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Genesis and geotectonic setting of podiform chromitites from the Zhob Valley Ophiolite, Pakistan: inferences from chromite composition

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Zhob valley ophiolite comprises Khanozai, Muslim Bagh, and Zhob chromitite occurrences located in Pakistan. These occurrences occur in massive, disseminated and nodular which exhibit both magmatic and deformational texture. The Muslim Bagh and Khanozai chromitites are classified into high-Cr chromitite ($Cr\# = 0.66-0.85$) while Zhob chromitite falls into high-Al chromitite ($Cr\# = 0.53-0.58$) composition. The calculated values of Al_2O_3 (wt%) and TiO_2 (wt%) for parental melts of high-Cr chromitites show similarities with boninitic melts, whereas those of the high-Al ones exhibit MORB melt affinity. Minor and trace element contents (Ti, V, Ni, Zn, and Ga (ppm)) are higher in high-Al chromitites than high-Cr chromitites and contrasting geochemical behavior of these elements with $Cr\#$ might be due to magma fractionation. MORB normalized major and trace element patterns of high-Cr chromitite show similar patterns with boninite while high-Al chromitite differs from boninite. Field and textural investigations, major and trace element geochemistry, and the presence of hydrous silicate inclusions, indicate that high-Cr chromitite were generated in equilibrium with boninitic melt, possibly in supra subduction zone. In contrast, high-Al chromitite crystallized from MORB-like melt during reaction with depleted mantle and probably originated in a back arc basin tectonic environment.

Introduction

The origin and nature of geotectonic setting of podiform chromitites is still not fully understood. The chromite composition is largely dependent on the nature and degree of partial melting of the mantle source. Therefore, the chromite composition can be helpful to deter-

mine the parental magma composition (Rollinson, 2008) and the geodynamic environment (Dick and Bullen, 1984; Arai et al., 2006; Cai et al., 2012; Ghosh et al., 2014). For instance, high-Cr and high-Al chromitites are considered to be crystallized from boninitic magmas and mid oceanic ridge basalt (MORB) like tholeiitic melts, respectively (Maurel and Maurel, 1982; Melcher et al., 1997; Kamenetsky et al., 2001; Arai et al., 2011; Zaccarini et al., 2011). Furthermore, supra-subduction zone and back-arc basin are the two most important geodynamic environment which influence the geochemical compositions of podiform chromitites (Roberts, 1988; Nicolas, 1989; Arai and Yurimoto, 1994; Zhou and Robinson, 1997; Ballhaus, 1998; Uysal et al., 2007a, b). Chromite is also a useful petrogenetic indicator to determine the composition of the primary mantle source.

The recent development of the techniques regarding the in situ analysis, like Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS), enable us to analyze a complete suite of minor and trace elements (Sc, Ti, V, Mn, Co, Ni, Zn, and Ga). Variations in the absolute concentrations of these minor and trace elements in chromian spinel are helpful to determine the composition of parental melt of chromitites and their geotectonic setting (Pagé and Barnes, 2009; Pagé et al., 2012; Colás et al., 2014; González-Jiménez et al., 2015). These elements are very sensitive to temperature and oxygen fugacity conditions prevailing during mantle melting (González-Jiménez et al., 2015; Kapsiotis et al., 2018).

In this study, we present petrographic description of chromitites and the first major (Cr, Al, Fe, Mg) and minor-trace element (Sc, Ti, V, Mn, Co, Ni, Zn, and Ga) concentrations in chromitites from the Zhob valley ophiolite. We purpose to determine the genesis of Zhob valley chromitite deposits including their parental melt composition and tectonic environment.

Regional Geological Setting

The rocks of the Zhob valley ophiolite belt and surrounding area

Figure 1. (a) Location map, (b) geological map of Zhob valley ophiolite and Western Sulaiman Fold and Thrust Belt (c) Khanozai ophiolite, (d) Muslim Bagh ophiolite and (e) Naweoba Block of Zhob ophiolite. Sample locations are shown and same symbols will be used for high-Cr and high-Al chromitites in all diagrams. (modified after Bannert et al., 1992).

can broadly be divided into three geologic zones (Fig. 1a, b). In the south, the Calcareous zone is tectonically the lowermost zone of the Indian continental plate margin. This zone contains sedimentary formations that range in age from Early Triassic to Paleocene. These successions are dominantly composed of limestone followed by shale with some sandstone and conglomerate that are deposited in pelagic to shallow marine environments (Hunting Survey Corporation (HSC), 1960). The Calcareous zone is thrust over by the Suture zone; lying between the Indian Plate and Afghan Block (Gansser, 1979) and consisting of the Muslim Bagh ophiolite and Bagh complex. The detailed descriptions of Muslim Bagh ophiolite and Bagh complex are given in their respective sections below. The third geological zone is the Flysch zone which lies to the north of the Suture zone (Fig. 1b). The stratigraphy of the Flysch zone, revised by Kasi et al. (2012), comprises limestone at the basal part which is succeeded by thick flysch sediments composed of cyclic successions of shale, siltstone and sandstone with locally minor conglomerates. These units are largely deltaic and fluvial in nature and range from Eocene to Pleistocene in age.

Geology of Zhob Valley Ophiolite

Pakistan contains an extended belt of ophiolites in the Bela-Zhob valley-Waziristan zone from south to north. Bela ophiolite is the largest ophiolite in Pakistan which begins from Bela town (near Arabian Sea coast) up to Khuzdar city while the Zhob valley ophiolite belt extends from northeast of Quetta up to Zhob town, followed by the Waziristan ophiolite further north. The Bela-Zhob valley-Waziristan ophiolite belt demarcates a suture zone between the Indian continental plate and the Afghan Block in northwestern Pakistan (Sengor, 1987). The Zhob valley ophiolitic belt consists of the Khanozai, Muslim Bagh and Zhob ophiolitic bodies (Fig. 1b). Among these bodies, the Khanozai ophiolite comprises both mantle peridotite and crustal mafic-ultramafic cumulates which are underlain by mélangé (Fig. 1c; Popal et al., 2018; Ulhaq, 2018). The mantle peridotite covers about two third of the area of the Khanozai ophiolite. The Muslim Bagh ophiolite is well-developed and the largest body in the Zhob valley ophiolite. This ophiolite was described by Vredenburg (1901) and Bilgrami (1964) as intrusive complex, but it was identified by Rossman et al. (1971) as ophiolite

complex. It contains a nearly complete ophiolitic succession (Penrose, 1972), with a less developed crustal section overlying a thick residual mantle section (Fig. 1d). The crustal portion is composed of ultramafic to mafic cumulate rocks which gradually grades into mafic cumulate or gabbros and poorly developed sheeted dykes at the top (Kakar et al., 2014). The mantle section consists of harzburgite, dunite and lherzo-

lite (Mahmood et al., 1995). These rocks are partially to completely serpentinized (30 to 100%) and intensively sheared (Mahmood et al., 1995). The swarms of 3 to 15 m thick mafic dyke cross cut the mantle section of this body (Kakar et al., 2015).

Ahmad (1974), Otsuki et al. (1989) and Sawada et al. (1992) proposed a mid-oceanic ridge tectonic setting for the Muslim Bagh ophiolite. But Hoshino and Anwar (1989), Siddiqui et al. (1996) and Kakar et al. (2014) disagreed and suggested that the Muslim Bagh ophiolite developed in a back arc basin or supra-subduction setting. Furthermore, the Zhob ophiolite consists of three detached bodies around Zhob town namely Naweoba, Omzha, and Ali Khanzai Blocks. Triassic-Jurassic rocks of the Calcareous zone surround all the three bodies (HSC, 1960). The Omzha Block contains mostly two elongated but parallel peridotite bodies. They are up to 3 km in length and 300 m in width, and diorite covers the margin of these bodies. The Ali Khanzai Block consists of peridotite and volcanic rocks (HSC, 1960 named it as Bahlolzai). Further, the Naweoba Block contains a thick unit of volcanic rocks with some gabbroic rocks. It also contains serpentinized peridotite which is largely composed of harzburgite and dunite (Ayoub, 2014; Fig. 1e).

