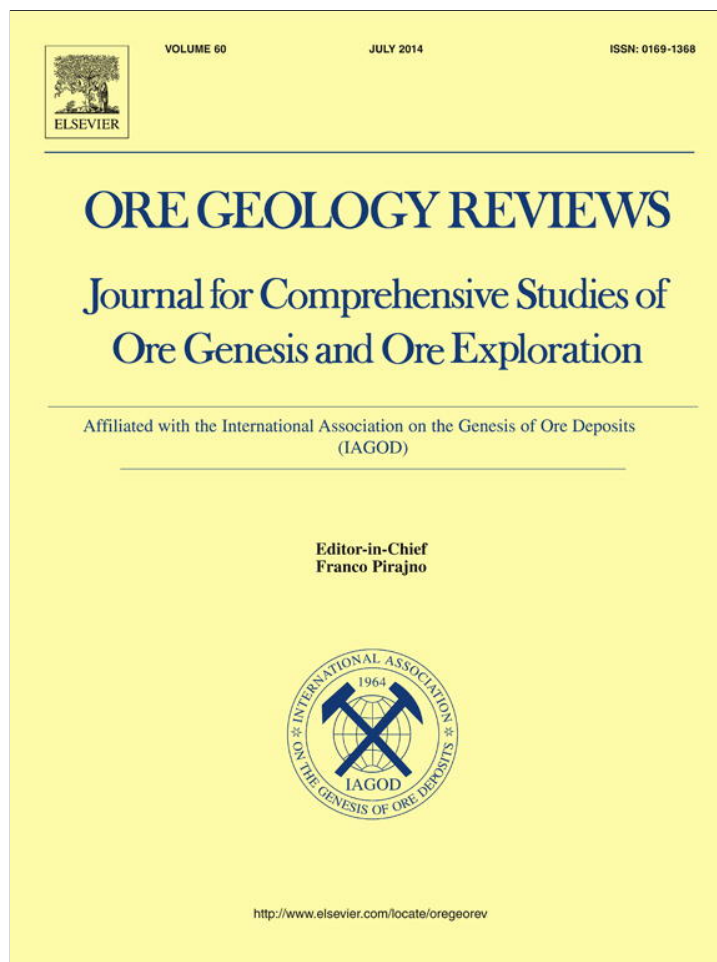


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Platinum group element (PGE) mineralisation and chromite geochemistry in the Berit ophiolite (Elbistan/Kahramanmaraş), SE Turkey



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ABSTRACT

The high-Al chromitite-bearing stratigraphic levels (Cr# ranges from 0.38 to 0.47) are located at the mantle/crust transition zone (MTZ) and in the cumulate dunites in the Berit ophiolite in SE Turkey. Iridium group elements-IPGE (Ir, Os and Ru) and related mineralisation were previously reported from ophiolitic high-Cr chromitites in the Berit-Elbistan area. Palladium group elements – PPGE (Pt, Pd and Rh) and associated mineralisation are predominantly found in the high-Al chromitites and they are presented in this study for the first time. Our results indicate that IPGE-enriched phases of the PGMs such as laurite are present in both the PPGE-enriched and the PPGE-poor chromitites in Berit.

The high-Al chromitite chondrite normalised patterns in the Berit ophiolite show an enrichment of PPGE, with values of up to 1700 ppb Pt and up to 4469 ppb Pd. During their occurrence sulphur saturation is consistent with the production of minor quantities of base metal sulphides (BMS) which took place in the form of droplets enclosed in chromite, commonly with PPGE-enriched patterns. These PPGM assemblages include Pd–Pt–tellurides, sperrylite, platarsite, Pd–antimonide, Pd–Sb–As, and Pt–Pd–Cu–Au– alloys. The PPGE enrichment in the Berit ophiolite is unusual, and the presence of such occurrences is known only in a few other ophiolites worldwide.

The geochemical evolution of the high Cr# ratios of the high-Cr chromitites indicates an origin due to high degrees of partial melting, whereas the high-Al chromitites indicate lower degrees of partial melting. Both high-degree and low-degree melts may have been fluxed through the upper mantle, either synchronously or possibly with a hiatus between the generation of different melts.

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1. Introduction

Siderophile elements are significant geochemical tools as they have the potential to trace mantle petrogenetic processes, such as the degree of partial melting and occurrence of sulphur saturation events; and thus, they reveal complementary information to the more commonly used lithophile elements. On the basis of their melting temperatures, the platinum group elements (PGEs) are classified into two groups: the iridium group (IPGE; melting temperature > 2000 °C) consists of Os, Ir and Ru; and the platinum group (PPGE < 2000 °C) consists of Rh, Pt and Pd. The PGEs have the potential to fractionate during geological processes as a result of their varying geochemical behaviour and their presence within different mantle phases (Woodland et al., 2002).

Orthomagmatic ore deposits are formed from ultramafic–mafic magmas due to high temperature crystallisation processes and they

are directly linked to the evolution of the parent magmas. The geochemistry of the podiform chromitite deposits is distinctly different from stratiform chromitite deposits found within continental complexes (e.g., the Bushveld Igneous Complex in South Africa) (Barnes and Roeder, 2001). Both ophiolitic and continental chromitite deposits are frequently enriched in PGE relative to their host silicate rocks. Within stratiform chromitite deposits this enrichment is in all six PGEs (Pt, Pd, Rh, Ru, Os and Ir), and often economic in terms of grade and tonnage (e.g., the Merensky and UG2 reefs in the Bushveld Complex) (Cawthorn et al., 2002). However, for the chromitites in ophiolitic deposits the enrichment is mostly in IPGEs (Constantinides et al., 1980; Economou-Eliopoulos and Vacandios, 1995; Gervilla et al., 2005; Page et al., 1979; Talkington et al., 1984; Tsoupas and Economou-Eliopoulos, 2008) and subeconomic, with either the grade or tonnage being too low for exploitation. Ophiolitic chromitite with associated BMS and PPGE mineralisation has been documented from only a few ophiolitic complexes e.g., Shetland in Scotland (Prichard et al., 1986), Acoje in Zambales in the Philippines (Bacuta et al., 1990),

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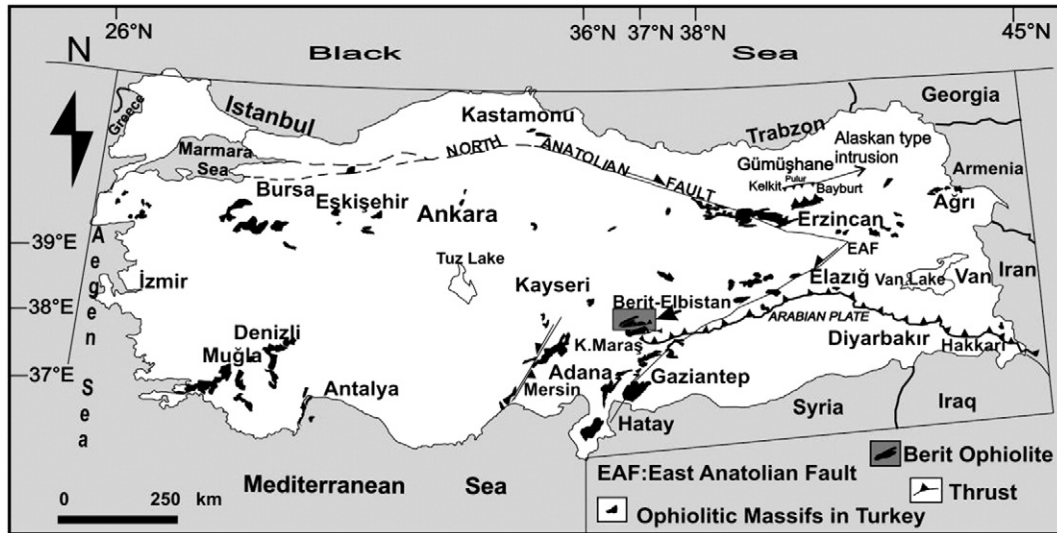


Fig. 1. Distribution of major chromitite-bearing ophiolitic massifs in Turkey and study area (Bingöl, 1989; Eyuboğlu et al., 2010).

Vourinos in Greece (Konstantopoulou and Economou-Eliopoulos, 1991), Berit in Turkey (Kozlu, 2009; Kozlu and Rudashevsky, 2010a, 2013; Kozlu-Erdal and Melcher, 2006), and Al 'Ays in Saudi Arabia (Prichard and Brough, 2009; Prichard et al., 2008a). The presence of Pt and Pd usually accompanied by BMS indicates sulphur saturation of the magma as it rose through the mantle especially during the crystallisation of chromitite (Prichard et al., 2008b).

A number of studies have focused on the PGE content of economic podiform chromitite occurrences in Turkey (Akbulut et al., 2010; Anil, 1992; Engin et al., 1986; Erdal, 2002, 2007b,c; Kozlu, 2009; Kozlu and Rudashevsky, 2010b; Kozlu et al., 2010; Kozlu-Erdal, 2007a; Özpeker et al., 1999; Page et al., 1984; Taşkın and Demiray, 1979; Uçurum et al., 2000; Uysal, 2008; Uysal et al., 2007). The chromitite deposits are mainly distributed from S to SE–E of Turkey in Fig. 1 (after Bingöl, 1989). A recent and important interpretation of the geology and

ultramafic rocks in Turkey, is occurrence reversely zoned Alaskan type intrusions described from the Pulur massif in NE of Turkey by Eyuboğlu et al. (2010, 2011) in Fig. 1.

