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Formation processes of dunites and chromitites in Orhaneli and Harmanck ophiolites (NW Turkey): Evidence from in-situ Li isotopes and trace elements in olivine

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Abstract: Trace elements and Li isotopic compositions of olivine from the mantle-crust transition zone of the Bursa ophiolites (including Orhaneli ophiolite and Harmancık ophiolite) in NW Turkey were measured to constrain the genesis of these dunites and chromitites. A cumulate origin for dunite can be ruled out due to the depletion of incompatible trace elements (Zr, Ti, and heavy rare earth elements) in olivine, instead the chemical signatures point to a replacive origin via melt-rock interaction. The olivine grains in the dunites have lower MnO (0.06-0.15 wt.%), Co (106-137 ppm), Ca (73-323 ppm), and higher NiO (0.23-0.44 wt.%) concentrations than olivine phenocrysts in MORB, suggesting these transition-zone dunites have equilibrated with extremely depleted melts. Additionally, the relatively small $\delta^{7}\text{Li}$ variations of olivine (average $\delta^{7}\text{Li}$ +4.8 to +8.7‰) of the Orhaneli suite indicate the Li isotopic compositions of melts percolating through these dunites are relatively homogeneous. However, the large $\delta^{7}\text{Li}$ variations of olivine (-2.5 to 20.3‰) in Harmancık dunites can be explained by incomplete diffusive equilibration with melts percolating through these dunites, suggesting infiltration happened not long before obduction of the ophiolite. Olivine in chromitites has higher Fo (92.6-94.7) than coexisting dunites, likely induced by subsolidus Mg-Fe exchange between olivine and chromite. The higher chromite contents of the chromitites can also explain the lower concentrations of Sc, V, Co and Zn in coexisting olivine grains. Mixing of depleted mantle-derived melts and boninitic magmas is suggested to induce a compositional shift from the olivine-chromite cotectic line to the liquidus field of chromite, causing the precipitation of chromite and formation of chromitite layers in the dunites. The heavy Li isotopic compositions (+5 to +11‰) of olivine in chromitites and dunites compared to MORB, together with the estimated compositions of parental magmas (Al_2O_3 : 9.8-11.4 wt.%; TiO_2 : 0.22-0.38 wt.%) for the chromitites, indicate an arc-like geochemical affinity, hence a subduction-related setting in which these mantle-crust transition zones formed.

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Title: Data for: Formation processes of dunites and chromitites in Orhaneli and Harmancik ophiolites (NW Turkey): evidence from in-situ Li isotopes and trace elements in olivine
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<https://data.mendeley.com/datasets/6nwr9d8z78/draft?a=ebf4efdf-b318-4ee5-8fc4-d1d0276533ea>

Formation processes of dunites and chromitites in Orhaneli and Harmançik ophiolites (NW Turkey): evidence from in-situ Li isotopes and trace elements in olivine

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Dear editor,

We really appreciate the insightful comments on our submission by you and the two reviewers, which gave us the opportunity to clarify several important aspects of our manuscript. We revised the manuscript according to the comments, with the major changes as follows:

1. Figure 9 and 12 are modified, and the corresponding explanations are provided in the figure captions. Previous Figure 6 and Figure 10 are removed from the revised version. The related sentences in the text are revised accordingly.
2. The “Highlights” have been shortened.
3. Unrelated references have been removed from the revised version and the total number of references is now 79.

In addition, all editorial comments by the reviewers have been incorporated in the revised version, and point-to-point responses to more detailed comments are listed below. All changes have been highlighted in yellow in the revised manuscript.

We hope you find this revised version of the manuscript suitable for publication in *Lithos*, and look forward to any further comments.

Best regards,
Chen Chen and co-authors

Detailed responses to comments (our responses in red font)

Editor's comments:

Both reviewers find the topic of interest and suggest minor revisions. Based on the two favorable reviews and my own reading of the paper, I am pleased to inform that your paper should be acceptable for publication in the journal after suitable revision is made following the reviewer comments.

1. Highlights 1-3 are too long. Each bullet point of highlights should be no more than 85 characters, including spaces.

Reply: The highlights have been shortened.

2. The number of references exceeds the *Lithos* maximum of 80. Please reduce the number of references.

Reply: Unrelated references have been removed from the revision and reference number is now 79.

3. Submit data tables 1 to 3 as supplementary material for online publication.

Reply: Data tables 1 to 3 have now been prepared supplementary material for online publication.

Reviewer #1:

The authors have made in-situ analyses on trace element and Li isotopic compositions of olivine from dunites and chromitites in Orhaneli and Harmancik ophiolites (NW Turkey) to unravel the genesis of the host rocks. The data were clearly reported; the manuscript is well structured and fully referenced. Based on the data, the authors made reasonable discussion for the genesis of the dunites and chromitites.

I have only minor comments on the manuscript as shown below:

1. The authors proposed that dunites have equilibrated with the depleted melts as revealed by trace element compositions of olivine in dunites from both Orhaneli and Harmancik ophiolites. But the large $\delta^7\text{Li}$ variations among individual samples and the negative correlation between Li concentrations and $\delta^7\text{Li}$ values for the Harmancik dunites indicate the incomplete equilibrium of Li isotopes between dunites and incorporated melts shortly before obduction and exhumation. As Li has higher diffusivity than other trace elements in olivine, these observations implicate that they belong to different stages of melt percolation. In the manuscript, I suggest that the authors clarify the temporal and original relationship of percolated melts responsible for the formation of dunites, and the formation of chromitites, and the large $\delta^7\text{Li}$ variations among individual samples, respectively.

Reply: Some Templeton experiments found that the isotopic gradients dissipate slower than gradients in the parent element. Richter et al. (2014) reported that very large lithium isotopic fractionations persisted after the lithium concentration had become effectively homogenized during diffusion process, suggesting that it still takes longer for the isotopic composition to become uniform compared to the time it takes for diffusion to homogenize the total lithium concentration. Thus, we can observe the Li element and other trace element concentrations of olivine in dunites from Harmancik ophiolite are equilibrated with the infiltrating melts, whereas the $\delta^7\text{Li}$ variations of olivine are large, which is caused by incomplete equilibrium of Li isotopes between dunites and incorporated melts. Therefore, these observations are the same stage of melt percolation, and not belong to different stages of melt percolation. In the revision, a detailed discussion has been added to Section 6.4.

2. The authors could identify whether there is any correlation between the concentrations of other trace elements (or other geochemical signatures, e.g., Fo) and Li (or $\delta^7\text{Li}$ values) in olivine. It may have some implications for the histories of melt percolation.

Reply: According to the reviewer's suggestion, we plotted the figures of concentrations of other trace/major elements and Li concentrations/ $\delta^7\text{Li}$ values, found there are relatively apparent correlations between Li concentrations/ $\delta^7\text{Li}$ values and Ca concentrations or Ni concentrations of olivine, which is also caused by melt-rock interaction. This conclusion is consistent with this paper. Because the reviewer pointed that the manuscript has many figures and suggested deleting or merging some of them, we do not show these figures in the manuscript.

3. The authors ascribed the large heterogeneity of olivine Li isotopic compositions in dunites from the Harmancik ophiolite as the result of disequilibrated Li diffusion during melt percolation. The diffusive addition of Li from melts in short periods can induce relatively higher Li concentrations and lower $\delta^7\text{Li}$ values in some samples. However, for samples with heavy Li isotopic compositions ($\delta^7\text{Li}$ as high as 20‰), the disequilibrated Li diffusion seems not accountable, as Li concentrations (as low as 0.7 ppm) are markedly lower compared to MORB or IAB (meaning that the diffusive loss of Li from dunites to melts is difficult). In Figure 9, the authors illustrated that these high $\delta^7\text{Li}$ values may result from partial melting (inherited from source rocks, depleted peridotites?). For this point, more discussion is needed to make it clear.

Reply: In the olivine of dunite from ophiolites, many studies have reported that there is a negative correlation between Li concentrations and $\delta^7\text{Li}$ isotopic compositions and the Li concentrations of olivine with high $\delta^7\text{Li}$ values can be similar to or slightly lower than those in the normal mantle (1.0-1.8 ppm), which can be explained by the interaction between melt and peridotite. For example, in the dunite from Trinity ophiolite, Lundstrom et al. (2015) observed that the $\delta^7\text{Li}$ values and Li concentrations olivine vary from -5 to 21 ‰ and from 0.6-1.2 ppm, respectively, and Li concentrations vary widely and negatively correlate with $\delta^7\text{Li}$ for olivines. These features could reflect mineral interaction with hydrothermal fluids where Li partitioning behavior changes with temperature. Su et al. (2016) reported that the olivine in the dunite from the Luobusa ophiolite have Li concentrations (Li isotopic compositions) varying from 0.30 to 0.60 ppm (~10 to 20 ‰). The trend of higher $\delta^7\text{Li}$ with decreasing Li concentration is also attributed to the diffusion from melts to the surrounding peridotites (Su et al., 2016).

The olivine grains dunites from the Harmancik ophiolite have Li concentrations and Li isotopic compositions varying from 0.7 to 1.9 ppm and from 2.5 to 20.3‰, the ranges and patterns comparable with those in Trinity dunite (Lundstrom et al., 2015), indicating the result of melt-rock interaction process. In the revision, the related discussion has been added to Section 6.4.

Sorry for the confusion, we have deleted the “partial melting” in the Fig. 9.

4. 12 figures in the manuscript are too many for a paper. I suggest deleting or merging some of them. The captions of several important figures are too simple (e.g., Figure 9 and 10). It will be better for understanding if more illustrations are added in

the captions.

Reply: According to the reviewer's suggestion, we have deleted Fig. 6 and Fig. 10 and added detailed description of some important figures.

Reviewer #2:

The paper by Chen et al deals with the formation processes of dunites and chromitites in some Turkish ophiolites via Li isotopes and trace elements in olivine.

The manuscript is well written with only some minor points that should be clarified or added to help the reader.

One of these points is at lines 270-278, where it is written "The chromitites from the two ophiolites display similar Li contents and ^7Li values " and then "the data presented here demonstrate that the composition of trace elements and Li isotopes are different". Maybe, the two sentences need some more explanations. They can't be similar and different at the same time.

Reply: Sorry for this confusion. We meant that compared to different $\delta^7\text{Li}$ compositions of olivine in Orhaneli dunites (3.7 to 11.0‰) and Harmancık dunites (-2.5 to 20.3‰), the $\delta^7\text{Li}$ compositions of olivine in chromitite from the two ophiolites are similar (5.0 to 14.7‰ in Orhaneli and 4.1 to 15.6‰ in Harmancık). This was clarified in the revision.

It is written that there are good correlations between Mn, Ni and Co but Fig. 7c displaying Co vs Mn shows that for some samples Co values are almost constant while Mn changes, while for some other Mn is constant and Co changes. So, I can't see this good correlation.

Reply: There are good correlations between Ni and Mn, whereas the correlation between Co and Mn is un conspicuous. This description has been modified in the revision.

In fig. 12a it is quite difficult to see the boninitic field. Kamenetsky et al (2001) defined a limit between BON and IAT at about 0.4 wt. % TiO_2 , while Derbyshire et al (2013 LITHOS) show an overlapping area but in a logarithmic scale it is difficult to see this without some more scale labels.

Reply: According to the figure 10 of Derbyshire et al. (2013), we added the field of boninite in the Fig. 12a, and found our studied samples are plotted in the field of boninite or the nearby IAT field. In the Fig. 12a, we just want to show that the chromite TiO_2 and Al_2O_3 contents plotted directly into the arc field, suggesting the formation of chromite is closely related to the melts from island arc. In the next Fig 12b-c, we further confirmed that the boninite or boninitic melts could be the parental magma of chromite, based on the Cr# of chromite and the calculated composition of melts in equilibrium with chromitite.

In my opinion Fig. 4 is a bit chaotic and difficult to read.

Reply: More detailed descriptions have been added in the captions, so it is clear to read and understand.

