Subduction initiation for the formation of high-Cr chromitites
in the Kop ophiolite, NE Turkey

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Abstract

The Kop ophiolite in NE Turkey is a forearc fragment of Neo-Tethys ocean, consisting mainly of a paleo-Moho transition zone (MTZ) and a harzburgitic upper mantle unit. Locally, the Kop MTZ contains cumulate dunites and high-Cr chromitites (Cr# up to ca. 79), which are cut by pyroxenites. Dunites and chromitites in the MTZ have REE concentrations that are 1-2 orders of magnitude lower than those of chondrite; they are either depleted in LREE or have concave REE shapes. The LREE depleted patterns are interpreted to reflect production of cumulate rocks by magmas derived from a depleted mantle, the concave patterns the modification of these rocks by LREE-enriched fluids. Clinopyroxenes from pyroxenites are diopsidic and characterized by high Mg#s (ca. 92-96) and high CaO contents (ca. 24-25%); their Al₂O₃ contents (1.0-3.0 wt.%) fall between those of clinopyroxenes in N-MORB and komatiite/boninite, suggesting that the parental melts originated from more refractory mantle than abyssal lherzolites. However, these clinopyroxenes display LREE depleted patterns consistent with those of clinopyroxenes in abyssal lherzolites, indicating their genetic connection with decompression melting of asthenosphere. The cross-cutting relationship between pyroxenite veins and chromitiferous rocks suggests that depleted mantle remained beneath the proto-forearc after chromitite formation; it

had not been significantly modified by slab-derived components and continued interacting with the upwelling asthenosphere until pyroxenite crystallization. This study provides a temporal constraint on the formation of high-Cr chromitites; they possibly began to be produced during the transition between early and late proto-forearc spreading, during which subduction dehydration had not well developed.

Keywords: Kop ophiolite, high-Cr chromitite, proto-forearc, depleted mantle, asthenosphere upwelling, metasomatism.

1. Introduction

High-Cr chromitites have been widely discovered in forearc ophiolites (Arai and Yurimoto, 1995; Pearce et al., 1984; Stowe, 1994). They are concentrated near the Moho and are closely associated with dunites (John and Dickey, 1975; Paktunc, 1990). The forearc affinities of high-Cr chromitites link them to the spreading of proto-forearc, and they have often been thought to be genetically related to boninites (Robinson et al., 1997; Zhou et al., 1996), which are derived from refractory but

hydrous mantle sources (Hickey and Frey, 1982; Bloomer, 1987; Pearce et al., 1992; Stern et al., 1991). However, these relationships need to be further investigated. Firstly, few studies have determined when high-Cr chromitites might be produced during proto-forearc spreading. Boninites have diverse major and trace element compositions (Danyushevsky et al., 1995; Pearce et al., 1992), but it remains unclear which types of boninites are responsible for the formation of high-Cr chromitites, if they were indeed the parental magmas. Despite numerous reports of hydrous mineral inclusions in chromite (Arai, 2013; Lorand and Ceuleneer, 1989; Matveev and Ballhaus, 2002), little is known about how important a role water may have in generating the parental magmas of high-Cr chromitites.

The flux of slab-derived fluids becomes progressively higher during the initial stage of subduction, increasingly modifying the composition of the overlying mantle with time (Reagan et al., 2010; Stern et al., 2012; Whattam and Stern, 2011). The chondrite-normalized REE patterns of magmatic rocks produced at that period change from LREE depleted to LREE enriched forms. Because light and heavy REE cannot be easily fractionated during the differentiation of mantle-derived magmas (Ariskin et al., 1993; Hanson, 1980), the REE patterns of chromitites are theoretically effective in restoring the features of their parental magmas. During the formation of chromitites,

dunites can be produced through melt-harzburgite interaction or magmatic accumulation (Arai and Yurimoto, 1994; Proenza et al., 1999; Rollinson, 2008; Xiong et al., 2015; Zhou et al., 1994). Given this genetic relationship, the geochemical features of dunites provide another important mean of exploring the relationship between high-Cr chromitite and magmatism during the initial stage of subduction.

Different REE patterns have been reported for chromitite-associated dunite (Proenza et al., 1999; Su et al., 2015; Zhou et al., 2005), implying that the parental magmas of high-Cr chromitites also have diverse REE distributions. However, the LREE enriched and U-shaped REE patterns of peridotites in supra-subduction zones could be generated by metasomatism (Parkinson and Pearce, 1998; Saccani and Photiades, 2004; Ulrich et al., 2010), casting doubt on whether these REE patterns of dunites are primary or secondary. However, this problem has seldom been discussed in previous studies, and further work is urgently needed to address it. Compared with reactive dunites, which may derive their REE compositions from both melt and peridotite, cumulate dunites are formed by accumulation alone; their geochemical features therefore can only be inherited from their parental magmas. As a result, cumulate dunites could represent very effective tools for deciphering the nature of the parental magmas of high-Cr chromitites if no remarkable post-magmatic modification

happened.

