-group element (PGE) in chromite ores suggested that they represent uppermost parts of the mantle sequence (close proximity to the petrological Moho) and/or lower parts of the cumulate sequence, and that they have formed in a supra-subduction zone (SSZ) environment.

3. SAMPLES AND ANALYTICAL METHODS

The studied chromite ore samples from the Kempirsai massif were collected from a) The southern part, the Main ore field, high-Cr ore. In particular, the samples labelled as U.Ki.2 to U.Ki.13 (Table 1) are from the XL Let Kazakh SSR - Molodezhnoe deposits (Fig. 1), from various drill-holes and undergroud workings. All samples are composed of >90 vol% coarse chromite (massive) to 70-80 vol% (dense disseminated). Sample U.G.93 was collected from the V-oe Geophizisheskoe (the 5th Geophysicheskoe deposit) orebody, which is of sub-vertical shape, relativelly small, fine grained and characterized by high temperature deformation superimposed on primary magmatic textures (Gravchenko and Grigoryeva, 1986). b) Samples U.Ki.115, -169, -175 and -224 were collected from the northern part, the Batamshink-type, which is high-Al ore. They are massive to dense disseminated, middle and coarse grained ore. The minor and trace elements Ni, Co, Cu, Zn, V , Ti, Pt, Pd and Au, and rare earth elements (REE) were analyzed at XRA Laboratories, Ontario, Canada, using ICP/PS method, after preconcentration by lead fire-assay technique for platinum, palladium and gold. The detection limit is 10 ppb for Pt, 1 ppb for Pd and 5 ppb for Au.

Electron microprobe analyses of chromite ores were carried out at the Institute of Geology and Mineral Exploration (IGME), Athens, using the Cameca Superprobe wavelength-dispervive automated system.

