

OPHIOLITIC CHROMITITES FROM THE KAHRAMANMARAŞ AREA, SOUTHEASTERN TURKEY: THEIR PLATINUM-GROUP ELEMENTS (PGE) GEOCHEMISTRY, MINERALOGY AND Os-ISOTOPE SIGNATURE

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ABSTRACT

Mantle-hosted podiform chromitites from ophiolites of the Kahramanmaraş area (south-eastern Turkey), have been investigated with regard to the chromite composition, Platinum-group elements (PGE) concentration and mineralogy, as well as Os-isotope geochemistry. Chromitites vary from Al-rich to Cr-rich, however they indifferently display enrichment in Os-Ir-Ru over Rh-Pt-Pd, with concentrations of PGE lower than 510 ppb. Consistently, the most abundant Platinum-group minerals (PGM) are Ru-Os-Ir sulfides and alloys with subordinate Ir-Ru-Rh sulfarsenides and one grain of unidentified Pd-Sb phase. Textural relationships indicate that the PGM sulfides and alloys are mostly magmatic in origin, i.e. formed at high temperature prior to or concomitant with the crystallization of chromite, whereas the sulfarsenides and the Pd bearing minerals were formed during post-magmatic processes. The Kahramanmaraş chromitites display relatively high Re/Os ratios, that coupled with error-chron calculated ages, point to a mixing of mantle-derived Os with Os from a source characterized by a relatively high radiogenic signature, possibly subduction-related fluids. If the genesis of the Kahramanmaraş ophiolites is related to subduction, the concomitant presence of Al-rich and Cr-rich chromitites suggests chromite precipitation from melts varying in composition from MORB-like back-arc basalts (Al-rich chromite) to boninites (Cr-rich chromite). The geochemical and mineralogical data indicate that most of the Kahramanmaraş chromitites have low PGE potential, due to low PGE concentration, small size of the PGM grains, and predominance of Ru-Os-Ir over Rh-Pt-Pd.

Only one sample from Elbistan, exceptionally, was found to have a pronounced positive Pt anomaly, up to 99 ppb, that is supported by identification of magmatic Pt specific phases. Genetic relationships of this chromitite with the others in the area are still unknown. This chromitite represents a potential target for Pt recovery, such that detailed study of the Pt mineralogy, distribution in the chromite ore, and identification of the magmatic sources of Pt, and the mechanisms of Pt concentration, may be useful tools to future exploration in the Kahramanmaraş ophiolite.

INTRODUCTION

Podiform chromitites hosted by Tethyan ophiolites in the Western Mediterranean are economically important, and represent a major economic source of chromium. Relevant deposits have been extensively exploited in the former Yugoslavia, Albania, Greece, Cyprus and Turkey (Cina et al., 1986; Economou et al., 1986; Engin et al., 1986; Jankovic, 1986; Panayiotou et al., 1986). Some of the most interesting exposures are in Tethyan ophiolites of Turkey, where a great number of complexes occur within five main zones. These are, specifically, from north to south: 1) Pontide, 2) Anatolia, 3) Tauride, 4) Southeast Anatolia, and 5) Peri-Arabian belts (Parlak et al. 2004 and references therein). According to Parlak et al. (2002; 2004) and Uysal et al. (2005; 2007) most ophiolite complexes of Turkey record Cretaceous ages, and formed in subduction-related dynamic settings, most exhibiting large-scale, economical important podiform-type chromite deposits.

In recent decades, podiform chromitites in ophiolites have attracted the attention of the economic geologists as a significant potential target for the recovery of platinum-group elements (PGE), their concentration being several orders of magnitude in excess of their country rocks (Economou-

Eliopoulos, 1993; 1996). It is generally agreed that PGE mostly form specific phases, so-called Platinum-group minerals (PGM), and do not occur as solid solution in the chromite lattice (Stockman and Hlava, 1984; Augé, 1985; Capobianco and Drake, 1990; McElduff and Stumpfl, 1990; Nilsson, 1990; Thalhammer et al., 1990; Capobianco et al., 1994; Garuti and Zaccarini, 1997; Melcher et al., 1997; Garuti et al., 1999a; 1999b; Cina et al., 2002; Zaccarini et al., 2005; 2007; Proenza et al., 2007; Tsoupas and Economou-Eliopoulos, 2007;). This conclusion has stimulated investigation of the chromitites in order to verify the mineralogical nature, morphology, grain size and textural position of PGM, in view of mineral processing for their recovery from the host rock.

Moreover, the nature of chromite composition, PGE geochemistry and host mineralogy, as well as Os-isotope signatures of ophiolitic chromitites are significant indicators of mantle source characters and geodynamic setting (Arai and Yurimoto, 1994; 1995; Melcher et al., 1997; Zhou et al., 1998; Proenza et al., 2004; Uysal et al., 2005), thereby offering a useful tool for exploration.

Despite their economic importance, most Turkish chromitites have not been extensively studied with respect to their compositions and PGE potential (Engin et al., 1986; Uysal et al., 2005; 2007). Accordingly, the present work fo-

cuses on a mineralogical, geochemical and isotopic investigation of chromitites from the Kahramanmaraş area, in southeast Turkey. The data are used to better understand the origin of these chromitites and their host ophiolite complexes, and to evaluate them as potential economic resources.

GEOLOGICAL BACKGROUND AND DESCRIPTION OF THE INVESTIGATED CHROMITITES

The chromitite samples studied were collected in southeastern Anatolia (Fig. 1A) at the following localities: Adiyaman, Elbistan, Hekimhan, Malatya and Türkoğlu (Fig. 1B). In this region, several tectonic units have been recognized, including metamorphic massifs, granitoids, ophiolites and their respective metamorphic products (Parlak 2006). The metamorphic units are dominated by metacarbonates, mica schists, phyllites, meta-clastic rocks, and meta-cherts. The highest metamorphic grade recorded is greenschist facies (Robertson et al., 2006, and references therein), while granitoid intrusives cut across all the above units in a NE-SW direction. Based on K-Ar geochronology, these intrusions occurred in a volcanic arc setting, between about 85 and 77 Ma (Parlak, 2006). Given a subduction-related provenance, the ophiolite-related metamorphic rocks are believed to have formed either during the initiation of intraoceanic subduction or possible late-thrusting (about 90 Ma). The ophiolites themselves consist of mantle tectonites and an oceanic crustal section including ultramafic and mafic cumulates. Sheeted dykes, massive gabbros, locally showing pegmatitic textures, cut by isolated basaltic dykes, have also been recognized. Chromitites form small podiform bodies within the mantle tectonite sequence, invariably surrounded by dunite envelopes. The chromitites and their mantle tectonite hosts were tectonically bounded by the metamorphic units. Chromite textures vary from massive to more nodular, disseminated types, and rarely appear as banded schlierens. The investigated samples are typical of massive chromitites, with less than 30 volume percent of silicate matrix. They are generally fresh, alteration being limited to the development of ferrian chromite along cracks and grain boundaries. The matrix mainly consists of clinopyroxene and altered silicates such as chlorite, serpentine and rare, Ca-rich garnet.