The Kop ophiolite in NE Turkey is a lithospheric fragment of the Neo-Tethys ocean. It displays supra-subduction affinity and contains harzburgitic mantle and Moho transition zone (MTZ) components (Uysal et al., 2010). Well-developed cumulate high-Cr chromitite and dunite are locally distributed in the MTZ (Kolaylı, 1996; Okay and Tüysüz, 1999; Uysal et al., 2007), making the Kop ophiolite ideal for studying the genesis of high-Cr chromitite. In addition, widespread pyroxenite veins occur in harzburgites and dunites. They could also help place genetic constraints on magmatism in the Kop ophiolite. In this paper, we present results of systematic whole-rock and in-situ analyses of the different lithologies, including the cumulate chromitites and dunites from the MTZ, the harzburgites and dunites from the mantle-MTZ boundary; and pyroxenite veins. The trace element features of the cumulate dunite and clinopyroxene reveal that high-Cr chromitite probably formed no later than the transition between the early and late stages of proto-forearc spreading after the initiation of subduction. Their parental magmas are interpreted to have originated from depleted mantle without intensive modification by slab-derived fluids.

2. Geological Background

The emplacement of ophiolites between Gondwana and Eurasia was caused by the closure of Neo-Tethys in Eocene (Clift and Robertson, 1989; Ghasemi and Talbot, 2006; Wang et al., 2002). These ophiolites define series of suture zones and divide the Tethyan domain into numerous micro-continents. Turkey is located in the western part of the Tethyan domain and can be divided into five major tectonic units, including Potides domain, Anatolian terrane, Taurus terrane, South Taurides exotic units, and Peri-Arabian domain (Fig. 1a; Moix et al., 2008). These different blocks collided in Late Cretaceous (Bozkurt and Mittwede, 2001; Moix et al., 2008; Sengör and Yilmaz, 1981; Okay, 2008).

The Kop ophiolite in NE Turkey occurs along the Izmir-Ankara-Erzincan suture zone, (Fig. 1a; Bozkurt and Mittwede, 2001; Moix et al., 2008; Uysal et al., 2007). It is about 15 km wide and stretches in a NE-SW direction over 50 km long (Uysal et al., 2007). Eyuboglu et al. (2015) proposed the Kop ophiolite were probably produced in Paleozoic or even earlier, but its age needs to be further constrained. The Kop ophiolite can be divided into a dunite-dominated belt along the northern margin and a harzburgite unit in the south and northwest (Fig. 1b). The dunite-dominated belt is likely to be equivalent to the lower part of the Moho transition zone and is about 2.5-3 km wide (Fig. 1b, c); it also contains some harzburgitic bodies locally associated with

dunites and chromitites. The harzburgite unit stratigraphically corresponds to the uppermost part of the mantle and makes up 90% of the Kop ophiolite (Fig. 2a). Chromitites occur in both harzburgite and dunite bodies; their reserves range from hundreds to millions of tons (Kolaylı, 1996). In the dunite-dominated belt, chromitites usually interlayer with dunites and were sometimes affected by shearing process (Fig. 2b, c). Pyroxenite veins can be frequently seen in the Kop ophiolite; they are usually gray green in color and cut both lithologies of harzburgite and dunite (Fig. 2c). In addition, there are also minor amounts of wehrlites and lherzolites in the Kop ophiolite (Kolaylı, 1996; Uysal et al., 2007).

3. Sampling and Petrography

Three composite samples of chromitite and dunite, two pyroxenite veins and their host rocks, and two cpx-harzburgites were specially selected in this study. The composite samples were collected from the MTZ and display layered structures in the field (Fig. 1-c). They were named as Kop-B, Kop-C and Kop-E, respectively (Fig. 2d-f). Two pyroxenite veins are hosted in cpx-harzburgite (Kop14-03) and chromitiferous dunites (Kop14-05), both of which were collected from the boundary between mantle and MTZ where harzburgites and dunites coexist (Fig. 1-c); these two

pyroxenite veins were named as Kopy-03 and Kopy-05 accordingly. The last two cpx-harzburgites are Kop14-18 and Kop14-21; they were collected from the MTZ harzburgitic bodies (Fig. 1-c).

In the three composite samples, chromitites are moderately disseminated and mainly consist of chromite, olivine and minor clinopyroxene (Fig. 3a). Chromite grains make up around 65% of the whole rock, and they are subhedral to anhedral with diameters ranging from 0.15 to 2.50 mm. Surrounding the chromites are olivine grains with a total volume around 35%. These olivine grains have been highly fractured. Olivines predominate in dunite and present similar textures to those in chromitite. There are also some subhedral to euhedral chromite grains in dunites (Fig. 3b). They scatter among olivine grains and take up modal fractions around 1-3%. Their diameters range generally from 0.1 to 0.4 mm. Anhedral clinopyroxene can be observed in both chromitite and dunite. They are unevenly distributed in both lithologies, comprising about 1% of the whole rock. These clinopyroxenes sometimes engulf olivine grains (Fig. 3b).