In the tables I can't find the values of Mn in ppm but only as wt. %. Did you calculate the ppm values from the wt. % or did you analyzed it by LA-ICP-MS but it was not reported in the tables?

Reply: The values of Mn and Ni in ppm are analyzed by LA-ICP-MS. We have added these values in the Table 3.

There is a diagram with Mg and Fe²⁺ values for both chromites and olivines but these values are not reported in the tables. Could you, please, add the cation per formula unit of the analyzed minerals.

Reply: We have added the Mg/Fe²⁺ ratios of olivine and chromite to the Table 1 and Table 2, respectively. The MgO and FeO contents of olivine and chromite have been in the Table 1 and Table 2. There is no need to add the Mg and Fe²⁺ values in the tables because the cation Mg and Fe²⁺ is calculated by the MgO and FeO contents of minerals.

Fig. 6 shows Zn vs Co (6a) and Sc vs. Co (6b) of olivine in the dunites and chromitites but in Fig. 6a the scale is 60-160 for Co while it is 250-550 in fig. 6b. I can't understand how it is possible that the range of cobalt is different in the two diagrams. And, however, I'm unable to find a trace element ranging between 250 and 550.

Reply: Sorry for the confusion. The Co contents in the Fig. 6a are the olivine Co contents, while the Co contents in the Fig. 6b are the Co contents of chromite. The Fig. 6 has been deleted in the revision.

Once, Prof Rollinson, author of the book "Using geochemical data", told me that in describing diagram you should say Y vs X so it is MnO vs Fo (Fig. 1) and the same for all the other figures.

Reply: We have modified it in all figure captions.

Other minor points

Line 263: it is written "from 4 to 11" but it seems that the lowest value is 3.7 (OL1 core 5m dunite)

Reply: We modified it.

Line 320: it is written olivine

Reply: We corrected it.

References

Line 56: it is written Pakunc instead of Paktunc

Reply: We corrected it.

Line 713: it should be Jeffcoate with double f

Reply: We modified it.

In the text there are some references that are not present in the reference list such as Zhang et al 2018, Akbulut 2018, Bonavia et al 1993, Ballhaus et al 1991 and Tomascak et al 2000. There is Abily et al 2013 that maybe corresponds to Abily and Ceuleneer 2013, and Tang et al 2009 that could be Tang et al 2011.

The following are written in the reference list but are not cited in the text: Arai and Yurimoto 1994, Coogan et al 2005b, Dick and Bullen 1984, Keleman et al 1992, Richter et al 2014, Su et al 2017, Uysal et al 2009, Xiao et al 2017.

In the text there are two papers by Rospabè et al, one is 2018, the other 2019. In the reference list both are 2018. Check.

Reply: We have checked the references in the text and the references in the reference list, deleted the references which are not cited, added the references which are not present in the reference list but in the text, and confirmed that the references in the text and reference list are same.

Trace elements and Li isotopic compositions of olivine from the mantle-crust transition zone of the Bursa ophiolites (including Orhaneli ophiolite and Harmancık ophiolite) in NW Turkey were measured to constrain the genesis of these dunites and chromitites. A cumulate origin for dunite can be ruled out due to the depletion of incompatible trace elements (Zr, Ti, and heavy rare earth elements) in olivine, instead the chemical signatures point to a replacive origin via melt-rock interaction. The olivine grains in the dunites have lower MnO (0.06-0.15 wt.%), Co (106-137 ppm), Ca (73-323 ppm), and higher NiO (0.23-0.44 wt.%) concentrations than olivine phenocrysts in MORB, suggesting these transition-zone dunites have equilibrated with extremely depleted melts. Additionally, the relatively small $\delta^7\text{Li}$ variations of olivine (average $\delta^7\text{Li}$ +4.8 to +8.7‰) of the Orhaneli suite indicate the Li isotopic compositions of melts percolating through these dunites are relatively homogeneous. However, the large $\delta^7\text{Li}$ variations of olivine (-2.5 to 20.3‰) in Harmancık dunites can be explained by incomplete diffusive equilibration with melts percolating through these dunites, suggesting infiltration happened not long before obduction of the ophiolite. Olivine in chromitites has higher Fo (92.6-94.7) than coexisting dunites, likely induced by subsolidus Mg-Fe exchange between olivine and chromite. The higher chromite contents of the chromitites can also explain the lower concentrations of Sc, V, Co and Zn in coexisting olivine grains. Mixing of depleted mantle-derived melts and boninitic magmas is suggested to induce a compositional shift from the olivine-chromite cotectic line to the liquidus field of chromite, causing the precipitation of chromite and formation of chromitite layers in the dunites. The heavy Li isotopic compositions (+5 to +11‰) of olivine in chromitites and dunites compared to MORB, together with the estimated compositions of parental magmas (Al_2O_3 : 9.8-11.4 wt.%; TiO_2 : 0.22-0.38 wt.%) for the chromitites, indicate an arc-like geochemical affinity, hence a subduction-related setting in which these mantle-crust transition zones formed.

(1) $\delta^7\text{Li}$ study of Orhaneli-Harmancık mantle-crust transition zone dunite and chromitite

(2) Orhaneli dunite formed by interaction of peridotite with homogeneous melt batches

(3) Harmancık dunite reflects incomplete diffusive equilibration during melt percolation

(4) Parental magmas of the chromitites show boninitic geochemical affinities.

1 **Formation processes of dunites and chromitites in Orhaneli and Harmancık**
2 **ophiolites (NW Turkey): evidence from in-situ Li isotopes and trace elements in**
3 **olivine**

4

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22

Abstract

Trace elements and Li isotopic compositions of olivine from the mantle-crust transition zone of the Bursa ophiolites (including Orhaneli ophiolite and Harmancık ophiolite) in NW Turkey were measured to constrain the genesis of these dunites and chromitites. A cumulate origin for dunite can be ruled out due to the depletion of incompatible trace elements (Zr, Ti, and heavy rare earth elements) in olivine, instead the chemical signatures point to a replacive origin via melt-rock interaction. The olivine grains in the dunites have lower MnO (0.06-0.15 wt.%), Co (106-137 ppm), and higher NiO (0.23-0.44 wt.%) concentrations than olivine phenocrysts in MORB, suggesting these transition-zone dunites have equilibrated with extremely depleted melts. Additionally, the relatively small $\delta^7\text{Li}$ variations of olivine (average $\delta^7\text{Li}$ +4.8 to +8.7‰) of the Orhaneli suite indicate the Li isotopic compositions of melts percolating through these dunites are relatively homogeneous. However, the large $\delta^7\text{Li}$ variations of olivine (-2.5 to 20.3‰) in Harmancık dunites can be explained by incomplete diffusive equilibration with melts percolating through these dunites, suggesting infiltration happened not long before obduction of the ophiolite. Olivine in chromitites has higher Fo (92.6-94.7) than coexisting dunites, likely induced by subsolidus Mg-Fe exchange between olivine and chromite. The higher chromite contents of the chromitites can also explain the lower concentrations of Sc, V, Co and Zn in coexisting olivine grains. Mixing of depleted mantle-derived melts and boninitic magmas is suggested to induce a compositional shift from the olivine-chromite cotectic line to the liquidus field of chromite, causing the precipitation of chromite

and formation of chromitite layers in the dunites. The heavy Li isotopic compositions (+6 to +11‰) of olivine in chromitites compared to MORB, together with the estimated compositions of parental magmas (Al_2O_3 : 9.8-11.4 wt.%; TiO_2 : 0.22-0.38 wt.%) for the chromitites, indicate an arc-like geochemical affinity, hence a subduction-related setting in which these mantle-crust transition zones formed.

Key words: olivine; trace element; Li isotopes; ophiolite; chromitite; mantle-crust transition zone

1. Introduction

The mantle-crust transition zone is well documented in many ophiolites, and marks the petrological transition from mantle peridotites to lower crustal cumulates (e.g., [Zhang et al., 2017](#); [Rollinson, et al., 2018](#); [Rospabé et al., 2018](#)). Ophiolitic mantle-crust transition zones typically consist of dunite-dominated ultramafic rocks and stratiform-like chromitites, and can reach a thickness of several kilometers ([Paktunc, 1990](#)). These dunites are made of mostly olivine with minor chromite and their thickness ranges from a few meters to a few hundred meters (e.g., [Zhang et al., 2017](#)). Although the transition zone chromitites are distinguished by their layered morphology from the mantle podiform chromitites which occur as irregular lenses and pods, their compositions are similar in many cases (e.g., [Arai et al., 2004](#); [Rollinson, 2008](#)). Despite many years of investigation, the genesis of the dunites and chromitites in the ophiolitic mantle-crust transition zone is still debated, and different models have been proposed, such as magmatic cumulates stagnating at the base of the crust

(e.g., [Abily and Ceuleneer, 2013](#)), crustal assimilation ([Arai et al., 2004](#)), reactions between melts and mantle harzburgites (e.g., [Abily and Ceuleneer, 2013](#)), and mixing of mantle-derived melts with differentiated magmas (e.g., [Ballhaus, 1998](#)). In addition, the nature of the mixed or infiltrated melts and their influences on the mantle-crust transition zone are not yet well known, limiting our understanding of the evolution of ophiolites. A close link between subduction initiation and chromitite/ophiolite genesis has been documented (e.g., [Reagan et al., 2017](#); [Zhang et al., 2017](#)) in several studies of the extensive ophiolites in Turkey (e.g., [Uysal et al., 2017](#); [Chen et al., 2019](#)). Therefore, careful study of the formation processes of the chromitite and their tectonic setting could shine further light on the relationship between subduction initiation and ophiolite emplacement.

Olivine is a ubiquitous mineral in both the ultramafic and mafic igneous rocks, and in most cases, it is the first silicate phase to crystallize from ultramafic-mafic melts ([Foley et al., 2013](#)). Olivine thus controls early magmatic differentiation processes, but its Fo content can provide little information about its origin and evolution ([De Hoog et al., 2010](#); [Foley et al., 2013](#)), which forces us to focus on its trace element geochemistry. Consequently, it has become increasingly important to improve our knowledge of the trace element composition of olivine, and to test the use of its geochemical signature as a tracer of early igneous and mantle melting processes ([Foley et al., 2013](#); [Rampone et al., 2016](#)). Several studies have shown that olivines in peridotites from different tectonic environments and/or various origins exhibit distinct geochemical characteristics and define systematic elemental

correlations for a series of trace elements (Ni, Mn, Zn, Co, Zr and heavy rare earth elements (HREE)), recording different magmatic processes (Sobolev et al., 2007; De Hoog et al., 2010; Foley et al., 2013; Rampone et al., 2016). Recent work on the Purang and Luobusa ophiolites (Su et al., 2019) advocates that the incompatible trace elements of olivine are more sensitive to melting processes, whereas the concentrations of compatible trace elements are mostly constrained by their source composition.

Lithium and its isotopes (^6Li and ^7Li) are increasingly used to trace multiple high-temperature processes due to their moderate incompatibility, strong fluid mobility, and large mass difference (17%) between its two isotopes (e.g., Tomascak et al., 2016). Olivine is the dominant Li reservoir in the upper mantle (Seitz and Woodland, 2000; De Hoog et al., 2010), and olivine-melt partition coefficients of Li are virtually independent of pressure, temperature and olivine composition (Seitz and Woodland, 2000; Qian et al., 2010). The equilibrium fractionation of Li isotopes is likely to be negligible at high temperatures (Vlastelic et al., 2009). However, many natural peridotites display heterogeneous $\delta^7\text{Li}$ compositions, which has been attributed to Li diffusion or interaction between percolating melts and peridotites (e.g., Lundstrom et al., 2005; Rudnick and Ionov, 2007; Su et al., 2014). Thus, olivine Li isotopic systematics can be used to trace magmatic processes of mantle-crust transition zone dunites and chromitites.