RESULTS

Chromite composition

Chromite compositions were determined by electron microprobe at the Universities of Hamburg (Germany) and Modena and Reggio Emilia (Italy). A selection of analyses is shown in Table 1. The chemical data for chromite were stoichiometrically recalculated distinguishing FeO from Fe₂O₃ following the procedure of Carmichael (1967).

In general, the chromite compositions plot in the podiform field (Fig. 2), although significant differences in each group may be observed. Those from Adiyaman, Malatya, Türkoğlu and some of those of Elbistan and Hekimhan have Cr₂O₃ contents higher than 50 wt% and Al₂O₃ lower than 20 wt% (Fig. 2A), confirming their attribution to the Cr-rich ores. In contrast, most of the Elbistan and Hekimhan chromitites show Cr₂O₃ to be less than 50 wt%, with Al₂O₃ higher than 20 wt%, corresponding to Al-rich chromitites. Mg contents are quite similar in all the investigated chromi-

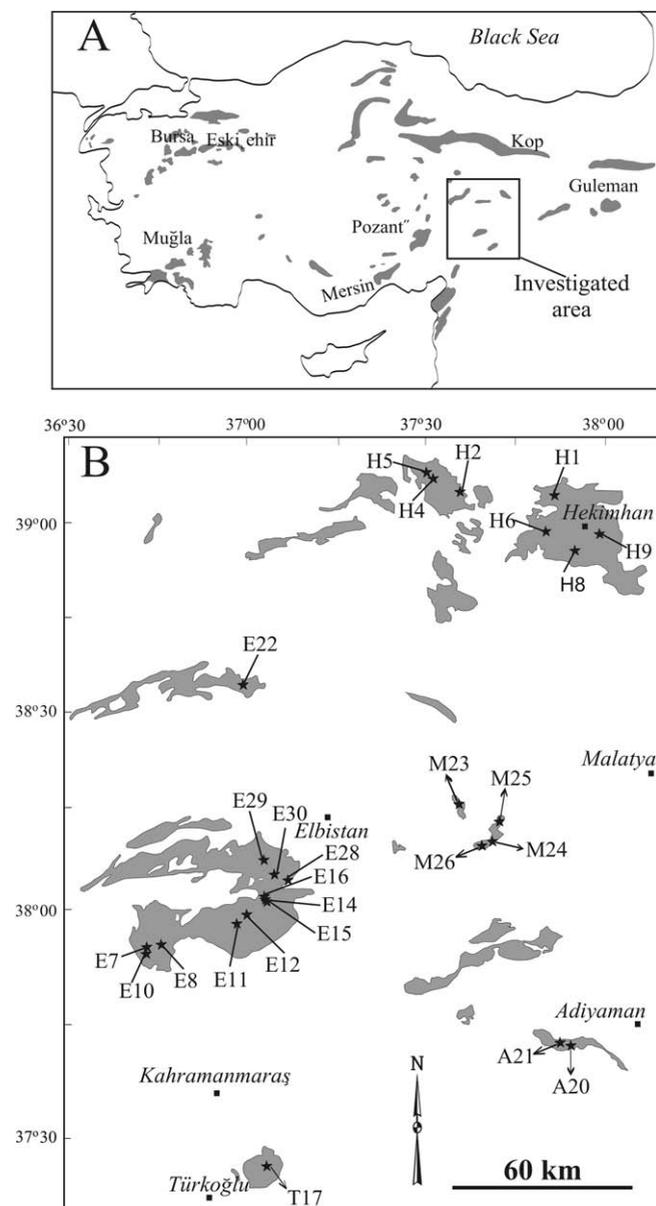


Fig. 1 - A. Location of the major ophiolite complexes in Turkey. Complexes containing chromite deposits are indicated. B. Ophiolite complexes (grey) in the area of the investigated chromitites, showing the samples location.

tites despite of their variable Cr, Mg numbers ($\#Mg = Mg/(Mg + Fe^{2+})$) varying between 80 to 60 (Fig. 2B). Only one group of chromitites from Elbistan, those with the highest Cr contents, have $\#Mg$ as low as 40 (Fig. 2B). TiO₂ contents are generally lower than 0.3 wt%, typical of ophiolitic chromitites, a few samples from Hekimhan only showing a weak enrichment in TiO₂ (Fig. 2C).

Geochemistry of Platinum-group elements

Chromitites were analyzed for the six PGE in the Laboratory of Genalysis (Australia) by ICP-MS after preconcentration of Ni-sulfide and at the University of Leoben (Austria) using the innovative procedure described in Meisel et al. (2003) and Meisel and Moser (2004). Total PGE concentrations in the analyzed chromitites vary from 28 to 510 ppb (Table 2).

Table 1 - Representative microprobe analyses of chromite in the Kahramanmaraş chromitites.

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	Fe ₂ O ₃	MgO	MnO	Cr ₂ O ₃	NiO	Totals
<i>Adiyaman</i>										
A21 11	0.05	0.12	10.99	10.13	5.42	15.54	0.14	58.46	0.00	100.86
A21 2	0.02	0.12	10.67	9.85	5.54	15.58	0.17	59.01	0.00	100.96
A21 3	0.04	0.11	12.60	11.24	3.95	14.95	0.16	57.35	0.00	100.39
A21 8	0.04	0.09	11.21	10.02	5.65	15.56	0.10	58.07	0.00	100.73
<i>Elbistan (Cr-rich)</i>										
E10 2	0.07	0.15	11.01	14.02	1.42	12.81	0.25	60.01	0.09	99.83
E10 3	0.06	0.15	11.14	13.95	1.58	12.81	0.26	59.58	0.08	99.61
<i>Elbistan (Al-rich)</i>										
E14 2	0.05	0.18	24.25	11.43	3.58	15.71	0.21	44.06	0.14	99.60
E29 4	0.00	0.14	26.68	11.16	5.99	16.15	0.24	39.02	0.00	99.38
<i>Hekimhan</i>										
H5 1	0.04	0.14	15.66	10.16	4.76	15.87	0.22	53.25	0.00	100.10
H5 5	0.10	0.13	14.26	10.60	4.62	15.65	0.27	55.38	0.00	101.01
H8 4	0.00	0.29	16.11	11.03	7.53	15.38	0.24	49.55	0.00	100.13
H8 9	0.05	0.26	14.58	11.12	7.62	15.17	0.20	50.99	0.00	99.98
<i>Malatya</i>										
M23 2	0.00	0.11	13.03	10.76	4.17	15.04	0.22	56.14	0.00	99.47
M23 2	0.04	0.08	12.55	10.37	4.90	15.45	0.27	56.88	0.00	100.54
M26 7	0.00	0.22	11.57	12.21	4.21	14.14	0.17	57.45	0.00	99.97
M26 5	0.01	0.26	13.52	10.83	5.35	15.32	0.22	54.91	0.00	100.43
<i>Türkoğlu</i>										
T17a 1	0.06	0.17	11.48	12.23	2.45	13.88	0.24	58.82	0.16	99.50
T17a 2	0.06	0.14	11.51	11.90	2.88	13.84	0.20	57.73	0.14	98.40
T17a 3	0.07	0.17	11.49	12.23	2.56	13.77	0.25	58.70	0.17	99.40
T17a 4	0.28	0.18	11.38	12.27	2.62	13.88	0.23	58.38	0.15	99.36