Samples Kopy-03 and 05 (Pyroxenite veins) are mainly composed of orthopyroxene and clinopyroxene. They usually have relatively sharp boundaries with their hosting peridotites (Fig. 3c, d). These minerals are usually quite irregular in

shape (Fig. 3e), and their grain sizes vary largely from part to part and range from 100 μm to 2 cm. Generally, orthopyroxene (60-70%) outnumbered clinopyroxene (30-40%) in each vein. The sample Koppy-05 is partly altered given the alteration margins of orthopyroxenes.

Samples Kop14-03, 18, and 21 (cpx-harzburgite) consist of olivine, orthopyroxene, clinopyroxene and chromite. These harzburgites present an overall fine-medium granular texture (Fig. 3f, g). The modal proportions of minerals vary in different samples. Olivines are highly fractured and make up of about 80-90% of the whole rocks. Orthopyroxene grains constitute about 7-15% of whole rock and are generally 0.5-1.5 mm in size. Rounded olivine inclusions could be seen in orthopyroxene (Fig. 3h). Clinopyroxene grains comprise about 2-4% of the rock but are quite unevenly distributed. They are euhedral in shape and range from tens to hundreds of microns. Chromite grains are sparsely distributed. They typically have anhedral and resorbed textures; their grain sizes range from 0.2 to 1 mm.

4. Analytical Methods

The major element compositions of chromite, olivine and clinopyroxene in this

study were measured with electron microprobes. The three composite samples (Kop-B, C and E) were divided into several parts and used for the whole-rock major and trace element analysis. Clinopyroxenes from cpx-harzburgite (Kop14-18) and the pyroxenite veins (Koppy-03 and 05) were used for in-situ trace element analysis.

The major element compositions of olivine, chromite and clinopyroxene in samples C and E and clinopyroxene in sample B were measured on the Cameca SX-100 system with a LaB6 cathode at the Department of Earth and Environmental Sciences in Ludwig Maximilian University of Munich (Germany). The analysis conditions were as follows: wavelength dispersive spectrometers at 15 kV and 20 nA; 1 μm beam diameter; 10 to 30 s counting time for different elements in silicates; 10 to 100 s counting time for different elements in chromite. The major element compositions of chromite in sample B were analyzed using the JEOL JXA-8100 electron micro probe (EMP) with a WDS/EDS combined micro-analyzer at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS). The analyses were operated in conditions as follows: 15 kV accelerating voltage, 20 nA beam current, 3 μm spot diameter, and counting time ranging from 10 to 30 s for different elements. The major element compositions of clinopyroxene and chromite in pyroxenite veins (Koppy-03 and 05) and cpx-harzburgites (Kop14-03, 05, 18 and 21)

were obtained using the JEOL JXA-8230 electron microprobe with a WDS/EDS combined micro-analyzer at the Earth Science Department, The University of Hong Kong (HKU). The analyses were carried out with a 15 kV accelerating voltage, a 20 nA beam current and a 1 μm spot diameter. The counting times range from 10 to 30 s for most elements and 120s for Ti. In these experiments, natural and synthetic oxides were used as the standards. Relevant calibrations were carried out with the PAP matrix correction and ZAF procedure based program for data obtained at Munich and Beijing, respectively. SEM images were also obtained using the JEOL JXA-8230 EMP in the department of Earth Sciences, The University of Hong Kong.

Whole-rock major element compositions of different parts of samples C and E were obtained with the X-ray fluorescence (XRF) at the ACME Analytical Laboratory at Vancouver (Canada). Concentrations of trace elements were measured with the Thermo Scientific X-Series 2 Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) in the Department of Earth Sciences at the University of Durham. Detailed analytical procedures can be referred to Ottley et al. (2003) and Uysal et al. (2012). The final results are presented in Appendix Table 6, including detection limits of all elements, blank values, and standard deviation and RSD% values of in-house peridotite standard (GP13).

The in-situ trace element analysis of clinopyroxene of sample B was carried out on polished thin sections using the laser ablation-inductively coupled plasma mass spectrometer (LA-ICP-MS) at IGGCAS. The instrument consists of a Lambda Physik LPX 120I pulsed ArF excimer laser coupled with an Agilent 7500 ICP-MS. Ablated materials were carried by helium gas. The out energy was around 80 mJ. The spot diameters range from 30 to 60 μm depending on the grain sizes of clinopyroxenes. Counting time for background and analysis were 20 s and 40 s, respectively. ^{43}Ca was used as the internal standard, and its absolute content was determined by the electron microprobe (24.26 on average in this study). NIST 610 was used as the external standard. The trace element data were rectified with GLITTER 4.0 Online Interactive Data Reduction for LA-ICP-MS program developed by GEMOC, Macquaries University. The analysis accuracy is better than 5% based on the results of USGS rock standards.