In the Bursa ophiolites (Orhaneli and Harmancık ophiolites) in northwestern Turkey, mantle-crust transition zones typically contain interlayered dunites and

chromitites (Uysal et al., 2015), the successions of which can reach up a few kilometers thick. In this paper, we provide in-situ trace element and Li isotope analyses of olivine in the chromitites and dunites from the mantle-crust transition zones of Orhaneli and Harmancık ophiolites. These datasets, together with petrological investigations and mineral major oxide compositions, are used to constrain the magmatic processes involved in the formation of dunites and chromitites in ophiolitic mantle-crust transition zones.

2. Geological Setting

Tethyan ophiolites in Anatolia occur in several E-W trending belts, which are separated by a series of Gondwana-derived continental fragments (e.g., Uysal et al., 2014) (Fig. 1a). The Izmir-Ankara Suture Zone (IASZ) in northern Turkey occurs between the Sakarya Zone (continent) to the north and the Anatolide-Tauride continental block to the south (Fig. 1a), and has relatively intact ophiolite blocks, which are locally extensive and well preserved (Dilek and Thy, 2006). The Orhaneli and the Harmancık ophiolites, situated in the western part of the IASZ, are considered as remnants of the Izmir-Ankara-Erzincan ocean, a local term for the northern branch of the Neotethys ocean (Sarıfakioğlu et al., 2009). The Orhaneli ophiolite was tectonically emplaced onto northwestern Anatolia along the IASZ (Fig. 1a). The Harmancık ophiolite is located ca. 30 km south of the Orhaneli ophiolite (Fig. 1b) (Sarıfakioğlu et al., 2009). These two ophiolites were thrust southwards over the metamorphic basement rocks of the Tavşanlı zone in the Anatolide-Tauride platform

([Sarifakioğlu et al., 2017](#)).

The Orhaneli ophiolite is approximately 50 km long, 15 km wide and 1500 m thick ([Fig. 1b](#); [Sarifakioğlu et al., 2009](#)), and mainly consists of mantle-crust transition zone comprising mostly basal ultramafic cumulates. The transition zone is dominated by chromitite interlayered dunites, followed by wehrlites, lherzolites, harzburgites and pyroxenites and to a lesser extent mafic cumulates such as gabbros and gabbroonorites (e.g., [Sarifakioğlu et al., 2009](#); [Uysal et al., 2015](#)). The chromitites interlayer with dunite in the two ophiolites and have typically semi-massive and banded (stratiform, cumulate) structures ([Fig. 2](#)). The mantle-crust transition zone of the Harmancık ophiolite, which reaches up to 1000 m thickness, has similar rock assemblages to those of the Orhaneli ophiolite ([Tankut, 1980](#)). The Harmancık ophiolite contains additional podiform chromitites in its mantle section ([Sarifakioğlu et al., 2009](#)). The podiform chromitites form centimeters to meters scale lenticular/tabular orebodies enclosed in thick dunite envelopes within mantle harzburgites. The mantle harzburgites and dunites from Harmancık ophiolite have been almost completely altered to serpentine and talc, and are unconformably overlain by Neogene sedimentary units (e.g., [Uysal et al., 2014, 2015](#)).

3. Petrography of dunites and chromitites

In the Orhaneli ophiolite, dunites display adcumulate textures and consist of mostly medium- to fine-grained olivine crystals with minor chromites ([Fig. 3a, b](#)). Chromitites generally show adcumulus- to orthocumulus-like textures with euhedral

to subhedral chromite grains (Fig. 3c). They occur as bands and layers in dunites (Fig. 2a-c), and massive chromitites are very rare. The banded chromitite orebodies display schlieren textures, characterized by parallel layers of chromitite alternating with dunite (Fig. 2b). The thickness of the chromitite bands in the Orhaneli ophiolite typically ranges between 0.2 and 3 cm, rarely reaching up to 5 cm (Fig. 2b-c). In contrast, chromitites from the Harmancık mantle-crust transition zone occur as schlieren/bands, semi-massive, and disseminated textures. Chromite grains are mostly euhedral to subhedral. Dunites are made up predominantly of olivine (> 95%) and have a dominant cataclastic texture (Fig. 3d).

In the Orhaneli ophiolite, the mantle-crust transition zone is nearly horizontal (Fig. 2a), and we have selected 13 samples (dunites and chromitites) from the mantle-crust transition zone profile. The thickness of this profile is about 90 m and we fixed the base of the dunite as 0 m and its roof is +90 m. In the Harmancık ophiolite, 12 drill hole samples from the mantle-crust transition zone were selected for chemical analyses, owing to their pristine olivine grains. The drill hole samples including dunite and chromitite were collected from depths of 63.4 m to 73.4 m.

4. Analytical methods

4.1 Major oxide analysis of minerals

Major oxide compositions of olivine and chromite were determined by wavelength-dispersive X-ray spectrometry using a JEOL JXA8100 electron probe micro-analyzer at the Institute of Geology and Geophysics, Chinese Academy of

Sciences (IGGCAS). The analyses were carried out using an accelerating voltage of 15 kV, a 10 nA beam current, a 5 μm spot size and 10-30 s peak counting time. Natural and synthetic mineral standards were used for calibration. A ZAF procedure was used for matrix corrections. Typical analytical uncertainty for the analyzed elements was better than 1.5% (1RSD%).

4.2 Trace element analysis of olivine

In-situ trace element analyses of olivine were conducted on thin sections using a laser ablation inductively coupled plasma mass spectrometer (LA-ICP-MS) at IGGCAS. The LA-ICP-MS system consists of a 193 nm Coherent COMPex Pro ArF Excimer laser coupled to an Agilent 7500a ICP-MS. About 6-8 spots were measured for different olivine grains in each sample. The laser spot size was 140 μm , and the repetition rate was 8 Hz. Each analysis consisted of 60 s measurement of gas blank and 60 s ablation. The following isotopes were measured: ^7Li , ^{27}Al , ^{29}Si , ^{31}P , ^{39}K , ^{43}Ca , ^{45}Sc , ^{49}Ti , ^{51}V , ^{53}Cr , ^{59}Co , ^{66}Zn , ^{91}Zr , ^{163}Dy , ^{166}Er , ^{172}Yb . De Hoog et al. (2010) reported that potential interferences in olivine from matrix components MgO , SiO_2 and FeO , which are generated during ablation only and therefore unaccounted for by gas blank subtraction. The contribution of $^{26}\text{Mg}^{40}\text{Ar}$ to the ^{66}Zn signal is about 0.2 ppm, and the $^{29}\text{Si}^{16}\text{O}$ interference on ^{45}Sc accounted for 0.2 ppm of the signal (De Hoog et al., 2010), hence those are small enough to be ignored. A glass standard, NIST 610, was used for external calibration. For most of the trace elements NIST 612 standard was used to monitor instrument drift, and silicon (^{29}Si) was selected as an internal standard. The SiO_2 contents of NIST 610 and NIST 612 are 69.7% and 72.1%,

respectively. Reference values of NIST 610 and NIST 612 are from GeoREM (<http://georem.mpch-mainz.gwdg.de>). The data were reduced using the GLITTER 4.0 program.

4.3 Li concentration and isotope analyses of olivine

In-situ analyses of Li concentrations and isotopic ratios of olivine were carried out on gold-coated polished thin-sections using a Cameca IMS 1270 SIMS at the Edinburgh Ion Microprobe Facility, in the University of Edinburgh, United Kingdom. A $^{16}\text{O}_2$ primary ion beam with an intensity of 12-16 nA was accelerated to 22.5 kV and impacted onto the sample surface using Kohler illumination. The elliptical spot area was approximately $20 \times 30 \mu\text{m}$. The secondary ion beam position in the field aperture and the ^7Li peak position were automatically centered before each measurement during a 60-s pre-sputter without beam rastering. Secondary ions were counted in mono-collection, pulse-counting mode. Fifty cycles were measured with counting times of 6 and 2.5 s for ^6Li and ^7Li , respectively. The count rate for ^7Li ranged from 30,000 to 120,000 cps, depending on the Li concentration of the sample and primary beam intensity, resulting in 1 s uncertainties of $\delta^7\text{Li}$ of 0.5-1.2‰. Lithium concentrations were calculated using beam current corrected ^7Li count rates of samples using 06JY34Ol as a standard (Li concentration = 1.73 ppm; [Su et al., 2015](#)). The Li isotopic ratios are expressed as $\delta^7\text{Li}$ relative to the NIST L-SVEC standard $\{\delta^7\text{Li} = [(^7\text{Li}/^6\text{Li})_{\text{sample}}/(^7\text{Li}/^6\text{Li})_{\text{L-SVEC}} - 1] \times 1000\}$. Basaltic standards BCR2-G and ML3B-G were analyzed to monitor instrument drift, whereas 06JY34Ol ($\delta^7\text{Li} = 3.1\text{‰}$; [Su et al., 2015](#)) was used for calibration. Matrix composition (Fo

content) has an effect on measured olivine Li isotopic compositions; e.g., [Su et al. \(2015\)](#) showed that $\delta^7\text{Li}$ values increase by 1.0‰ for each mole percent decrease in the Fo content of olivine, and this was taken into account for calibration. As Fo contents of the olivines span a narrow range from 91.6 to 94.7, the matrix correction amounted to no more than 3‰, compared to a range of > 20‰ in $\delta^7\text{Li}$ for the whole dataset.

5. Results

5.1 Major oxide contents of minerals

Olivine in the Orhaneli and Harmancık dunites has Fo values of 92.4-94.0 and 91.6-93.5, respectively ([Table S1](#); [Fig. 4a-c](#)). The chromitites contain olivine with somewhat higher Fo values (92.6-94.7 in Orhaneli; 93.3-94.4 in Harmancık) than those in the dunites ([Table S1](#)). The dunites from the two ophiolites have similar MnO (0.06-0.15 wt.%) and NiO (0.23-0.44 wt.%) contents in their olivine ([Table S1](#)). In the Orhaneli and Harmancık profile analyses, the variations of Mn concentrations in olivines are not continuous and yield abrupt change at the contact with chromitite layers. Compared to Mn, Ni concentrations show the reverse patterns ([Fig. 5](#)).

Chromite grains in dunites of the both ophiolites are generally uniform in TiO_2 contents (0.14-0.23 wt.% in Orhaneli; 0.11-0.22 wt.% in Harmancık), similar to those in the chromitites (0.14-0.26 wt.% and 0.13-0.22 wt.%), whereas their Cr# ($100 \times \text{Cr}/(\text{Cr}+\text{Al})$) and Mg# ($100 \times \text{Mg}/(\text{Mg}+\text{Fe})$) values are variable within ranges of 79.1-81.8 and 47.6-53.5 in the Orhaneli dunites, 70.6-80.2 and 41.9-52.9 in the

Harmancık dunites, 81.1-82.8 and 58.7-67.3 in the Orhaneli chromitites and 78.8-80.0 and 46.4-64.2 in the Harmancık chromitites (Table S2; Fig. 4).

5.2 Trace element compositions of olivine

From base to top, the mantle-crust transition zone in the Orhaneli ophiolite includes many cyclic dunite and chromitite layers (Fig. 2a-b) with a total thickness of 90 m. Overall, olivines in chromitites show lower Co, Zn, Sc and V concentrations than those in dunites (Fig. 5a, b). The Co concentrations of olivine in the dunites (106-132 ppm in Orhaneli, 128-137 ppm in Harmancık) are higher than those of primitive mantle (105 ppm; McDonough and Sun, 1995), whereas the concentrations of Zn (6.0-44.8 ppm), Sc (2.14-3.68 ppm) and V (0.07-0.36 ppm) in all samples are lower than primitive mantle (Zn: 55 ppm; Sc: 16.2 ppm; V: 82 ppm; McDonough and Sun, 1995). The olivine in both dunites and chromitites from the two ophiolites has lower incompatible trace element concentrations (Ti = 4.0-7.8 ppm, Zr = 0.010-0.034 ppm, and Yb = 0.007-0.027 ppm) than the counterparts in olivine phenocrysts in MORB (Table S3; Fig. 6) (e.g., Piccardo et al., 2007; Foley et al., 2011). In the Orhaneli section and Harmancık drill hole samples, there is no apparent correlation between trace element compositions of olivine and the relative position of the layers (Figs. 5, 6).