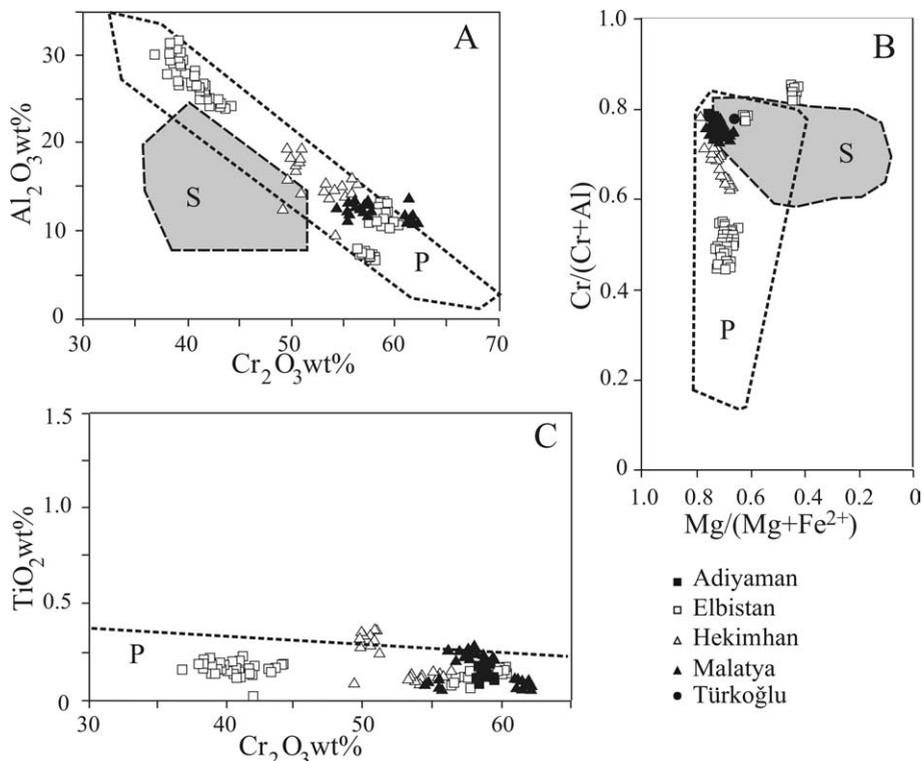


Fig. 2 - Chemical composition of chromite from chromitites of Kahramanmaraş. Abbreviations: P = podiform chromitites, S = stratiform chromitites.

Chondrite-normalized distribution patterns are presented in Fig. 3, compared with those reported for other mantle-hosted ophiolitic chromitites worldwide (Gauthier et al., 1990; McElduff and Stumpfl, 1990; Economou-Eliopoulos, 1996; Proenza et al., 1999; Kojonen et al., 2003; Büchl et al., 2004; Uysal et al., 2005). Despite the variation in total PGE amounts, all the analyzed chromitites are enriched in Os+Ir+Ru relative Rh+Pt+Pd, involving a negative slope of PGE, with exceptional weak positive Ru anomaly. One sample from Elbistan is characterized by Pt enrichment (Fig. 3). No significant difference in PGE distribution and concentration was noted between the Cr-rich and Al-rich chromitites.

Platinum-group element mineralogy

Polished sections, obtained from samples of massive chromitite were investigated by reflected-light microscope. Subsequently, PGM distribution was studied by electron microscopy and analyzed with an electron microprobe at the University of Modena and Reggio Emilia (Italy) following the procedure described in Zaccarini et al. (2005; 2007). The PGM are very small in size (generally less than 10 μm) and occur as single or polyphase grains in association with clinopyroxene, amphibole, base metals sulfides and other PGM. They are located in fresh chromite, along cracks of chromite filled with chlorite and in the matrix, which mainly

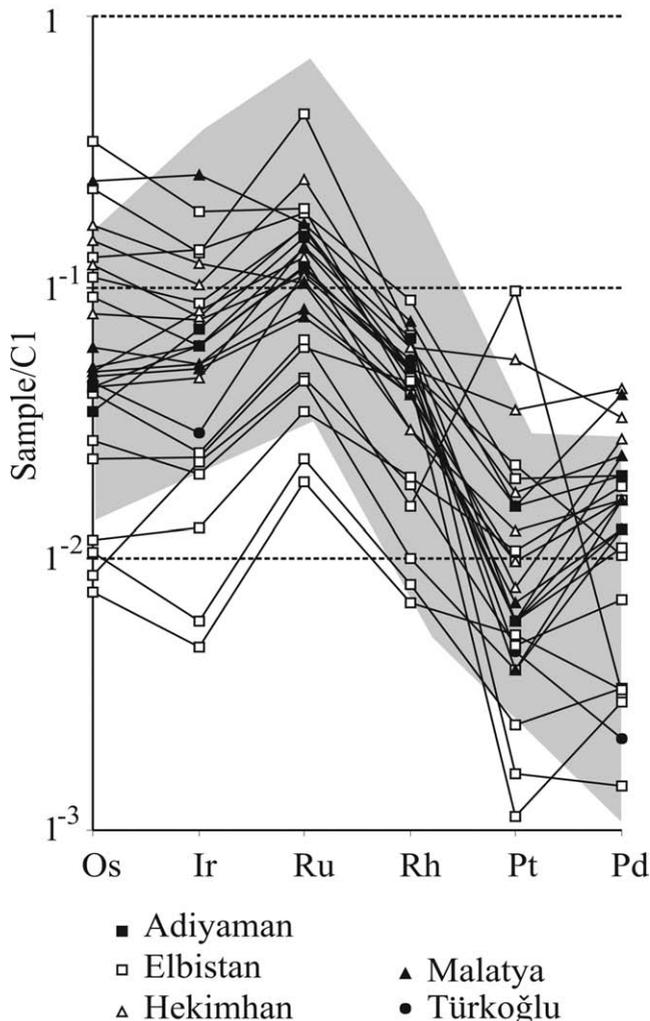


Fig. 3 - C1 chondrite (Naldrett and Duke 1980) normalized patterns of the Kahramanmaraş chromitites and comparison with the chromitites hosted in the ophiolitic mantle (see text for data source).