The in-situ trace element analysis of pyroxenes from pyroxenites and cpx-harzburgerite was operated on polished thin sections using the LA-ICP-MS at Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIGCAS). The instrument consists of an Agilent 7500a ICP-MS coupled with a Resonetics RESolution M-50 laser-ablation system. Ablated materials were carried by helium

gas. The out energy was around 80 mJ. The spot size of 70 μm was used. Counting time for background and analysis was 30 s and 40 s, respectively. Reference material KL2-G was used as the external standard. The analysis accuracy is better than 5%. Off-line selection and integration of background and analyte signals, and time-drift correction and quantitative calibration were performed by ICPMSDataCal (Liu et al., 2008).

5. Results

5.1. Major elements of olivine and chromite

Olivine grains from samples C and E are all forsterite and have Mg#s $[(100 \times \text{Mg} / (\text{Mg} + \text{Fe}^{2+}))]$ ranging from 91.2 to 94.9 (Appendix Table 1). However, olivine grains in chromitites have higher Mg#s than those from dunites. The former Mg#s are between 92.7 and 94.9, whereas the latter ones are between 91.2 and 93.0.

Chromite grains in this study belong to magnesiochromite. Those in chromitites and dunites are all characterized by high Cr#s $[100 \times \text{Cr} / (\text{Cr} + \text{Al})]$, generally between 70.3 and 78.9 (Appendix Table 2; Fig. 4). In samples B, C and E, magnesiochromite from chromitites and dunites have little differences in Cr#. The overall Mg#s of

magnesiochromites ranges from 45.4 to 57.6, and magnesiochromite in chromitites present distinguishable higher Mg#s than those in dunites. In cpx-harzburgites (Kop14-03 and 18; Appendix Table 3), the Cr#s and Mg#s of magnesiochromites vary from 14.7 to 37.6 and 60.7 to 72.3, respectively. These values are comparable to those of magnesiochromites from lherzolites and harzburgites (Fig. 4).

5.3. Compositions of clinopyroxene

Three occurrences of clinopyroxenes were recognized in this study; they are hosted in the composite samples (Fig. 3a, b), pyroxenite veins (Fig. 3c-e) and cpx-harzburgites (Fig. 3f, g). The first two types of clinopyroxenes will be termed as dispersed and vein-type clinopyroxenes, respectively.

All these clinopyroxenes belong to diopside based on their major element compositions (Appendix Table 4), but they have quite different contents of CaO, Al₂O₃ and Cr₂O₃ (Fig. 5). The dispersed clinopyroxene have the lowest Al₂O₃ (<1.0 wt.%) and highest CaO content (ca. 25 wt.%) and Mg#s (ca. 96.0); they are compositionally close to the pure end member of diopside. Clinopyroxenes in pyroxenite Koppy-03 and cpx-harzburgites (Kop14-18 and 21) have similar

compositions and are featured by distinctively higher contents of Al_2O_3 (ca. 1.5-3.0 wt.%) than the dispersed ones. Compared with those in Kopyy-03, clinopyroxenes in Kopyy-05 have lower Al_2O_3 contents (ca. 1.0 wt.%); their major element features are closer to the dispersed ones.

There are also large differences between the trace element compositions of different clinopyroxenes. Overall, the dispersed clinopyroxenes have more variable trace element compositions than those in pyroxenites and cpx-harzburgites. The dispersed clinopyroxenes have higher concentrations of Sr (4.30-27.4 ppm) than those in pyroxenites and harzburgites (1.9-2.6 ppm), but their concentrations of transition metals, e.g., Sc, Ni and Co, are either higher or lower than the latter ones (Appendix Table 5). The dispersed clinopyroxenes present varying degrees of LREE differentiations with $(\text{La}/\text{Nd})_{\text{N}}$ ratios ranging from 0.46 to 17.3 (Fig. 6a; Appendix Table 5), but those in pyroxenites and cpx-harzburgites have quite uniform REE distributions, and all are featured by LREE depleted patterns (Fig. 6b). The spider diagrams of dispersed clinopyroxenes look nearly flat with their spikes of U and Pb neglected (Fig. 6c). However, those in pyroxenites and cpx-harzburgite display quite remarkable depleted features despite their slightly enriched mobile elements like Rb and Pb (Fig. 6d).

5.3. Compositions of chromitite and dunite in composite samples

Major element compositions of chromitites differ vastly from dunites. Chromitites have higher contents of Cr_2O_3 and FeO than dunites. The percentages of Cr_2O_3 in chromitite are 31.5 wt.% and 31.6 wt.% for samples C and E, respectively (Appendix Table 6). Dunites have 1-2 times higher contents of SiO_2 and MgO than those in chromitites. Chromitites and dunites have low concentrations of REE, ranging from 0.045 ppm to 0.104 ppm in total. Most parts in samples C and E are relatively depleted in middle REE, but the patterns of E2a and E2b are depleted in LREE (Fig. 7).