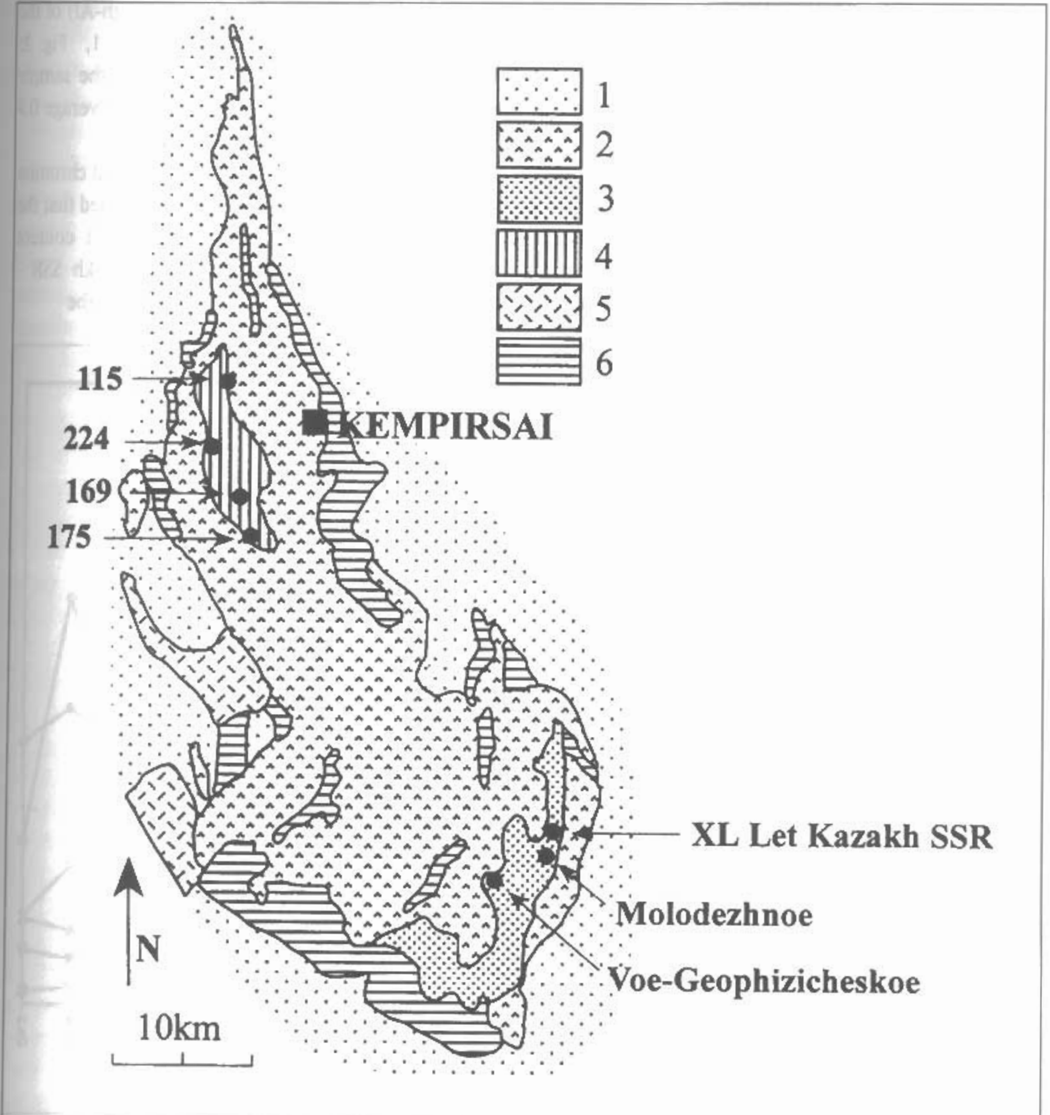

Fig. 1: Simplified geological map of the Kempirsai massif, showing the location of the studied chromite ores. Symbols: 1= Proterozoic rocks (sediments and volcanogenic), 2= serpentinized peridotites, 3= serpentinized highly depleted harzburgites and large dunite bodies, 4= serpentinized harzburgites with small dunite bodies and/or envelopes accompanied chromite ores, 5= gabbro and 6= gabbro-amphibolite (modified after Pavlov et al., 1968; Kravechenko and Grigoryeva; Merchet et al., 1994).

Representative samples of chromite ore from the Rhodope massif have been analyzed for major elements and platinum groum elements in a previous study (Zhelyaskova-Panayotova and Economou-Eliopoulos, 1993). In the present study same samples were analyzed for minor and trace elements.

4. CHEMICAL COMPOSITION OF CHROMITE ORES

Electron microprobe analyses completed for the present study (Table 1) confirm the presence of two chromite types (high-Cr and -Al) and that the chromite ores throughout both in the southern part (XL-Let Kazakh SSR - Molodezhnoe mines, high-Cr), and northern part (Batamshink -type, high-Al) of the Kimpersai massif, including the Molodezhnoe mine, show a very small variation (Table 1, Fig. 2; Kravchenko and Grigoryeva, 1986; Melcher et al., 1994). However, the composition of the sample U.G.93 from the V-oe Geophizisheskoe orebody is characterized by a high titanium content (average 0.9 wt% TiO_2), and relatively high iron content (20.0 wt% FeO).

With respect to the trace element content, the Pt, Pd and Au content of both high-Cr and -Al chromite ores it is very low (Table 1) and falls in the range given by Melcher et al., (1994) who concluded that the PGE-patterns of chromites are characterized by negative slopes. Nickel, Co, Zn, V, Mn and Ti content in chromite ores from in the southern part of the Kempirsai massif, the XL Let Kazakh SSR - Molodezhnoe mines, exhibit only a small variation, in contrast to those from the northern part, the