5.3 Li concentrations and isotopic compositions

In the Orhaneli dunites, olivine has Li concentrations varying from 0.9 to 1.5 ppm, and $\delta^7\text{Li}$ from 3.7 to 11.0‰ (Fig. 7), with no correlation between Li concentrations and Li isotopic compositions (Fig. 8). In contrast, Li concentrations

(0.7 to 1.9 ppm) and $\delta^7\text{Li}$ values (-2.5 to 20.3‰) of olivine in the Harmancık dunites vary widely (Table S1), and the $\delta^7\text{Li}$ values are negatively correlated with the Li concentrations (Fig. 8). Most olivine grains in the two ophiolites show little change in Li concentrations and $\delta^7\text{Li}$ values from core to rim (Table S1). Nevertheless, different olivine grains in the same sample from Harmancık can have strongly variable Li isotopic compositions (up to 15‰ difference) (Table S1; Fig. 7). On the other hand, the chromitites from the two ophiolites display Li contents and $\delta^7\text{Li}$ values of olivine with 0.8 to 1.6 ppm and 5.0 to 14.7‰ in Orhaneli and 0.7 to 1.2 ppm and 4.1 to 15.6‰ in Harmancık (Table S1; Fig. 7).

6. Discussion

Based on trace elements and Li isotopes compositions of olivine in the dunites and chromitites from the mantle-crust transition zones for both ophiolites, we first evaluate the various processes that may account for the observed trace elemental and Li isotope variations, followed by models for the formation of dunites and chromitites.

6.1 Origin of mantle-crust transition zone dunites in the Orhaneli and Harmancık ophiolites

Dunite consists almost entirely of olivine and is usually formed by one of three processes (e.g., Su et al., 2016; Yao et al., 2018): 1) ultrahigh-degree partial melting of mantle with nearly all orthopyroxene being exhausted; 2) cumulate dunite left behind by the fractionation and accumulation of abundant olivine from an ultramafic-mafic

magma; 3) reaction between silica-undersaturated melt migrating in channels and pyroxene-rich wall rock triggering the formation of replacive dunite.

Cumulate dunites are formed via crystal accumulation from magmas and therefore olivine generally has low Fo (88-91) and feature a rapid decrease in the NiO content with decreasing Fo (Santos et al., 2002; Song et al., 2007; Arai et al., 2012; Seo et al., 2013; Su et al., 2016; Rospabé et al., 2018). Moreover, the coexisting chromites show a wide range of Cr# from 15 to 76 as well as high TiO₂ contents (up to 0.8 wt.%) (Santos et al., 2002; Song et al., 2007; Arai et al., 2012; Seo et al., 2013) (Fig. 4a-c). In contrast, olivine in replacive dunites generally has higher Fo values (up to 94), because the high-MgO melts reacting with peridotites convert olivine and pyroxene in peridotite to high-Fo olivine (Rollinson et al., 2018). Besides, no obvious correlation exists between the Fo and NiO of olivine grains within the replacive dunites (Mazzucchelli et al., 2009). In the Orhaneli and Harmancık dunites, olivine has higher Fo (91.6-94.0) and lower MnO contents (0.06-0.15 wt.%) than that from cumulate dunites, while chromites display higher Cr# (79.1-82.8) and lower TiO₂ contents (0.14-0.26 wt.%) (Fig. 4c-d). These observations, together with the absence of a clear correlation between Fo and NiO in olivine, demonstrate that the dunites from both ophiolites could not be related to fractional crystallization (Fig. 4b). Instead, all our data fall within the fields of replacive dunites (Fo: 90.4-94.6; MnO of olivine: 0.07-0.15 wt.%; Cr# of chromite: 23-89) (Suhr et al., 2003; Piccardo et al., 2007; Ackerman et al., 2009; Mazzucchelli et al., 2009; Oh et al., 2012; Sanfilippo et al., 2014, 2017) (Fig. 4), indicating that these dunites were formed by melt-peridotite

interaction rather than have a cumulate origin. Furthermore, although the olivines from these dunites show a good correlation between Ni and Mn, the correlation between Co and Mn is poor (Fig. 6b-c). According to olivine-melt partition coefficients (e.g., Beattie et al., 1991), Co and Ni are compatible in olivine, whereas Mn is incompatible, and hence segregation of olivine from its parental magma should produce a decrease of Co and Ni with increasing Mn (Sanfilippo et al., 2014). However, Co contents in olivine from the Orhaneli and Harmancık dunites are poorly correlated with Mn contents, and therefore incompatible with olivine fractionation and likely to be induced by melt migration.

For the Orhaneli and Harmancık ophiolites, the mineralogical and geochemical characteristics of mantle-crust transition zone dunites indicate that they were formed by melt-peridotite interaction: orthopyroxene + melt 1 $\rightarrow$ olivine + melt 2. In this reaction, melt 1 (reactant) is silica-undersaturated and melt 2 (product) is relatively enriched in SiO₂ and Cr₂O₃ due to progressive melt-rock reaction (e.g., Suhr, 1999; Zhou et al., 2005). Since the majority of all dunites are of refractory chemical nature and not akin to MORB (Figs. 4, 6), we argue that the reactant (melt 1) was highly depleted.

6.2 Origin of chromitites of the Orhaneli and Harmancık ophiolites

Olivines in Orhaneli and Harmancık chromitites have somewhat higher Fo than that contained in dunites, which likely implies an additional process for the chromitites. Subsolidus Mg-Fe exchange between olivine and chromite has been

usually reported in chromitites (e.g., [Xiao et al., 2016](#)):

The Mg diffuses from chromite to olivine and Fe from olivine to chromite. The compositional effect of Fe-Mg exchange on olivine depends on the elemental contents and relative modal abundances of olivine and chromite in the rocks ([Xiao et al., 2016](#)). The Fe-Mg exchange effect on olivine in the dunites is negligible because of the extremely low amount of chromite. Recent studies (e.g., [Qian et al., 2010](#)) reported that despite differences in ionic size and charge, Sc and V diffuse at approximately similar rates to Mg, Fe and other divalent cations (e.g., Co and Zn). Cobalt and Zn are more compatible in chromite than in olivine, with crystal-melt partition coefficients from 8.3 to 2.1, and 7.9 to 3.6, respectively (<https://earthref.org>). Vanadium compatibility decreases in the order of chromite >> pyroxene >> olivine ([Witt-Eickschen and O'Neill et al., 2005](#)). In addition, the partitioning of Sc between chromite and olivine is strongly dependent upon the major element composition of chromite ([Stosch et al., 1981](#)). Thus, as expected, Co, Zn, Sc and V concentrations of olivine in the Orhaneli profile and Harmancık chromitites are lower than those in the associated dunites ([Figs. 5a-b](#)), which points to the relative modal abundances of chromite and olivine being a factor in determining the Sc, V, Co and Zn concentrations in olivine in chromitites ([Xiao et al., 2016](#); [Zhang et al., 2017](#)). For example, in the Orhaneli profile, chromitite sample (+50 m) contains the highest modal amount of chromite and its olivine has the lowest Co, Zn, Sc and V concentrations ([Fig. 5a](#)).

Mantle-derived magmas generally have ca. 500 ppm Cr concentrations, whereas the chromites derived from these melts contain 30-50 wt.% Cr₂O₃ (Zhou et al., 2014; Zhang et al., 2017). During the evolution of magmatic systems, the oversaturation of chromite in the magma is an important factor for the formation of chromitite. Addition of silica to magmas has been widely accepted as a means of triggering chromite precipitation, because SiO₂ addition can decrease Cr solubility (Irvine et al., 1986). The increase in silica has been usually attributed to assimilation/reaction of more siliceous materials or magma mixing (e.g., Arai et al., 2004; Zhou et al., 1994, 2014; Zhang et al., 2017). In this regard, chromitites in the Orhaneli and Harmancık mantle-crust transition zones are exclusively associated with dunites, and hence it is unlikely that the oversaturation of chromite was caused by extensive assimilation of siliceous-rich crust. Instead, the oversaturation of chromite induced by magma mixing becomes the most likely scenario here. Mantle-derived mafic magma A rises through the upper mantle and mixes with more Si-rich and Cr-rich magma (e.g., Lissenberg and Dick, 2008), upon which the newly-formed, mixed magma B would move into the field of chromite crystallization (Fig. 9). Additionally, the residual melt (melt 2) following melt-peridotite reaction and orthopyroxene dissolution will also be enriched with Cr and SiO₂ relative to the infiltrating melt (Arai and Yurimoto, 1995). Therefore, it would further facilitate the oversaturation of chromite in the mixed magma (Zhou et al., 1994, 2014; Su et al., 2019), driving crystallization of abundant chromite and forming chromitite layers. Due to precipitation of chromite, mixed magma 'B' would evolve to point 'C', i.e., back to the chromite-olivine cotectic line.

6.3 Origin of infiltrating melts

During melt-peridotite interaction, trace elements between minerals and melts can be redistributed. The trace elements of olivine in the Orhaneli and Harmancık dunites do not show any zoning (Tables S1, S3), indicating that they were fully equilibrated with the percolating melts. Since dunites predominantly consist of olivine grains, and other silicate minerals (e.g., pyroxene) are rare or absent, the trace element concentrations of olivine cannot be affected by subsolidus re-equilibration among silicate minerals. Thus, the olivine trace elements can be used to trace the composition of the melt in chemical equilibrium with these crystals. The lower incompatible trace element concentrations (Zr, Ti and HREE) in olivines from the Orhaneli and Harmancık dunites relative to those of the olivines from the lower crustal sections of ophiolites (Sanfilippo et al., 2014) (Fig. 6a) indicate that our dunites are not in equilibrium with a melt derived from the lower oceanic crust. In addition, compared to mantle harzburgites of the Orhaneli and Harmancık ophiolites (chromite Cr#: 43-55; Fo < 91.6) (Uysal et al., 2017), the mantle-crust transition zone dunites have Cr# in chromite of 79-82, NiO in olivine of 0.2-0.4 wt.% and Fo of 91.6-94.0, which are far more refractory. The Mn and Co abundances of olivines in both the Orhaneli and Harmancık dunites are lower than those of olivine phenocrysts within MORB (Sobolev et al., 2007) (Fig. 6b-c), in conjunction with the lower trace-element concentrations relative to primitive mantle (McDonough and Sun, 1995), suggesting that these dunites were equilibrated with melts that are more depleted than MORB

(e.g., [Piccardo et al., 2004](#); [Sanfilippo and Tribuzio, 2011](#)).

We can use the composition of the chromitites to put further constraints on the composition of its parental melts. In contrast to the incompatible elements, diffusion of compatible elements Cr, Al and Ti out of chromite is negligible ([Abily and Ceuleneer, 2013](#)), because Al and Ti enter olivine and/or serpentine in only very low amounts (e.g., [Kamenetsky et al., 2001](#)). As a consequence, we can use these elements to calculate the composition of equilibrated melts based on chromite compositions. The TiO₂ content of chromite is a key indicator of tectonic setting of where chromitite forms (e.g., [Kamenetsky et al., 2001](#)). The Orhaneli and Harmancık chromites have very low TiO₂, and plot in the arc or boninitic fields ([Fig. 10a-b](#)), suggesting crystallization from low-Ti island arc tholeiitic melts or boninitic melts. In addition, several studies have also shown that chromite compositions in chromitites reflect the composition of their parental melt ([Kamenetsky et al., 2001](#); [Rollinson, 2008](#); [Zhou et al., 2014](#); [Rollinson and Adetunji, 2015](#); [Chen et al., 2019](#)). The following equations were proposed by [Rollinson and Adetunji \(2015\)](#) to more closely reflect the empirical correlations defined by [Kamenetsky et al. \(2001\)](#) and applies to melt with an arc affinity:

$$(\text{Al}_2\text{O}_3)_{\text{melt}} = 5.2181 \times \ln(\text{Al}_2\text{O}_3)_{\text{Chr}} - 1.0505 \text{ (Eq. 2)}$$

$$(\text{TiO}_2)_{\text{melt}} = 1.0963 \times (\text{TiO}_2)_{\text{Chr}}^{0.7863} \text{ (Eq. 3)}$$

The implementation of equations (2) and (3) demonstrates that the melts in equilibrium with chromitite have the following composition: 9.8-10.8 wt.% Al₂O₃ and 0.23-0.38 wt.% TiO₂ in Orhaneli, and 10.7-11.4 wt.% Al₂O₃ and 0.22-0.33 wt.% TiO₂

in Harmancık. The inferred parental melts of the chromitites from the two ophiolites have similar Al_2O_3 and TiO_2 contents to boninitic melts (Fig. 10c), suggesting that the Orhaneli and Harmancık chromitites possibly originated in a forearc setting during the early stage of subduction. The zigzag pattern (Fig. 5) of the olivine trace element contents in the chromitites from the Orhaneli profile and Harmancık drill hole, in conjunction with the widespread occurrence of interlayered chromitites and dunites, could be the witness of multiple magma replenishments in the mantle-crust transition zone.