6. Discussion

The high Cr#s of chromitites and Mg#s of olivines define the forearc affinity (Arai, 1994) of the Kop ophiolite, suggesting this ophiolite was genetically related to subduction initiation. Coexistence of depleted and concave REE patterns of composite sample E and disparate trace element features of clinopyroxenes reflect multiple processes and different geological settings in the Kop ophiolite. These data provide

new insight about the origin of high-Cr chromitites and are important to understand the early stage of intra-ocean subduction.

In the following parts, we discussed the genesis of different types of clinopyroxenes firstly, and then proposed a two-stage model for the genesis of concave REE patterns of composite samples. Finally, we link the formation of high-Cr chromitites with the tectonic evolution of the Kop ophiolite.

6.1. Formation of dispersed clinopyroxenes by CaO-rich fluids

The clinopyroxene grains dispersed in composite samples are always anhedral and distributed irregularly in dunites and chromitites. Some of them even engulf olivine grains (Fig 3b), indicative of their later generation than olivine. Because Al is more fusible than Cr during partial melting (Bernstein et al., 1998; Dick and Bullen, 1984; Hellebrand et al., 2001), the positive correlation between Cr_2O_3 and Al_2O_3 of these clinopyroxenes rules out the possibility that their low Al_2O_3 contents were caused by high degrees of partial melting (Fig. 5a). Overall, the Al_2O_3 contents of these clinopyroxenes are all below 1 wt.%, distinguishing themselves from magmatic clinopyroxenes which usually have more than 1 wt.% Al_2O_3 (Leterrier et al., 1982).

Instead, their major element compositions largely overlap those hydrothermal diopsides from the northern Oman ophiolite (Fig. 5b; Akizawa et al., 2011; Python et al., 2007a, 2007b), possibly suggesting they were produced by Ca-rich fluids at high temperature conditions (over 900 °C; Python et al., 2007a).

The dispersed clinopyroxene grains are characterized by negative anomalies of Nb and Zr; their REE patterns vary from slightly depleted to enriched (Fig. 6c). However, the diopsides in the diopsidites from the mantle part of Oman ophiolite display remarkable positive anomalies of Sr (average δ_{Sr} 4.66) and Eu (average δ_{Eu} 5.22) (Akizawa et al., 2011; Python et al., 2007b), which are not found for the dispersed clinopyroxenes. Compared with clinopyroxenes from different backgrounds, the clinopyroxenes in this study is more similar to those from the subduction zones or subcontinental lithospheric mantle, which are commonly featured by the enrichment of LILE and depletion of HFSE (Bizimis et al., 2000; Bodinier and Godard, 2007; Xu et al., 2000). In contrast, clinopyroxene from the newly-born mantle, e.g., abyssal lherzolite, are smooth in normalized elemental distributions (Bodinier and Godard, 2007). Considering the forearc affinity of the Kop ophiolite, it is plausible to attribute the formation of dispersed clinopyroxenes here to the subduction related dehydration. Such a process could differentiate U from Th in oxidized conditions (Bali et al., 2011;

Hawkesworth et al., 1997a, 1997b; Kogiso et al., 1997), and also decouple Nb from Ta and Zr from Hf during the degassing (Danyushevsky et al., 1995).

6.2. Magmatic origin of pyroxenite veins

Different from the dispersed ones, clinopyroxenes in pyroxenite veins (vein-type clinopyroxenes) are usually associated with orthopyroxenes, which are completely absent in dunites and chromitites. The lack of orthopyroxenes in the hydrothermal diopsidites of Oman ophiolite indicates that orthopyroxenes were unstable in the diopside related hydrothermal processes (Akizawa et al., 2011; Python et al., 2007b). As a result, the pyroxenite veins should be formed in disparate chemical environments from those dispersed clinopyroxenes. Despite sharing similar Mg# values and CaO contents, the vein-type clinopyroxenes show higher Al₂O₃ contents than those of dispersed ones, reducing their CaO/Al₂O₃ ratios to the level of magmatic clinopyroxenes (Fig. 5). The major elements of clinopyroxenes in Koppy-05 are closer to those of dispersed ones, but their trace element compositions, e.g. Sr and transition metals, are more consistent with those in Koppy-03 and Kop14-18 (Appendix Table 5). Based on the Cpx-Opx thermometer of Wood and Banno (1973), the equilibrium temperatures of pyroxenes in pyroxenite veins and cpx-harzburgites

range from 995 °C to 1031 °C (Appendix Table 4), consistent with the records of other pyroxenites in the mantle (Berly et al., 2006; Sen, 1988). Moreover, the vein-type clinopyroxenes are uniformly featured by depleted REE patterns (Fig. 6b); their REE concentrations are in accordance with clinopyroxenes in abyssal lherzolites (Batanova et al., 1998; Bodinier and Godard, 2007; Bizimis et al., 2000; Johnson et al., 1990; Sano and Kimura, 2007; Seyler et al., 2001). All these differences above corroborate the vein-type clinopyroxenes were supposed to be magmatic in origin.

