



Compositional variations of chromite and solid inclusions in ophiolitic chromitites from the southeastern Turkey: Implications for chromite genesis



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ABSTRACT

Chromitites, associated with upper mantle peridotites of ophiolites from southeastern Turkey, are lenticular bodies or veinlets made up of massive, banded and disseminated chromite. Chromite shows a wide range of Cr# [$\text{Cr}/(\text{Cr} + \text{Al})$] varying between 0.42 and 0.81, and Mg# [$\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$] of 0.45 to 0.75. Geochemically, they are divided into two compositional groups, such as high-Cr (Cr# \geq 0.7) and high-Al (Cr# $<$ 0.6). The contents of the platinum-group elements (PGE) in high-Cr chromitites range between 42 and 348 ppb (average 158 ppb), whereas high-Al ones are represented by a lower total PGE, ranging between 70 and 94 ppb (average 84 ppb). However, two high-Cr chromitite samples showed significant enrichments especially of Ir-subgroup of PGE (IPGE: Os, Ir, Ru) with total PGE contents reaching up to 2.7 ppm. The chromitites mostly contain tiny inclusions ($<5 \mu\text{m}$) of platinum-group minerals (PGM). The most abundant PGM is laurite which is rarely associated with irarsite \pm Os–Ir alloys; these minerals in particular are more abundant in high-Cr chromitites, especially in PGE enriched chromitites. The primary base-metal sulfide (BMS) inclusions consist of millerite and to a lesser extent pentlandite, and very rarely pyrite. Violarite, polydymite and heazlewoodite form the secondary BMS phases found mostly in altered silicate matrix. Both PGM and BMS are frequently associated with the silicates: amphibole, olivine and clinopyroxene. Textural relationships and the composition of PGM and BMS inclusions suggest that they crystallized at varying temperature (1300 °C–1000 °C) and sulfur fugacity conditions, before or during the event of crystallization of chromite. The high-Cr chromitites crystallized in equilibrium with boninite melt, probably originated in a supra-subduction zone (SSZ), while the high-Al chromitites crystallized in equilibrium with middle oceanic ridge basalt (MORB) type melts. The presence of amphiboles in high-Al chromitites suggests hydrous parental melts that could be produced, most probably, in back-arc tectonic setting.

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1. Introduction

Many researchers have stated that podiform-type chromitites formed by melt-rock reaction in supra subduction zone (SSZ) geodynamic environment, in the presence of parental melts, saturated in olivine–chromite, and rich in water (Arai and Yurimoto, 1994, 1995; Büchl et al., 2004; Matveev and Ballhaus, 2002; Melcher et al., 1999; Proenza et al., 1999; Roberts, 1988; Uysal et al., 2005; Zhou et al., 1998). It has also been emerged that high-Cr chromitites may have been crystallized in equilibrium with boninitic or Mg-rich andesite melts in the deeper mantle sequence (Ahmed and Arai, 2002; Pagé and Barnes, 2009; Proenza et al., 1999; Zhou et al., 1998) whereas, high-Al chromitites are possibly formed from back-arc basalts, and tend to occur at the shallowest levels of the upper mantle, within the Moho-Transition Zone, and very close to the lower layered sequence

(Leblanc and Nicolas, 1992; Leblanc and Violette, 1983; Proenza et al., 1999).

Chromite composition and, geochemistry and mineralogy of PGE in chromitites have been used to determine the partial melting processes, plus the estimation of the thermochemical conditions prevailing in the magmatic systems in which chromite and PGM are formed (Ahmed and Economou-Eliopoulos, 2008; Ferrario and Garuti, 1990; Garuti et al., 1999; Kapsiotis et al., 2011; Nakagawa and Franco, 1997; Uysal et al., 2005). In addition, BMS and silicate inclusions have been used to give an idea regarding the crystallization processes, and geodynamic environments of chromitites (González-Jiménez et al., 2011a; Jannessary et al., 2012; Uysal, 2008; Uysal et al., 2007a). The distribution of PGE in chromitites provides valuable information on the partial melting history of the upper mantle and fractionation process of the parental melt of the chromitites (González-Jiménez et al., 2011a; Kapsiotis et al., 2011; Uysal et al., 2007b, 2009a,b; Zaccarini et al., 2011). This information combined with the T - fS_2 conditions for the crystallization of the PGM is a powerful tool in understanding the origin of chromitites in ophiolites (González-Jiménez et al., in press).