One of the economic chromitite deposits in Turkey is hosted in the Berit ophiolite, exposed at Berit Mountain in Elbistan town, in the SE of Turkey. Here, we describe the PGM paragenesis of the Berit chromitites on the basis of both previous and recent results (Kozlu-Erdal and Melcher, 2007). Furthermore, this is the first description of PGMs which are rich in Pt, Pd and Rh (PPGM) formed in the high-Al chromitites in the Kahramanmaraş–Elbistan area of SE Turkey. The aim of this work is to identify links between the composition of the chromites and their high PPGM content. The objectives are to determine the variation in geochemical composition of the chromite and to examine the PGE concentrations and PGE mineralogy in chromitites from different localities. This paper discusses how

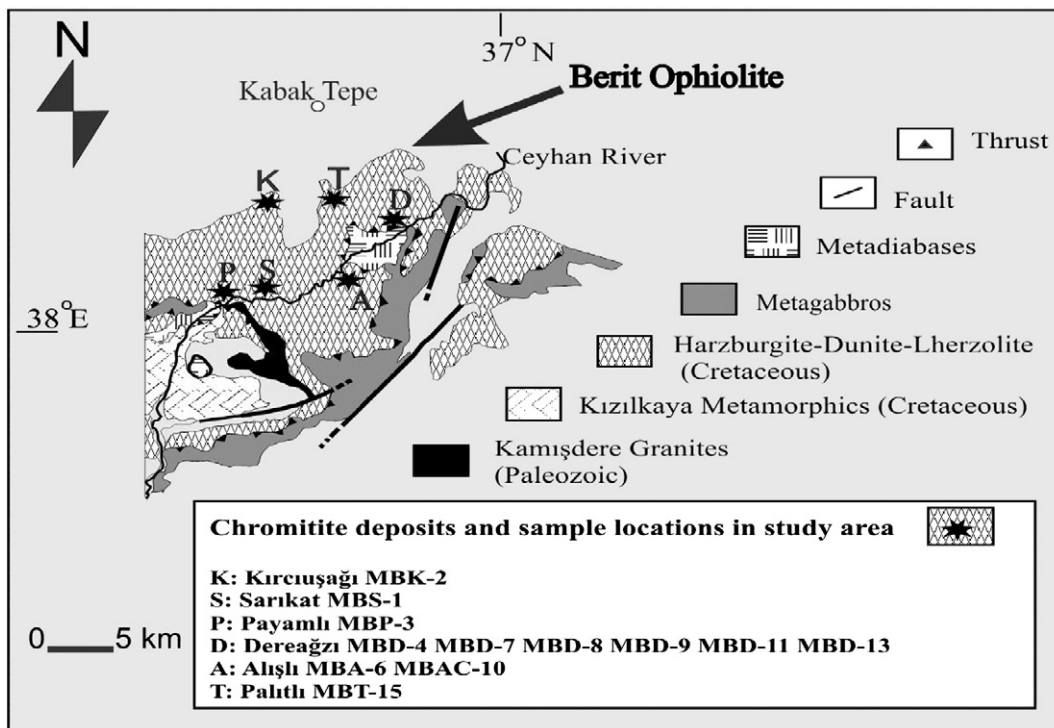


Fig. 2. Simplified geological map of the Berit ophiolite and sample locations (modified from Yiğitbaş, 1989).

various magmatic processes combined to produce PGE-enriched chromitites in the Berit ophiolite. The PGM paragenesis within the high-Al chromitites in Berit indicate that they constitute a much more important potential target for the location of Pt and Pd mineralisation than the high-Cr chromitites within the ophiolitic suite within and around Elbistan.

2. Geological setting

Neotethyan ophiolites occur in four east–west trending subparallel zones within the Tauride tectonic belt in the southern part of Turkey (Dilek et al., 1999). The Berit ophiolite massif is located in the SE Tauride thrust belt of Turkey (Fig. 2) as a part of the Tauride Ophiolite Belt in SW of Elbistan. The Berit ophiolite is thought to have formed in an incipient oceanic arc within the southern Neo-Tethys Ocean during the Late Cretaceous (Robertson et al., 2006; Yiğitbaş, 1989; Yılmaz et al., 1987). It was accreted onto the Tauride active continental margin to the north around 85 Ma ago and was later intruded by granites c. 70–85 Ma ago (Robertson et al., 2006). Geochemical analysis shows that the amphibolites within the metamorphic sheet fall into two geochemical groups, corresponding to subduction influenced tholeiites and N-MORB type tholeiites (Parlak et al., 2002).

The ophiolite consists of harzburgites, dunites and minor amphibole- and plagioclase bearing-lherzolite (Fig. 3A and B). The upper levels of the Berit ophiolite consist of ultramafic units such as dunite–wehrlite, pyroxenite and websterite (Yiğitbaş, 1989). Above these lie mafic cumulates and pegmatitic metagabbro–amphibolite overlain by a sheeted dyke complex as well as orthopyroxenite and diabase dykes are present.

Polymetamorphic stages affecting the Berit ophiolite include ocean floor, contact dynamothermal metamorphism and retrograde metamorphism. Furthermore granulite and eclogite facies rocks were reported by Yiğitbaş (1989) and Robertson et al. (2006). The eclogitic rocks are observed in the Ekinözü–Ilica area within the ophiolite body (Fig. 3C)

(Kozlu and Rudashevsky, 2013). Ultramafic rocks were previously reported as intercalated with metamorphic rocks, including amphibolite, plagioclase–amphibole schist, epidote–amphibole schist, garnet and amphibole-bearing metagabbros, together with high grade rocks of granulite facies (e.g., pyroxene granulites) Robertson et al. (2006). The corundum-bearing metapyroxenite and their stratigraphic relationship with Mantle Transition Zone (MTZ) dunites within the ophiolitic suite, has been investigated as a separate study subject (Kozlu and Rudashevsky, 2013).

3. Analytical techniques

Fourteen chromitite samples from the Berit ophiolite were first analysed for PGEs at the Institute of Karlsruhe Technical University in Germany in 2006 (Kozlu-Erdal and Melcher, 2006). They were analysed for Ir, Ru, Rh, Pt, and Pd using an ICP-MS after Ni-sulphide fire assay collection at the lab of Institute of Mineralogy-Geochemistry in Karlsruhe. The detection limits are: Ir, 0.1, Ru, 0.2, Rh, 0.004, Pt, 0.2, and Pd, 0.3 ppb. The results of this PGE analysis showed that most of the samples from Berit were enriched in PPGes. MBT-15 was the only sample with an enrichment in IPGE (Ru + Ir > 1 ppm). The PGE data for new samples from previous and new locations were analysed by Ni-sulphide fire assay and ICP-MS finish at Genalysis Laboratories in Western Australia. Detection limits were 2 ppb for all the PGEs except for Rh with a detection limit of 1 ppb. Standards run included AMIS009 and HGMN1 along with repeat analyses and blanks.

Twenty polished sections were examined for chromites, BMS and PGMs using reflected light microscopy at 200–500× magnification at the Institute of Mineralogy and Geochemistry in Karlsruhe Technical University. The chromite grains were analysed for chromite mineral chemistry by means of wavelength-dispersive (WDS) and energy-dispersive (EDS) electron microprobe analyses (EPMA), as well as back-scattered electron (BSE) images were performed with a CAMECA SX50 microprobe on polished, carbon-coated thin sections at the

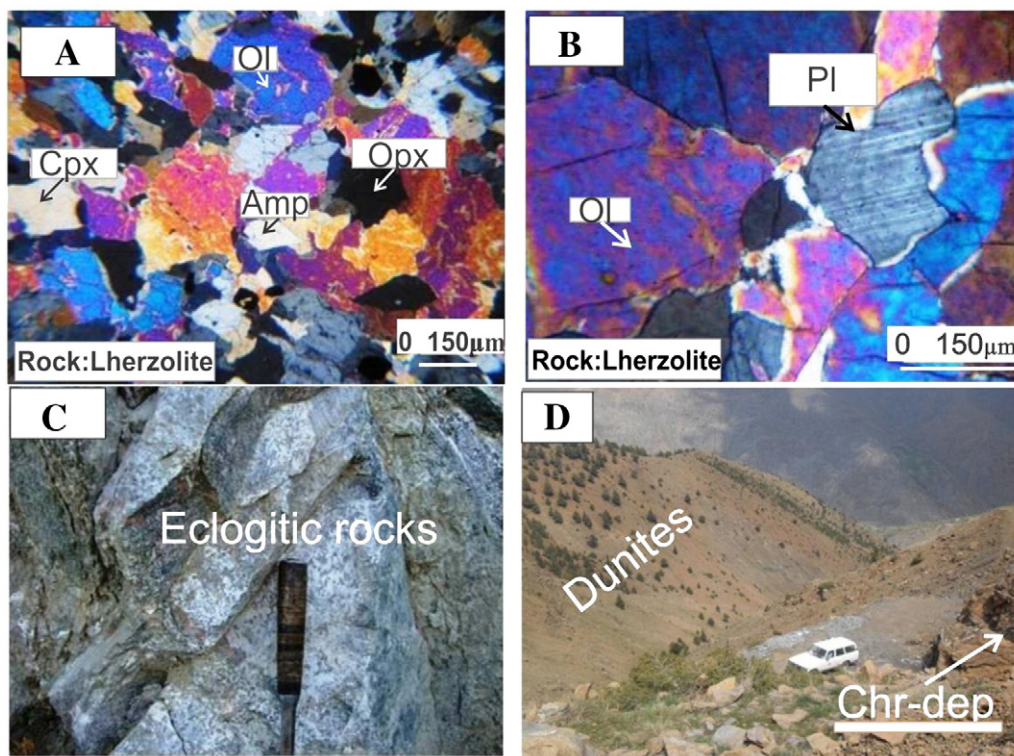


Fig. 3. A: accessory amphibole (Amp) and B: plagioclase (Pl) minerals in plane polarised light in the lherzolite (Ol: Olivine, Opx: Orthopyroxene, Cpx: Clinopyroxene), C: outcrops of the garnet (Grn) bearing eclogitic rocks and D: chromite deposit (Chr-dep) in MTZ dunites in Berit field.

Laboratory for Electron Microscopy, University of Karlsruhe in Germany. Quantitative (WDS) microprobe analyses were carried out using the crystals TAP (Si, Al), PET (Ti, Ca, K), RAP (Mg, Na) and LiF (Fe, Mn). All quantitative major element analyses were calibrated with the following standards: Fe: Fe₂O₃; Si: wollastonite; Mg: MgO; K: orthoclase; Ca, Al: anorthite; Ti: MnTiO₃; Na: albite. Accelerating voltage was set to 15–20 kV with a primary beam of 15 nA; counting times of 20–40 s were used per element. Detection limits are in the range between 0.5 and 1 wt.%. Oxide percentages were calculated using a ZAF correction programme (Fialin, 1988). Microprobe analyses of PGM grains were conducted using a CAMECA SX100 instrument at BGR in Germany where the spherical BMS inclusions in chromite and some of the laurite and irarsite were investigated. Analytical details are given in Melcher and Lodziak (2007) and El Ghorfi et al. (2008). Further analyses of PGMs were undertaken at Cardiff University where 12 polished blocks of chromitite were examined for PGM including 4 from Dereağzı, the locality with elevated PPGE. Samples with the highest concentrations of IPGE and PPGE were chosen for this PGM study. The PGMs were located with a LEO 360 SEM using a four-quadrant back-scattered detector to locate the PGM at a magnification of ×50. Analyses were made using an Oxford Instruments INCA energy dispersive X-ray system (EDX). Operating conditions included an accelerating voltage of 20 kV, a probe current of 1 nA, a working distance of 25 mm and an effective beam diameter of ~1–5 μm. Cobalt standards were frequently analysed to check for instrument drift. Pure element standards for PGE, Au, Co, Ni, Fe, Cu and Cr and Al₂O₃ (Al), FeS₂ (S), InAs (As) and SiO₂ (Si and O) were used which were supplied by Microanalysis Consultants (UK). Quantitative analyses were made for laurite, members of the hollingworthite–irarsite–platarsite solid solution series, PGE alloys, sperrylite (PtAs₂) and a Pd–Sb arsenide. Several grains of PGE-oxides were also analysed.