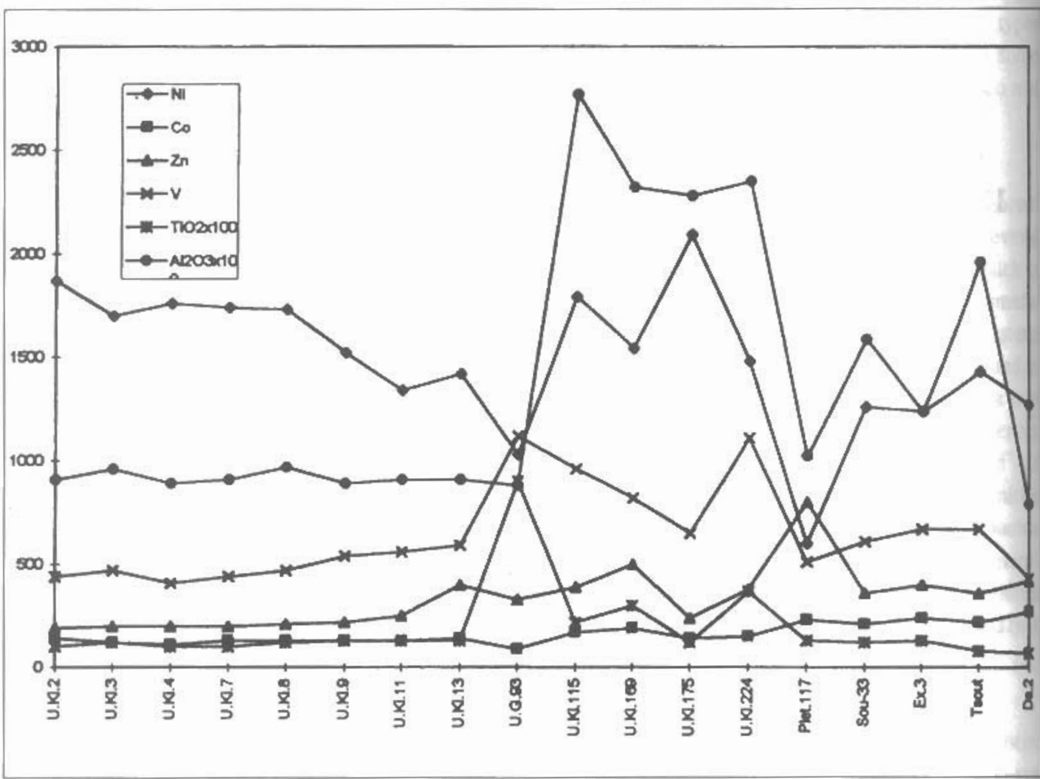

Fig. 2: Compositional variation of chromite ores from the Kempirsai massif, Urals, Data from the Table 1.

Batamshinskoe type(Table 1; Fig. 2). In addition, the average content of these elements is higher in the refractory type than the metallurgical one. The V-oe Geophizicheskoe chromite ore seems to differ from the average composition of ores from the Molodezhnoe mine in having higher Fe, Ti, Cu, Zn and V content, and lower Mg and Ni content, although Cr and Al content is similar. With respect to the trace element content of chromitites from the Rhodope massif there is a wide variation, in particular in the part of Bulgaria, but any correlation with the major element composition is not obvious (Table 2, Fig. 2). The rare earth element content (both light and heavy), in the studied chromite samples from Kempirsai and Bulgaria is lower than the detection limit of the method.