consists of serpentine, chlorite and clinopyroxene. Examples of PGM grains are illustrated in Figs. 4 and 5, in which four mineral species were identified: sulfides, alloys, sulfarsenides and one antimonide. At all the investigated localities, the Ru-sulfide laurite is the most abundant PGM, occurring as polygonal crystal included in fresh chromite, in the altered silicate matrix or in contact with cracks (Figs. 4, 5E, F). It may consist of single phase (Fig. 4A), or may form composite grains associated with base metals sulfides (mainly millerite, pentlandite and chalcopyrite), Na-rich amphibole, clinopyroxene, chlorite and other PGM (Figs. 4B-E, 5C-F). Element abundances in two sulfides included in fresh chromite in the Elbistan chromitites, containing Pt-Ir-Rh-Fe-Cu and Ni and Ir-Pt-Rh-Fe and Cu respectively, were only qualitatively estimated due to their relatively small size (less than 5 μm). The Pt-Ir-Rh-Fe-Cu-Ni sulfide was found associated with laurite and the Ir-Pt-Rh-Fe-Cu sulfide with a small silicate aggregate (Fig. 5B). Osmium and iridium alloys were found included in fresh chromite in the chromitites of Elbistan and Türkoğlu respectively. Osmium occurs associated with laurite whereas iridium was found in contact with a silicate phase. The sulfarsenides identified are irarsite, ruarsite and hollingworthite. Irarsite occurs as a porous grain in contact with a laurite crystal that displays a spectacular “graphitic-like” texture, being completely filled with tiny lamellae of irarsite. This PGM has been found in contact with ferrian chromite, chlorite and clinopyroxene (Fig. 5C, D) in the chromitite from Elbistan. A small ruarsite, about 3 μm in size, characterized by an irregular shape, was detected in the crack of chromite close to a laurite crystal, in the Türkoğlu chromitite. One grain of hollingworthite has been identified in the Malatya chromitite, as part of a polyphasic PGM composed of zoned laurite and unidentified Pd-Sb phase (about 1 μm in size). The PGM occur in the altered matrix of chromite in contact with chlorite (Fig. 5E, F).

Selected analyses of laurite are listed in Table 3, their compositions plotted, as atomic proportion, in the Ru-Os-Ir ternary diagram in Figure 6. Most of the analyzed laurite crystals have Ru-Os ratios higher than C1 chondrite values (Fig. 6A-C). Only some laurites from Hekimhan are relatively enriched in Os. In most cases laurites are homogeneous, only a few grains displaying Os-rich rims, suggesting that laurite compositions had not been significantly influenced by their textural setting. Iridium (Fig. 6D) is characterized by the following composition, as atomic %: Ir = 56.53, Os = 16.69, Ru = 10.05, Pt = 9.76, Rh = 3, Fe = 3.38 and Ni = 0.6.

Os-isotopic composition

Re and Os concentrations, along with Os-isotopic compositions, were determined using ICP-QMS (quadrupole ICP-MS) at the University of Leoben (Austria) and are presented in Table 4. The chromitites are generally characterized by very low Re/Os ratios, thus only a small increase of $^{187}\text{Os}/^{188}\text{Os}$ through the radiogenic ingrowths with time is to be expected, and such that measured $^{187}\text{Os}/^{188}\text{Os}$ ratios should be close to the initial isotopic composition of the mantle at the time of formation. The $^{187}\text{Os}/^{188}\text{Os}$ isotopic compositions of the chromitites are in general super-chondritic, having $^{187}\text{Os}/^{188}\text{Os}$ values higher than those expected from average mantle. Since the Re/Os ratios of the Kahramanmaraş chromitites are relatively high, the radiogenic ingrowths through time cannot be neglected. Although the uncertainties of $^{187}\text{Os}/^{188}\text{Os}$ determined via ICP-QMS