4. Description of the chromite occurrences

The chromitites in the study area are distributed over an area of 100 km², and are located SW of Elbistan in Kahramanmaraş. Representative chromitite samples were collected from six ore bodies within the cumulates (Kurtini), MTZ (Sarıkat, Kırçuşağı, Payamlı, Dereağzı, Alışlı) and mantle tectonites (Palıtlı) (Table 1, Fig. 2). In the study area, the podiform chromitite deposits are mainly hosted by dunites at the MTZ. The thickest dunite layers host massive chromitites at Dereağzı. The dunitic layers have also been observed from the southwestern to southeastern edge of the ophiolite (e.g., from Sarıkat to Alışlı). In Dereağzı, diabase dykes commonly occur as elongated lenses in layered dunites and alternating layers of massive chromite and dunite along the MTZ. Dereağzı chromitites have thicknesses between 2 and 25 m, with a total layer length of 500 m following the NE–SW trend (N 33–64°E/

55°SW) of the dunitic host rock. In this location, chromitites sometimes appear as small pockets within the dunites. These samples include MBD-7, MBD-8, MBD-11, and MBD-13. The largest chromitite deposits are hosted by cumulate dunites at Dereağzı whereas the smallest chromitite occurrences are hosted by harzburgites at Palıtlı (MBT-15). The chromitites are of lensoidal shape and also massive in the harzburgites at Palıtlı, whereas banded, disseminated, nodular and massive types all exist at Berit (Table 1).

5. Mineralogy and petrography of the chromitite and host rocks

The chromitites in the Berit ophiolite are hosted in thick dunites at the mantle/crust boundary where they are interlayered with cumulate dunites and less commonly occur in harzburgite. The chromitites are extensively faulted and deformed (e.g., at Dereağzı).

Modal compositions of the harzburgite include olivine (up to 80 modal percent), enstatite (up to 15 modal percent, 2–4 mm in size), clinopyroxene, amphibole and chromian spinel (0.5–2 modal percent, 0.5–1 mm in size). Dunite contains olivine grains (up to 85 modal percent, 2–6 mm in size), and accessory clinopyroxene (up to 10 modal percent, 0.5–2 mm in size). Chromian spinel grains are 1–2 mm in size and make up 2–4 vol.% in the dunite. Above the mantle tectonite, cyclic cumulate sequences of ultramafic and mafic rocks include dunite, wehrlite and olivine gabbro. Reconnaissance mapping suggests that the mantle tectonite is more abundant in the north western ultramafic section including Kırçuşağı and Palıtlı and cumulate dunite is more abundant in the east around Dereağzı, Alışlı with clinopyroxenite present in discontinuous layers to the south (Fig. 2).

The chromite forms massive to disseminated ore types composed of up to 80–95% by volume chromian-spinel with grain sizes varying from 0.4 to 25 mm. Some of the Berit chromitites have an orthocumulate texture with euhedral chromite grains hosting numerous silicate inclusions. These inclusions may be divided into 2 groups: (1) anhydrous silicates such as olivine and orthopyroxene (enstatite); (2) hydrous silicates such as pargasitic hornblende and edenite. Rutile is common especially in chromitites at the MTZ of the complex (e.g., at Payamlı, Dereağzı, and Alışlı). The interstitial matrix to the chromite grains is composed of serpentine, chlorite, minor olivine, and accessory sulphides, which are, in order of abundance, pentlandite, chalcopyrite, bornite and pyrrhotite.

6. Composition of the chromitites

Chromite hosted by harzburgite at Palıtlı has the highest Cr₂O₃ (57 wt.%) content with the highest corresponding Cr# [Cr / (Cr + Al) ratio] of 0.79 (Table 2A). However the chromite mineral chemistry

Table 1
Sample locations, type-size-trend and related host rocks of chromitite deposits in Berit field (Mas: Massive, Dis: Disseminated, Dun: Dunite, Hrz: Harzburgite).

Sample	Location	Type	Max width/length m	Host rock	Trend
MBS-1	Sarıkat	Mas	20/400	MTZ-Dun	E19–50°W
MBK-2	Kırçuşağı	Mas–Dis	5/100	MTZ-Dun	S 35–57°W
MBK-10	Kırçuşağı	Mas–Dis	5/50	MTZ-Dun	
MBK-14	Kırçuşağı	Mas–Dis	5/50	MTZ-Dun	
MBP-3	Payamlı	Mas–Dis	6/200	MTZ-Dun	E 30–43°W
MBD-4	Dereağzı	Mas	4/100	MTZ-Dun	N 33–64°W
MBA-6	Alışlı	Mas	2/80	MTZ-Dun	S 36°E/86°SE
MBD-7	Dereağzı	Mas	5/50	MTZ-Dun	N 64°E/55°SW
MBD-8	Dereağzı	Mas	5/20	MTZ-Dun	
MBD-9	Dereağzı	Mas	5/250	MTZ-Dun	
MBAC10A	Alışlı	Mas	2/100	MTZ-Dun	S 36°E/86°SE
MBD-11	Dereağzı	Mas	2/50	MTZ-Dun	
MBD-13	Dereağzı	Mas	3/50	MTZ-Dun	
MBT-15	Palıtlı	Mas	2/10	Hrz	E 27–46°W

Table 2A
Mineral chemistry results of the high-Cr chromitites (Al_2O_3 wt.% < 25) from Berit.

Location	Kircuşağı		Dereağzı	Palıtlı			
Sample wt.%	MBK2-2	MBK2-12	MBD4-1	MBD4-2	MBD4-3	MBT15-1	MBT15-2
SiO ₂	0.00	0.01	0.05	0.00	0.00	0.03	0.02
TiO ₂	0.12	0.11	0.19	0.19	0.17	0.15	0.19
Al ₂ O ₃	17.16	16.73	14.60	15.42	15.44	10.19	14.85
Cr ₂ O ₃	45.90	46.52	51.04	49.94	48.94	56.64	51.39
Fe ₂ O ₃	5.45	5.13	4.94	5.63	5.76	4.15	4.78
FeO	22.24	22.51	19.01	17.84	17.44	18.94	18.22
MgO	7.83	7.56	9.69	10.57	10.56	9.33	10.39
MnO	0.26	0.30	0.20	0.10	0.08	0.11	0.03
CaO	0.00	0.01	0.00	0.01	0.00	0.00	0.03
Na ₂ O	0.07	0.03	0.03	0.01	0.05	0.00	0.02
K ₂ O	0.01	0.04	0.01	0.00	0.05	0.04	0.02
Total	98.50	98.40	99.80	99.70	98.50	99.60	99.50
Ti	0.003	0.003	0.005	0.005	0.004	0.004	0.005
Al	0.665	0.652	0.559	0.585	0.592	0.400	0.565
Cr	1.194	1.215	1.311	1.270	1.259	1.489	1.310
Fe ²⁺	0.612	0.622	0.530	0.495	0.490	0.538	0.504
Fe ³⁺	0.135	0.127	0.121	0.136	0.141	0.104	0.116
Mn	0.007	0.008	0.006	0.003	0.002	0.003	0.001
Mg	0.384	0.372	0.469	0.507	0.512	0.462	0.499
Cr/(Cr + Al)	0.64	0.65	0.70	0.68	0.68	0.79	0.70
Mg/(Mg + Fe ²⁺)	0.39	0.37	0.47	0.51	0.51	0.46	0.50

Table 2B
Mineral chemistry results of the high-Al chromitites (Al_2O_3 wt.% > 25) from Berit.

Location	Dereağzı												
Sample wt. %	MBD7-3	MBD7-6	MBD7-7	MBD7-9	MBD8-1	MBD8-2	MBD8-3	MBD8-7	MBD9-1 centre	MBD9-2 centre	MBD9-3 rim	MBD13-1	MBD13-5
SiO ₂	0.00	0.00	0.00	0.01	0.01	0.01	0.03	0.03	0.00	0.01	0.00	0.00	0.00
TiO ₂	0.36	0.27	0.35	0.32	0.40	0.26	0.26	0.32	0.21	0.21	0.19	0.09	0.11
Al ₂ O ₃	29.80	30.01	32.09	31.59	30.24	30.08	30.44	29.17	29.77	29.81	14.36	36.37	36.13
Cr ₂ O ₃	36.49	35.72	34.07	34.50	35.59	35.85	35.51	37.17	38.76	37.02	52.11	33.21	33.67
Fe ₂ O ₃	4.27	4.01	3.25	3.81	3.88	3.88	3.75	4.16	2.82	4.23	4.53	1.42	0.37
FeO	12.85	12.91	13.45	12.92	12.49	12.23	12.16	12.99	12.95	11.38	15.73	12.06	12.92
MgO	15.35	15.03	15.14	15.41	15.52	15.53	15.59	15.15	15.54	16.18	11.72	16.75	16.14
MnO	0.19	0.22	0.05	0.10	0.07	0.06	0.07	0.17	0.03	0.15	0.06	0.08	0.02
CaO	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.03	0.02	0.00	0.04	0.00	0.00
Na ₂ O	0.00	0.02	0.00	0.03	0.03	0.00	0.02	0.00	0.01	0.04	0.00	0.02	0.00
K ₂ O	0.00	0.02	0.00	0.02	0.03	0.01	0.02	0.00	0.00	0.02	0.03	0.00	0.02
Total	99.30	98.20	98.40	98.70	98.30	97.90	97.90	99.20	100.10	99.10	98.80	100.00	99.40
Ti	0.008	0.006	0.008	0.007	0.009	0.006	0.006	0.007	0.005	0.005	0.005	0.002	0.002
Al	1.037	1.056	1.117	1.098	1.059	1.057	1.069	1.021	1.030	1.035	0.548	1.219	1.223
Cr	0.852	0.842	0.795	0.804	0.836	0.845	0.836	0.872	0.899	0.862	1.333	0.747	0.764
Fe ²⁺	0.328	0.332	0.340	0.328	0.320	0.315	0.312	0.333	0.325	0.291	0.438	0.290	0.311
Fe ³⁺	0.095	0.090	0.072	0.085	0.087	0.087	0.084	0.093	0.062	0.094	0.110	0.030	0.008
Mn	0.005	0.006	0.001	0.002	0.002	0.002	0.002	0.004	0.001	0.004	0.002	0.002	0.000
Mg	0.675	0.668	0.666	0.677	0.687	0.690	0.692	0.670	0.679	0.710	0.565	0.710	0.691
Cr/(Cr + Al)	0.45	0.44	0.42	0.42	0.44	0.44	0.44	0.46	0.47	0.45	0.71	0.38	0.38
Mg/(Mg + Fe ²⁺)	0.67	0.67	0.66	0.67	0.68	0.69	0.69	0.67	0.68	0.71	0.56	0.71	0.69