Zhob Valley Chromitites

Chromitite deposits occur in the mantle portion of the Zhob valley ophiolite which is largely composed of highly serpentinized harzburgite and dunite. Chromitite bodies form lenses, pods and banded structures (Fig. 2a, b, c). At many places, these structures do not show any apparent directional relationship with the boundaries of intrusive while at some places chromitite layers are parallel with and have same to dip with host rocks (Bilgrami, 1963, 1969). Pods reach up to 4 m in thickness while lenses of chromitite are found up to 25 cm. The pods and lenses are surrounded by dunite envelopes which are highly serpentinized. Dunite envelopes make sharp to slightly gradual contact with harzburgite. Chromitites form alternate layers with dunite of varied thickness. Chromitites form massive to semi-massive, nodular, disseminated, and layered or banded textures. Massive chromitite and semi massive chromitite contains aggregates of medium to coarse, subhedral to anhedral grains of chromite (Fig. 2d, e). Furthermore, nodular chromitite is observed at some locations (Fig. 2f) which is massive in nature and has anhedral grain shape. The nodules reach in size up to 10 mm and are embedded in serpentinized matrix. Disseminated chromitite is

Figure 2. Photographs of Zhob valley chromitites, (a) Chromitite pods with massive textures and sharp contacts with dunite envelopes, (b) chromitites lenses in dunite envelope, (c) banded chromitites, (d) massive texture in Zhob Valley chromitites, (e) chromitites with semi-massive texture, (f) chromitites with nodular textures, (g) disseminated texture in chromitites, (h) layered structure in Zhob valley chromitites. The coin is 27.5 mm in diameter.

made up of fine grained subhedral chromite grains (Fig. 2g). Layering in the Zhob valley chromitite is also observed locally in which chromites usually form disseminated texture (Fig. 2h).

Petrography

Lherzolite forms thin layers at the base of the ophiolitic sequence. The layers are less serpentinized and show porphyroclastic to mylonitic textures. Modal composition of lherzolite is olivine (70%), clinopyroxene (14%), orthopyroxene (14%) and spinel (2%) (Kakar et al., 2013). Harzburgite shows serpentinization, is generally medium to coarse grained, granoblastic and hypidiomorphic textures. It contains orthopyroxene (25–35%), serpentine (56–60%, mostly after olivine), olivine (5–10%) and chrome spinel (3–6%) (Siddiqui et al., 1996). Dunite is the most important rock type of the mantle section and it is highly serpentinized across all bodies. It shows granoblastic texture and in some samples the relict core of olivine is surrounded by a serpentinized mesh. Dunite is composed of olivine (15–20%), serpentine (65–70%), diopside (3–5%) and spinel (2–3%) (Siddiqui et al., 1996). Serpentinites in the Muslim Bagh body of the Zhob valley ophiolite contain 90% serpentine with minor opaque oxides and olivine. It is massive and greenish in color (Mahmood et al., 1995).

The investigated chromitites from Zhob valley ophiolite are massive–semi massive, disseminated, banded, and nodular in texture. Massive–semi massive chromite grains are surrounded by alteration product such as serpentine (Fig. 3a, b). Also, massive chromitites show brecciated textures in which grains are fragmented in small pieces (Fig. 3c). However, disseminated chromitites contain largely subhedral grains embedded in serpentinized matrix (Fig. 3d).

Chromite is largely unaltered, at the same time a few grains show alteration (Fig. 3e). The ferritchromite alteration occurs along fractures and boundaries of some chromite grains, the development of ferritchromite is not limited to fractures and grain margin, and covers up to 75 vol% of chromite grain. The formation of ferritchromite yields spongy textures in chromite grains (Fig. 3e).

Anhydrous-hydrous silicates, and sulfide minerals occur in chromitite samples as inclusions and matrix in chromite grains. Olivine is the most frequent silicate phase that occurs as matrix among chromite grains as well as inclusions (Fig. 3f). Olivine is typically altered into serpentine minerals in the matrix, which is subhedral in shape and 40 µm in size. Hydrous silicates are amphibole and chlorite. Chlorite is found in the matrix of chromitite (Fig. 3g) while amphibole occurs in chromite grains as inclusions (Fig. 3f, h). These are largely anhedral to subhedral in shape and range in size up to 20 µm. Occasionally minute sulfide grains occur between chromite grains in the matrix (Fig. 3i).

Analytical Methods

Petrographic analysis of host rocks and chromitites were carried out with transmitted and reflected light microscopy. Micro X-ray Fluorescence (micro-XRF) was used to analyze the microstructure as well as phase composition. Polished blocks of representative samples were used for the analysis. The X-ray fluorescence analysis was conducted with the Bruker M4 Tornado X-ray apparatus at the Institute of Geoscience at Aarhus University, Denmark. The source used was a

single rhodium target X-ray tube. For all samples the following criteria were the same. The spot size used was 20 µm and the distance between measured points was 25 µm. Two spectrometers were running at a range of 40 keV/130 kcps. The X-ray tube was running at 50 kV electron voltage and the current was set to 600 µA. All analysis was carried out in vacuum.

The major element composition of chromites and silicate inclusions was analyzed using a JEOL JXA-8600 superprobe at the Department of Geoscience, Aarhus University, Denmark. The method for quantitative analysis was EDS (energy dispersive X-ray spectroscopy) with an acceleration voltage set to 15 KeV and a current beam of 10 nA. The beam diameter was 5 µm with a counting time of 20 seconds. For the calibration of the microprobe natural mineral standards, including quartz, sanidine, apatite, jadeite, corundum, hematite, rutile, chromite, or oxides (NiO, MgO) were used. The analysis quality was monitored with two in-house standards; clinopyroxene BBI and labradorite (Oslo plagioclase). These standards were measured intermittently and compared with the known chemical composition to check the quality of the analysis. They contain all the major elements measured and the relative reproducibility was better than 1%.

The minor and trace element concentrations of chromite were analyzed by LA-ICP-MS at the Aarhus Geochemistry and Isotope Research (AGIR) platform, Department of Geoscience at Aarhus University. The instrument consists of a 193 nm ArF Excimer laser from Resonetics attached to an Agilent 7900 ICPMS. The analysis was carried out with single spot ablations which had a spot size of 80 µm. The ablation rate was 8 Hz at an energy of 80 mJ/cm². Helium was used as the carrier gas, which then was mixed with Ar before it entered the ICP. The measurements included 15 seconds of background and 25 seconds of ablation. The NIST 610 reference standards was used as the external calibration standards, and Fe-values determined by electron microprobe/stoichiometry were used as internal standards. The data processing and quantification was done in Iolite software (Paton, 2011) and follows the procedure outlined in Heinrich et al. (2003).

Results

Major Element Geochemistry of Chromite

The composition of fresh chromite grains from the Zhob valley chromitite deposits of all three bodies are given in Table 1. Chromite in these bodies shows a wide range of composition. The range of major element concentration (wt%) in the chromite from the Zhob body is; Cr₂O₃ (39.8–44.9), Al₂O₃ (21.3–23.7), FeO (11.00–13.20), MgO (12.34–17.70) and TiO₂ (0.1–0.3). In the Muslim Bagh chromite the values are as wt%: Cr₂O₃ (49.4–60.6), Al₂O₃ (9.4–17.3), FeO (10.40–17.50), MgO (10.30–15.60) and TiO₂ (0.01–0.2). The chromite from the Khanozai chromitite contains Cr₂O₃ (52.7–55.2), Al₂O₃ (9.4–12.9), FeO (11.90–16.30), MgO (10.30–15.20) and TiO₂ (0.08–0.4) (wt%). Generally, Muslim Bagh and Khanozai chromites have similar composition while the Zhob chromite shows higher Al₂O₃ and MgO values, but lower Cr₂O₃ compared to the others (Fig. 4). Nevertheless, nearly all data from all the three chromitite ore deposits fall into the podiform chromitites region on the TiO₂ vs Cr₂O₃ diagram (Fig. 5a). The Al₂O₃ and Cr₂O₃ show a negative correlation (Fig. 5b) in the Zhob

Figure 3. Photomicrographs, micro-XRF, and BSE images showing petrographic characteristics, a) and b) massive-semi massive chromite grains are surrounded by serpentine, c) chromitites with brecciated texture, d) disseminated texture with subhedral to anhedral grains, e) ferrian alterations of chromitites, f) olivine and amphibole inclusions in chromite grain, g) chlorite in matrix h) amphibole inclusions in chromite and chlorite in interstitial matrix and i) sulfide grains. Ol=Olivine, Srp=serpentine, Chr=chromite, Amp=Amphibole, Sul=Sulfide. Note that (b) and (h) are micro-XRF images.