Olivine grains in the Kop14-18 (cpx-harzburgite) have an average Fo value of 91.8, and the Cr# values of magnesiochromites grains range from 28.7 to 39.2. These results are comparable to the typical mantle harzburgite that have experienced about 15-20% partial melting (Fig. 4). However, clinopyroxenes in the Kop14-18 have almost the same ranges of major and trace element compositions to the vein-type clinopyroxenes, and their REE patterns well match those clinopyroxenes in abyssal lherzolites (Fig. 6b). These features support that the clinopyroxenes in Kop14-18 were not melting residues, and they should have similar origins to the vein-type clinopyroxenes. Given the uneven distribution of clinopyroxenes and presence of olivines devoured by orthopyroxenes (Fig. 3h), the parental magmas of vein-type clinopyroxenes had probably permeated heterogeneously into the harzburgites and

reacted with olivine grains, converting the original harzburgites locally into lherzolites.

Although clinopyroxenes in cpx-harzburgites have similar REE patterns with those in abyssal lherzolites, they have higher Mg# values and lower contents of Al_2O_3 than the latter ones, and their $\text{CaO}/\text{Al}_2\text{O}_3$ ratios plot into the area close to those from boninites and komatiites (Fig. 5). Because abyssal lherzolites could be generated by either decompressional melting of upwelling asthenosphere or refertilization harzburgite with MORB-like melts (Bodinier and Godard, 2007; Johnson et al., 1990; Seyler et al. 2004), the parental magmas of clinopyroxenes in cpx-harzburgites should be more refractory than MORBs. Theoretically, pyroxenite veins can be considered as cumulate products of pyroxenes in narrow melt corridors; the compositions of vein-type clinopyroxenes were mainly dominated by their parental melts, quite similar to the clinopyroxene phenocrysts in extrusive rocks. As a result, the parental melts of pyroxenite veins were probably fertile than boninites and komatiites because of their relatively higher contents of Al_2O_3 . Given that boninites and komatiites are derived from refractory mantle (Herzberg et al., 2007; Storey et al., 1991; Wilson et al., 2003), the parental magmas of pyroxenite veins were possibly derived from mantle sources chemically between abyssal lherzolites and refractory harzburgite.

6.3. Metasomatism in depleted cumulate rocks

REE are usually considered as immobile during low-temperature alteration (Hulme et al., 2010; Menzies et al., 1993), and they have no correlation with degrees of serpentinization in peridotite (Savov et al., 2005; Zhou et al., 2005). Whole-rock major element analysis of samples C and E shows that most subdivided parts in them present limited loss on ignition (ca. < 5 wt.%; Appendix Table 6), consistent with the observed slight alteration in both samples. As a result, the whole-rock REE features of chromitites and dunites in samples C and E are potentially primary and not disturbed by the secondary alteration.

Although most parts of samples C and E display concave REE patterns, LREE depleted curves are also observed in the parts of E2a and E2b as well (Fig. 7); they are similar to the spoon shaped patterns reported for some reactive dunites from the Tibetan ophiolites in China (Su et al., 2015; Zhou et al., 2005). Because REE are highly incompatible in both olivine and chromite (Nagasawa et al., 1980; Nielse et al., 1992; Mckay, 1986; Spandler et al., 2007), continuous crystallization of both minerals cannot largely fractionate the REE patterns in residual magmas. As a result, dunite and chromitite pairs formed during a successive accumulation are supposed to have

similar REE patterns. In this case, the two disparate types of REE distributions in sample E cannot be obtained in a single magmatic event, and at least two processes are required to generate the coexistence of depleted and concave REE patterns.

The concave REE patterns have been repeatedly reported to magmatic rocks from the SSZ environment, and they were explained with the combined effects of earlier melt extraction and later metasomatism in the source regions of magmas (Parkinson and Pearce, 1998; Proenza et al., 1999; Saccani and Photiades, 2004; Ulrich et al., 2010). Regarding the cumulative genesis of dunites and chromitites in this study, it is probable that the rough depleted REE patterns were contributed by the primary magmatic process, whereas the concave ones were generated by later modification, which were likely achieved by multiple events of fluid activities related to the formation of dispersed clinopyroxenes. In-situ trace element analysis shows the LREE patterns of dispersed clinopyroxenes vary from being depleted to enriched (Fig. 6a). This reflects these clinopyroxenes had been reacted or equilibrated with different types of metasomatic fluids (Liu et al., 2010), which had diversities of REE distribution features. With the late modification events, some incompatible elements were heterogeneously introduced into dunite and chromitite after their formation, which reshaped the REE patterns into concave ones and might also cause the

inflection of La and Ce in spoon-shaped REE patterns.