Location	Sarıkat			Payamlı			Alıştı	
Sample-wt. %	MBS1-1	MBS1-3	MBS1-4	MBP3-1 centre	MBP3-2 rim	MBP3-5	MBA6-1	MBA6-2
SiO ₂	0.02	0.01	0.06	0.04	0.02	0.04	0.00	0.00
TiO ₂	0.13	0.12	0.02	0.19	0.27	0.11	0.33	0.28
Al ₂ O ₃	27.83	26.58	26.53	25.10	21.90	24.14	24.90	25.21
Cr ₂ O ₃	40.27	41.30	40.63	42.40	47.00	44.52	42.05	42.38
Fe ₂ O ₃	3.42	3.27	4.51	3.72	2.73	2.74	4.51	3.53
FeO	12.08	12.39	11.97	12.25	13.52	12.66	13.91	14.40
MgO	15.71	15.43	15.64	15.18	14.32	14.88	14.32	14.03
MnO	0.00	0.05	0.11	0.07	0.05	0.03	0.16	0.13
CaO	0.01	0.02	0.01	0.03	0.00	0.01	0.00	0.02
Na ₂ O	0.00	0.00	0.00	0.04	0.01	0.02	0.05	0.00
K ₂ O	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Total	99.50	98.80	99.00	99.00	99.80	99.20	100.2	100.0
Ti	0.003	0.003	0.000	0.004	0.006	0.003	0.007	0.006
Al	0.973	0.941	0.936	0.894	0.789	0.864	0.883	0.897
Cr	0.945	0.980	0.962	1.013	1.136	1.069	1.000	1.011
Fe ²⁺	0.308	0.311	0.300	0.319	0.353	0.329	0.361	0.372
Fe ³⁺	0.076	0.074	0.102	0.085	0.063	0.063	0.102	0.080
Mn	0.000	0.001	0.003	0.002	0.001	0.001	0.004	0.003
Mg	0.695	0.690	0.698	0.684	0.652	0.673	0.642	0.631
Cr/(Cr + Al)	0.49	0.51	0.51	0.53	0.59	0.55	0.53	0.53
Mg/(Mg + Fe ²⁺)	0.69	0.69	0.70	0.68	0.65	0.67	0.64	0.63

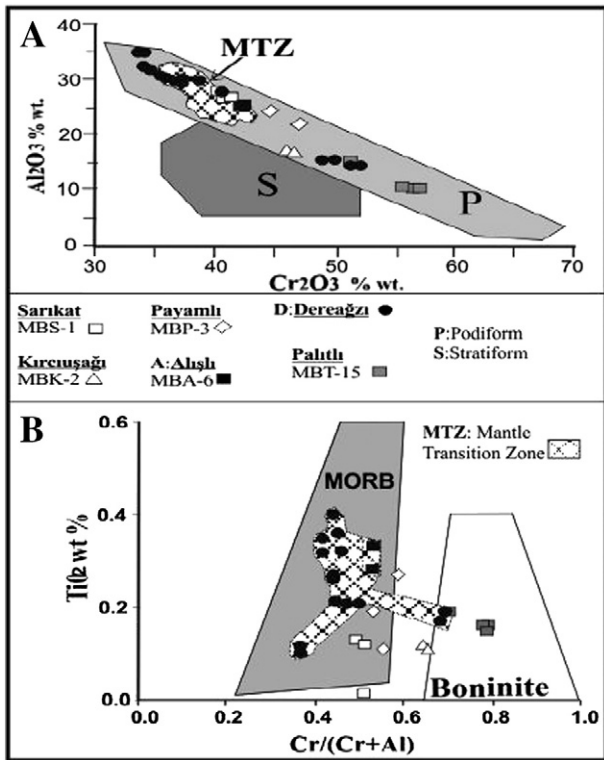


Fig. 4. Chrome-spinel compositions from the Berit chromitite A: plotted as a graph of Cr₂O₃ wt.% versus Al₂O₃ wt.% from Bonovia et al. (1993), Ahmed and Arai (2003). Reference field data for Mantle Transition Zone chromitites (MTZ) from Kozlu and Rudashevsky (2013) for Berit chromitites. P: Podiform chromitites, S: Stratiform chromitites. B: plotted from Dick and Bullen (1984) and Arai (1992).

results for the Berit chromitites from MTZ hosted-dunite show that they are dominantly of high-Al compositions (Al₂O₃: 21–36 wt.%, in Table 2B). These chromitites are highly variable in terms of their Al₂O₃ and Cr₂O₃ contents. The compositions of the MTZ-hosted chromitites from Sarikat, Payamlı and Alışlı exhibit Cr# ratios between 0.49 and 0.50 (Table 2B). Their Al₂O₃ concentration ranges between 17 and 25 wt.%. Beside the Palıtlı chromitites, high Cr# are also detected in the chromitites from Dereağzı (MBD-4: 0.70 and MBD-9: 0.71), along with some of the lowest Cr# (0.38 in MBD-13). Chromitites from Dereağzı have 14–36 wt.% Al₂O₃ and 33–52 wt.% Cr₂O₃ (Tables 2A and 2B). They plot in the podiform and MTZ hosted chromitite field in the Cr₂O₃ vs. Al₂O₃ diagram (Fig. 4A). The chromite compositions from the MTZ-hosted Berit chromitite indicate a podiform type ophiolitic origin in Fig. 4A (Ahmed and Arai, 2003; Arai et al., 2004; Bonovia et al., 1993). The magnesium number of Berit chromitites [Mg # = Mg / (Mg + Fe²⁺)] ranges from 0.37 to 0.71 and TiO₂ ranges between 0.01 and 0.4 wt.%. The distribution of chromite composition of the Berit chromitites shows a transition from boninite to MORB type when plotted on a graph of Cr# vs TiO₂ wt.% [fields of MORB and boninite in Fig. 4B are from Dick and Bullen (1984), and Arai (1992)].

7. PGE geochemistry of Berit chromitites

Fourteen chromitite samples from 6 different locations in the Berit ophiolite are analysed for PGE (Table 3). Among these samples MBK-2, MBD-7, MBD-8, MBAC-10A and MBD-13 are enriched in Pt and Pd (PPGE). The chromitites show both IPGE and PPGE enrichment with spot values of Ru and Pt greater than 1 ppm and Pd greater than 4 ppm (Table 3). Up to 4.5 ppm Pd and 1.7 ppm Pt have been recorded in one of the high-Al chromitites (MBD-8 in Fig. 5A). This represents the highest PPGE enrichment among all previously studied high-Al

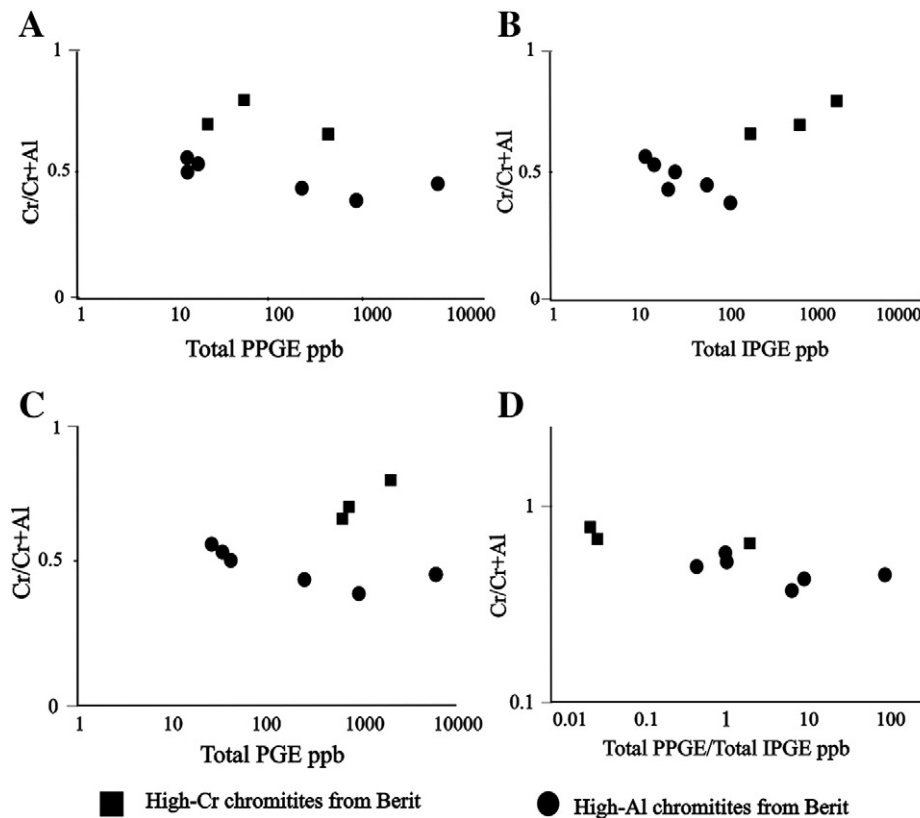


Fig. 5. The composition of chromite [Cr / Cr + Al (#Cr)] versus the amount of total (ppb) A: PPGE, B: IPGE, C: PGE and D: PPGE/IPGE in the logarithmic diagram on the differences of their magmatic evolution on the basis of high-Cr and high-Al chromitite compositions.

Table 3
Bulk PGE analyses results from Berit chromitites.

ppb sample	Sarıkat				Kırıcıuşağı				Payamlı				Dereağzı		Alışlı		Palıtlı
	MBS-1	MBK-2	MBK-10	MBK-14	MBP-3	MBD-4	MBD-7	MBD-8	MBD-9	MBD-11	MBD-13	MBA-6	MBA-10A	MBT-15			
Os		28					5	41			33			39	523		
Ir	8	62	27	17	3	110	6	25	6	7	32	3	38	286			
Ru	19	108	206	46	9	618	11	35	25	16	51	12	52	1275			
Rh	2	23	8	5	1	14	6	31	2	2	18	1	28	28			
Pt	9.5	271	5	5	10	8	74	1700	21	25	321	11	1500	14			
Pd	2	143	2	11	3	1	144	4469	11	31	509	6	2385	14			
Total PGE	40.5	635	248	84	26	751	246	6301	65	81	964	33	4042	2140			
Pt/Pd	4.75	1.89	2.5	0.45	3.3	8	0.5	0.4	1.9	0.8	0.63	1.83	0.63	1			
Pt/Ir	1.2	4.37	0.2	0.3	3.1	0.1	12	68	3.5	3.6	10	3.66	39.5	0.05			
Pd/Ir	0.25	2.31	0.07	0.65	1	0.01	24	178.8	1.83	4.4	15.9	2	62.8	0.05			

and/or high-Cr chromitites from Berit and Elbistan in the SE Taurides (Kozlu-Erdal, 2007b, 2008).