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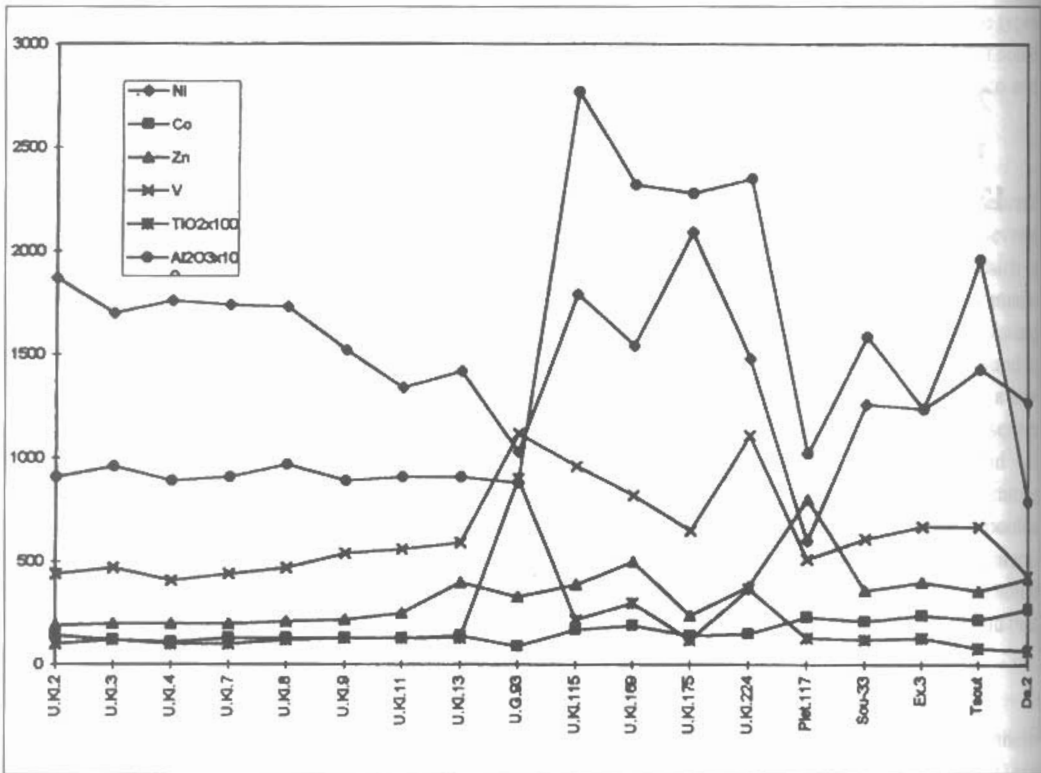

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Table 1. Major* and trace element data on chromite ores from the Kimpersai deposits, Urals

Location	Samples	description of the ore	ppb			ppm						Ni/V	Wt%				
			Pt	Pd	Au	Ni	Co	Cu	Zn	V	Mn		TiO2	Cr2O3	Al2O3	FeOt	MgO
Kempersai deposit																	
Southern part, XL Let Kazakh SSR- Molodezhnoe mine																	
	U.Ki.2	disseminated	<10	2	54	1870	140	<10	190	440	910	4,25	0,1	60,2	9,1	12,4	15,1
	U.Ki.3	disseminated	<10	<1	20	1700	120	15	200	470	910	3,62	0,12	58,7	9,6	13,1	14,8
	U.Ki.4	disseminated	<10	<1	7	1760	110	<10	200	410	940	4,3	0,1	59,7	8,9	13,8	15,2
	U.Ki.7	disseminated	<10	<1	10	1740	130	35	200	440	1030	3,95	0,1	59,8	9,1	14,1	14,6
	U.Ki.8	schlieren	<10	1	13	1730	130	10	210	470	910	3,68	0,12	58,9	9,7	13,9	15,4
	U.Ki.9	massive	15	<1	6	1520	130	42	220	540	950	2,81	0,13	59,2	8,9	14,1	14,4
	U.Ki.11	massive	<10	2	8	1340	130	173	250	560	980	2,39	0,13	58,9	9,1	13,8	14,7
	U.Ki.13	massive	<10	2	18	1420	140	19	400	590	980	2,4	0,13	59,1	9,1	13,7	14,6
Average						1640	130	50	230	490	950	3,4	0,11	59,3	9,2	13,6	14,8
Geophizicheskoe	U.G.93	massive	<10	8	9	1030	90	130	330	1120	980	0,92	0,9	58,5	8,8	19,6	9,7
Northern part																	
Batamshinskoe	U.Ki.115	massive	<10	<1	10	1790	170	22	390	960	1000	1,86	0,22	43,1	27,7	12,6	14,5
	U.Ki.169	massive	<10	<1	7	1540	190	15	500	820	1340	1,88	0,3	47,1	23,2	13,1	14,2
	U.Ki.175	massive	<10	<1	4	2090	140	<10	240	650	840	3,21	0,12	47,7	22,8	14,6	13,2
	U.Ki.224	massive	<10	1	6	1480	150	12	380	1110	1050	1,33	0,37	46,6	23,5	12,8	14,52
Average						1730	160	12	380	890	1060	2,8	0,25	46,1	24,3	13,3	14,1