6.4. Petrogenesis and tectonic implication

The origin of high-Cr chromitites have been thought genetically related to the boninitic magmatism (Robinson et al., 1997; Zhou et al., 1996), which typically happens in proto-forearc setting during the initiation of subduction. development of proto-forearc involves two stages of spreading (Stern et al., 2012; Whattam and Stern, 2011). The early stage is featured by asthenosphere upwelling over the sinking oceanic slab, producing MORB-like forearc basalts (FAB) and leaving a harzburgitic residual. In the late stage, slab-derived fluids migrate into the harzburgitic mantle and induce their further melting, generating boninites or volcanic arc basalts. Obtained studies show the REE patterns of boninites largely vary from being depleted to concave and right-dip. Based on the REE patterns of dunites in this study, the parental magmas of high-Cr chromitites were probably akin to those boninites with depleted REE features.

Due to the weaker compatibility of LREE than HREE in peridotite (Sun and McDonough, 1989), the parental magmas of high-Cr chromitites in the Kop ophiolite

were contributed mainly by depleted mantle; metasomatism by fluids could not have remarkably happened before the magmas were produced. Considering most incompatible elements came from the subducting slabs, it is quite probable that dehydration were not maturely developed during the formation of high-Cr chromitites. Moreover, the widespread pyroxenite veins in the Kop ophiolite were also originated from depleted mantle; their cross-cutting relationship with chromitiferous dunites well constrains that fluid activities still remained limited even after the formation of high-Cr chromitites. As a result, the parental magmas of high-Cr chromitites in the Kop ophiolite were not likely to be produced from highly hydrous mantle.

The boninitic parental magmas of high-Cr chromitites have been traditionally regarded to be derived from refractory harzburgitic mantle (Hickey and Frey, 1982; Pearce et al., 1992; Stern et al., 1991). They are silica under-saturated and highly magnesian (Arai and Yurimoto, 1994; Zhou et al., 1994). In contrast, the formation of pyroxenite veins requires their parental magmas were silica saturated and had compositions between N-MORB and boninite/komatiite. Studies on the Izu-Bonin-Mariana (IBM) zone demonstrated the existence of transitional lavas chemically between FAB and boninite (Reagan et al., 2010), and changing magma compositions from MORB-like to boninitic could account for the large Cr# variations

of magnesiochromite in the IBM forearc mantle (Morishita et al., 2011). Similarly, magnesiochromite in the Kop ophiolite also present large range of Cr# values (Fig. 4); this provides evidence for the occurrence of different magmas during the regional proto-forearc spreading. Based on these comparisons, it is possible that the parental magmas of pyroxenites resembled the transitional lavas.

Lithological shift from chromitites to pyroxenites reflects the transfer of their source regions from refractory to relatively fertile ones. However, this differs from the overall tendency of magmatism variation and long-term mantle evolution in the proto-forearc setting (Pearce et al., 1992; Reagan et al., 2010; Stern et al., 2012; Whattam and Stern, 2011). To make a compromise between the inconsistency above, it is quite probable that chromitites and pyroxenites were formed in a short time interval, during which boninite and transitional lava could be produced alternatively. Furthermore, asthenosphere possibly remained upwelling in appropriate degrees during the formation of high-Cr chromitites and pyroxenites (Fig. 8; Stage I), just like when high-Ca boninites were produced at the Tongga ridge (Falloon and Crawford, 1991). Interaction between asthenosphere and harzburgitic mantle could diversify the lithologies below proto-forearc (Rampone et al., 2008; Seyler et al., 2004), facilitating the production of various magmas under changing physico-chemical conditions. This

assumption well matches the fact that harzburgitic mantle in ophiolites are often underlain by cpx-poor lherzolites (Bodinier and Godard, 2007).

Compared to the magmatism during subduction initiation, high-Cr chromitites in the Kop ophiolite possibly began to be produced around the transition period between early and late stages of proto-forearc spreading, at which release of slab-derived fluids was not intensive enough, and depleted geochemical features were still predominated in the mantle. As subduction continued, the previous proto-forearc in NE Turkey transformed into forearc regions where little magmatism occurred. Fluids released from the subsiding slab penetrated into both the mantle and crustal parts of the forearc regions (Fig. 8; Stage II). Heterogeneous infiltration of these fluids generated the dispersed clinopyroxenes and introduced incompatible components to peridotites, blurring their original depleted features. Consequently, the Kop ophiolite preserves abundant detailed information about the initiation of subduction, from proto-forearc spreading to the start of true subduction.

7. Conclusions

1. The parental magmas of high-Cr chromitites in the Kop ophiolite were possibly

originated from depleted mantle and akin to LREE-depleted boninites.

Accumulation of olivine and magnesiochromite from such magmas resulted in LREE-depleted dunites and chromitites in the MTZ.