The PGE concentrations of these chromitites are grouped into two different sets based on their geochemical behaviour. The typical IPGE-enrichment (Pt/Ir and Pd/Ir < 1) of ophiolitic high-Cr chromitites is represented by higher Cr# in Fig. 5B, whereas the more unusual PPGE-enrichment (Pt/Pd < 1, Pt/Ir and Pd/Ir > 10) of high-Al chromitites is characterised by lower Cr# in the diagram of [Cr / Cr + Al (#Cr)] versus the amount of total PGE and PPGE/IPGE in Fig. 5C and D.

The high-Cr chromitites located at Dereağzı (MBD-4; Cr #: 0.68–0.71) and Palıtlı (MBT-15; Cr #: 0.79) (Table 2A) have the highest IPGE concentrations (Ru ranges from 618 to 1275 ppb) in Fig. 5B. The high-Cr chromitite (MBK-2; Cr #: 0.64–0.65) from Kırıcıuşağı contains variable PGE content and up to 437 ppb PPGE and 198 ppb IPGE (Table 3 and Fig. 6A). IPGE-enriched samples from Berit chromitites have characteristic negatively sloped chondrite normalised PGE patterns such as MBK-10 and MBT-15 (Fig. 6A, chondrite normalization values are from Naldrett and Duke, 1980). Their total whole rock PGE contents vary from 248 to 2140 ppb. However only one sample (MBK-2) from the Kırıcıuşağı area displays a positively sloped chondrite normalised pattern with a Pd/Ir ratio of > 1 (Figs. 5A and 6A).

The high-Al (Al₂O₃ > 25 wt.%) chromitites from different locations (Alışlı and Dereağzı) are enriched in Pt and Pd relative to the IPGE. They have positively sloped chondrite normalised PGE patterns (Fig. 6B). The maximum concentration of Pt is 1.7 ppm, and of Pd is 4.5 ppm (MBD-8, from Dereağzı). Other PPGE-enriched samples (MBD-7 and MBD-13) from Dereağzı range from 246 to 964 ppb total PGE. The Pt/Pd, Pt/Ir and Pd/Ir ratios of the richest sample (MBD-8, total PGE 6.3 ppm) are 0.4, 68 and 178.8, respectively. The rest of the samples from Dereağzı (MBD-9 and MBD-11) have low total PGE content (65–81 ppb) despite their high PPGE/IPGE ratios (3.5–3.6). The PPGE-enriched high-Al chromitites are not only restricted to Dereağzı; one of the high-Al chromitite samples at Alışlı (MBAC-10A) is also enriched in PPGE, exhibiting a high Pd/Ir ratio (62.8) and about 4 ppm total PGE. In contrast, MBA-6 which is another high-Al chromitite from Alışlı carries only 33 ppb total PGE (Fig. 6C). A high-Al chromitite sample from Sarıkat (MBS-1) has a total PGE content of 40.5 ppb, typically Pt/Pd and Pt/Ir ratios are both > 1 (Fig. 6C). The chromitite from Payamlı (MBP-3) has the lowest total PGE content (26 ppb) among all the investigated chromitites (Table 3, Fig. 6C).

8. PGM composition

PGMs were identified in the chromitites as IPGMs and PPGMs. IPGE-bearing PGMs are common in the high-Cr chromitites from mantle (harzburgite) and MTZ-hosted chromitite bearing levels, and both IPGE- and PPGE-bearing PGMs are found in the high-Al chromitites from Dereağzı (Tables 4 and 5, Fig. 7A–L).

70 individual PGMs (among them 30 laurite grains), commonly forming composite grains or clusters, have been discovered in 5 samples. These grains are mainly IPGE-bearing PGMs including laurite,

irarsite and erlichmanite. The PPGMs in Berit are Pt–Rh-bearing sulpharsenides belonging to the platarsite/hollingworthite/irarsite solid solution series, Pt–Pd base metal alloys, Pd–Sb, sperrylite and Pd–Pt tellurides.

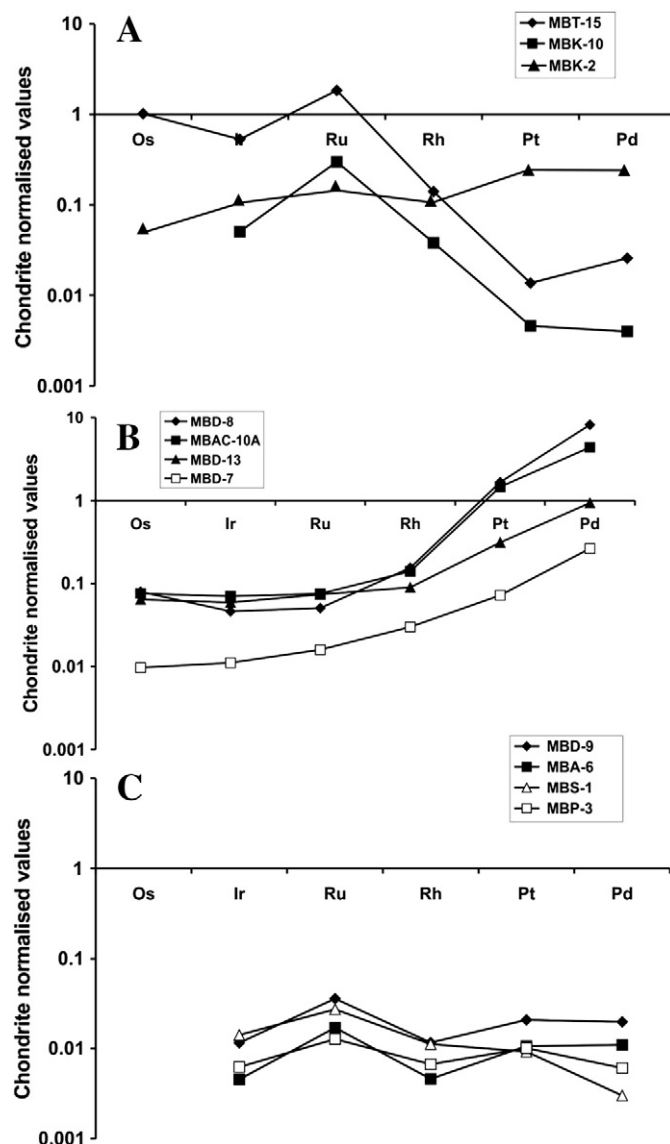


Fig. 6. PGE patterns of the Berit chromitites on normalised diagram. A: PGE distribution of IPGE-enriched chromitites (high-Cr), B: PGE distribution of PPGE-enriched chromitites (high-Al) and C: chromitites with Rh depleted patterns. Chondrite normalization values are from Naldrett and Duke (1980).

Table 5
Selected analytical results of PGMs from Dereağzı chromitites.

Sample	MBD-7	MBD-8A	MBD-8B	MBD-8A	MBD-8	MBD-13	MBD-13
Mineral	Pd–Pt–Te	Cu–Pt O	Ho	Cu–Pd–Au	Pt–Fe	Spy	Vic
wt.%	BM-1	A1	A1-2	A2	C1	B1	F1
S			14.00				0.3
Fe		5		4	10.33		
Cr		0.6					
Ni		0.6	3.00	1	2		1
Cu		38		44	3		2
As			34.00			43	10.5
Ru			6.00				
Rh			27.00				
Pd	10.53	2		10			74
Te	77.93						
Sb							13
Pt	9.9	36	17.00		85	57	
Au				40			
Bi	1.32						
O		17.5					
Total	99.68	99.7	101.00	99	100.33	100	100.8
At. %							
S			32.33				0.94
Fe		5.51		6.64	26.35		
Cr		1.48					
Ni		0.63	3.78	1.58	4.85		1.7
Cu		36.8		64.22	6.73		3.15
As			33.6			66.26	14.01
Ru			4.4				
Rh			19.43				
Pd	12.90	1.16		8.72			69.53
Te	79.65						
Sb							10.68
Pt	6.62	11.36	6.45		62.07	33.74	
Bi	0.82						
Au				18.84			
O		43.07					
Total	100	100	100	100	100	100	100
Sample	An. no	Mineral					
MBD-8	A1-2	Hollingworthite	(Rh _{0.57} Pt _{0.19} Ru _{0.13} Ni _{0.11}) _{1.00} As _{1.01} S _{0.96}				
MBD-8	A2	Cu–Au–Pd alloy	Cu _{0.64} Au _{0.19} Pd _{0.09} Fe _{0.07} Ni _{0.02}				
MBD-8	C1	Pt–Fe alloy	Pt _{2.48} (Fe _{1.05} Cu _{0.27} Ni _{0.19}) _{1.51}				
MBD-13	B1	Sperrylite	Pt _{1.02} As _{1.99}				
MBD-13	F1	Vicentite	(Pd _{2.79} Cu _{0.13} Ni _{0.07}) _{3.00} (As _{0.56} Sb _{0.43} S _{0.04}) _{1.01}				

has a gold grain associated with it (Fig. 7K, analysis A2 in MBD-8, Table 5). In addition, one Ag–Au–Cu (Hg, Fe) grain was identified. A number of PGE-oxides were analysed (e.g., Analysis A1 in MBD-8, Table 5) including a Pt–Cu-oxide (Fig. 7 L) and a Pt–Pd–Cu oxide suggesting that these PGMs have been subjected to late alteration. Structural formulae of PPGMs which have been found in Berit chromitites are given in Table 5.