Table 1. Representative chromite compositions (wt%) of chromites from the Zhob valley ophiolite and calculated melt compositions. $Cr\# = Cr/(Cr+Al)$, $Mg\# = Mg/(Mg+Fe^{2+})$, $Fe^{2+}\# = Fe^{2+}/(Mg+Fe^{2+})$

Locations		Muslim Bagh									
Sample No	B43	B43a	B44	B45cb	B48	B49	B54	B63	B64	B65	B69
Type	High-Cr	High-Cr	High-Cr	High-Cr	High-Cr	High-Cr	High-Cr	High-Cr	High-Cr	High-Cr	High-Cr
SiO ₂	1.50	1.30	0.10	0.20	0.50	0.40	0.00	0.20	0.10	0.80	0.40
TiO ₂	0.19	0.10	0.14	0.08	0.19	0.20	0.10	0.06	0.01	0.20	0.10
Al ₂ O ₃	10.20	10.58	11.80	11.90	17.10	16.20	9.00	7.20	9.40	12.20	17.30
Cr ₂ O ₃	56.50	59.58	52.70	52.90	51.20	52.10	60.00	60.60	58.10	49.40	50.80
Fe ₂ O ₃	2.60	0.30	6.40	6.70	3.20	3.60	3.70	5.70	4.90	7.50	4.40
FeO	15.30	14.80	14.80	14.70	12.60	12.90	13.20	10.40	10.40	17.50	10.90
MnO	0.23	0.60	3.00	3.90	0.18	0.50	0.60	2.70	1.90	0.29	0.60
MgO	13.20	11.87	10.60	10.30	15.10	14.90	12.50	13.30	13.60	11.10	15.60
NiO	0.10	0.10	0.20	0.20	0.21	0.10	0.40	0.20	0.10	0.10	0.00
TotalΣ	99.82	99.24	99.74	100.88	100.28	100.90	99.50	100.36	98.51	99.09	100.10
Cations (structural formula on the basis of 4 oxygen)											
Si	0.04	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.02	0.01
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	0.38	0.41	0.40	0.45	0.62	0.57	0.35	0.27	0.36	0.47	0.62
Cr	1.44	1.55	1.36	1.36	1.24	1.25	1.54	1.56	1.50	1.25	1.24
Fe ³⁺	0.06	0.00	0.16	0.16	0.07	0.13	0.09	0.14	0.12	0.18	0.10
Fe ²⁺	0.41	0.40	0.40	0.40	0.32	0.28	0.36	0.28	0.28	0.48	0.28
Mn	0.00	0.00	0.08	0.10	0.00	0.01	0.01	0.07	0.05	0.00	0.00
Mg	0.63	0.58	0.51	0.49	0.68	0.71	0.61	0.64	0.66	0.54	0.71
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Cr#	0.79	0.79	0.77	0.75	0.66	0.68	0.81	0.85	0.80	0.72	0.66
Mg#	0.60	0.59	0.56	0.55	0.68	0.71	0.62	0.69	0.70	0.52	0.71
Fe ²⁺ #	0.39	0.40	0.43	0.44	0.32	0.28	0.37	0.30	0.29	0.47	0.28
Al ₂ O ₃ -melt	11.06	11.25	11.82	11.87	13.76	13.48	10.41	9.25	10.64	12.00	13.82
TiO ₂ -melt	0.29	0.17	0.23	0.15	0.29	0.30	0.17	0.12	0.02	0.30	0.17
Locations		Khanozai						Zhob			
Sample No	KO30	KO30a	KO31	KO32	KO33	KO34b	Z103c	Z104	Z105a	Z100	Z100d
Type	High-Cr	High-Cr	High-Cr	High-Cr	High-Cr	High-Cr	High-AL	High-AL	High-AL	High-AL	High-AL
SiO ₂	0.10	0.10	0.50	0.60	0.50	0.30	2.10	1.80	0.40	0.19	0.16
TiO ₂	0.14	0.08	0.11	0.20	0.15	0.40	0.18	0.10	0.30	0.17	0.10
Al ₂ O ₃	12.80	12.90	16.20	15.20	9.40	10.30	21.90	23.70	23.20	21.30	23.23
Cr ₂ O ₃	52.70	52.90	51.70	53.40	55.20	54.90	42.10	39.80	44.30	44.95	42.44
Fe ₂ O ₃	5.00	4.90	4.20	3.50	7.40	5.40	4.70	4.60	2.90	5.30	5.50
FeO	15.60	16.30	11.90	12.80	14.20	16.30	11.00	12.80	13.20	12.30	11.50
MnO	2.00	2.00	0.16	0.50	0.23	0.80	0.20	0.40	0.30	3.28	2.46
MgO	10.70	10.30	15.20	14.60	12.40	11.20	17.70	16.90	14.80	12.34	14.31
NiO	0.20	0.20	0.08	0.00	0.08	0.30	0.17	0.10	0.20	0.24	0.35
TotalΣ	99.24	99.68	100.05	100.80	99.56	99.90	100.05	100.20	99.60	100.07	100.05
Cations (structural formula on the basis of 4 oxygen)											
Si	0.00	0.00	0.01	0.10	0.00	0.00	0.06	0.05	0.01	0.00	0.00
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	0.49	0.49	0.59	0.55	0.36	0.39	0.76	0.83	0.83	0.76	0.83
Cr	1.36	1.36	1.27	1.30	1.43	1.42	0.99	0.94	1.06	1.08	1.02
Fe ³⁺	0.12	0.12	0.09	0.08	0.18	0.13	0.10	0.10	0.06	0.17	0.12
Fe ²⁺	0.42	0.44	0.30	0.33	0.38	0.44	0.27	0.32	0.33	0.33	0.29
Mn	0.05	0.05	0.00	0.10	0.00	0.02	0.00	0.02	0.00	0.08	0.06
Mg	0.52	0.50	0.70	0.67	0.60	0.54	0.78	0.71	0.67	0.60	0.64
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr#	0.73	0.73	0.68	0.70	0.79	0.78	0.56	0.53	0.56	0.58	0.55
Mg#	0.55	0.53	0.70	0.67	0.61	0.55	0.74	0.68	0.67	0.64	0.68
Fe ²⁺ #	0.44	0.46	0.30	0.33	0.38	0.44	0.25	0.31	0.33	0.35	0.31
Al ₂ O ₃ -melt	12.25	12.29	13.48	13.14	10.64	11.11	15.05	15.46	15.35	14.91	15.36
TiO ₂ -melt	0.23	0.15	0.19	0.30	0.24	0.53	0.28	0.17	0.42	0.27	0.17

Figure 4. Comparison of major elements in the three chromite occurrences. Average concentrations of major elements in chromites from Khanozai, Muslim Bagh and Zhob ore deposits, showing uniform compositions with slight differences in SiO_2 , Al_2O_3 and MnO .

Figure 5. Composition of chromite from Zhob valley chromitites plotted on (a) TiO_2 vs Cr_2O_3 (b) Al_2O_3 and Cr_2O_3 diagrams. Fields of podiform and stratiform chromitites are from Bonovia et al., (1993) and Ahmed and Arai (2003).

valley chromitites which is characteristic for ophiolitic chromitites.

On the basis of compositional variation of chromite, the studied chromitites can be classified into two groups as high-Cr ($\text{Cr}\# = \text{Cr}/(\text{Cr} + \text{Al}) > 0.6$) and high-Al ($\text{Cr}\# = \text{Cr}/(\text{Cr} + \text{Al}) < 0.6$). Muslim Bagh and Khanozai chromitites are high-Cr composition which contains high Cr#

values ranging from 0.66 to 0.85 and from 0.73 to 0.79, respectively. In contrast, the Zhob chromitite is high-Al character and shows Cr# values from 0.53 to 0.58. Generally, both high-Cr and high-Al chromitites are low in Fe_2O_3 concentrations (approx. 5 wt%) but a few samples from high-Cr chromitites contain higher Fe_2O_3 contents, reaching up to 7.4 wt%.

Profile analyses of chromite are mostly unzoned but a few grains in high-Cr and high-Al chromite show weak and strong zonation, respectively. The zoned chromite grains from high-Al chromitite exhibit an increase from rim to core in Mg# (Fig. 6a). But Cr# and $\text{FeO}_{\text{total}}$ (wt%) values decrease from rim to core in grains from high-Al chromitite (Fig. 6a). On other hand, values of Cr#, Mg# and $\text{FeO}_{\text{total}}$ (wt%) are approximately uniform from rim to core in chromite grains from high-Cr chromitites but some grains show slight zonation. In high-Cr chromitites, values of Cr# increase from rim to core while $\text{FeO}_{\text{total}}$ (wt%) values decrease from rim to core and Mg# values increase partially from rim to core (Fig. 6b).

Minor and Trace Element Geochemistry of Chromite

The 174 spots on fresh parts of chromite grains were analysed for minor and trace element concentrations (Sc, Ti, V, Mn, Co, Ni, Cu, Zn, and Ga) in both high-Cr and high-Al chromitites. The average contents are listed in Table 2. Average contents of Ti, V, Ni, Zn and Ga in chromite of high-Cr chromitites (1523, 718, 1002, 551, and 26.2 ppm, respectively) are lower than those in high-Al chromitites (1880, 1158, 1979, 730.5, and 64.3 ppm, respectively) (Fig. 7). Average concentrations of Sc and Mn are higher in chromite (9 and 2264 ppm, respectively) of high-Cr chromitites than those in the high-Al chromitites (5.9 and 1882 ppm, respectively) while average contents of Co and Cu are approximately similar in both types of chromitites (Fig. 7).