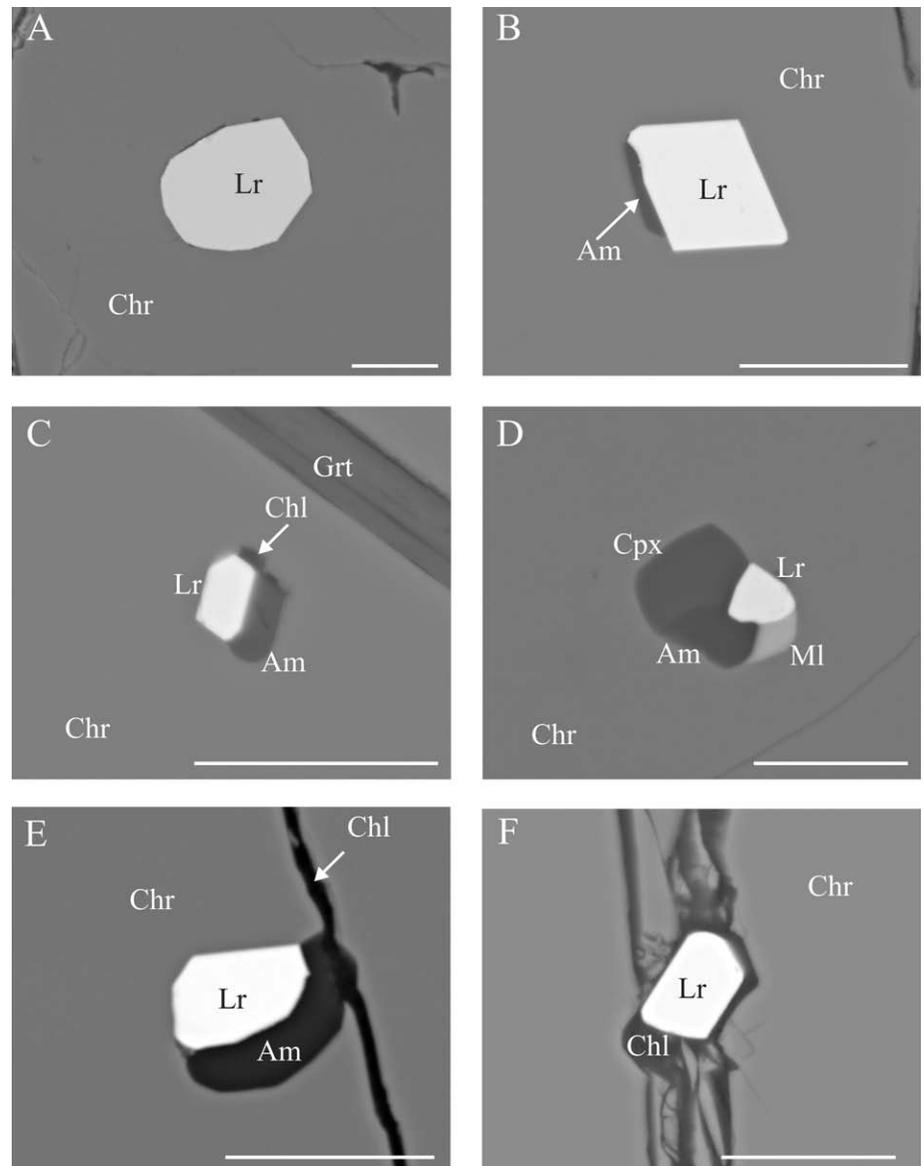


Fig. 4 - Scanning electron microscope images showing morphology, texture and mineral assemblage of the Kahramanmaraş laurite. A = single phase laurite included in fresh chromite, B = Laurite + Na-rich amphibole in fresh chromite. C = inclusion composed of laurite + Na-rich amphibole + chlorite in chromite, close to a vein filled with Ca-rich garnet, D = polyphasic grain composed of laurite + Na-rich amphibole + clinopyroxene + chlorite included in fresh chromite, E = laurite + Na-rich amphibole in contact with a crack filled with chlorite, F = single phase laurite in veins filled with chlorite. Abbreviations: Lr = laurite, Chr = chromite, Am = amphibole, Chl = chlorite, Grt = Ca-rich garnet, Cpx = clinopyroxene, Ml = millerite. Scale bar = 10 μ m.

(quadrupole ICP-MS) are about 1%, it is possible to calculate a pseudo-isochron, the age of which, about 1 Ga, is significantly higher than that expected (Fig. 7). In computing this regression, samples S8 and S11 were not included since their composition is too high for a given $^{187}\text{Re}/^{188}\text{Os}$ and Pt/Ir ratio is much higher than for the other samples and for typical ophiolitic chromitites in general. The initial isotopic composition of the remaining samples calculated from this regression ($^{187}\text{Os}/^{188}\text{Os} = 0.12856 \pm 0.00172$) is consistent with a Mesozoic or even younger chondritic (or "primitive") mantle composition (Fig. 7).

DISCUSSION AND CONCLUSIONS

Genesis of PGE-Cr mineralization in ophiolitic mantle

The origin of mantle-hosted podiform ophiolitic chromitites has been debated for many years (Lago et al., 1982; McElduff and Stumpfl, 1990, Arai and Yurimoto 1995, Zhou et al. 1998, Proenza et al., 1999). One of the major questions concerns whether they form solely in high-temperature magmatic systems, or if it is possible to precipitate

significant amounts of chromite in the presence of fluids during melt-rock or melt-melt interaction. Recently, a general consensus has emerged that podiform chromitites formed by melt-rock reaction in subduction-related geodynamic environments (Roberts, 1988; Arai and Yurimoto, 1994; 1995; Yumul and Balce, 1994; Zhou et al., 1998; Proenza et al., 1999; Melcher et al., 1999; Büchl et al., 2004; Uysal et al., 2005) in the presence of primitive melts saturated in olivine and chromite, and enriched in water (Matveev and Ballhaus, 2002). It has also been demonstrated that Cr-rich ophiolitic chromitites are commonly associated with boninitic or andesitic melts of high #Mg (high Mg andesites or HMA) generated in refractory peridotite upper mantle sources. Al-rich ophiolitic chromitites tend to be associated with MORB-like back-arc basalts, generated by decompression melting at seafloor spreading centers. The presence of Al-rich and Cr-rich chromitites in the Kahramanmaraş area, therefore, suggests that chromite could have precipitated from different melts varying in composition from MORB-like basalts formed in back-arc setting (Al-rich chromite) to boninites related with subduction zone (Cr-rich chromite). On the other hand, the bimodal composition of the Kahramanmaraş chromitites may also reflect vertical

Table 2 - PGE concentration (ppb) of the Kahramanmaraş chromitites (*Analyses from the University of Leoben (Austria)).

	Os	Ir	Ru	Rh	Pt	Pd	PGE Sum
<i>Adiyaman</i>							
A20	18	38	106	13	6	7	188
A21	22	33	81	10	16	11	173
<i>Elbistan</i>							
E10*	12	13	42	9	1	2	78
E11*	21	13	44	3	99	2	182
E12*	4	12	32	4	5	4	61
E13*	5	3	16	2	3	2	31
E14*	4	3	13	1	5	2	28
E15A*	119	72	303	13	2	1	510
E28	66	74	129	18	20	11	318
E29	6	7	24	4	11	10	62
E30	14	11	31	2	4	9	71
E8*	48	33	82	10	23	6	201
<i>Hekimhan</i>							
H1	22	25	98	12	18	13	188
H2	41	41	76	10	8	15	191
H3	87	66	71	6	13	9	252
H4	177	103	134	8	10	9	441
H5	62	42	116	10	36	23	289
H6	76	55	172	12	55	18	388
H7	25	44	89	6	10	9	183
<i>Malatya</i>							
M22	31	28	72	8	7	7	153
M23	127	141	118	15	16	22	439
M24	25	28	57	8	6	9	133
M25	24	27	54	8	6	13	132
M26	26	33	96	10	4	7	176

zoning due to: 1) fractionation of a single magma batch (increase of Al in the liquid) during its ascent, implying accumulation of Cr-rich chromitites at deep mantle levels and formation of the Al-rich ones close to the Moho-Transition Zone, or 2) progressive depletion of the mantle tectonite upwards in the mantle sequence, with increase of the #Cr number in podiform chromitites hosted in the most residual mantle (Leblanc and Violette, 1983; Leblanc and Nicolas, 1992; Stowe, 1994). Both these alternative hypotheses can hardly be applied to the Kahramanmaraş chromitites, since fractionation of a single magma batch or high degrees partial melting should have caused marked PGE fractionation between the Cr-rich and Al-rich chromitites, that was not the case.

A subduction-related geodynamic setting is supported by the Os isotopic signature of the Kahramanmaraş chromitites. They display relatively high Re/Os ratios that coupled with errorchron age calculated point to a mixing of Os from the upper mantle with Os from a source characterized through a

more radiogenic signature. Such a source could be fluids originating in the SSZ region of the upper mantle (Brandon et al., 1996).

Most podiform chromitites are enriched in Os, Ir and Ru, although a small number display enrichments in Pt and Pd. These rare cases include some chromitites from ophiolites of Greece, Albania (Konstantopoulou and Economou-Eliopoulos, 1992; Cina et al., 2002), the Zambales ophiolites in Philippines (Bacuta et al., 1990), the Shetlands (Prichard et al., 1996) and Oman (Ahmed and Arai, 2002). In these cases, Pt and Pd enrichment is related to the presence of magmatic sulfides. Formation of discrete PGM of Os-Ir-Ru in the pre-chromite stage can be explained by invoking the "metal cluster" hypothesis, proposed by Tredoux et al. (1995). These authors suggested that the fractionation of Os, Ir and Ru into chromite is controlled by the entrapment of submicroscopic PGE clusters, composed of few hundred atoms in the metallic state, that are initially present in the chromite-forming system at high temperature. Subse-

Table 3 - Representative microprobe analyses of laurite in the Kahramanmaraş chromitites.