A spectacular feature of the chromitites is the occurrence of spherical polyphase BMS composites included within chromite grains that were commonly observed in the high-Al chromite samples from Dereağzı (MBD-7, MBD-8 and MBD-13) and from Alışlı (MBAC-10A). They usually contain chalcopyrite and pentlandite, though these may also be altered to bornite, pyrrhotite, violarite and PGM. Two of these spherical BMS composites were found to contain precious metal-bearing minerals (Fig. 8A and B, Table 5). Chemical compositions of primary sulphides and structural formulae are listed in Table 6. The polyphase pentlandites [average (Ni_{5.2}Fe_{3.6})_{8.8}S_{8.2}] contain 35–42 wt.% Ni, 25–32 wt.% Fe and 32.5–33.5 wt.% S. Associated chalcopyrite carries 24–25 wt.% Cu, 30–31 wt.% Fe, and 33–34 wt.% S. These chalcopyrite grains include trace amounts of Ni (0.08–0.36 wt.%). A Pd–Pt–telluride grain was detected in association with BMS (pentlandite and chalcopyrite, analysis BM-2 and BM-3 in MBD-7, Table 4) in the high-Al chromitites in Berit. The microprobe analysis data (from Kozlu-Erdal, 2007b) of this grain

is problematic due to the small size; however, the quantitative analysis includes high Te (59.3 wt.%), Pd (19.9 wt.%), Pt (18.7 wt.%) and some Bi (2.19 wt.%). This indicates the presence of a Pd–Pt (bismuto-) telluride in Berit chromitites (Kozlu-Erdal, 2007b).

9. Discussion

9.1. Chromitite composition

The chemical composition of the Berit chromite and the presence of nodular chromite attest to their ophiolitic nature and podiform type origin (Fig. 4A). The formation of dunite within the host harzburgite through the process of melt/rock reaction was proposed by Kelemen et al. (1992), following the observation that liquids formed at high pressures in the upper mantle will only become olivine saturated at the lower pressures observed in the upper mantle. Thus, as melts migrate up through lherzolitic lithosphere (through intergranular pathways) they will dissolve clinopyroxene and orthopyroxene leaving a residual dunite. This process has been applied to the formation of podiform chromitites (Zhou and Robinson, 1994, 1997; Zhou et al., 1996, 1998) with the observation that incongruent melting of pyroxene through melt/rock reaction will result in silica saturation of the liquid. This may force the melt into the chromite only saturation field and hence into chromitite crystallisation. In the Berit ophiolite, chromite compositions range from Al-rich (>25 wt.% Al₂O₃) to Cr-rich (Cr# > 60) (e.g., Dereağzı samples MBD-4 and MBD-9 in Fig. 9A). High chromium-chromitites are thought to be derived from boninitic magmas, whereas high alumina-rich chromitites could be derived from tholeiitic magmas (Zhou et al., 1998). Al-rich chromitite bodies within the upper part of the mantle and in the transition zone close to the crust–mantle boundary may be explained by fractional crystallisation of chromite from a basaltic magma derived from partial melting of fertile lherzolite (Melcher et al., 1997). Alternatively they may be derived from tholeiitic magmas which have not undergone fractionation. Thus, high alumina chromitites hosted by the ophiolitic upper mantle could be the products of the fractionated melt systems or they could be derived from tholeiitic partial melts in a supra-subduction zone tectonomagmatic setting (Figs. 6B–C and 9A–B).

Interestingly the PPGE enrichment and prominent sulphur saturation occur with the high-Al chromitites which correlate with tholeiitic melts, rather than with boninitic melts.

9.2. Cr# vs. PGE concentrations

Podiform chromitites within ophiolites are generally known to have negative chondrite normalised PGE patterns, although a few chromitite deposits worldwide have been described that exhibit both positive and negative chondrite normalised patterns (Economou, 1986; Edwards, 1990; Ohnenstetter et al., 1999; Pedersen et al., 1993; Prichard et al., 1986; Prichard and Tarkian, 1988; Proenza et al., 1998; Tarkian et al., 1996). The Berit ophiolite presents another example of these PGE-enriched chromitite deposits which exhibit enrichment in IPGE and PPGE with both positive and negative chondrite normalised patterns (Kozlu-Erdal et al., 2007). The PPGE-rich high-Al chromitites, which sometimes reveal precious metal-bearing sulphide droplets enclosed in chromite, occur at Dereağzı and Alışlı in Berit. However, not all high-Al chromitites contain high total PPGE values, with total PGE contents occasionally as low as 33–65 ppb. The mostly inverse relationship of higher PPGE-enrichment associated with lower Cr# can be interpreted in two different ways depending on the nature of chromium and alumina spinel formation. If chromitites were formed by a fractionation from an originally high-chromian melt, then the PGE mineralisation is related to a high degree of fractionation and higher degree of partial melting. This coincides well with the observation that IPGE minerals are locked within chromite grains in the high-Cr chromitites. However, the crystallisation of Pd with some remaining Pt with sulphur saturation in high-Al

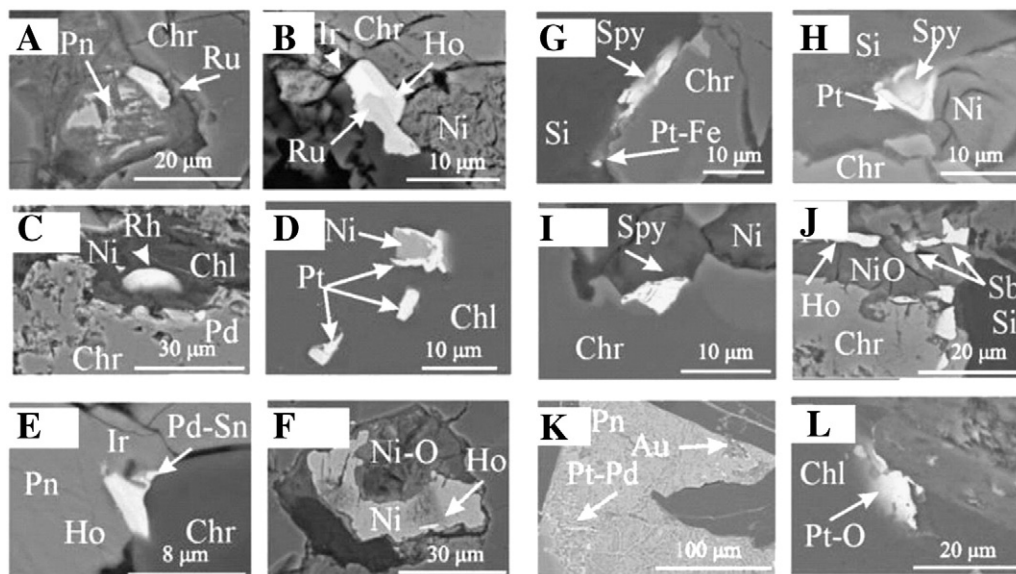


Fig. 7. Scanning electron microscope images of PGMs within the Berit chromitites. A: Laurite (Ru) on the edge of a patchwork of pentlandite (Pn) adjacent to chromite (Chr). B: composite PGM of laurite, hollingworthite (Ho) and irarsite (Ir) situated between chromite and millerite (Ni). C: Ni-Fe-Ir-Rh-sulphide in chlorite (Chl) associated with a Pd-As-S (Pd) at the junction of the chlorite and chromite and associated with millerite. D: Platarsite (Pt) associated in one case with millerite surrounded by chlorite. E: Composite grain of zoned irarsite and hollingworthite partially enclosed by pentlandite on the edge of chromite and associated with a Pd-Sn alloy (Pd-Sn). F: Hollingworthite (Ho) enclosed by millerite in a Ni-Fe oxide and Ni-silicate filled inclusion in chromite. G: Sperrylite (Spy) on the edge of chromite and adjacent to silicate with a grain of Pt-Fe alloy (Pt-Fe) in a more altered silicate. H: Sperrylite surrounded by platarsite all on the edge of millerite and chromite and silicate. I: Sperrylite on the edge of chromite and millerite. J: Pd-antimonide (Sb) and hollingworthite surrounded Ni-silicate all on the edge of chromite and silicate (Si). K: Altered pentlandite that is now a mixture of Fe-Ni ± Cu oxides (NiO) containing an elongate Pt-Pd alloy (Pt-Pd) filling a vein and an Au grain (Au) on the edge. L: Pt-Cu oxide in chlorite.

chromitites suggests formation from a lower degree of partial melting of the mantle. We propose that the crystallisation of PGMs in the high-Al chromitites may have been produced during sulphur saturation conditions and was enriched in PPGE because of the lower degree of mantle melting. Thus, sulphide associated PPGMs in the high Al chromitites indicate a formation from crystallisation of a different melt than those of the chromitites with higher Cr#, generally characterised by IPGE-enrichment (Figs. 6A–B and 9A–B).

The high PPGE values in the high-Al chromitites in Berit are related to Pd-Pt-bearing PGMs within sulphide assemblages (e.g., PGE-bearing spherical pentlandite–chalcopyrite inclusions in Berit chromite). We suggest that the PGEs have been concentrated into an immiscible sulphide liquid that crystallised to form a primary magmatic assemblage. All six PGEs have similar partition coefficients between sulphide and silicate melt, with a strong preference for sulphide melt. The PGE enrichment in the Berit chromitites also indicates that sulphur saturation occurred during the crystallisation of chromite resulting in the crystallisation of both Os–Ir–Ru and Pt–Pd–Rh-rich BMS. Evidence for sulphur saturation includes the presence of interstitial Fe–Ni bearing

sulphides and drop-like or spherical inclusions of Ni–Cu–Fe sulphides (Fig. 8A) in the chromite (Gonzalez-Jimenez et al., 2009; Malitch, 2001; Melcher, 2000). If the sulphur content in the melt remains below the saturation level, an extensive fractionation between Os–Ir–Ru and Pt–Pd occurs. As a consequence, Pt and Pd will concentrate in the fractionated immiscible sulphide melts. The great range of Pt/Pd ratios (0.4 to 8) in Berit suggests that Pd has been mobilised during late alteration processes within the ophiolite resulting in variable Pt/Pd ratios producing differing slopes on chondrite normalised diagrams, as observed elsewhere (Fuchs and Rose, 1974; Loucks, 1978; Prichard and Lord, 1994; Seabrook et al., 2004).