6.4 Lithium isotope constraints on the origin of Orhaneli and Harmancık dunites and chromitites

Due to the highly depleted composition of dunites and chromitites, traditional chemical indicators of tectonic setting can generally not be applied. However, Li isotope systematics of olivine may provide clues about the tectonic setting of the infiltrating melts. High-temperature partial melting is thought to induce negligible Li isotope fractionation (e.g., Tomascak et al., 1999; Ionov and Seitz, 2008) and Jeffcoate et al. (2007) estimated that the $\delta^7\text{Li}$ value of magmas generated by equilibrium melting would be $< 0.5\text{‰}$ different from their source. In addition, most studies have shown that Li isotopes do not fractionate during fractional crystallization of silicate magmas (e.g., Tomascak et al., 1999; Teng et al., 2006). Many studies also demonstrated that diffusion is an important mechanism controlling Li abundances and isotopic distribution (e.g., Su et al., 2014; Tomascak et al., 2016). Lithium

concentrations and isotopes do not show core-to-rim zoning in individual olivine grains in most samples of the Orhaneli and Harmancık ophiolites (Table S2), and chromite contains little or no Li (e.g., Jeffcoate et al., 2007; Chen et al., 2019). Thus, the Li isotopic compositions of olivine have not been affected by inter-mineral diffusion. Therefore, the Li isotopic compositions of olivines in the Orhaneli and Harmancık dunites record the history of melt-rock interaction.

Compared to typical mantle peridotites with $\delta^7\text{Li}$ values of 2-6‰ and 1.0-1.8 ppm Li (Seitz and Woodland, 2000; Su et al., 2014), the olivines from the Orhaneli dunites show a similar range of Li concentrations (0.9-1.5 ppm), but a slightly larger range of $\delta^7\text{Li}$ values (+4.0 to +11.0‰) (Table S1; Figs. 7, 8), offset to higher values. As the samples are relatively homogeneous (1s 0.8-1.7‰ based on multiple olivine analyses in each sample) (Fig. 7) and the olivines are unzoned, these samples likely reached Li isotope equilibrium during rock-melt interaction, and therefore could reflect the composition of the infiltrating melt. Average $\delta^7\text{Li}$ per sample shows a more restricted range from +4.8 to +8.7‰ with 1.1-1.3 ppm Li, suggesting reaction with relatively homogeneous melt batches.

The Orhaneli chromitites have somewhat higher $\delta^7\text{Li}$ values (average $\delta^7\text{Li}$ per sample +6.0 to +10.6‰ with 1.0-1.3 ppm), but the two samples with highest $\delta^7\text{Li}$ shows considerable heterogeneity (based on multiple olivine analyses in each sample) of > 4-7‰ even though individual olivines are unzoned. Excluding these samples, the range of Orhaneli chromitites is +6.0 to +8.2‰, an even smaller range than the dunites. These Li isotopic characteristics could be attributed to infiltrating melts in a

subduction zone setting. Dehydration of altered oceanic crusts during subduction can induce that the Li isotope fractionation generates isotopically heavy-Li fluids and light-Li slab residues (e.g., [Elliott et al., 2004](#); [Penniston-Dorland et al., 2017](#)), but the Li isotopic range of arc lavas (-1 to +12‰) reflects the heterogeneity of the altered oceanic plate and overlying sediments ([Tomascak et al., 2002](#); [Elliott et al., 2004](#)). Mixing of various slab components and re-equilibration with Li already present in the mantle wedge results in arc lavas with $\delta^7\text{Li}$ values that only slightly extend beyond that of MORB. The dominance of $\delta^7\text{Li}$ values in the Orhaneli mantle-crust transition zone that extends well beyond the MORB/mantle peridotite range point to a ubiquitous subducting slab component present in the infiltrating melts. The survival of these signatures suggests that the source of the interacting agent was rather shallow, as Li isotopic signatures will re-equilibrate with ambient mantle at short length and timescales ([Halama et al., 2009](#)). This is consistent with a subduction initiation.

Compared to Orhaneli, olivine from the Harmancık dunites shows much larger $\delta^7\text{Li}$ variations of -2.5‰ up to +20.3‰, but also larger sample heterogeneity, with only one sample having a ranging of $\delta^7\text{Li}$ of < 3‰ ([Figs. 7, 8](#)). The Harmancık dunites were considerably more altered than the Orhaneli dunites, but the olivine grains selected for Li isotope analyses were fresh and unzoned, and hence the influences of alteration (such as serpentinization) on $\delta^7\text{Li}$ values between different grains are likely to be small (e.g., [Lundstrom et al., 2005](#)). The larger range of $\delta^7\text{Li}$ values in the Harmancık dunite may indicate the infiltrating melts with a wider range of $\delta^7\text{Li}$ values, especially given that the slab-derived fluids and melts have a broad

range of compositions and are highly variable from one location to another (Elliott et al., 2004; Yao et al., 2018). However, the heterogeneous distribution of $\delta^7\text{Li}$ in individual samples from the Harmancık dunites and the negative correlation between $\delta^7\text{Li}$ values and Li concentrations is indicative of incomplete diffusive equilibration between olivines and infiltrating melts (Fig. 8) (e.g., Jeffcoate et al., 2007; Penniston-Dorland et al., 2017), which is consistent with the studies of olivine Li isotope of dunite from Trinity ophiolite (Lundstrom et al., 2005) and Luobusa ophiolite (Su et al., 2016). Many studies have demonstrated that ^6Li diffuses about 2-3% faster than ^7Li through melts and minerals (e.g., Lundstrom et al., 2005; Teng et al., 2006). As Li diffuses from percolating melt into olivine, the $\delta^7\text{Li}$ of olivine will become lower at first, but will then increase to higher values until $\delta^7\text{Li}$ equilibrates with that of the infiltrating melt, due to equilibrium partitioning (Lundstrom et al., 2005). During this process, temperature and time are the fundamental parameters that control the efficiency of the isotopic exchange (Tomascak et al., 2016). We, therefore, estimated the equilibration temperatures of the Harmancık and Orhaneli dunites and chromitites based on the Al (Coogan et al., 2014) and Mg-Fe exchange (Ballhaus et al., 1991) between olivine and chromite (Table 1). The Al-in-olivine thermometry results (Coogan et al., 2014) show that the temperature range for Harmancık dunites (933-979°C) is similar to that of the Orhaneli suite (960-993°C), while Mg-Fe exchange temperatures (Ballhaus et al., 1991) are considerably lower: 714-778°C for Orhaneli dunites and 663-755°C for Harmancık dunites. This suggests no significant difference in temperature between Harmancık and Orhaneli ophiolites, so this cannot

explain the heterogeneity of the Harmancık samples. The main another factor of diffusion is time. Richter et al. (2014) found that very large lithium isotopic fractionations persisted after the lithium concentration had become effectively homogenized during diffusion process, suggesting that it still takes longer for the isotopic composition to become uniform compared to the time it takes for diffusion to homogenize the total lithium concentration. Thus, if infiltration of melts into the rocks occurred shortly before obduction and exhumation, Li isotopes would not fully equilibrate, and isotope heterogeneity would be preserved during relatively rapid cooling. Heterogeneities in the Harmancık samples could indicate rapid cooling was essential to preserve the observed isotope heterogeneities.

In summary, excluding two heterogeneous samples (Fig. 7), the Li isotope signatures of olivine in dunites and chromitites from the Orhaneli ophiolite are likely primary features inherited from their parental melts, with all olivines falling between $\delta^7\text{Li}$ values of +5‰ and +9‰, which is within the range of arc lavas but isotopically heavier than MORB (Fig. 7) (Chan et al., 2002; Tomascak et al., 2002), suggesting an affinity with arc magmatism. The olivine Li isotopic compositions of Harmancık mantle-crust transition zone chromitites are similar to those from Orhaneli, but still, likely have diffusional heterogeneities due to incomplete equilibration between infiltrating melt and olivine. Nevertheless, their average compositions (+6 to +11‰) does suggest a melt source similar to the one that crystallized Orhaneli chromitites.

The estimated Al_2O_3 and TiO_2 contents of the parental magmas of chromitites in the two ophiolites are similar to the signatures of boninitic melts. Given that boninitic

magmas have been widely found in preserved fore-arcs related to subduction initiation (e.g., [Reagan et al., 2017](#); [Stern et al., 2012](#)), this suggests that the Orhaneli and Harmancık ophiolites possibly originated in a subduction initiation setting, which gives additional support to studies suggesting that these settings represent an ideal environment for forming ophiolites with economically viable chromitite deposits ([Johnson, 2012](#)).

7 Conclusions

This study presents in-situ trace elements and Li isotopic compositions of olivine in dunites and chromitites from the Orhaneli and Harmancık mantle-crust transition zone. The following conclusions can be drawn:

1. Compared to olivine from cumulate dunites, the olivine in the Orhaneli and Harmancık dunites is distinct by higher Ni, lower Mn concentrations and extreme depletion of incompatible trace elements (Ti, Zr and HREE), which are consistent with the formation of dunites driven by interaction of peridotite with depleted melts.
2. The relatively uniform Li isotopic compositions (+4 to +11‰) of olivines from Orhaneli dunites indicate these samples reached Li isotope equilibrium, and suggest a reaction driven by relatively homogeneous melt batches with a subduction component, whereas the large $\delta^7\text{Li}$ variations (-2.5 to +20.3‰) in olivine from Harmancık dunites reflect incomplete diffusive equilibration during the melt percolation through these dunites.

3. The formation of chromitites in the mantle-crust transition zone of the two ophiolites was likely triggered by the magma mixing. The calculated Al_2O_3 (9.8-11.4 wt.%) and TiO_2 (0.22-0.38 wt.%) contents of the parental magmas of chromitites demonstrate a boninite-like geochemical affinity, i.e., a subduction initiation setting, which is in good agreement with the Li isotopic compositions of their olivines.
4. In contrast to the dunites, the higher Fo contents of olivine in the chromitites could be caused by the Mg-Fe exchange between olivine and chromite. The lower Sc, V, Co and Zn concentrations of olivine in the chromitites are controlled by the modal abundances of chromite.

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Figure Captions:

Fig. 1 (a) Map showing distribution of the continental blocks, major sutures and related ophiolites in the Eastern Mediterranean region (modified after [Chen et al., 2018](#)). (b) Simplified geological map of the Orhaneli and Harmancık ophiolites (after [Uysal et al., 2015](#)). Red stars in (b) are the sampling locations. IASZ: Izmir-Ankara Suture Zone; ITSZ: Inner-Tauride Suture Zone; BZSZ: Bitlis-Zagros Suture Zone.

Fig. 2 Photographs of field sites with numbered sampling locations and hand specimens of dunites and chromitites from the Orhaneli mantle-crust transition zone.