Symbols: * = the oxides of Cr, Al, Fe and Mg were determined by electron microprobe, FeOt = total Fe

Table 2. Trace element data on chromite ores from the Rhodope massif

Location	Samples	ppb							ppm								
		Os	Ir	Ru	Rh	Pt	Pd	Au	Ni	Co	Zn	V	Mn	%TiO2	%Al2O3	Ni/V	Pd/Ir
BULGARIA																	
Dobromirci																	
243/63	243/63	16	32	120	6	4	14	2	520	240	370			0,11	11,7		0,44
13/63	13/63	3	8,8	25	3	2	12	6	520	110	150			0,07	21,5		1,36
DCH	DCH	30	58	210	7	3	5	4	520	180	240			0,08	17,7		0,09
Brucevtci																	
497/9	497/9	12	18	56	3	1	2	5	780	180	370			0,1	27,9		0,11
Jakovitsa																	
2007/67	2007/67	37	41	88	8	4	19	5	780	240	400			0,04	5,4		0,46
Pletena																	
117/76	117/76	220	98	220	13	5	7	11	600	230	800	510	3300	0,13	10,2	1,17	0,07
G.Kamenyane																	
29/68	29/68	18	21	30	4	11	3	8	1080	500	1900			0,1	4,5		0,14
GREECE																	
Soufli	Sou-33	24	37	124	9	3	1	2	1260	210	360	610	1850	0,12	15,8	2,06	0,03
Exochi	Ex.3	25	20	70	4	4	6	4	1240	240	400	670	1280	0,13	12,4	1,85	0,3
Tsoutoura	Tsout	25	6	40	3	2	5	2	1430	220	360	670	1270	0,08	19,6	1,85	0,83
Dadia	Da.2	20	35	120	4	2	1	4	1270	270	420	430	2380	0,07	7,9	2,95	0,03

5. DISCUSSION

Since the trace elements Zn, Mn and Co can substitute for Mg and Fe^{2+} into the tetrahedral site of the chromite structure, they are considered to diffuse easily between chromite and other mineral, during postmagmatic processes, in contrast to the V and Ti, which substitute for Cr and Al into the ocrahedral site and diffuse less easily. Although Al and Zn are considered to be less stable elements in the structure of spinel and a Zn-enrichment (< 1 wt% Zn) in disseminated and/or small concentrations of chromite could be attributed to postmagmatic processes (spinels (Zhelyaskova-Panayotova, 1962; Wylie et al., 1987; Zhelyaskova-Panayotova et al., unpubl. data) the available analytical data on chromite ores (massive or dense disseminated) from the Pindos , Othrys, Vourinos ophiolite complexes of Greece and elsewhere indicate that the magma composition rather than alteration and postmagmatic processes is a major factor controlling the chromite composition (Economou-Eliopoulos, 1996; Economou-Eliopoulos et al., 1997; unpub. data). Thus, the degree of melting of the mantle source and/or subsequent modifications (due to the extent of interaction between residue and melt and the fractional crystallization) may affect the composition of chromite ores (Jaques and Green 1980; Bacuta et al. 1990; Zhou et al. 1994; Leblanc 1995; Economou-Eliopoulos 1996).