Silicate Inclusions

Olivine and amphibole are the primary silicate inclusions found in fresh grains of chromite. In both types of chromitites, the chemical

Figure 6. Profile analysis of chromite grains from Zhob valley chromitites; (a) high-Al and (b) high-Cr chromitite.

composition of these inclusions are almost similar (Table 3). Olivine is the most common inclusions that contains up to 0.80 wt% NiO and 0.5 wt% MnO which is represented by high Fo content (average Mg#

= 0.97, Table 3), showing forsterite composition. Amphibole contains high Mg# ranges from 0.92 to 0.96 and Si contents ranges from 6.53 to 7.25 which classify amphibole as magnesio-hornblende. Major ele-

Table 2. Minor and trace elements concentrations (ppm) of representative chromites from the chromitites of Zhob valley ophiolite

Element		Sc	Ti	V	Mn	Co	Ni	Cu	Zn	Ga
Muslim Bagh	Type									
B43-1	High-Cr	7.52	1752	569	2161	342	1177	1.49	578	30.20
B43-2	High-Cr	8.87	1726	558	2391	367	962	2.87	636	28.70
B43-3	High-Cr	8.99	1745	563	2401	369	988	4.80	620	28.60
B43-4	High-Cr	7.83	1743	572	2250	359	1112	2.00	574	29.10
B43-5	High-Cr	8.58	1780	578	2397	373	1024	2.33	613	31.00
B43-6	High-Cr	7.59	1743	575	2183	350	1168	1.54	589	30.30
B43-7	High-Cr	7.90	1741	583	2226	352	1190	1.21	583	30.90
B43-8	High-Cr	7.99	1789	577	2065	335	1285	1.53	569	31.08
B43-9	High-Cr	8.71	1804	588	2350	375	1032	1.27	585	31.90
B43-10	High-Cr	9.00	1762	580	2437	371	973	0.54	617	31.10
B43a-1	High-Cr	7.71	1741	561	2063	340	1186	0.38	581	30.10
B43a-2	High-Cr	7.57	1774	577	2076	343	1221	1.76	576	30.44
B43a-3	High-Cr	7.89	1776	580	2272	363	1179	0.89	593	30.58
B43a-4	High-Cr	7.88	1774	580	2332	371	1033	1.17	587	31.60
B43a-5	High-Cr	8.28	1732	573	2281	369	1092	1.33	586	30.30
B43a-6	High-Cr	8.04	1749	581	2145	349	1232	1.79	578	31.70
B43a-7	High-Cr	7.46	1768	576	2136	352	1239	2.12	583	30.50
B43a-8	High-Cr	7.70	1716	575	2191	342	1237	3.20	613	30.30
B43a-9	High-Cr	7.38	1761	573	2121	342	1211	1.36	559	30.10
B43a-10	High-Cr	8.16	1747	569	2172	349	1185	1.65	610	30.80
B43a-11	High-Cr	8.23	1783	583	2383	383	952	0.83	617	29.00
B43a-12	High-Cr	9.18	1763	577	2402	385	949	0.90	603	28.30
B43a-13	High-Cr	7.90	1789	580	2030	334	1265	2.19	586	30.70
B43a-14	High-Cr	7.92	1738	574	2233	356	1118	0.71	579	30.00
B43a-15	High-Cr	7.47	1755	580	2083	341	1241	5.00	574	30.60
B43a-16	High-Cr	6.85	1744	576	2059	334	1253	0.65	583	30.03
B43a-17	High-Cr	7.73	1711	567	2124	333	1246	2.78	557	31.00
B43a-18	High-Cr	7.81	1746	572	2040	334	1256	1.15	563	31.60
B43a-19	High-Cr	7.90	1747	574	2037	335	1254	1.16	572	29.60
B43a-20	High-Cr	8.30	1749	577	2135	345	1194	16.00	568	30.10
B43a-21	High-Cr	8.49	1786	574	2406	378	966	0.45	632	29.30
B43a-22	High-Cr	7.66	1738	569	2388	372	942	0.82	593	28.90
ST DEV		0.53	22.11	6	135	16	115.49	2.76	20.71	0.94
Average		8.01	1755	575	2218	354	1136.3	2.12	589.3	30.26
B65-1	High-Cr	11.67	1876	877	2894	359	1051	1.34	730	32.80
B65-2	High-Cr	11.03	1920	888	2892	357	1061	1.01	701	33.70
B65-3	High-Cr	12.32	1929	895	2937	377	1010	13.00	694	34.00
B65-4	High-Cr	14.20	1880	884	3555	395	3040	3.00	816	35.80
B65-5	High-Cr	10.89	1931	898	2938	377	1063	0.98	704	33.60
B65-6	High-Cr	10.99	1882	879	2956	377	1021	0.78	703	34.00
B65-7	High-Cr	11.21	1870	879	2895	365	1055	0.74	668	32.00
B65-8	High-Cr	11.53	1953	912	2911	367	1078	0.61	688	33.30
B65-9	High-Cr	11.47	1993	937	2941	372	1068	0.57	699	35.20
B65-10	High-Cr	11.51	1926	901	2916	359	1058	2.30	700	33.70
B65-11	High-Cr	10.57	1887	907	2852	358	1088	1.65	700	34.00
B69-1	High-Cr	10.83	1852	888	2917	363	1033	1.25	701	33.60
B69-2	High-Cr	11.82	1890	904	2916	362	1046	1.31	699	34.40

Table 2. (Continued)

Element		Sc	Ti	V	Mn	Co	Ni	Cu	Zn	Ga
Type										
B69-3	High-Cr	11.21	1912	919	2916	361	1081	1.06	705	35.60
B69-4	High-Cr	11.13	1942	926	2835	360	1124	0.77	718	34.70
B69-5	High-Cr	11.82	1934	920	2971	379	1067	0.82	706	34.10
B69-6	High-Cr	11.25	1920	928	2908	366	1078	1.26	691	34.60
B69-7	High-Cr	11.04	1988	954	2954	364	1062	0.78	701	34.80
B69-8	High-Cr	11.89	1932	944	2888	365	1124	1.08	717	34.60
B69-9	High-Cr	11.84	1952	929	2869	365	1100	0.96	688	35.30
B69-10	High-Cr	11.36	1921	933	2884	367	1043	1.24	728	34.00
B69-11	High-Cr	11.68	1916	924	2846	357	1091	1.55	699	34.00
B69-12	High-Cr	11.54	1976	947	2965	367	1092	0.67	700	33.90
B69-13	High-Cr	11.95	2006	951	2954	380	1098	0.81	728	34.70
B69-14	High-Cr	13.10	1930	940	3056	385	1041	0.94	724	34.80
B69-15	High-Cr	12.07	2006	951	2915	369	1075	0.75	740	34.20
B69-16	High-Cr	12.23	2019	954	2963	375	1052	0.67	743	34.60
B69-17	High-Cr	11.71	1976	948	2837	363	1152	0.82	738	37.00
B69-18	High-Cr	11.77	2011	956	2867	369	1114	0.89	732	35.50
B69-19	High-Cr	12.13	1977	949	2976	383	1044	1.13	711	34.30
ST DEV		0.71	45.94	26	126	9	360.81	2.23	26.30	0.95
Average		11.65	1937	921	2937	369	1137	1.49	712.4	34.36
Khanozai										
KO33-1	High-Cr	9.96	1506	595	2271	373	836	1.90	508	23.99
KO33-2	High-Cr	9.75	1535	597	2349	374	865	1.64	493	25.30
KO33-3	High-Cr	9.65	1492	602	2275	368	873	1.80	479	24.66
KO33-4	High-Cr	9.29	1476	592	2305	371	829	1.60	492	23.60
KO33-5	High-Cr	9.16	1471	597	2345	371	840	2.00	502	24.49
KO33-6	High-Cr	9.50	1470	596	2331	369	843	1.57	497	24.50
KO33-7	High-Cr	9.35	1471	590	2252	366	840	1.61	493	24.40
KO33-8	High-Cr	8.28	1471	594	2266	365	833	2.02	509	24.40
KO33-9	High-Cr	9.38	1530	608	2329	375	853	1.85	500	25.67
KO33-10	High-Cr	8.16	1498	594	2260	372	821	1.68	498	24.18
KO33-11	High-Cr	9.11	1437	585	2282	365	831	1.74	490	24.17
KO33-12	High-Cr	9.39	1512	593	2289	366	837	2.10	503	24.12
KO33-13	High-Cr	7.33	1494	591	2334	370	841	1.89	495	23.87
KO33-14	High-Cr	8.40	1403	573	2287	365	799	1.62	506	23.23
KO33-15	High-Cr	9.08	1511	591	2314	371	836	1.84	512	24.20
KO33-16	High-Cr	9.87	1472	589	2336	368	759	1.62	519	25.00
KO33-17	High-Cr	8.04	1462	574	2260	371	814	2.69	507	23.10
KO33-18	High-Cr	9.46	1523	587	2284	373	846	1.86	523	23.22
KO33-19	High-Cr	9.22	1512	588	2316	378	839	1.39	514	25.00
KO33-20	High-Cr	9.73	1532	594	2330	376	838	2.16	519	24.30
KO33-21	High-Cr	7.32	1521	601	2344	374	840	1.55	527	24.29
KO33-22	High-Cr	8.50	1557	599	2378	381	861	2.10	527	23.86
KO33-23	High-Cr	9.73	1507	587	2388	378	850	1.71	503	23.10
KO33-24	High-Cr	8.53	1506	591	2358	377	846	1.77	513	24.60
KO33-25	High-Cr	9.05	1503	584	2376	381	856	1.56	530	23.51
KO33-26	High-Cr	9.55	1525	580	2419	391	892	1.82	552	23.19
KO33-27	High-Cr	8.34	1491	577	2341	381	844	1.66	527	23.24