Weight %	Os	Ir	Ru	Rh	Pt	Pd	Fe	Ni	Cu	S	As	Total
<i>Elbistan</i>												
E15A 6 2	12.76	5.57	43.11	0.23	0.00	0.25	0.94	0.19	0.00	35.78	0.00	98.83
E15C 2 2	5.47	5.71	37.49	0.23	0.00	0.00	5.39	5.48	0.31	40.05	0.00	100.12
E15A 3 4	9.84	2.64	50.19	0.00	0.00	0.07	0.96	0.07	0.08	37.54	0.00	101.39
E15C 3 3	13.13	8.18	41.75	0.15	0.00	0.00	0.76	0.13	0.08	34.99	0.00	99.16
<i>Hekimhan</i>												
H5 1 2	30.46	13.99	23.47	0.34	0.00	0.14	0.50	0.01	0.00	31.01	0.00	99.93
H5 2 1	28.26	13.73	26.58	0.51	0.00	0.00	0.58	0.00	0.10	31.56	0.00	101.32
H5 3 2	29.83	12.00	24.56	0.31	0.00	0.00	0.89	0.00	0.51	31.42	0.00	99.52
H8 2 2	13.55	3.86	41.57	1.04	0.00	0.00	1.59	0.57	0.27	36.69	0.00	99.13
<i>Malatya</i>												
M26 1 1	16.29	6.48	39.99	0.21	0.00	0.04	0.80	0.27	0.12	34.75	0.00	98.95
M26 1 4	16.79	6.04	41.55	0.00	0.00	0.26	0.87	0.13	0.00	35.20	0.00	100.83
M26 2 2	15.26	6.35	42.50	0.37	0.00	0.00	0.79	0.06	0.12	36.12	0.00	101.57
M23b 1 2	13.70	12.39	35.48	2.38	0.00	0.00	0.32	0.07	0.08	32.23	2.28	98.92
M23b 1 3	15.44	10.40	36.23	2.35	0.00	0.00	0.24	0.11	0.00	33.06	2.37	100.19
Atomic %	Os	Ir	Ru	Rh	Pt	Pd	Fe	Ni	Cu	S	As	
<i>Elbistan</i>												
E15A 6 2	4.03	1.74	25.65	0.13	0.00	0.14	1.01	0.19	0.00	67.10	0.00	
E15C 2 2	1.53	1.58	19.78	0.12	0.00	0.00	5.15	4.98	0.26	66.61	0.00	
E15A 3 4	2.95	0.78	28.33	0.00	0.00	0.04	0.98	0.07	0.07	66.78	0.00	
E15C 3 3	4.22	2.60	25.27	0.09	0.00	0.00	0.83	0.13	0.07	66.77	0.00	
<i>Hekimhan</i>												
H5 1 2	11.07	5.03	16.06	0.23	0.00	0.09	0.62	0.01	0.00	66.88	0.00	
H5 2 1	10.01	4.81	17.72	0.33	0.00	0.00	0.70	0.00	0.11	66.32	0.00	
H5 3 2	10.68	4.25	16.54	0.21	0.00	0.00	1.08	0.00	0.55	66.70	0.00	
H8 2 2	4.19	1.18	24.21	0.59	0.00	0.00	1.68	0.57	0.25	67.33	0.00	
<i>Malatya</i>												
M26 1 1	5.28	2.08	24.39	0.13	0.00	0.02	0.89	0.28	0.11	66.82	0.00	
M26 1 4	5.35	1.91	24.93	0.00	0.00	0.15	0.94	0.13	0.00	66.58	0.00	
M26 2 2	4.77	1.97	25.01	0.21	0.00	0.00	0.84	0.06	0.12	67.02	0.00	
M23b 1 2	4.63	4.15	22.58	1.49	0.00	0.00	0.37	0.08	0.08	64.66	1.96	
M23b 1 3	5.12	3.41	22.61	1.44	0.00	0.00	0.27	0.12	0.00	65.03	1.99	

quently, due to their physical and chemical properties, these clusters coalesce forming specific PGM phases that are enclosed by early-crystallizing minerals, principally chromite. It has also been demonstrated that the crystallization of primary PGM associated with chromitite mainly depends on the proportion of Os, Ir and Ru, and on the availability of sulfur and temperature conditions prevailing during the chromite formation (Augé and Johan, 1988; Garuti et al., 1999a; 1999b). Sulfur fugacity is expected to increase with decreasing temperature in the magmatic system, this variation being reflected in the paragenesis of magmatic PGM, which are characterized by early precipitation of Os-Ir-Ru alloys \pm Os-Ir-Ru sulfides followed by the crystallization of

sulfides alone especially those of the laurite-erlichmanite series (Augé and Johan, 1988). Recent experiments by Brenan and Andrews (2001) and Andrews and Brenan (2002) confirmed that temperature and sulfur fugacity are important factors controlling the precipitation of Os-Ir-Ru sulfides or Os-Ir-Ru alloys. At about 1300 °C laurite crystallizes in equilibrium with Os-Ir alloys. The experimental results also demonstrated that Os solubility in laurite increases with decreasing temperature, or increasing sulfur fugacity. Therefore, by increasing the sulfur fugacity and decreasing temperature, the stability field of laurite expands thereby accommodating more Os, producing the Os-rich laurite and erlichmanite prior to its entrapment within the chromite. De-