The low concentrations of PGEs in MORB magmas have been attributed to retention of sulphide in the source region by Hamlyn et al. (1985) who proposed that MORB is sulphide saturated upon leaving its source, and a residual chalcophile element-rich sulphide phase remains in the mantle. It has been suggested that moderately high degrees of melting in a subduction zone are necessary to extract PGE from the mantle producing a PGE-enriched melt (Prichard et al., 1996). The generation of boninitic magmas by subsequent melting of a mantle source

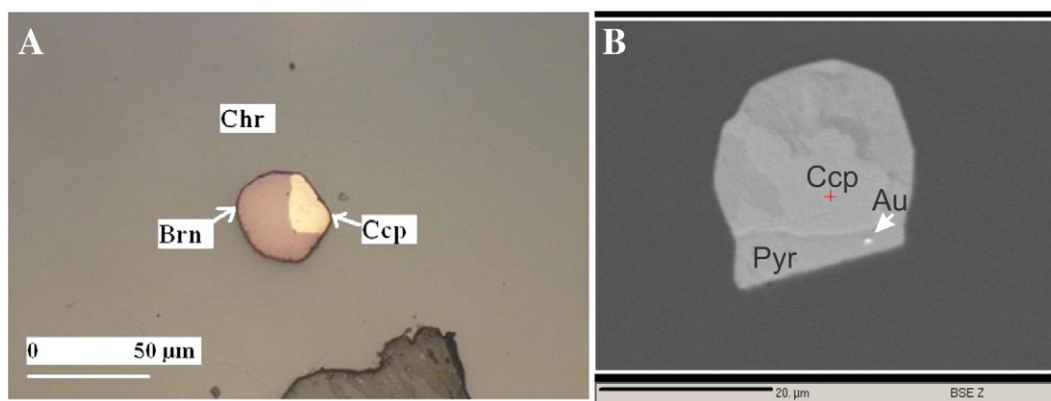


Fig. 8A: Base metal sulphide inclusions of chalcopyrite and bornite (Brn) in reflected light in the chromites (Chr). B: Back scattered image of a gold (Au) grain in the chalcopyrite (Ccp)-pyrrhotite (Pyr) sulphide association.

Table 6
Representative primary base metal sulphide mineral compositions from Berit chromitites.

Sample	MBD-7	MBD-7	MBD-7	MBD-11	MBD-11	MBD-13	MBD-13
	BM-2	BM-3	BM-4	BM-5	BM-6	BM-7	BM-8
Mineral	Pn	Ccp	Brn	Hzl	Pn	Pn	Ccp
<i>wt.%</i>							
S	33.51	34.02	26.16	26.46	32.78	32.51	33.27
Fe	25.8	30.89	11.91	2.20	31.87	24.6	29.96
Ni	39.06	0.08		71.22	35.15	41.99	0.36
Cu		34.18	59.51				33.5
Total	98.37	99.17	97.58	99.88	99.8	99.1	97.09
<i>at.%</i>							
S	48.1069	49.27	41.51	39.71	46.64	46.73	49.24
Fe	21.2634	25.69	10.85	1.90	26.03	20.30	25.46
Ni	30.6297	0.06		58.39	27.32	32.97	0.29
Cu		24.98	47.64				25.01
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00
<i>Z</i>							
S	8.1782	1.971	4.151	1.986	7.930	7.944	1.970
Fe	3.6148	1.027	1.085	0.095	4.426	3.451	1.018
Ni	5.2070	0.003		2.919	4.645	5.605	0.012
Cu		0.999	4.764				1.001
Total	17	4	10	5	17	17	4
Sample	An. no	Mineral					
MBD-7	BM-2	Pentlandite	Ni _{5.2} Fe _{3.6} S _{8.2}				
MBD-7	BM-3	Chalcopyrite	Cu ₁ Fe _{1.03} S _{1.98}				
MBD-7	BM-4	Bornite	Cu _{4.8} Fe _{1.09} S _{4.2}				
MBD-11	BM-5	Heazlewoodite	Ni _{2.9} S _{1.99}				
MBD-11	BM-6	Pentlandite	Ni _{4.65} Fe _{4.43} S _{7.93}				
MBD-13	BM-7	Pentlandite	Ni _{5.6} Fe _{3.5} S _{7.94}				
MBD-13	BM-8	Chalcopyrite	Cu ₁ Fe _{1.02} S _{1.97}				

already depleted by the extraction of MORB magma totally consumes the enriched sulphide phase and results in relatively PGE-rich melts. This process has been modelled by O'Hara et al. (2001) who suggested that PGE would be released as the last BMS in the mantle were incorporated into the magma during partial melting. This would produce a PGE-enriched partial melt that would become progressively less enriched in PGE as further PGE-barren mantle is melted. A critical amount of melting to extract PGE, but not further dilute the magma in PGE is needed to produce a PGE-rich magma capable of producing PGE concentrations in ophiolitic chromitite as occurred in Al 'Ays (Prichard et al., 2008a,b).

9.3. PGM and sulphide association

Many researchers have observed that Ir, Os and Ru-bearing PGM form early as part of the chromite precipitating mechanism in ophiolitic chromitites (Ahmed, 2007; Auge, 1988; Ferrario and Garuti, 1990; McElduff and Stumpfl, 1990; Prichard et al., 1994; Stockman and Hlava, 1984; Thalhammer et al., 1990; Torres-Ruiz et al., 1996; Zaccarini et al., 2007).

PGM mineralogy in ophiolitic chromitites mainly consists of disulphides of the laurite (RuS₂)-erlichmanite (OsS₂) solid solution series, Os-Ir-Ru alloys and irarsite (IrAsS), and to a lesser extent, sperrylite (PtAs₂), and Pt-Pd-Rh base-metal alloys (Gonzalez-Jimenez et al., 2009). Os-, Ir- and Ru-rich minerals make up about 72% of the PGM in podiform chromitites. They are even more abundant in unaltered chromite (up to 93% Os-, Ir- and Ru-rich PGM), whereas the population of grains found in altered chromite is characterised by equal proportions of IPGMs and PPGMs (Gonzalez-Jimenez et al., 2009). The generally low content of primary sulphides in podiform chromitites and their frequent association with alloys suggest sulphur undersaturation of their parental magma, normally preventing precipitation of chromite with PPGMs.

A genetic model for PGE-bearing sulphide ore bodies in layered intrusions invokes separation and segregation of an immiscible sulphide

liquid from a fractionating magma, and its accumulation in sulphide-rich layers or on the floor of magma chambers (Campbell et al., 1983; Naldrett, 1993). The compatible PGEs (Os, Ir, Ru) are incorporated in crystalline monosulphide, whereas incompatible Pt and Pd prefer to remain in the silicate melt (Ballhaus et al., 2006). In the case of ophiolite complexes, Pt and Pd enrichment is not commonly encountered, BMS are rare and the silicate magmas are sulphur-poor. However, the presence of only a small amount of immiscible sulphide liquid may lead to high concentrations of Pt and Pd within these sulphides as observed in the high-Al chromitites of Berit. Spherical BMS composites are interpreted as crystallisation products of primary immiscible sulphide liquid trapped within chromite grains (Fig. 8A, Table 6). As a consequence, immiscible sulphide-rich liquid is encapsulated by crystallising chromite grains. During the cooling of this system this liquid may segregate into a copper-rich liquid and a crystalline monosulphide solid solution MSS. With continued cooling the copper-rich liquid crystallises intermediate solid solution (ISS). Further cooling results in the exsolution of ISS into chalcopyrite and PGM, e.g. Pd-Pt-telluride (Table 5), with MSS exsolving pentlandite and pyrrhotite (Table 6).

After MSS crystallisation, Pt, Pd and Au in the residual sulfide liquid are concentrated with semi metals such as As, Te and Bi (Holwell and McDonald, 2007). Pt and Pd tellurides and gold crystallise at the rims of the pentlandite and pyrrhotite grains (Fig. 8B, Table 7).

The As-rich PGM encountered with primary minerals (e.g., irarsite with laurite in the high-Cr chromitites) and within the other minerals (e.g., sperrylite, surrounded by platarsite at the edge of chromite in the high-Al chromitites) form part of the PGM assemblages in both types of chromitites in Berit. PtAs₂ (sperrylite), IrAsS (irarsite) and RhAsS (hollingworthite) inclusions in olivine in mafic/ultramafic intrusive complexes near Lavatrafu, Madagascar (Ohnenstetter et al., 1999) were described by McDonald (2008) as an early crystallisation from a sulphide liquid with a high As/S ratio. Genkin and Evstigneeva (1986) described the concentration of Pt, Pd, Sn, Te, Pb, As, Sb and Bi into a residual liquid for the Noril'sk-Talnakh ores. The presence of As, Bi and Te

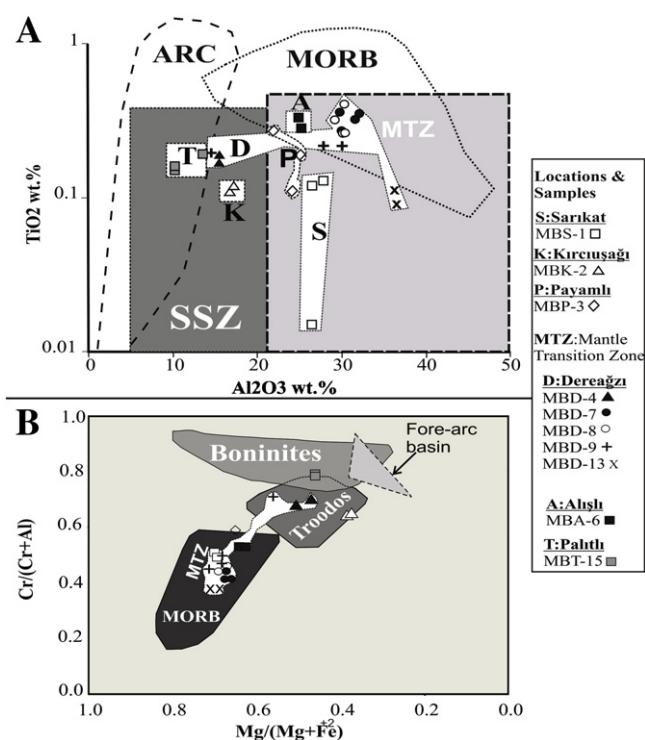


Fig. 9. Composition of the chromian spinel data from Berit A: Al₂O₃ (wt.%) versus TiO₂ (wt.%) and B: the distribution of chromian spinel of Berit in terms of Cr/(Cr + Al) versus Mg/(Mg + Fe²⁺). Fields of MORB and SSZ are from Kamenetsky et al. (2001). Fields of MORB and boninite in panel A are from Dick and Bullen (1984) and Arai (1992).

Table 7
Representative base metal sulphide mineral and PGM paragenesis of Berit chromitites.

Sample	IPGM	PPGM	BMS	Alloys	Cr #
MBK-10	Laurite erlichmanite		Pentlandite–millerite		Cr# 65
MBD-4			Laurite–irarsite pentlandite–millerite		Cr# 70
MBD-7		Pd–Pt–Te	Pentlandite–chalcopyrite		Cr# 43
MBD-8	Hollingworthite–laurite Irarsite		Millerite		Cr# 44
		Pd–As–S Ni–Fe–Ir–Rh	Millerite		
	Hollingworthite–irarsite	Sperrylite	Pentlandite Millerite	Pd–Sn Pt–Fe Pt–Pd–Au Ag–Au–Cu–(Hg, Fe)	
MBD-13		Sperrylite	Millerite		Cr# 38
MBT-15	Laurite–irarsite		Pentlandite millerite		Cr# 0.79

in PGM of Berit also suggests a concentration of volatile elements in these composites. Alternatively, antimony and arsenic are known to be commonly introduced during serpentinization. Thus, some of the PGM-bearing arsenides and antimonides in Berit chromitites could be secondary in nature (Corrivaux and Laflamme, 1990; Genkin and Evstigneeva, 1986).