2. Magmatic clinopyroxenes in pyroxenite veins and cpx-bearing harzburgites have REE compositions indicative of crystallization from magmas derived from moderately refractory mantle which interacted with asthenosphere; these magmas possibly resemble the transitional lavas in the IBM forearc zone.
3. Nearly pure end-member of diopsides in dunites and chromitites were possibly generated by subduction-related high-Ca fluids, which enriched cumulate rocks in the MTZ in mobile elements and LREE.
4. The initial batches of high-Cr chromitites were possibly produced no later than the transition period between the early and late stages of proto-forearc spreading, during which asthenosphere continued upwelling without extensive slab dehydration, and boninitic and transitional lavas could be produced alternatively.

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Figure Captions

Figure 1. A: tectonic units in Turkey and location of the Kop ophiolite. The dashed yellow line represents the Izmir-Ankara-Erzincan suture (IAES). B: geological map of the Kop ophiolite. C: schematic cross-section drawn based on our own observation and previous studies (Çiftçi et al., 2008; Kolaylı, 1996; Uysal et al., 2007). The three composite samples Kop-B, C and E and two cpx-harzburgites Kop14-18 and 21 were sampled from the inner MTZ, and Kop14-03 and 05 were collected from the boudary between MTZ and upper mantle. The legends are not applicable to Fig.1a.

Figure 2. Photos showing the outcrops and lithologies in the Kop ophiolite. A: outcrop of harzburgite in the mantle part of Kop ophiolite; B: outcrops of cumulate chromitites and dunites; C: chromitiferous dunite and its hosted pyroxenite vein; D, E and F: composite sample B, C and E.

Figure 3. Petrographic pictures of different lithologies. A: chromitites in Sample B containing chromite, olivine and accessory clinopyroxene. B: dunite in composite sample B. Engulfed olivine by clinopyroxene can be seen in the white rectangle. C:

lithologic boundary between pyroxenite and harzburgite in Kop14-03. D: lithologic boundary between pyroxenite and chromitiferous dunite in Kop14-05. E: Two types of anhedral pyroxenes in pyroxenites. F and G: cpx-harzburgite of Kop14-03 and 18, respectively. H: olivine partly enclosed in orthopyroxene in Kop14-18.

Figure 4. Plot of Cr# against TiO₂ of magnesiochromite from different lithologies, including harzburgite, chromitite and dunite. The compositions of magnesiochromite indicate that harzburgites in the Kop ophiolite have experienced 10-20% degrees of partial melting. Magnesiochromite from dunites and chromitites have large ranges of Cr# values. IBM, FMM, Lz, Hz, and Dn are the abbreviations of Izu-Bonin-Mariana, fertile MORB mantle, lherzolite, harzburgite and dunite, respectively. The subscripts b, i and m represent boninite, island arc tholeiite and MORB, respectively. This diagram is modified after (Pearce et al., 2000). The gray crosses represent magnesiochromites in other chromitites from the Kop ophiolite. Magnesiochromites from Kop14-21 (cpx-harzburgite) are also added in the diagram. These data are from Zhang et al. (unpublished).

Figure 5. Plot of Al₂O₃ against Cr₂O₃ (A) and CaO/Al₂O₃ against Mg# (B) of clinopyroxenes in this study. The data of clinopyroxenes in basalt, komatiite, boninite, and hydrothermal rocks are from Leterrier et al. (1982); Parman et al. (2003);

Bloomer and Hawkins (1987) and Sobolev and Danyushevsky (1994); and Akizawa et al. (2011), respectively.

Figure 6. Normalized REE and trace element diagrams of different types of clinopyroxenes (normalized data from Sun and McDonough, 1989). The grey field of clinopyroxenes from abyssal peridotites are from Johnson and Dick (1992) and Johnson et al., (1990). The solid black lines give the REE compositions of clinopyroxenes in the source mantle of MORBs after about 10%, 15%, 20% and 25% fractional melting in the spinel field (Sano and Kimura, 2007).

Figure 7. Chondrite normalized REE diagrams of chromitites and dunites in the composite samples C and E (normalized data from Sun and McDonough, 1989). The curves of E2a and E2b are highlighted with white circles. The dashed line in the upper diagram represent the detection limits for the whole-rock trace element analysis of these samples.

Figure 8. Two-stage formation model of the Kop ophiolite. Stage I shows the general scenario when the first batches of high-Cr chromitites were produced. This stage was possibly featured by weak dehydration and upwelling of asthenosphere, which are represented by solid blue and dashed yellow arrowed lines, respectively. Magmas produced then displayed depleted REE patterns and were mainly contributed by

depleted mantle regions. Stage II involved intensive activity of slab-derived fluids, which caused the formation of dispersed clinopyroxene (yellow green hexagons) and introduced mobile elements into cumulate rocks, generating the concave REE patterns.