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Recent refinements of the techniques concerning the in situ analysis, such as the Laser Ablation Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS), allow us to analyze a complete suite of minor and trace elements (Ni, Mn, Ti, V, Zn, Co, Ga and Sc). These elements provide additional information regarding the type of parental melts and their tectonic setting of formation (González-Jiménez et al., 2011b; Pagé and Barnes, 2009).

In this paper, we aim to resolve the geodynamic uncertainties of southeastern Turkey chromitites, using the composition of chromite combined with PGE geochemistry, and a systematic investigation of silicate, PGM and BMS in chromite.

2. Geological background

The geology of Turkey consists of lithospheric fragments of the mega-continental margins (Gondwana and Laurasia), that were combined during the Alpine Orogeny when the Arabian plate collided with the Anatolian plate during the Late Cretaceous–Tertiary time (Bozkurt and Mittweide, 2001). The investigated chromitite occurrences are located within the ophiolites of southeastern Anatolia. Southeastern Anatolia comprises of an east-west trending mountain belt of Alpine orogenic segment in the north, and flat, low-lying plain of Arabian Platform to the south (Yılmaz, 1993). The metamorphic rocks, known as Bitlis and Pötürge massifs, and ophiolitic units, covering an area larger than the metamorphic rocks, crop out along the orogenic belt, whereas sedimentary rocks form the Arabian Platform. Although the ophiolitic rocks are observed mainly in the suture zones, they are also present in nappes on the Arabian Platform. The ophiolites in the nappe region commonly demonstrate a polyphase metamorphism; however, those on the Arabian Platform are nonmetamorphic (Yılmaz, 1993).

The Berit metaophiolite, located in the southern Neotethyan oceanic basin in southeastern Anatolia, is the most significant ophiolite in the investigated region. It consists of both metamorphosed and unmetamorphosed rocks, of an ophiolite sequence, of the late Cretaceous age. The metamorphosed rocks are characterized by pyroxene granulite, garnet amphibolite, amphibolite, garnet and amphibole-bearing metagabbro, amphibole schist, plagioclase–amphibole schist and epidote–plagioclase–amphibole schist. However, the unmetamorphosed rocks are represented by chromite-bearing dunite, harzburgite, wehrlite and serpentine. The contact between metamorphic and nonmetamorphic rocks are observed in the Doğanşehir region (Malatya) (Parlak et al., 2009 and references therein). The nonmetamorphic ophiolitic rocks are mostly dismembered, and composed mainly of mantle peridotites (dunite and harzburgite), which are mostly serpentinized, displaying foliation and lineation, which reflect plastic deformation (Bağcı, 2013).

3. Geological and petrographic description of the chromitites

Many ophiolitic units, which contain significant chromitite bodies, are present in various parts of Turkey (Fig. 1a). In this paper, we investigated fifty ophiolitic chromitite samples from the Berit Mountain and Afşin (Kahramanmaraş, Fig. 1b), Doğanşehir (Malatya, Fig. 1c) and İslahiye (Gaziantep, Fig. 1d) ophiolites from southeastern Turkey. Most of the chromitites investigated were heterogeneously distributed in the deeper part of the ophiolitic mantle section and were discordant with host peridotites. However, some of them formed close to the Moho-Transition Zone, and are concordant with host peridotites. All samples were taken from chromitite exposures and mines which are associated with depleted mantle peridotites (mainly harzburgite and dunite), in the form of veinlets and lenticular bodies of variable size (1–5 m thick and 5–20 m wide). The investigated chromitites are separated from the host harzburgite by dunite envelopes of variable thickness. The transitions from chromitite bodies to surrounding dunite and harzburgite are generally sharp and slightly gradual. No

observations were made of any structures such as boudins, flow folds, and the like, within the chromitites which may attest to high-T mantle deformation.