Table 2. (Continued)

Element		Sc	Ti	V	Mn	Co	Ni	Cu	Zn	Ga
Type										
ST DEV		0.73	32.73	8	44	6	24.05	0.26	15.74	0.69
Average		9.01	1496	591	2319	373	839.33	1.80	508.8	24.11
KO31-1	High-Cr	6.55	1096	557	1571	263	887	4.94	384	19.03
KO31-2	High-Cr	6.55	1126	551	1586	265	881	6.12	388	18.96
KO31-3	High-Cr	6.34	1143	547	1549	261	881	6.32	385	18.57
KO31-4	High-Cr	6.77	1128	539	1604	260	835	3.54	387	18.36
KO31-5	High-Cr	6.27	1125	530	1552	261	911	8.50	384	18.44
KO31-6	High-Cr	6.49	1112	511	1570	263	899	9.16	371	18.30
KO31-7	High-Cr	6.56	1128	496	1608	263	873	5.33	375	17.91
KO31-8	High-Cr	6.49	1111	493	1594	268	846	4.42	388	18.01
KO31-9	High-Cr	6.08	1106	476	1572	263	878	5.88	379	18.72
KO31-10	High-Cr	6.23	1106	470	1592	263	876	5.48	381	18.05
KO31-11	High-Cr	6.98	1109	474	1585	263	866	5.32	372	17.98
KO31-12	High-Cr	6.43	1098	468	1560	261	874	5.98	370	17.55
KO31-13	High-Cr	6.30	1099	510	1565	258	881	5.31	372	17.70
KO31-14	High-Cr	6.28	1125	520	1550	261	941	8.65	375	18.70
KO31-15	High-Cr	6.80	1102	522	1576	263	867	5.86	382	18.18
KO31-16	High-Cr	6.61	1140	552	1570	262	892	4.00	389	19.93
KO31-17	High-Cr	6.41	1114	537	1538	264	892	6.50	379	18.54
KO31-18	High-Cr	6.32	1069	508	1621	268	821	4.93	367	18.52
KO31-19	High-Cr	6.58	1112	521	1610	266	860	3.34	369	17.58
KO31-20	High-Cr	6.44	1123	524	1582	269	881	5.79	374	18.90
KO31-21	High-Cr	6.48	1094	496	1608	265	829	1.12	376	16.93
KO31-22	High-Cr	6.63	1087	502	1588	266	841	4.92	369	18.58
KO31-23	High-Cr	6.22	1098	479	1594	266	875	5.64	381	18.10
KO31-24	High-Cr	6.57	1101	477	1594	267	882	5.72	383	18.41
KO31-25	High-Cr	6.27	1092	476	1575	264	857	3.80	371	17.99
KO31-26	High-Cr	6.67	1018	455	1626	271	781	3.42	379	17.04
KO31-27	High-Cr	6.46	1075	466	1592	263	851	3.53	393	18.52
KO31-28	High-Cr	6.56	1139	489	1580	265	877	4.92	381	19.02
KO31-29	High-Cr	6.90	1100	497	1572	264	910	5.74	368	18.42
KO31-30	High-Cr	6.74	1123	500	1573	268	879	5.11	378	17.79
KO31-31	High-Cr	6.42	1110	546	1566	277	858	4.39	392	17.87
KO31-32	High-Cr	6.71	1127	568	1584	268	863	4.12	385	18.41
KO31-33	High-Cr	6.02	1140	566	1570	267	875	4.98	379	18.90
KO31-34	High-Cr	6.59	1162	574	1574	268	876	4.66	372	18.59
KO31-35	High-Cr	6.45	1116	550	1565	270	897	7.00	382	19.29
KO31-36	High-Cr	6.36	1132	556	1603	270	882	5.79	374	17.92
KO31-37	High-Cr	6.56	1139	574	1568	268	894	4.11	381	18.69
KO31-38	High-Cr	6.22	1057	550	1580	258	839	3.24	352	17.25
KO31-39	High-Cr	6.18	1115	524	2011	347	709	1.88	492	16.90
ST DEV		0.21	16.15	34	72	14	38.01	1.61	19.96	0.64
Average		6.47	1110	517	1592	267	867.1	5.11	381	18.27
Zhob										
Z100-1	High-Al	4.92	1845	1339	1894	307	1786	0.00	880	72.90
Z100-2	High-Al	4.32	1919	1347	1734	297	2008	1.27	788	70.90
Z100-3	High-Al	5.22	1871	1282	1786	289	1765	2.60	784	62.90

Table 2. (Continued)

Element		Sc	Ti	V	Mn	Co	Ni	Cu	Zn	Ga
Type										
Z100-4	High-Al	5.81	1913	1300	1797	296	1769	0.00	828	64.80
Z100-5	High-Al	5.47	1871	1309	1754	301	1999	2.82	800	68.70
Z100-6	High-Al	6.86	1846	1282	1783	292	1939	2.19	767	64.40
Z100-7	High-Al	6.26	1764	1279	1804	293	1970	2.66	791	66.40
Z100-8	High-Al	5.14	1888	1318	1724	294	2058	3.39	794	68.00
Z100-9	High-Al	5.58	1923	1358	1755	301	2130	3.12	821	71.50
Z100-10	High-Al	4.84	1929	1332	1825	299	1888	0.00	781	64.80
Z100-11	High-Al	5.58	1961	1371	1747	303	2055	1.53	866	72.40
Z100-12	High-Al	4.89	1873	1342	1839	303	1915	1.04	879	69.70
Z105a-1	High-Al	5.89	1913	1351	1755	296	2138	3.12	823	68.10
Z105a-2	High-Al	5.98	1852	1367	1743	302	2207	0.00	836	72.50
Z105a-3	High-Al	5.02	1942	1344	1714	308	2127	1.85	858	67.10
Z105a-4	High-Al	6.10	1846	1333	1789	301	1844	1.68	869	70.20
Z105a-5	High-Al	5.08	1908	1346	1816	297	1949	2.30	824	67.90
Z105a-6	High-Al	3.57	1972	1385	1742	309	2157	1.33	895	66.80
Z105a-7	High-Al	6.14	1884	1352	1778	303	2137	4.95	811	68.30
Z105a-8	High-Al	6.13	1954	1369	1763	308	2173	2.81	856	72.00
Z105a-9	High-Al	6.18	1880	1348	1779	304	2108	3.04	844	69.80
Z105a-10	High-Al	5.59	1944	1386	1771	308	2135	2.82	863	70.70
Z105a-11	High-Al	6.15	1857	1366	1780	308	2035	2.63	861	73.10
Z105a-12	High-Al	5.50	1911	1388	1798	307	2179	1.99	850	70.90
Z105a-13	High-Al	5.03	1943	1352	1790	300	1981	0.00	789	67.20
ST DEV		0.71	47.43	32	39	6	134.74	0.91	36.66	2.88
Average		5.49	1896	1342	1778	301	2018.1	2.45	830.3	68.88
Z103c - 1	High-Al	6.76	1836	984	1777	302	1927	6.01	678	60.80
Z103c - 2	High-Al	6.17	1854	960	1745	300	1944	5.06	657	60.50
Z103c - 3	High-Al	5.93	1889	964	1800	301	1965	6.16	587	57.30
Z103c - 4	High-Al	5.85	1849	984	1757	306	1999	5.95	616	60.50
Z103c - 5	High-Al	5.66	1865	967	1792	303	1971	6.32	644	61.50
Z103c - 6	High-Al	6.02	1830	967	1721	307	1999	5.57	616	58.70
Z103c - 7	High-Al	6.29	1843	965	1750	300	2008	3.70	615	60.90
Z103c - 8	High-Al	6.19	1863	967	1809	310	1883	5.14	646	57.90
Z103c - 9	High-Al	5.94	1856	981	1793	306	1949	4.27	599	60.40
Z103c - 10	High-Al	5.45	1865	984	1790	314	1963	10.20	634	62.80
Z103c - 11	High-Al	5.47	1818	952	1758	317	1913	6.04	613	58.20
Z103c - 12	High-Al	5.79	1856	972	1746	301	2076	6.88	646	60.40
Z103c - 13	High-Al	5.63	1858	982	1880	333	1820	4.56	642	58.30
Z103c - 14	High-Al	5.56	1870	984	1774	306	2030	6.93	627	59.00
Z103c - 15	High-Al	6.37	1858	977	1768	307	2044	7.01	642	59.80
Z103c - 16	High-Al	4.95	1874	982	1745	314	1935	1.51	641	61.60
Z103c - 18	High-Al	5.74	1894	983	1796	308	1985	6.38	641	60.60
Z103c - 19	High-Al	4.95	1898	987	1922	339	1704	2.52	632	57.70
Z103c - 20	High-Al	6.38	1871	970	1783	312	1869	3.87	646	59.40
Z103c - 21	High-Al	6.65	1933	988	1827	317	1833	5.40	607	60.00
ST DEV		0.48	25.81	10	47	10	87.05	1.84	21.47	1.46
Average		5.88	1864	975	1787	310	1940.9	5.47	631.5	59.81