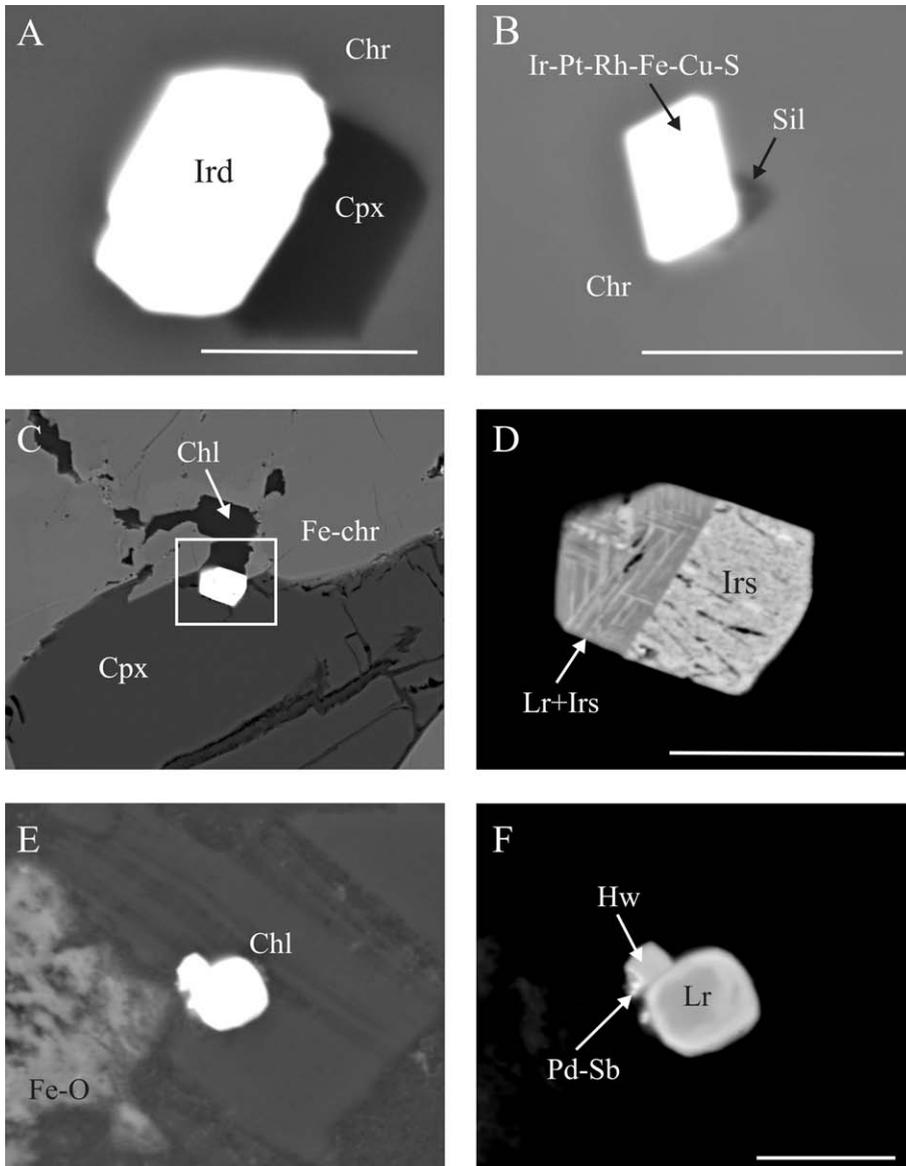


Fig. 5 - Scanning electron microscope images showing morphology, texture and mineral assemblage of the Kahramanmaraş PGM. A = iridium + clinopyroxene included in fresh chromite, B = inclusion composed of the unidentified Ir-Pt-Rh-Fe-Cu sulfides + silicate, in fresh chromite, C = laurite + irarsite in contact with chlorite, ferrian-chromite and clinopyroxene, D = enlargement of the Figure C, showing the “graphitic-like” texture of laurite and irarsite, E = laurite + hollingworthite + unidentified Pd-antimonide in the chromite matrix composed of chlorite and Fe oxide or hydroxide, F = enlargement of the grain in Figure E, showing the laurite zonation. Abbreviations: Ird = iridium, Cpx = clinopyroxene Lr = laurite, Irs = irarsite, Fe-O = Fe oxide or hydroxide, Hw = hollingworthite. Scale bar = 10 μm.

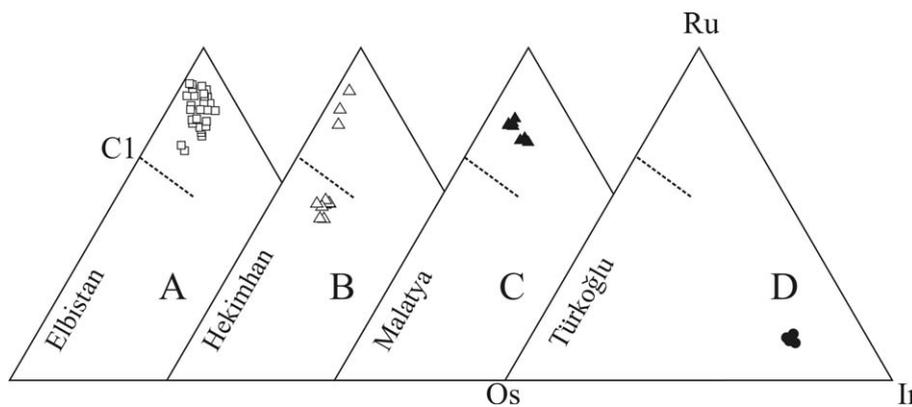


Fig. 6 - Composition of Kahramanmaraş laurite (A,B,C) and iridium (D) plotted in the ternary diagram Ru-Os-Ir (at%). Os-Ru ratio calculated from the C1 chondrite (Naldrett and Duke 1980).

spite their association with altered silicates, on the basis of their composition, shape and chemical zoning, most of the Kahramanmaraş laurite and other PGM crystallized at high temperature, prior to or concomitantly with the crystallization of the host chromite. Therefore the composition of laurite is indicative of the physico-chemical conditions prevailing during its entrapment. In consequence, we are able to conclude that sulfur fugacity was low during the precipita-

tion of the chromitites of Elbistan, Malatya but was relatively high during crystallization of laurite in the Hekimhan chromitites (Fig. 6). Although erlichmanite is absent in the investigated chromitites, the presence of abundant base metals sulfides associated with the magmatic PGM suggests that the sulfur fugacity was increasing up to the stabilization field of millerite. The absence of erlichmanite, despite high sulfur fugacities, has been attributed to the low Os activity

Table 4 - Os and Re abundances (ppb), and Os–isotopic composition of Kahramanmaraş chromitites.

	Os		Re		$^{187}\text{Re}/^{188}\text{Os}$	$^{187}\text{Os}/^{188}\text{Os}$
E10	12.0	0.5%	0.25	0.9%	0.1015	0.1319
E11	20.9	0.6%	0.13	3.0%	0.0306	0.1371
E13	5.4	0.8%	0.35	1.6%	0.3141	0.1340
E14	3.9	0.5%	0.35	1.5%	0.4374	0.1367
E15A	119.4	0.9%	0.18	1.1%	0.0073	0.1289
T17B	22.8	0.7%	0.28	1.4%	0.0582	0.1283
H8	47.6	1.1%	0.15	0.9%	0.0149	0.1361

in the system, possibly due to early precipitation of this metal in Os-Ir-Ru alloys. As noted above, the formation of podiform chromitites and associated PGM may have occurred in the presence of volatile- (including H_2O) and sodium-rich fluids (Johan et al., 1983; Augé and Johan, 1988; Melcher et al., 1997). The presence of these fluids is indicated by the presence of abundant primary Na-rich amphibole crystals associated with PGM in the Kahramanmaraş chromitites (Fig. 4B, C, E). These fluids are believed to have been preferentially released in a subduction zone environment. Thus the association of abundant primary hydrated silicates, along with high PGE concentration and composition of Kahramanmaraş chromitites appear to testify subduction-related ophiolitic sequences.