(a) Banded chromitites that occur by the rhythmic layering of chromitite and dunite.
(b) Banded chromitite. (c) Disseminated chromitite.

Fig. 3 Back scattered electron images of thin sections of dunites and chromitites from the Orhaneli (a)-(c) (sample Ol-1, 2-2 and 4-2) and Harmancık (d) (sample 71.5 m) ophiolites.

Fig. 4 Plots of (a) MnO vs. Fo of olivine, (b) NiO vs. Fo of olivine, (c) Cr# of chromite vs. Fo, and (d) Cr# vs. TiO₂ of chromite in dunites from the Orhaneli and Harmancık ophiolites. The gray and pink fields represent literature olivine/chromite composition ranges of cumulate dunites and dunites formed by peridotite-melt interaction, respectively. The cumulate dunite field is defined using data from Santos et al. (2002), Song et al. (2007), Arai et al. (2012) and Seo et al. (2013). The replacive dunite field is defined using data from Suhr et al. (2003), Piccardo et al. (2007), Ackerman et al. (2009), Mazzuchelli et al. (2009), Oh et al. (2012), Sanfilippo et al. (2014, 2017).

Fig. 5 Elemental (Fo, Ni, Mn, Li, Co, Zn, Sc and V) and isotopic ($\delta^7\text{Li}$) variations of olivine compositions in the Orhaneli profile (a) and Harmancık drill hole (b). Olivine grains from dunites are shown as blue circles, whereas pink circles are olivine grains from chromitites. Scanned photographs of dunites and chromitites are shown to clearly describe the effect of chromite proportion on olivine trace element

compositions.

Fig. 6 (a) Primitive mantle-normalized pattern of olivine in the dunites from Orhaneli and Harmancık ophiolites. Plots of (b) Ni (ppm) vs. Mn (ppm), (c) Co (ppm) vs. Mn (ppm) of olivine in the dunites from the two ophiolites. Primitive mantle values are from [Anders and Ebihara \(1982\)](#). Compositions of lower crust data in (a) are from [Sanfilippo et al. \(2014, 2017\)](#) and [Rampone et al. \(2016\)](#). The compositions of olivine phenocrysts in MORB are from [Sobolev et al. \(2007\)](#).

Fig. 7 Li isotopic compositions of olivines in dunite and chromitites from the Orhaneli and Harmancık ophiolites. The $\delta^7\text{Li}$ range of MORB is from [Tomascak et al. \(2008\)](#), and the $\delta^7\text{Li}$ range of arc lava is from [Tomascak et al. \(2002\)](#) and [Chan et al. \(2002\)](#).

Fig. 8 Diagram of $\delta^7\text{Li}$ vs. Li of olivine in the Orhaneli and Harmancık dunites. The arrow is the trend of Li diffusion during melt-rock interaction (after [Lundstrom et al. \(2005\)](#)).

Fig. 9 A petrologic model for chromitite formation in the Orhaneli and Harmancık ophiolites in the simplified system olivine (Ol) - quartz (Q) - chromite (Chr). The trends in the phase diagrams are after [Zhou et al. \(1994\)](#) and [Zhang et al. \(2017\)](#).

Fig. 10 (a) TiO_2 vs. Al_2O_3 (after [Kamenetsky et al., 2001](#) and [Derbyshire et al., 2013](#)),

879 (b) Cr# vs. TiO_2 (after [Pearce et al., 2000](#)) of chromite in the chromitites and (c) TiO_2
880 vs. Al_2O_3 (after [Peighambari et al., 2016](#)) of parental melts for the Orhaneli and
881 Harmancık chromitites. FMM: fertile MORB mantle. The subscripts b and I represent
882 boninite and island arc tholeiite, respectively. BON: boninite; IAT: island arc tholeiite;
883 MORB: mid-ocean ridge basalt. Data of grey hexagons, triangles and circles
884 representing lherzolite, harzburgite and dunite, respectively, are from [Uysal et al.](#)
885 [\(2014\)](#).

1 **Formation processes of dunites and chromitites in Orhaneli and Harmancık**
2 **ophiolites (NW Turkey): evidence from in-situ Li isotopes and trace elements in**
3 **olivine**

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Abstract

Trace elements and Li isotopic compositions of olivine from the mantle-crust transition zone of the Bursa ophiolites (including Orhaneli ophiolite and Harmancık ophiolite) in NW Turkey were measured to constrain the genesis of these dunites and chromitites. A cumulate origin for dunite can be ruled out due to the depletion of incompatible trace elements (Zr, Ti, and heavy rare earth elements) in olivine, instead the chemical signatures point to a replacive origin via melt-rock interaction. The olivine grains in the dunites have lower MnO (0.06-0.15 wt.%), Co (106-137 ppm), and higher NiO (0.23-0.44 wt.%) concentrations than olivine phenocrysts in MORB, suggesting these transition-zone dunites have equilibrated with extremely depleted melts. Additionally, the relatively small $\delta^7\text{Li}$ variations of olivine (average $\delta^7\text{Li}$ +4.8 to +8.7‰) of the Orhaneli suite indicate the Li isotopic compositions of melts percolating through these dunites are relatively homogeneous. However, the large $\delta^7\text{Li}$ variations of olivine (-2.5 to 20.3‰) in Harmancık dunites can be explained by incomplete diffusive equilibration with melts percolating through these dunites, suggesting infiltration happened not long before obduction of the ophiolite. Olivine in chromitites has higher Fo (92.6-94.7) than coexisting dunites, likely induced by subsolidus Mg-Fe exchange between olivine and chromite. The higher chromite contents of the chromitites can also explain the lower concentrations of Sc, V, Co and Zn in coexisting olivine grains. Mixing of depleted mantle-derived melts and boninitic magmas is suggested to induce a compositional shift from the olivine-chromite cotectic line to the liquidus field of chromite, causing the precipitation of chromite

and formation of chromitite layers in the dunites. The heavy Li isotopic compositions (+6 to +11‰) of olivine in chromitites compared to MORB, together with the estimated compositions of parental magmas (Al_2O_3 : 9.8-11.4 wt.%; TiO_2 : 0.22-0.38 wt.%) for the chromitites, indicate an arc-like geochemical affinity, hence a subduction-related setting in which these mantle-crust transition zones formed.

Key words: olivine; trace element; Li isotopes; ophiolite; chromitite; mantle-crust transition zone

1. Introduction

The mantle-crust transition zone is well documented in many ophiolites, and marks the petrological transition from mantle peridotites to lower crustal cumulates (e.g., [Zhang et al., 2017](#); [Rollinson, et al., 2018](#); [Rospabé et al., 2018](#)). Ophiolitic mantle-crust transition zones typically consist of dunite-dominated ultramafic rocks and stratiform-like chromitites, and can reach a thickness of several kilometers ([Paktunc, 1990](#)). These dunites are made of mostly olivine with minor chromite and their thickness ranges from a few meters to a few hundred meters (e.g., [Zhang et al., 2017](#)). Although the transition zone chromitites are distinguished by their layered morphology from the mantle podiform chromitites which occur as irregular lenses and pods, their compositions are similar in many cases (e.g., [Arai et al., 2004](#); [Rollinson, 2008](#)). Despite many years of investigation, the genesis of the dunites and chromitites in the ophiolitic mantle-crust transition zone is still debated, and different models have been proposed, such as magmatic cumulates stagnating at the base of the crust

(e.g., [Abily and Ceuleneer, 2013](#)), crustal assimilation ([Arai et al., 2004](#)), reactions between melts and mantle harzburgites (e.g., [Abily and Ceuleneer, 2013](#)), and mixing of mantle-derived melts with differentiated magmas (e.g., [Ballhaus, 1998](#)). In addition, the nature of the mixed or infiltrated melts and their influences on the mantle-crust transition zone are not yet well known, limiting our understanding of the evolution of ophiolites. A close link between subduction initiation and chromitite/ophiolite genesis has been documented (e.g., [Reagan et al., 2017](#); [Zhang et al., 2017](#)) in several studies of the extensive ophiolites in Turkey (e.g., [Uysal et al., 2017](#); [Chen et al., 2019](#)). Therefore, careful study of the formation processes of the chromitite and their tectonic setting could shine further light on the relationship between subduction initiation and ophiolite emplacement.

Olivine is a ubiquitous mineral in both the ultramafic and mafic igneous rocks, and in most cases, it is the first silicate phase to crystallize from ultramafic-mafic melts ([Foley et al., 2013](#)). Olivine thus controls early magmatic differentiation processes, but its Fo content can provide little information about its origin and evolution ([De Hoog et al., 2010](#); [Foley et al., 2013](#)), which forces us to focus on its trace element geochemistry. Consequently, it has become increasingly important to improve our knowledge of the trace element composition of olivine, and to test the use of its geochemical signature as a tracer of early igneous and mantle melting processes ([Foley et al., 2013](#); [Rampone et al., 2016](#)). Several studies have shown that olivines in peridotites from different tectonic environments and/or various origins exhibit distinct geochemical characteristics and define systematic elemental

correlations for a series of trace elements (Ni, Mn, Zn, Co, Zr and heavy rare earth elements (HREE)), recording different magmatic processes (Sobolev et al., 2007; De Hoog et al., 2010; Foley et al., 2013; Rampone et al., 2016). Recent work on the Purang and Luobusa ophiolites (Su et al., 2019) advocates that the incompatible trace elements of olivine are more sensitive to melting processes, whereas the concentrations of compatible trace elements are mostly constrained by their source composition.

Lithium and its isotopes (^6Li and ^7Li) are increasingly used to trace multiple high-temperature processes due to their moderate incompatibility, strong fluid mobility, and large mass difference (17%) between its two isotopes (e.g., Tomascak et al., 2016). Olivine is the dominant Li reservoir in the upper mantle (Seitz and Woodland, 2000; De Hoog et al., 2010), and olivine-melt partition coefficients of Li are virtually independent of pressure, temperature and olivine composition (Seitz and Woodland, 2000; Qian et al., 2010). The equilibrium fractionation of Li isotopes is likely to be negligible at high temperatures (Vlastelic et al., 2009). However, many natural peridotites display heterogeneous $\delta^7\text{Li}$ compositions, which has been attributed to Li diffusion or interaction between percolating melts and peridotites (e.g., Lundstrom et al., 2005; Rudnick and Ionov, 2007; Su et al., 2014). Thus, olivine Li isotopic systematics can be used to trace magmatic processes of mantle-crust transition zone dunites and chromitites.

In the Bursa ophiolites (Orhaneli and Harmancık ophiolites) in northwestern Turkey, mantle-crust transition zones typically contain interlayered dunites and

chromitites (Uysal et al., 2015), the successions of which can reach up a few kilometers thick. In this paper, we provide in-situ trace element and Li isotope analyses of olivine in the chromitites and dunites from the mantle-crust transition zones of Orhaneli and Harmancık ophiolites. These datasets, together with petrological investigations and mineral major oxide compositions, are used to constrain the magmatic processes involved in the formation of dunites and chromitites in ophiolitic mantle-crust transition zones.

2. Geological Setting

Tethyan ophiolites in Anatolia occur in several E-W trending belts, which are separated by a series of Gondwana-derived continental fragments (e.g., Uysal et al., 2014) (Fig. 1a). The Izmir-Ankara Suture Zone (IASZ) in northern Turkey occurs between the Sakarya Zone (continent) to the north and the Anatolide-Tauride continental block to the south (Fig. 1a), and has relatively intact ophiolite blocks, which are locally extensive and well preserved (Dilek and Thy, 2006). The Orhaneli and the Harmancık ophiolites, situated in the western part of the IASZ, are considered as remnants of the Izmir-Ankara-Erzincan ocean, a local term for the northern branch of the Neotethys ocean (Sarıfakioğlu et al., 2009). The Orhaneli ophiolite was tectonically emplaced onto northwestern Anatolia along the IASZ (Fig. 1a). The Harmancık ophiolite is located ca. 30 km south of the Orhaneli ophiolite (Fig. 1b) (Sarıfakioğlu et al., 2009). These two ophiolites were thrust southwards over the metamorphic basement rocks of the Tavşanlı zone in the Anatolide-Tauride platform

([Sarifakioğlu et al., 2017](#)).