Discussion

Nature of Parental Melts of the Zhob Valley Chromitite

The Al_2O_3 and TiO_2 (wt%) contents of chromium spinel are characteristics for determining the origin and tectonic setting of parental melt of chromitites (Auge, 1987; Melcher et al., 1997; Kamenetsky et al., 2001; Uysal et al., 2007a; Rollinson, 2008; Page and Barnes, 2009; Zaccarini et al., 2011). The parental melts occurring chromitites are formed by various processes such as partial melting (Kelemen et al., 1992; Arai, 1994; Zhou et al., 1996), melt/rock reaction and melt/melt interaction (Zhou et al., 1998; Melcher et al., 1999; Kamenetsky et al., 2001; Uysal et

al., 2005, 2009). Several authors noted that the concentration of Al_2O_3 (wt%) and TiO_2 (wt%), and FeO/MgO ratios of chromium spinel are

ments contents in amphibole range between 0.92 to 2.80 wt% for Na_2O , 0.01 to 0.03 wt% for K_2O and 0.17 to 0.79 wt% for TiO_2 .

Table 3. Composition of olivine and amphibole inclusions in chromite. Ol=Olivine and Amp=Amphibole, N=Number of spot analysis, bdl= below detection limit

Sample No	B43	B43a	B44 cr	B63 cr	KO30	Z100	Z100c	Z103c	B43	KO30	Z100
Mineral	Ol	Ol	Ol	Ol	Ol	Ol	Ol	Ol	Amp	Amp	Amp
Type	High-Cr	High-Cr	High-Cr	High-Cr	High-Cr	High-Al	High-Al	High-Al	High-Cr	High-Cr	High-Al
N	4	1	3	1	2	3	2	1	2	1	2
SiO_2	42.55	41.50	41.59	41.99	42.93	43.06	42.97	42.51	52.41	51.08	46.89
TiO_2	bdl	bdl	0.01	0.04	0.02	0.26	bdl	0.03	0.17	0.79	0.70
Al_2O_3	0.22	0.78	0.54	bdl	0.75	0.06	0.57	0.19	6.55	7.04	11.76
Cr_2O_3	0.29	0.27	0.35	0.62	0.36	0.64	0.41	0.80	1.76	0.90	1.70
FeO	3.25	3.62	2.70	2.88	3.21	3.48	3.38	2.86	3.35	1.60	2.08
MnO	0.50	bdl	0.20	bdl	0.27	0.10	0.18	0.30	bdl	0.04	0.02
NiO	0.80	bdl	0.28	0.69	0.05	0.21	0.05	0.50	0.15	0.30	0.15
MgO	52.76	52.92	53.51	54.53	51.88	51.85	51.76	52.25	21.19	21.02	20.01
CaO	bdl	bdl	0.03	0.02	0.06	0.15	0.05	0.07	11.48	12.07	12.11
Na_2O	0.36	bdl	bdl	bdl	bdl	0.06	bdl	bdl	0.92	1.40	2.80
K_2O	0.05	bdl	0.04	bdl	0.03	0.28	0.04	0.40	0.01	0.02	0.03
TotalΣ	99.46	99.10	99.24	100.78	99.12	99.90	99.33	99.92	97.88	96.24	98.25
Cations (structural formula on the basis of 4 oxygen for olivine and 23 oxygen for amphibole)											
Si	1.02	1.00	1.00	0.99	1.03	1.03	1.03	1.01	7.25	7.14	6.53
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.08	0.07
Al	0.00	0.02	0.02	0.00	0.01	0.01	0.02	0.01	1.07	1.16	1.93
Cr	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.19	0.10	0.19
Fe^{2+}	0.07	0.07	0.05	0.06	0.06	0.07	0.07	0.06	0.39	0.19	0.24
Mn	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.00
Ni	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.01
Mg	1.88	1.89	1.91	1.92	1.85	1.84	1.84	1.86	4.37	4.38	4.16
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.70	1.81	1.81
Na	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.25	0.38	0.76
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01
TotalΣ	2.98	2.99	2.99	2.99	2.96	2.96	2.96	2.97	15.22	15.25	15.70
Mg#	0.96	0.96	0.97	0.97	0.97	0.96	0.96	0.97	0.92	0.96	0.95

in direct relation with the composition of the parental melts (Kamenetsky et al., 2001; Rollinson, 2008).

The equation developed by Rollinson (2008) based on the data of chromite spinels from 36 different igneous suites from oceanic, arc, and intraplate tectonic setting of Kamenetsky et al. (2001), can be used to derive the composition of parental melts:

$$\text{Al}_2\text{O}_3_{\text{melt}} = 5.2181 * \text{Ln}(\text{Al}_2\text{O}_3_{\text{chromite}}) - 1.50505 \quad (\text{i})$$

$$\text{Ln}(\text{TiO}_2_{\text{melt}}) = 1.0963 * (\text{TiO}_2_{\text{chromite}})^{0.7863} \quad (\text{ii})$$

The calculated Al_2O_3 (wt%) and TiO_2 (wt%) compositions of the parental melts of both high-Cr and high-Al chromitites from the Zhob valley ophiolite are presented in Table 1. The concentrations of Al_2O_3 of the parental melts of high-Cr chromitites ranges from 9.2 to 13.8

wt%, while for the high-Al ones it varies between 14.9 and 15.4 wt%. Furthermore, the TiO_2 concentration of parental melts of high-Cr and high-Al chromitites varies from 0.02 to 0.53 wt% and from 0.17 to 0.42 wt%, respectively. The Al_2O_3 contents of the inferred parental melts of high-Cr chromitites (9.2–13.8 wt%) are in agreement with Al_2O_3 concentrations of chromitites of the Elekdag Ophiolite (northern Turkey) (9.4–13.2 wt%; Dönmez et al., 2014), Kop Mountain (Turkey) (10.1–13.5 wt%; Uysal et al., 2007a), Thetford Mines Ophiolite (9.2–12.9 wt%; Page and Barnes, 2009), Oman Ophiolite (11.8–12.9 wt%; Rollinson, 2008), and Luobusa Ophiolite (13.8 wt%; Zhou et al., 2014). In addition, the Al_2O_3 (wt%) values of high-Cr chromitites fall within the range of composition of chromite derived from boninite melt (10.6–14.4 wt%; Wilson, 1989). However, the calculated

Figure 8. $100 * \text{Cr} \#$ vs. $\text{Fe}^{2+} \#$ for chromite from podiform chromitites in the Zhob valley ophiolite. Boninite and MORB values taken from Page and Barnes, (2009). Fields for chromite from MORB and boninite are from Barnes and Roeder (2001). Hess Deep (a MOR setting) (Arai and Matsukage, 1998) and Japan Arc Xenolith (a supra-subduction setting) (Arai and Abe, 1994), Tari-Misaka (Arai and Yurimoto, 1994), TMO (Page and Barnes, 2009). Average contents of TMO, Tr and TM are plotted. MOR=Mid ocean ridge, SSZ=Supra-subduction zone, Tr= Turkish deposits, TM, Tari-Misaka, TMO=Thetford Mines Ophiolite.

Al_2O_3 (wt%) values of the parental magma of studied high-Al chromitites (14.9–15.4 wt%) are similar to the high-Al chromitites of southern Turkey (14.5–16.2 wt%; Akmaz et al., 2014), Sagua de Tanamo (eastern Cuba) (15–16 wt%; Gonzalez-Jimenez et al., 2011), Kempirsai-Batamshinsk (Kazakhstan) (13.5–16.7 wt%; Melcher et al., 1997), and Sartohay Ophiolite (16.3 wt%; Zhou et al., 2014) and comparable to the Al_2O_3 (wt%) concentrations with MORB melts (16 wt%; Wilson,

1989). Thus, the data indicates that parental magma of high-Cr chromitites were boninitic while high-Al chromitite was crystallized from MORB-like melts.