Apart from a complex influence of the variations of physico-chemical conditions of crystallization (fO_2, P, T) on the composition of chromite ores (Hill and Roeder, 1974), the composition of high-Al ores may be the result of either lower degree of melting in the mantle source or formation from more evolved magmas. The degree of melting removes elements to an extent that depends on their compatibility. Due to the incompatible behavior of Al, Ti, Pt and Pd, in contrast to the compatible nature of Cr, Os, Ir and Ru (Tindle and Pearce 1983; Barnes et al. 1985), high-Cr chromitites, have been interpreted as resulting from higher degree of partial melting in the mantle and/or less fertile source, compared to high-Al ores (Bacuta et al. 1990; Economou-Eliopoulos and Vacondios, 1990; Zhou et al. 1994 Economou-Eliopoulos 1996). Also, the vanadium and zinc content, appears to be higher in high-Al ores than in high-Cr ones. The average content is 980 ppm V and 300 ppm Zn in the Othrys ores, and 450 ppm V and 230 ppm Zn in the metallurgical chromite ores of Vourinos (Konstantopulou 1990; Economou-Eliopoulos et al., 1997). Such a difference in individual ophiolite complexes has been attributed to the composition of the parent magma, which in turn has derived by a lower degree of partial melting of the mantle source in the case of the Othrys complex than the Vourinos. Moreover, it has been suggested that during the evolution of a marginal basin the chromite mineralization in the Othrys complex is related to a Back-arc setting, whereas the Vourinos has all features of a typical Supra-subduction zone (SSZ) complex (Economou-Eliopoulos, 1996).

The presence of two different chromite types (metallurgical and refractory), the remarkably homogeneous composition throughout the southern part of the Kempirsai massif, and the higher V, Zn and Ti content in the high-Al ores (average 890 ppm, 380 ppm and 0.25 wt% respectively) than in the high-Cr ones (490 ppm 230 ppm and 0.11 wt% respectively), are comparable to that of the above largest chromite deposits of Greece, and may indicate that, the Batamshinskoe and Main ore field chromite ores have formed from parent magmas of different composition, derived by lower degree of partial melting of the mantle source in the former than in the latter. Moreover, Melcher et al., (1997) based on an integrated study of precious metals, rare earth elements, stable and radiogenic isotopes, and the composition of fluid inclusions in chromite, proposed a two stage formation of the Kempirsai ophiolite sequence and accompanied chromite ores, and concluded that the large chromite deposits of metallurgical type in the Main Ore Field, formed after a second-stage partial melting event of an already depleted mantle source, *postdating by 15-35 Ma the first stage.*

Besides the origin of the high-Al and -Cr chromite ores in the Kempirsai massif from separate magmas, the compilation of present trace element data (Table 1) and those published by Melcher et al., (1997) indicate that large chromite deposits related with the Kempirai massif were formed from primary magmas compared to those in the Rhodope massif and Pindos ophiolite complex of Greece, which exhibit a fractionation trend, as it is suggested by the ratios of incompatible/compatible (Table 2; Barnes et al., 1985; Economou-Eliopou[illegible] the Geohizicheskoe exhibit a fractionated trend, as it is suggested by the lower content of Ni and Co, and the higher content of Ti, Fe, V and Zn compared to ores from the large deposits of the southern part with similar Cr and Al content (Table 1). Also, a significant variation in the concentrations of these trace elements seems to be common in the Batamshinsk (refractory) chromite ores (Table 1) despite their similar major element composition. Moreover, high-Al chromite ores from the Voskod drill-holes are characterized by relatively high ratios of incompatible/compatible elements, like Pd/Ir ranging from 2.0 to 4.3 (Melcher et al., 1994), although they have comparable major element composition to the studied samples from Batamshinskoe. Although much more research is required to define and explain fractionation trends throughout the Kempirsai massif., it seems likely that the large high-Cr chromite deposits in the southern part are characterized by a remarkably limited compositional variation, which may reflect uniform conditions over large areas (large volumes of magma), in contrast to small chromite bodies, in both southern and northern parts of the massif.

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