Texturally banded, massive and disseminated chromites are usually unaltered, although some of them exhibit ferritchromite generation along the rim of grains and cracks. Many chromite grains display pull-apart fractures and cataclastic textures. The matrix consists mainly of olivine, clinopyroxene, amphibole and altered silicates, such as chlorite and serpentine. Chromite grains of the investigated chromitites are podiform and of variable in size (1–3 cm), containing inclusions of PGM, silicate and BMS that are mostly euhedral or subhedral in shape.

4. Analytical methods

In situ micro-chemical analyses of chromite, PGM, BMS and silicate inclusions were carried out using CAMECA SX-100 electron-probe micro-analyzer (EPMA) at the Department of Earth and Environmental Sciences, in the Ludwig Maximilian University of Munich, Germany. Platinum-group mineral, BMS and silicate inclusions in chromite were located on polished thick sections and scanned under reflected light at 200–500× magnifications. The PGM and base-metal phases were qualitatively examined first by energy dispersion spectrometry, and then analyzed quantitatively by wavelength-dispersion spectrometry (WDS). Analytical conditions for quantitative WDS analyses were 15–20 kV accelerating voltage, 30 nA probe current, and a beam diameter of 1 μm. Pure metals were used as standards for PGE, Ni and Cu, arsenopyrite for As, and pyrite for Fe. The following X-ray lines were used in the analyses: Lα for Ru, Ir, Rh and Pt, Mα for Os, Lα for Pd, As, and Kα for S, Ni, Fe and Cu. Ferric and ferrous iron contents of the chromites were calculated assuming spinel stoichiometry (AB₂O₄). The detection limits of the elements measured for chromite, PGM, BMS and silicates were presented in Tables 1, 4, 5 and 6, together with the analytical results. Back scattered electron (BSE) images of chromites, PGM, BMS and silicate phases were also obtained using the same instrument.

A total of 15 whole rock chromitite samples were analyzed for their PGE concentrations using a nickel sulfide fire-assay pre-concentration method followed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) at Genalysis Laboratory, Perth, Western Australia, with the following method described by Chan and Finch (2001). Detection limits of PGE were 1 ppb for Rh, and 2 ppb for Os, Ir, Ru, Pt and Pd.

Trace element concentrations of 16 chromite grains from five chromitite samples were analyzed using a Thermo X-Series 2 quadrupole ICP-MS coupled to a New Wave UP-213 Laser Ablation system at Geochemistry/ICP-MS Laboratory at the School of Earth and Ocean Sciences, University of Victoria, Victoria, BC Canada. The signal for each element was normalized to an internal standard (Aluminum) correcting for ablation efficiency and instrumental drift. NIST 611 Glass was used to calibrate the signal, and the quality of calibration was confirmed by re-analysis of NIST 611 after every four shots. Accuracy and precision were confirmed by daily replicate analyses of the USGS reference material BCR2g. NIST 611 Glass and BCR2g were analyzed at both the beginning and end of each session, and at regular intervals throughout the session. The data was calibrated to NIST 611 Glass (= NIST 610), as is common for many geological LA-ICP-MS studies. BCR2g was used as an independent check to (1) confirm the quality of the calibration and check for sensitivity drift and (2) offer an independent measure of precision and accuracy of the method. Laser frequency of 10 Hz, typical energy of ~10 J/cm² and the laser beam size of 80 μm were used during the measurements. For each analysis, 25–30 s of background was collected (gas blank before firing the laser – these signals were subtracted from the signals measured during analysis), followed by approximately 30 s of sample analysis time (while the laser was firing). Detection limits of elements were 10.7 ppm for Ni, 4.7 ppm for Mn, 2 ppm for Ti, 1.1 ppm for V, 0.6 ppm for Zn, 0.3 ppm for Co,

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