In the $\text{Fe}^{2+}\#$ vs Cr# diagram, chromitites from the Zhob valley ophiolite plot in the high-Cr and high-Al fields of podiform chromitites, which further extends from the high-Cr boninitic field to the high-Al MORB field (Fig. 8). With the exception of a few samples that have

Figure 9. (a) Ti vs. Cr#, (b) Ga vs. Cr#, (c) V vs. Cr#, (d) Sc vs. Cr#, (e) Zn vs. Cr#, (f) Co vs. Cr#, (g) Ni vs. Cr#, (h) Mn vs. Cr# for chromites from Zhob valley ophiolite. LO=Luobusa Ophiolite (Zhou et al., 2014), SO=Sartohay Ophiolite (Zhou et al., 2014), AO= Acoje Ophiolite (Zhou et al., 2014), CO=Coto Ophiolite (Zhou et al., 2014). Podiform chromitite, MORB and BON fields, other data source and acronyms are as in Figure 8. Note that average contents of elements are plotted.

higher Fe^{2+} , high-Cr chromitites of the Zhob valley ophiolite exhibit an identical range of compositions to the Thetford Mines Ophiolite (TMO), supra-subduction zone (SSZ), and high-Cr chromite from Troodos Ophiolite (Fig. 8) (Arai and Abe, 1994; Arai and Yurimoto, 1994; Panktunc and Cabri, 1995; Page and Barnes, 2009). The compositions of high-Al chromitites shows a similar range to the high-Al chromitites from the Tari-Misaka Complex (TM), and MOR (Auge, 1987; Arai and Yurimoto, 1994; Ahmed and Arai, 2002).

Ga, Ti, Zn, Ni and V concentrations of chromite from the Zhob valley chromitites show negative correlation with Cr# (Fig. 9) which reflects crystal fractionation in the parental melt of chromite (Page and Barnes, 2009). High-Cr chromitites from the Zhob valley ophiolite have a similar range of Ti contents to the northern Oman (NO), Luobusa Ophiolite (LO), and chromitites from supra-subduction zone, while high-Al chromitites have similar contents of Ti to the Tari-Misaka Complex (TM) and Sartohay Ophiolite (SO) (Fig. 9a). Gallium, vanadium and nickel show a more pronounced inverse correlation with Cr# than Ti and Zn (Fig. 9). Ga in high-Cr chromitites is similar with the TMO and Acoje ophiolite (AO) and close to chromites in boninites (Fig. 9b), while high-Al chromitites are enriched in Ga contents compared to those of the Sartohay Ophiolite and close to MORB content. Vanadium in high-Cr chromitites exhibits a similar range to the TMO and northern Oman chromitites while it is lower than chromites in boninites. High-Al chromitites are in agreement with TM and Sartohay chromitites in terms of vanadium contents (Fig. 9c). The depletion of V in high-Cr chromitite is believed to be the result of various oxidation conditions of boninitic parental melts (Page and Barnes, 2009). It is partly related to oxidizing conditions that vary from the mantle to the top of the crust or to oxidation of boninite magmas during shallow ascent and eruption (Page and Barnes, 2009).

Sc contents of high-Cr and high-Al chromitites show similar ranges to the TMO and boninite and Sartohay, Coto Ophiolites (CO) and MORB, respectively (Fig. 9d). In high Cr chromitites, Zn and Ni contents are comparable with boninite, TMO and LO, but Co and Mn are higher than boninite (Fig. 9e, f, g, h). On the other hand, high-Al chromitite is enriched in Ni, Mn, Zn and Co as compared to those from MORB (Fig. 9e, f, g, h). Especially, Mn, Zn and Co enrichments are interpreted as metamorphism of chromitites in the literature (Colás et al., 2014; Uysal et al., 2018). Similarly high concentrations of these elements are reported from highly altered chromite from Morocco (Gahlan and Arai, 2007), Greece (Paraskevopoulos and Economou, 1981; Michailidis, 1990; Economou-Eliopoulos, 2003), Dobromirski Chromitites, Bulgaria (Gonzalez-Jimenez et al., 2015) and some deposits from southeastern Turkey (Akmaz et al., 2014).

Trace elements of chromitites from the Zhob valley ophiolite were normalized to chromite compositions from MORB and arranged on the pattern of Page and Barnes (2009) in Figure 10. Moreover, high-Cr chromitites were compared to Luobusa Ophiolite (LO) (Zhou et al., 2014) and Thetford Mines Ophiolite (TMO) (Page and Barnes, 2009) whereas high-Al chromitites were compared to Sartohay Ophiolite (SO) (Zhou et al., 2014) and Zambales Ophiolite (ZO) (Gonzalez-Jimenez et al., 2012) (Fig. 10). With minor exceptions, concentrations of almost all elements of high-Cr chromitite are in agreement with TMO while they are partially enriched in Ga, Ti, Zn, and Mn compared with Luobusa Ophiolite (Fig. 10a). The high-Al chromitites show a similar pattern to the Zambales Ophiolite (ZO) and Sartohay Ophiolite (SO).

However, they are slightly enriched in Zn, Co, Mn (ppm) and Cr_2O_3 (wt%) and depleted in Al_2O_3 (wt%), Ti (ppm) and MgO (wt%) compared with those in ZO and higher in terms of Ga, Ni, Zn, Co, Mn (ppm) and Cr_2O_3 (wt%) compared to these elements in SO (Fig. 10b). The Ti, V, Ni, Zn and Ga contents in high-Al chromitites more enriched than high-Cr ones suggest that parental melts from which high-Al chromitites were formed. The similarity of high-Cr chromitite from studied deposits to the boninite and TMO indicates genetic link between them and suggests that high-Cr chromitites from Zhob valley ophiolite crystallized out from boninitic melts. On the other hand, high-Al chromitites exhibit similar patterns to the MORB. But high-Al chromitite is slightly depleted in Al_2O_3 and Ti compared to those from MORB while similar to those from Sartohay Ophiolite which reveals high-Al chromitites have thoiilitic/MORB affinity.

Compositional Variation and Alteration in Chromites

The profile analyses of chromite grains of both types of chromitites show that most of them are unzoned. However, in some grains of high-Cr chromitite, Cr contents decrease while Al_2O_3 (wt%) and $\text{FeO}_{\text{total}}$ (wt%) contents increase from core to rim. Therefore, the Cr# values are decreasing from core to rim in high-Cr chromite grains (Fig. 6b). This kind of zoning is considered to be the results of fractionation of melt during the formation of chromite, hence, reflect magmatic zoning (Akmaz et al., 2014). On the other hand, in some grains of high-Al chromitites, Al_2O_3 (wt%) and MgO (wt%) contents decrease from core to rim while Cr and $\text{FeO}_{\text{total}}$ (wt%) contents increase from core to rim, resulting in an increase of Cr# from core to rim (Fig. 6a). This kind of zonation indicates that secondary processes had affected the chromite grains which had resulted in the formation of ferritchromite.

The alteration process observed in ophiolitic chromitites is associated with many events which are serpentinization (Burkhard, 1993), regional metamorphism (Barnes, 2000; González-Jiménez et al., 2009), decomposition (Pooley, 2004) and lateritization (Economou-Eliopoulos, 2003). As a result of petrographic investigations, any decomposition and lateritization process was not observed in Zhob valley chromitites. Therefore, the main cause of ferritchromite formation can be explained as serpentinization and/or metamorphism (Kapsiotis, 2015).

The formation of ferritchromite in the Kalkan chromitites (southern Urals), has been described and three stages were suggested for its development (Merlini et al., 2009). In first stage chromite grains equilibrated with surrounding olivine. The second stage involved the serpentinization (lizardite and chrysotile) of the matrix rich with olivine at approximately 200 to 300 °C (Auzende et al., 2006; Hajialioghli et al., 2007). Almost all lizardite/chrysotile transformed by prograde metamorphism at more than 300 °C into the polymorph antigorite in the third stage. The metamorphic reaction $2(\text{Mg}_{0.60}\text{Fe}_{0.40})(\text{Cr}_{1.30}\text{Al}_{0.70})\text{O}_4$ [chromite] + $3/2(\text{Mg}_{2.57}\text{Al}_{0.32}\text{Fe}_{0.11})\text{Si}_2\text{O}_5(\text{OH})_4 + \text{H}_2\text{O} + 1/12\text{O}_2$ [antigorite] $\rightarrow 7/6(\text{Mg}_{0.40}\text{Fe}_{0.60})(\text{Cr}_{1.85}\text{Fe}_{0.08}\text{Al}_{0.07})\text{O}_4$ [Fe-chromite] + $1/2(\text{Mg}_{9.18}\text{Fe}_{0.34}\text{Al}_{1.60}\text{Cr}_{0.88})(\text{Al}_2\text{Si}_6\text{O}_{20}(\text{OH})_{16})$ [Cr-chlorite] converts chromite-serpentine into ferritchromite-chromian-chlorite assemblages in the presence of a hydrous fluid phase (Merlini et al., 2009). Thus, according to this reaction, the generation of ferritchromite in chromite grains of high-Al chromitite from the Zhob valley ophiolite indicates that this is due to metamorphic processes (Barnes, 2000; Proenza et al., 2004; Mukherjee et al., 2010; Gervilla et al., 2012).