The Orhaneli ophiolite is approximately 50 km long, 15 km wide and 1500 m thick ([Fig. 1b](#); [Sarifakioğlu et al., 2009](#)), and mainly consists of mantle-crust transition zone comprising mostly basal ultramafic cumulates. The transition zone is dominated by chromitite interlayered dunites, followed by wehrlites, lherzolites, harzburgites and pyroxenites and to a lesser extent mafic cumulates such as gabbros and gabbroonorites (e.g., [Sarifakioğlu et al., 2009](#); [Uysal et al., 2015](#)). The chromitites interlayer with dunite in the two ophiolites and have typically semi-massive and banded (stratiform, cumulate) structures ([Fig. 2](#)). The mantle-crust transition zone of the Harmancık ophiolite, which reaches up to 1000 m thickness, has similar rock assemblages to those of the Orhaneli ophiolite ([Tankut, 1980](#)). The Harmancık ophiolite contains additional podiform chromitites in its mantle section ([Sarifakioğlu et al., 2009](#)). The podiform chromitites form centimeters to meters scale lenticular/tabular orebodies enclosed in thick dunite envelopes within mantle harzburgites. The mantle harzburgites and dunites from Harmancık ophiolite have been almost completely altered to serpentine and talc, and are unconformably overlain by Neogene sedimentary units (e.g., [Uysal et al., 2014, 2015](#)).

3. Petrography of dunites and chromitites

In the Orhaneli ophiolite, dunites display adcumulate textures and consist of mostly medium- to fine-grained olivine crystals with minor chromites ([Fig. 3a, b](#)). Chromitites generally show adcumulus- to orthocumulus-like textures with euhedral

to subhedral chromite grains (Fig. 3c). They occur as bands and layers in dunites (Fig. 2a-c), and massive chromitites are very rare. The banded chromitite orebodies display schlieren textures, characterized by parallel layers of chromitite alternating with dunite (Fig. 2b). The thickness of the chromitite bands in the Orhaneli ophiolite typically ranges between 0.2 and 3 cm, rarely reaching up to 5 cm (Fig. 2b-c). In contrast, chromitites from the Harmancık mantle-crust transition zone occur as schlieren/bands, semi-massive, and disseminated textures. Chromite grains are mostly euhedral to subhedral. Dunites are made up predominantly of olivine (> 95%) and have a dominant cataclastic texture (Fig. 3d).

In the Orhaneli ophiolite, the mantle-crust transition zone is nearly horizontal (Fig. 2a), and we have selected 13 samples (dunites and chromitites) from the mantle-crust transition zone profile. The thickness of this profile is about 90 m and we fixed the base of the dunite as 0 m and its roof is +90 m. In the Harmancık ophiolite, 12 drill hole samples from the mantle-crust transition zone were selected for chemical analyses, owing to their pristine olivine grains. The drill hole samples including dunite and chromitite were collected from depths of 63.4 m to 73.4 m.

4. Analytical methods

4.1 Major oxide analysis of minerals

Major oxide compositions of olivine and chromite were determined by wavelength-dispersive X-ray spectrometry using a JEOL JXA8100 electron probe micro-analyzer at the Institute of Geology and Geophysics, Chinese Academy of

Sciences (IGGCAS). The analyses were carried out using an accelerating voltage of 15 kV, a 10 nA beam current, a 5 μm spot size and 10-30 s peak counting time. Natural and synthetic mineral standards were used for calibration. A ZAF procedure was used for matrix corrections. Typical analytical uncertainty for the analyzed elements was better than 1.5% (1RSD%).

4.2 Trace element analysis of olivine

In-situ trace element analyses of olivine were conducted on thin sections using a laser ablation inductively coupled plasma mass spectrometer (LA-ICP-MS) at IGGCAS. The LA-ICP-MS system consists of a 193 nm Coherent COMPex Pro ArF Excimer laser coupled to an Agilent 7500a ICP-MS. About 6-8 spots were measured for different olivine grains in each sample. The laser spot size was 140 μm , and the repetition rate was 8 Hz. Each analysis consisted of 60 s measurement of gas blank and 60 s ablation. The following isotopes were measured: ^7Li , ^{27}Al , ^{29}Si , ^{31}P , ^{39}K , ^{43}Ca , ^{45}Sc , ^{49}Ti , ^{51}V , ^{53}Cr , ^{59}Co , ^{66}Zn , ^{91}Zr , ^{163}Dy , ^{166}Er , ^{172}Yb . De Hoog et al. (2010) reported that potential interferences in olivine from matrix components MgO , SiO_2 and FeO , which are generated during ablation only and therefore unaccounted for by gas blank subtraction. The contribution of $^{26}\text{Mg}^{40}\text{Ar}$ to the ^{66}Zn signal is about 0.2 ppm, and the $^{29}\text{Si}^{16}\text{O}$ interference on ^{45}Sc accounted for 0.2 ppm of the signal (De Hoog et al., 2010), hence those are small enough to be ignored. A glass standard, NIST 610, was used for external calibration. For most of the trace elements NIST 612 standard was used to monitor instrument drift, and silicon (^{29}Si) was selected as an internal standard. The SiO_2 contents of NIST 610 and NIST 612 are 69.7% and 72.1%,

respectively. Reference values of NIST 610 and NIST 612 are from GeoREM (<http://georem.mpch-mainz.gwdg.de>). The data were reduced using the GLITTER 4.0 program.

4.3 Li concentration and isotope analyses of olivine

In-situ analyses of Li concentrations and isotopic ratios of olivine were carried out on gold-coated polished thin-sections using a Cameca IMS 1270 SIMS at the Edinburgh Ion Microprobe Facility, in the University of Edinburgh, United Kingdom. A $^{16}\text{O}_2$ primary ion beam with an intensity of 12-16 nA was accelerated to 22.5 kV and impacted onto the sample surface using Kohler illumination. The elliptical spot area was approximately $20 \times 30 \mu\text{m}$. The secondary ion beam position in the field aperture and the ^7Li peak position were automatically centered before each measurement during a 60-s pre-sputter without beam rastering. Secondary ions were counted in mono-collection, pulse-counting mode. Fifty cycles were measured with counting times of 6 and 2.5 s for ^6Li and ^7Li , respectively. The count rate for ^7Li ranged from 30,000 to 120,000 cps, depending on the Li concentration of the sample and primary beam intensity, resulting in 1 s uncertainties of $\delta^7\text{Li}$ of 0.5-1.2‰. Lithium concentrations were calculated using beam current corrected ^7Li count rates of samples using 06JY34Ol as a standard (Li concentration = 1.73 ppm; [Su et al., 2015](#)). The Li isotopic ratios are expressed as $\delta^7\text{Li}$ relative to the NIST L-SVEC standard $\{\delta^7\text{Li} = [(^7\text{Li}/^6\text{Li})_{\text{sample}}/(^7\text{Li}/^6\text{Li})_{\text{L-SVEC}} - 1] \times 1000\}$. Basaltic standards BCR2-G and ML3B-G were analyzed to monitor instrument drift, whereas 06JY34Ol ($\delta^7\text{Li} = 3.1\text{‰}$; [Su et al., 2015](#)) was used for calibration. Matrix composition (Fo

content) has an effect on measured olivine Li isotopic compositions; e.g., [Su et al. \(2015\)](#) showed that $\delta^7\text{Li}$ values increase by 1.0‰ for each mole percent decrease in the Fo content of olivine, and this was taken into account for calibration. As Fo contents of the olivines span a narrow range from 91.6 to 94.7, the matrix correction amounted to no more than 3‰, compared to a range of > 20‰ in $\delta^7\text{Li}$ for the whole dataset.

5. Results

5.1 Major oxide contents of minerals

Olivine in the Orhaneli and Harmancık dunites has Fo values of 92.4-94.0 and 91.6-93.5, respectively ([Table S1](#); [Fig. 4a-c](#)). The chromitites contain olivine with somewhat higher Fo values (92.6-94.7 in Orhaneli; 93.3-94.4 in Harmancık) than those in the dunites ([Table S1](#)). The dunites from the two ophiolites have similar MnO (0.06-0.15 wt.%) and NiO (0.23-0.44 wt.%) contents in their olivine ([Table S1](#)). In the Orhaneli and Harmancık profile analyses, the variations of Mn concentrations in olivines are not continuous and yield abrupt change at the contact with chromitite layers. Compared to Mn, Ni concentrations show the reverse patterns ([Fig. 5](#)).

Chromite grains in dunites of the both ophiolites are generally uniform in TiO_2 contents (0.14-0.23 wt.% in Orhaneli; 0.11-0.22 wt.% in Harmancık), similar to those in the chromitites (0.14-0.26 wt.% and 0.13-0.22 wt.%), whereas their Cr# ($100 \times \text{Cr}/(\text{Cr}+\text{Al})$) and Mg# ($100 \times \text{Mg}/(\text{Mg}+\text{Fe})$) values are variable within ranges of 79.1-81.8 and 47.6-53.5 in the Orhaneli dunites, 70.6-80.2 and 41.9-52.9 in the

Harmancık dunites, 81.1-82.8 and 58.7-67.3 in the Orhaneli chromitites and 78.8-80.0 and 46.4-64.2 in the Harmancık chromitites (Table S2; Fig. 4).

5.2 Trace element compositions of olivine

From base to top, the mantle-crust transition zone in the Orhaneli ophiolite includes many cyclic dunite and chromitite layers (Fig. 2a-b) with a total thickness of 90 m. Overall, olivines in chromitites show lower Co, Zn, Sc and V concentrations than those in dunites (Fig. 5a, b). The Co concentrations of olivine in the dunites (106-132 ppm in Orhaneli, 128-137 ppm in Harmancık) are higher than those of primitive mantle (105 ppm; McDonough and Sun, 1995), whereas the concentrations of Zn (6.0-44.8 ppm), Sc (2.14-3.68 ppm) and V (0.07-0.36 ppm) in all samples are lower than primitive mantle (Zn: 55 ppm; Sc: 16.2 ppm; V: 82 ppm; McDonough and Sun, 1995). The olivine in both dunites and chromitites from the two ophiolites has lower incompatible trace element concentrations (Ti = 4.0-7.8 ppm, Zr = 0.010-0.034 ppm, and Yb = 0.007-0.027 ppm) than the counterparts in olivine phenocrysts in MORB (Table S3; Fig. 6) (e.g., Piccardo et al., 2007; Foley et al., 2011). In the Orhaneli section and Harmancık drill hole samples, there is no apparent correlation between trace element compositions of olivine and the relative position of the layers (Figs. 5, 6).

5.3 Li concentrations and isotopic compositions

In the Orhaneli dunites, olivine has Li concentrations varying from 0.9 to 1.5 ppm, and $\delta^7\text{Li}$ from 3.7 to 11.0‰ (Fig. 7), with no correlation between Li concentrations and Li isotopic compositions (Fig. 8). In contrast, Li concentrations

(0.7 to 1.9 ppm) and $\delta^7\text{Li}$ values (-2.5 to 20.3‰) of olivine in the Harmancık dunites vary widely (Table S1), and the $\delta^7\text{Li}$ values are negatively correlated with the Li concentrations (Fig. 8). Most olivine grains in the two ophiolites show little change in Li concentrations and $\delta^7\text{Li}$ values from core to rim (Table S1). Nevertheless, different olivine grains in the same sample from Harmancık can have strongly variable Li isotopic compositions (up to 15‰ difference) (Table S1; Fig. 7). On the other hand, the chromitites from the two ophiolites display Li contents and $\delta^7\text{Li}$ values of olivine with 0.8 to 1.6 ppm and 5.0 to 14.7‰ in Orhaneli and 0.7 to 1.2 ppm and 4.1 to 15.6‰ in Harmancık (Table S1; Fig. 7).