Primary PGM formed at high temperature may become unstable at low temperatures as they undergo post-magmatic processes, thereby altering to secondary phases (Stockman and Hlava, 1984; McElduff and Stumpfl, 1990; Nilsson, 1990; Thalhammer et al., 1990; Garuti and Zaccarini, 1997; Tsoupas and Economou-Eliopoulos, 2007). Only the sulfarsenides irarsite, ruarsite, hollingworthite and the unidentified Pd-Sb found in the Kahramanmaraş chromitites, are probably secondary in origin. This interpretation is supported by the irregular morphology and exclusive occurrence of the PGM in contact with secondary minerals, and their absence as primary inclusions in fresh chromitites. Late-stage circula-

tion of hydrous fluids enriched in As and Pd during the serpentinization may have played an important role in the formation of the secondary PGM, causing small-scale remobilization of PGE. In fact, however, there is no evidence that secondary fluids have significantly modified the primary magmatic PGE concentration in the chromitite samples.

PGE potential of mantle-hosted ophiolitic chromitites

Platinum-group elements are strategically important metals because of: 1) their growing use in several advanced technologies, 2) their scarcity in the earth's crust, 3) up to 99% of the world production comes from few localities (e.g. South Africa and Russia) that supply 90% of Pt and the 85% of Pd respectively. In consequence, exponential increase in demand renders many deposits as potentially economic, and underpinning the need for exploration of unconventional types of PGE deposits. For these reasons, podiform chromitites hosted in ophiolite complexes have become potential important exploration targets given their extreme enrichment in these metals, and that PGE may be recovered as a by-product of chromium extraction, provided that problems concerning PGM separation from the chromite host are satisfactory re-solved.

Published data (Gauthier et al., 1990; McElduff and Stumpfl, 1990; Economou-Eliopoulos, 1996; Proenza et al., 1999; Kojonen et al., 2003; Büchl et al., 2004; Uysal et al., 2005; 2007; Zaccarini et al., 2005; 2007) show that PGE abundances in the great majority of mantle-hosted podiform chromitites are less than 1 ppm, and are generally enriched in Os-Ir-Ru over Rh-Pt-Pd. However, some of these chromitites have been shown to contain PGE concentration higher than 1 ppm and, in rare cases, exhibit marked enrichment in valuable elements such as Rh-Pt-Pd (Ohnenstetter et al., 1991; Cina et al., 1995; 2002; Prichard et al., 1996; Ahmed and Arai, 2002; Tsoupas and Economou-Eliopoulos, 2007). Prichard et al. (1996) attributed PGE enrichment in Shetland chromitites to the presence of magmatic sulfides occurring in association with chromite. The PGE-rich chromitites in Albania occurring in the uppermost level of ophiolitic mantle sequences contain abundant sulfides and sulfarsenides of Pt, accompanied by PGE alloys and the PGE enrichment

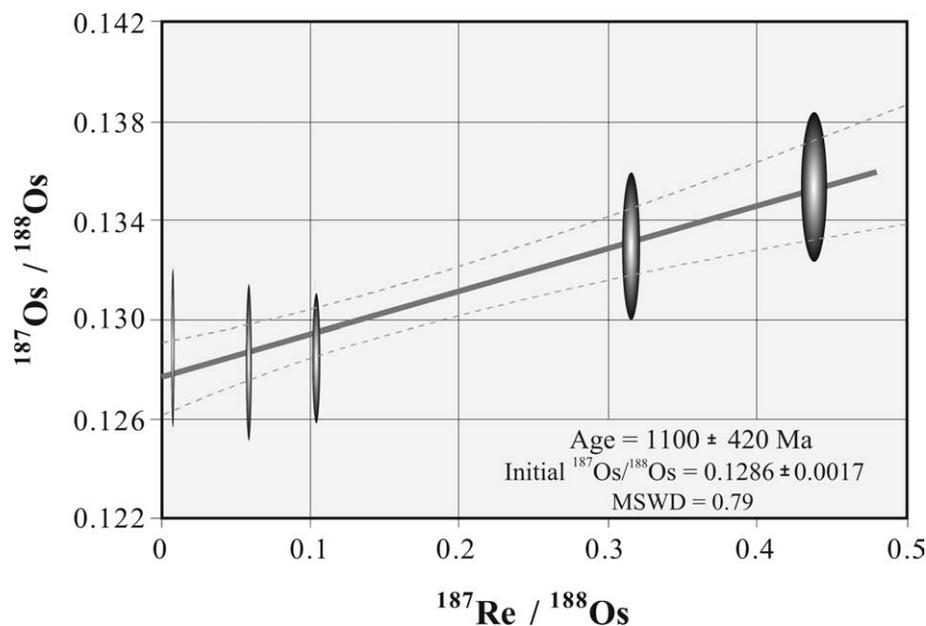


Fig. 7 - Re-Os errorchron, calculated for the chromitites from the Kahramanmaraş.

was linked to a PGE fractionation process (Cina et al., 2002). In contrast, the PGE-enriched Oman chromitites are settled in the deep part of the ophiolitic mantle (Ahmed and Arai, 2002). An anomalous PGE enrichment (up to 25 ppm) in the Veria chromitites (Greece) has been attributed to post-magmatic processes encompassing a long period of deformation episodes (Tsoupas and Economou-Eliopoulos, 2007).

On the basis of the above observations, it may be contended that local PGE enrichment in mantle-hosted podiform chromitites could be achieved in different ways, indicating that careful investigation of the PGE concentration mechanisms is important. A further problem is related with the mineralogical residence of the PGE. One of the most problematic aspects arises from the poor PGE recovery due to the minute grain size of PGM (generally less than 15 microns), and textural position relationships within the chromitite host (i.e. included versus interstitial). The identification and characterization of PGM is thus extremely useful, if not indispensable, despite the attendant time-consuming difficulties.

In summary, the geochemical and mineralogical data presented here indicate that the Kahramanmaraş chromitites have low PGE potential, due to the small size of PGM grains, low PGE concentrations (< 510 ppb total PGE), and the predominance of Ru-Os-Ir over Rh-Pt-Pd. Only one sample from Elbistan shows a pronounced positive Pt anomaly (up to 99 ppb), supported by identification of Pt-specific phases. The Pt-bearing PGM were found to be exclusively included in fresh chromites, indicative of a primary magmatic origin. Because these chromitites represent a potential target for Pt recovery, detailed studies of the Pt mineralogy, distribution in chromite ores, and precise identification of magmatic sources characterized by anomalous in Pt and mechanisms of Pt concentration, are necessary tools to future exploration.

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