Figure 10. $\text{Chromite}_{\text{MORB}}$ normalized major-trace elements of high-Cr (a) and high-Al (b) Zhob valley ophiolitic chromitites. Data source for TMO and boninite values were from (Page and Barnes, 2009), ZO chromitites values from (Gonzalez-Jimenez et al., 2012) Luobusa and Sartohay chromitites values were from (Zhou et al., 2014). Data source and acronyms are as in Figure 8. Note that average contents of elements are plotted.

Genesis and Geotectonic Environment

Today, the formation of podiform chromitites is not fully understood. Fractional crystallization from melt supplied through magmatic conduits is regarded as the primary model for the formation of podiform chromitites (Thayer, 1964; Lebac and Ceuleneer, 1992). Melt/rock reaction, multi stage partial melting, magma mixing and magma segregation processes can lead to chromite formation (Paktunc et al., 1990; Lebac and Ceuleneer, 1992). These models consider that melt/rock reactions and eventually melt/melt mixing are significant processes in

the genesis of podiform chromitites (Kelemen, 1990; Arai and Yurimoto, 1994; Zhou et al., 1996). A model proposed by Gonzales-Jimenez et al. (2014b) suggests that podiform chromitites form in networks and channels of highly porous dunite, which formed in the mantle peridotite by melt/rock reaction. In high permeability conduits, the mixing and crystallization of new basaltic magma yields a suitable environment for podiform chromitite formation. Size, type and texture of chromitites may indicate the pattern of melt flow at different melt/rock ratios within highly porous networks of channels and a range of temperature contrasts between melt and the host peridotite.

Many researchers have revealed that both high-Cr and high-Al chromitites can occur together within depleted peridotite in the same ophiolitic massif as well as in separate massifs (Zhou et al., 1994; Leblanc, 1995; Melcher et al., 1997; Proenza et al., 1999; Ahmed et al., 2001; Gervilla et al., 2005; Uysal et al., 2007a, 2009; Zaccarini et al., 2011; Kapsiotis, 2013). In addition, several authors explained the coexistence of high-Cr and high-Al chromitites in different ways. 1– It has been suggested that the melt responsible for the formation of chromite in a supra-subduction zone environment originates from several depleted mantle sources (MORB to boninitic type melt) (Uysal et al., 2009; Gonzales-Jimenez et al. 2011; Zaccarini et al., 2011). 2– Much depletion of mantle peridotite upwards in mantle sequence, with enhancement of Cr# values in ophiolitic chromitites situated in residual mantle (Leblanc and Nicolas, 1992; Stowe, 1994; Uysal et al., 2007b). Chromitites from the Zhob valley ophiolitic bodies have lenses and pods of variable size that have sharp contacts with their dunite envelopes, and interlayered dunite and chromitites. These are characteristics that support a model in which metasomatic-magmatic processes have occurred in a network of channels through which melts percolated and reacted with peridotite wall rocks.

Contents of Al_2O_3 and TiO_2 in chromite are related to the Al_2O_3 and TiO_2 contents of parental melts of chromites which provide useful indicators of tectonic settings (Kamenetsky et al., 2001). Calculated Al_2O_3 (wt%) contents of parental melts of high-Cr and high-Al from Zhob valley ore bodies suggest that they have an arc and MORB geochemical affinity, respectively. The very low TiO_2 content of parental

melt of high-Cr chromitites suggests that the chromitites were derived from boninitic melt formed in an island arc environment while parental fluid composition of high-Al chromitites indicates that it has been derived from MORB melts.

Inclusions of silicate minerals in chromite grains have been reported in several podiform chromitites (Johan and Lebel, 1978; Johan et al., 1983; Augé, 1987; Lorand and Ceuleneer, 1989; Graham et al., 1996; Melcher et al., 1997; Gervilla et al., 2005). Some authors like Johan and Lebel (1978), and Johan et al. (1983) argue that hydrous inclusions are evidence of unmixing of basaltic melt and an aqueous fluid phase and other volatile constituents. Furthermore, hydrous silicates indicate that during the chromite crystallization basaltic melt was contaminated with a fluid phase (Watkinson and Mainwaring, 1980; Lorand and Ceuleneer, 1989). We have observed mineral inclusions in unaltered chromites of the Zhob valley. Chromite grains of both kinds of chromitites contain a variety of silicate mineral inclusions. These inclusions occur together in a single chromite grain as well as in separate grains. Among the silicate inclusion, olivine and amphibole are detected (Fig. 3f and h). These silicate inclusions are typically anhedral to subhedral in shape and granular in texture. These assemblages and textures of minerals indicate that the mineral inclusions represent crystallization products of trapped liquids during crystallization of chromite (Zhou et al., 2014). The presence of amphibole inclusions and high Cr# values prove that high-Cr chromitites were formed by boninitic type melts in supra-subduction zone environment. However, minor-trace element composition and amphibole inclusions indicate that high-Al chromitites are generated by MORB-

Figure 11. Tectonic discrimination using $100 \times \text{Cr\#}$ vs. TiO_2 for chromites for podiform chromitites From Zhob valley ophiolite. The podiform chromitite field is from Page and Barnes (2009) and fields for chromite from MORB and boninite are from (Barnes and Roeder, 2001).

like melts in back-arc setting.

Cr# values and TiO₂ contents (wt%) of chromite from both chromitites are plotted in the diagram TiO₂ vs Cr# (Fig. 11). Both chromitites fall in the field of ophiolitic podiform chromitites while high-Cr chromitites show good similarities with chromitites that are derived from boninitic melts, generated in supra-subduction zones and high-Al chromitites analyses plot close to the MORB field.

Using the diagram (Al₂O₃ vs TiO₂ wt%) of Kamenetsky et al. (2001) which is used to separate chromites crystallized from OIB, LIP, MORB and arc related basaltic melts (Fig. 12), high-Cr chromitites related the Zhob valley ophiolite exhibit a positive correlation and plot in or near to the arc field which suggests boninitic affinity. The high-Al chromitites plot within or close to the MORB field and display MORB affinity. Further, trace elements also impart suitable evidences for tectonic environments. Ga is compatible in chromian spinel (Malvin and Drake, 1987) and its concentration in chromites is a sensitive indicator of magma compositions and degree of depletion (Paktunc and Cabri, 1995, Zhou et al., 2014). Ga decreases with increasing Cr# (Fig. 9b)

(from high-Al to high-Cr chromitite) and inversely correlations with Cr#. Thus, this correlation reveals a switch from a mid-ocean ridge setting to a supra-subduction zone setting (Alabaster et al., 1982; Umino et al., 1990; Dare et al., 2008; Pagé and Barnes, 2009).

Conclusions

In the Zhob valley ophiolite, the Khanozai and Muslim Bagh bodies contain high-Cr (> 0.6) chromitites while the Zhob body includes of high-Al (< 0.6) chromitites. Chromite of high-Cr chromitite is largely uniform in composition but a few grains are partially zoned, with decrease in Cr# from core to rim which reflects the melt fractionation during crystallization of chromite. In the chromite grains of high-Al chromitites, Cr# and FeO_{total} (wt%) decrease from rim to core which suggests that ferritchromite from high-Al chromitites had been generated by secondary processes.

The parental melt composition of high-Cr chromitites and the hydrous

Figure 12. Tectonic discrimination using Al and Ti of chromites from chromitites of the Zhob valley ophiolite (fields after Kamenetsky et al., 2001). MORB, mid-oceanic ridge basalt; BON, boninite; LIP, large igneous province basalt; OIB, ocean island basalt; ACR, arc-related volcanic rock; IAT, island arc tholeiite.

silicate inclusions reflect that the parental magma is boninitic, which formed by high degrees of partial melting of mantle, generating S-undersaturated and hydrous melt. In contrast, the calculated composition of parental melt of the high-Al chromitites is MORB-like melt and the presence of amphibole inclusions indicate that high-Al chromite are derived from MORB-like melt reaction with depleted mantle that produced hydrous melt.

Negative correlations of vanadium, gallium, zinc, nickel and titanium with Cr# reveal the fractionation of the parental melt. The trace elements of high-Cr chromite form an identical pattern to the boninitic lava which shows that the parental melt of high-Cr is boninitic in nature. High-Al chromites are enriched in Al, Ga, Ti, Ni, and Mg compared to boninite and form flat patterns similar to MORB and suggest that parental melt is basaltic with MORB affinity.

The field, petrographic and geochemical data suggest that the Zhob valley chromitites are crystallized from ascending melts through a network of channels, formed by melt-rock interactions at different degrees and high-Cr chromite are crystallized out from boninite magma and may be linked to a supra-subduction zone environment, whereas high-Al chromitites are derived from MORB-like melt during reaction with depleted mantle, most probably, originated in a back arc basin tectonic environment.

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