9.4. PGE variability of Berit chromitites compared with SW–S Taurides

The PPGE concentrations in high-Al chromitites at Berit are higher than in most Turkish chromitites investigated so far (Erdal, 2002; Kozlu-Erdal, 2007c; Kozlu-Erdal and Melcher, 2006; Kozlu-Erdal and Sendir, 2006; Uysal et al., 2009), except for the Muğla–Dalaman–Gürleyik chromitites with 4115 ppb Pt and 14950 ppb Pd values (from Uçurum et al., 2000). It is noteworthy that the PGE enrichments in Turkish chromitites were mostly found in high-Cr chromitites. Mantle-hosted podiform chromitites from ophiolites of the Kahramanmaraş area, SE-Turkey, had been previously investigated by Uysal et al. (2007), Uysal (2008). PGE concentrations lower than 510 ppb were reported from Cr-rich chromitites with IPGE > PPGE. The total PGE values of S Tauride chromitites (Mersin and Pozanti–Aladağ) range from 80–204 to 57–2730 ppb (Kozlu-Erdal, 2007a). The range of Cr# (0.71–0.81) and Mg# ratios (0.65–0.69) of these S Tauride chromitites,

is consistent with their podiform type and the boninitic character of their parental magma. One of the samples from the Elmaslar–Denizli chromitites in SW Turkey was reported as enriched in PPGE (1830 ppb Pt, 1815 ppb Pd) with a high-Cr chromitite composition of Cr# 0.75, Cr₂O₃: 57.5 wt.% and Al₂O₃: 12.87 wt.% (Akbulut et al., 2010). The high-Cr chromitites from the SW Taurides, were reported as enriched in IPGE (1240–1305 ppb); in all chromitites, IPGE dominate over PPGE (Uysal et al., 2009), who also summarised the PGE occurrences and suggested that Al-rich and Cr-rich chromitites have almost similar chondrite-normalised PGE patterns, although Al-rich ones seem to have slightly lower total PGE concentrations. In contrast, both IPGE-enriched (up to 2140 ppb total PGE) and PPGE-enriched (up to 6301 ppb total PGE) chromitites exist in the Berit ophiolite from the SE Taurides (Fig. 6A and B).

9.5. PGM formation related to the tectonomagmatic environment of the chromitites

The chemical compositions of chromite are sensitive petrogenetic indicators and are used to constrain the parent melt composition (Arai, 1992; Auge, 1987; Be'dard and He'bert, 1998; Dick and Bullen, 1984; Irvine, 1967; Kamenetsky et al., 2001; Melcher et al., 1997; Zhou et al., 1996). The chromitite pods occurring in the mantle zone below the cumulate sequence with well-developed cumulus textures could be produced by crystallisation of small pockets of parental melt (Robinson et al., 1997). The origin of podiform chromitite by the process of melt–rock interaction (Kelemen et al., 1992; Zhou et al., 1994) includes production of olivine at the expense of orthopyroxene, resulting in a more differentiated Cr-rich melt from which Cr-rich spinel could precipitate by mixing with more primitive melts (Zhou et al., 1994). However, the petrogenesis of ophiolitic podiform chromitites in different tectonomagmatic environments has been discussed for over two decades (Büchl et al., 2004; Gervilla et al., 2005; Lago et al., 1982; Malitch et al., 2003; Melcher et al., 1997; Paktunç, 1990; Pearce et al., 1984; Roberts, 1988; Stowe, 1994; Zhou and Robinson, 1997; Zhou et al., 1998). Chromitite formation may occur in the upper mantle as 'podiform' and 'stratiform' types both in the ultramafics and also at the mantle/crust transition zone. Typical textures of podiform chromitites may result from magma mingling (Ballhaus, 1998) or from fluid-rich melts (Matveev and Ballhaus, 2002). Within supra-subduction zone environments, fluxing of previously depleted peridotites by hydrous fluids and/or melts induces high degrees of secondary partial melting which results in chromium and PGE-rich melts that are able to migrate out of their source region (Kocks et al., 2007). The deposition of layered high-Al podiform chromitites at the base of the cumulate series has been reported from many ophiolites (Konstantopoulou and Economou-Eliopoulos, 1991; Proenza et al., 1998). In these instances, high Pt and Pd are attributed to the presence of Pt–Pd-rich sulphides (Prichard et al., 1996, 2008a,b). PGEs may be concentrated into BMS droplets and be trapped between crystallising silicate or chromite grains. PGMs may then exsolve out of

Table 8
Representative mineral chemistry results of silicate and rutile inclusion in chromites from Berit chromitites (Ol: Olivine, Opx: Orthopyroxene, Par: Pargasite, Rut: Rutile).

Sample wt.%	MBS1-1	MBS1-6	MBS1-2	MBK2-9	MBP3-1	MBD9-1
Mineral	Ol	Opx	Par	Par	Rut	Par
SiO ₂	41.50	57.1	45.26	42.14	0.03	45.46
TiO ₂	0.00	0.03	0.50	0.41	98.88	0.79
Al ₂ O ₃	0.01	1.19	10.80	13.42	0.00	11.30
Cr ₂ O ₃	0.68	0.80	2.09	2.84	1.60	1.79
FeO	3.90	3.70	2.23	4.04	0.12	0.17
MnO	0.09	0.12	0.00	0.03	0.00	0.00
MgO	53.00	36.4	19.67	17.28	0.03	19.48
CaO	0.04	0.22	12.67	12.12	0.00	12.81
Na ₂ O	0.00	0.00	2.73	3.63	0.00	2.37
K ₂ O	0.00	0.03	0.36	0.35	0.00	0.39
Total	99.22	99.63	96.35	96.81	100.66	97.09
Si	0.999	1.953	6.448	6.111	0.000	6.44
Ti	0.000	0.001	0.054	0.045	0.986	0.084
Al	0.000	0.048	1.813	2.293	0.000	1.88
Cr	0.013	0.022	0.235	0.326	0.017	0.200
Fe(+3)	0.000	0.023	0.261	0.219	0.000	0.266
Fe(+2)	0.078	0.082	0.005	0.271	0.001	0.020
Mn	0.002	0.003	0.006	0.000	0.000	0.000
Mg	1.902	1.860	4.178	3.736	0.001	4.106
Ca	0.001	0.008	1.934	1.883	0.000	1.940
Na	0.000	0.000	0.754	1.021	0.000	0.650
K	0.000	0.001	0.065	0.065	0.000	0.070
Total	2.995	4.000	15.753	15.968	1.005	15.660

the sulphides forming PGE-bearing grains (e.g., Ni–Fe–Ir–Rh sulphides) or PGE-rich grains (e.g., Pt–Pd–Te) (Melcher, 2000). Hattori et al. (2002) by analysing As, Sb, Se, and Te in primary sulphides in xenoliths from mantle wedges by micro proton-induced X-ray excitation probe (PIXE), documented a wide range of S/Se, S/Te, S/As, and S/Sb values in mantle sulphides that are primarily related to depletion by partial melting events.

High-Al (Cr# < 60) PPGE-rich chromitites in the Berit ophiolite carry polyphase sulphide droplets with small Pd–Pt telluride phases associated. In these chromitites, the PGMs are most commonly associated with primary BMS minerals such as pentlandite, chalcocopyrite, and to a lesser extent pyrite, pyrrhotite and bornite. Te, Sb, and Bi-bearing minerals are important carriers of precious metals, especially of Pt, Pd, Au, and Ag (Helmy et al., 2007). Sulphide–telluride assemblages in the Gabbro Akarem intrusion, Egypt, have been interpreted as magmatic (Helmy and Mogessie, 2001). In other cases, moncheite and merenskyite inclusions were reported in, or in close association with, low-temperature recrystallisation products of MSS, e.g., pyrrhotite, pentlandite, and chalcocopyrite (Garuti and Rinaldi, 1986; Helmy, 2005). Extensive substitution of Pd by Pt and Te by Bi in telluride phases was also taken as evidence for elevated crystallisation temperatures; by Gervilla and Kojonen (2002) who suggested a temperature in excess of 750 °C. Telluride inclusions in high temperature silicates or oxides also indicate a magmatic origin of these phases.

Non-sulphide and non-PGM inclusions in high-Al chromitites of Berit include olivine, orthopyroxene (enstatite), chromian Na-pargasite, and rutile (Table 8) (Kozlu-Erdal and Melcher, 2007). The composite sulphide-PGM phases in the PPGE-enriched samples are invariably hosted by high-Al chromitites (Table 7). The presence of hydrosilicate inclusions in chromitites from Berit point to melting of the shallow mantle at high temperature under fluid-saturated conditions, probably from second stage melting of a residual source. The PPGE-enriched melt may have formed as the last BMS was melted from the mantle during suprasubduction melting. The degree of partial melting might have been higher than typically assumed to produce MORB, but not as high as the melting that produced the high-Cr and IPGE-enriched chromitites. The Berit chromitites probably formed during supra-arc magmatism prior to obduction of the host ophiolite.

10. Conclusions

The Berit chromitites have geochemical compositions typical of those formed in a supra-subduction ophiolite complex. The chromitites are variably enriched in IPGE and PPGE and represent a further example of a growing number of ophiolitic chromitites that have anomalous values of both IPGE and PPGE. The PPGE-rich chromitites are those with a high-Al composition and have Pt values up to 1700 ppb and Pd values up to 4469 ppb with Pt/Ir ratios > 4. The PPGE-enrichment in these chromitites is primarily hosted with minor BMS and Pt- and Pd-bearing sulpharsenides and antimonides. Later modification has resulted in the removal of As and Sb to give PGE alloys. These PPGMs are mostly located interstitially to the chromite grains. The interstitial PGMs have been altered and in some cases PGE-alloys and -oxides formed. However the chromitites from the Berit ophiolite are unusual in that they contain abundant spherical precious metal-bearing base metal-filled inclusions in chromite.

All these different IPGE and PPGE associations in the ophiolitic chromitites are representative of the crystallisation of the magma of different compositions perhaps derived from different degrees of partial melting to produce tholeiitic and/or boninitic magma in the supra-subduction zone environment.

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