6. Discussion

Based on trace elements and Li isotopes compositions of olivine in the dunites and chromitites from the mantle-crust transition zones for both ophiolites, we first evaluate the various processes that may account for the observed trace elemental and Li isotope variations, followed by models for the formation of dunites and chromitites.

6.1 Origin of mantle-crust transition zone dunites in the Orhaneli and Harmancık ophiolites

Dunite consists almost entirely of olivine and is usually formed by one of three processes (e.g., Su et al., 2016; Yao et al., 2018): 1) ultrahigh-degree partial melting of mantle with nearly all orthopyroxene being exhausted; 2) cumulate dunite left behind by the fractionation and accumulation of abundant olivine from an ultramafic-mafic

magma; 3) reaction between silica-undersaturated melt migrating in channels and pyroxene-rich wall rock triggering the formation of replacive dunite.

Cumulate dunites are formed via crystal accumulation from magmas and therefore olivine generally has low Fo (88-91) and feature a rapid decrease in the NiO content with decreasing Fo (Santos et al., 2002; Song et al., 2007; Arai et al., 2012; Seo et al., 2013; Su et al., 2016; Rospabé et al., 2018). Moreover, the coexisting chromites show a wide range of Cr# from 15 to 76 as well as high TiO₂ contents (up to 0.8 wt.%) (Santos et al., 2002; Song et al., 2007; Arai et al., 2012; Seo et al., 2013) (Fig. 4a-c). In contrast, olivine in replacive dunites generally has higher Fo values (up to 94), because the high-MgO melts reacting with peridotites convert olivine and pyroxene in peridotite to high-Fo olivine (Rollinson et al., 2018). Besides, no obvious correlation exists between the Fo and NiO of olivine grains within the replacive dunites (Mazzucchelli et al., 2009). In the Orhaneli and Harmancık dunites, olivine has higher Fo (91.6-94.0) and lower MnO contents (0.06-0.15 wt.%) than that from cumulate dunites, while chromites display higher Cr# (79.1-82.8) and lower TiO₂ contents (0.14-0.26 wt.%) (Fig. 4c-d). These observations, together with the absence of a clear correlation between Fo and NiO in olivine, demonstrate that the dunites from both ophiolites could not be related to fractional crystallization (Fig. 4b). Instead, all our data fall within the fields of replacive dunites (Fo: 90.4-94.6; MnO of olivine: 0.07-0.15 wt.%; Cr# of chromite: 23-89) (Suhr et al., 2003; Piccardo et al., 2007; Ackerman et al., 2009; Mazzucchelli et al., 2009; Oh et al., 2012; Sanfilippo et al., 2014, 2017) (Fig. 4), indicating that these dunites were formed by melt-peridotite

interaction rather than have a cumulate origin. Furthermore, although the olivines from these dunites show a good correlation between Ni and Mn, the correlation between Co and Mn is poor (Fig. 6b-c). According to olivine-melt partition coefficients (e.g., Beattie et al., 1991), Co and Ni are compatible in olivine, whereas Mn is incompatible, and hence segregation of olivine from its parental magma should produce a decrease of Co and Ni with increasing Mn (Sanfilippo et al., 2014). However, Co contents in olivine from the Orhaneli and Harmancık dunites are poorly correlated with Mn contents, and therefore incompatible with olivine fractionation and likely to be induced by melt migration.

For the Orhaneli and Harmancık ophiolites, the mineralogical and geochemical characteristics of mantle-crust transition zone dunites indicate that they were formed by melt-peridotite interaction: orthopyroxene + melt 1 → olivine + melt 2. In this reaction, melt 1 (reactant) is silica-undersaturated and melt 2 (product) is relatively enriched in SiO₂ and Cr₂O₃ due to progressive melt-rock reaction (e.g., Suhr, 1999; Zhou et al., 2005). Since the majority of all dunites are of refractory chemical nature and not akin to MORB (Figs. 4, 6), we argue that the reactant (melt 1) was highly depleted.

6.2 Origin of chromitites of the Orhaneli and Harmancık ophiolites

Olivines in Orhaneli and Harmancık chromitites have somewhat higher Fo than that contained in dunites, which likely implies an additional process for the chromitites. Subsolidus Mg-Fe exchange between olivine and chromite has been

usually reported in chromitites (e.g., [Xiao et al., 2016](#)):

The Mg diffuses from chromite to olivine and Fe from olivine to chromite. The compositional effect of Fe-Mg exchange on olivine depends on the elemental contents and relative modal abundances of olivine and chromite in the rocks ([Xiao et al., 2016](#)).

The Fe-Mg exchange effect on olivine in the dunites is negligible because of the extremely low amount of chromite. Recent studies (e.g., [Qian et al., 2010](#)) reported that despite differences in ionic size and charge, Sc and V diffuse at approximately similar rates to Mg, Fe and other divalent cations (e.g., Co and Zn). Cobalt and Zn are more compatible in chromite than in olivine, with crystal-melt partition coefficients from 8.3 to 2.1, and 7.9 to 3.6, respectively (<https://earthref.org>). Vanadium compatibility decreases in the order of chromite >> pyroxene >> olivine ([Witt-Eickschen and O'Neill et al., 2005](#)). In addition, the partitioning of Sc between chromite and olivine is strongly dependent upon the major element composition of chromite ([Stosch et al., 1981](#)). Thus, as expected, Co, Zn, Sc and V concentrations of olivine in the Orhaneli profile and Harmancık chromitites are lower than those in the associated dunites ([Figs. 5a-b](#)), which points to the relative modal abundances of chromite and olivine being a factor in determining the Sc, V, Co and Zn concentrations in olivine in chromitites ([Xiao et al., 2016](#); [Zhang et al., 2017](#)). For example, in the Orhaneli profile, chromitite sample (+50 m) contains the highest modal amount of chromite and its olivine has the lowest Co, Zn, Sc and V concentrations ([Fig. 5a](#)).

Mantle-derived magmas generally have ca. 500 ppm Cr concentrations, whereas the chromites derived from these melts contain 30-50 wt.% Cr₂O₃ (Zhou et al., 2014; Zhang et al., 2017). During the evolution of magmatic systems, the oversaturation of chromite in the magma is an important factor for the formation of chromitite. Addition of silica to magmas has been widely accepted as a means of triggering chromite precipitation, because SiO₂ addition can decrease Cr solubility (Irvine et al., 1986). The increase in silica has been usually attributed to assimilation/reaction of more siliceous materials or magma mixing (e.g., Arai et al., 2004; Zhou et al., 1994, 2014; Zhang et al., 2017). In this regard, chromitites in the Orhaneli and Harmancık mantle-crust transition zones are exclusively associated with dunites, and hence it is unlikely that the oversaturation of chromite was caused by extensive assimilation of siliceous-rich crust. Instead, the oversaturation of chromite induced by magma mixing becomes the most likely scenario here. Mantle-derived mafic magma A rises through the upper mantle and mixes with more Si-rich and Cr-rich magma (e.g., Lissenberg and Dick, 2008), upon which the newly-formed, mixed magma B would move into the field of chromite crystallization (Fig. 9). Additionally, the residual melt (melt 2) following melt-peridotite reaction and orthopyroxene dissolution will also be enriched with Cr and SiO₂ relative to the infiltrating melt (Arai and Yurimoto, 1995). Therefore, it would further facilitate the oversaturation of chromite in the mixed magma (Zhou et al., 1994, 2014; Su et al., 2019), driving crystallization of abundant chromite and forming chromitite layers. Due to precipitation of chromite, mixed magma 'B' would evolve to point 'C', i.e., back to the chromite-olivine cotectic line.

6.3 Origin of infiltrating melts

During melt-peridotite interaction, trace elements between minerals and melts can be redistributed. The trace elements of olivine in the Orhaneli and Harmancık dunites do not show any zoning (Tables S1, S3), indicating that they were fully equilibrated with the percolating melts. Since dunites predominantly consist of olivine grains, and other silicate minerals (e.g., pyroxene) are rare or absent, the trace element concentrations of olivine cannot be affected by subsolidus re-equilibration among silicate minerals. Thus, the olivine trace elements can be used to trace the composition of the melt in chemical equilibrium with these crystals. The lower incompatible trace element concentrations (Zr, Ti and HREE) in olivines from the Orhaneli and Harmancık dunites relative to those of the olivines from the lower crustal sections of ophiolites (Sanfilippo et al., 2014) (Fig. 6a) indicate that our dunites are not in equilibrium with a melt derived from the lower oceanic crust. In addition, compared to mantle harzburgites of the Orhaneli and Harmancık ophiolites (chromite Cr#: 43-55; Fo < 91.6) (Uysal et al., 2017), the mantle-crust transition zone dunites have Cr# in chromite of 79-82, NiO in olivine of 0.2-0.4 wt.% and Fo of 91.6-94.0, which are far more refractory. The Mn and Co abundances of olivines in both the Orhaneli and Harmancık dunites are lower than those of olivine phenocrysts within MORB (Sobolev et al., 2007) (Fig. 6b-c), in conjunction with the lower trace-element concentrations relative to primitive mantle (McDonough and Sun, 1995), suggesting that these dunites were equilibrated with melts that are more depleted than MORB

(e.g., [Piccardo et al., 2004](#); [Sanfilippo and Tribuzio, 2011](#)).

We can use the composition of the chromitites to put further constraints on the composition of its parental melts. In contrast to the incompatible elements, diffusion of compatible elements Cr, Al and Ti out of chromite is negligible ([Abily and Ceuleneer, 2013](#)), because Al and Ti enter olivine and/or serpentine in only very low amounts (e.g., [Kamenetsky et al., 2001](#)). As a consequence, we can use these elements to calculate the composition of equilibrated melts based on chromite compositions. The TiO₂ content of chromite is a key indicator of tectonic setting of where chromitite forms (e.g., [Kamenetsky et al., 2001](#)). The Orhaneli and Harmancık chromites have very low TiO₂, and plot in the arc or boninitic fields ([Fig. 10a-b](#)), suggesting crystallization from low-Ti island arc tholeiitic melts or boninitic melts. In addition, several studies have also shown that chromite compositions in chromitites reflect the composition of their parental melt ([Kamenetsky et al., 2001](#); [Rollinson, 2008](#); [Zhou et al., 2014](#); [Rollinson and Adetunji, 2015](#); [Chen et al., 2019](#)). The following equations were proposed by [Rollinson and Adetunji \(2015\)](#) to more closely reflect the empirical correlations defined by [Kamenetsky et al. \(2001\)](#) and applies to melt with an arc affinity:

$$(\text{Al}_2\text{O}_3)_{\text{melt}} = 5.2181 \times \ln(\text{Al}_2\text{O}_3)_{\text{Chr}} - 1.0505 \text{ (Eq. 2)}$$

$$(\text{TiO}_2)_{\text{melt}} = 1.0963 \times (\text{TiO}_2)_{\text{Chr}}^{0.7863} \text{ (Eq. 3)}$$

The implementation of equations (2) and (3) demonstrates that the melts in equilibrium with chromitite have the following composition: 9.8-10.8 wt.% Al₂O₃ and 0.23-0.38 wt.% TiO₂ in Orhaneli, and 10.7-11.4 wt.% Al₂O₃ and 0.22-0.33 wt.% TiO₂

in Harmancık. The inferred parental melts of the chromitites from the two ophiolites have similar Al_2O_3 and TiO_2 contents to boninitic melts (Fig. 10c), suggesting that the Orhaneli and Harmancık chromitites possibly originated in a forearc setting during the early stage of subduction. The zigzag pattern (Fig. 5) of the olivine trace element contents in the chromitites from the Orhaneli profile and Harmancık drill hole, in conjunction with the widespread occurrence of interlayered chromitites and dunites, could be the witness of multiple magma replenishments in the mantle-crust transition zone.

6.4 Lithium isotope constraints on the origin of Orhaneli and Harmancık dunites and chromitites

Due to the highly depleted composition of dunites and chromitites, traditional chemical indicators of tectonic setting can generally not be applied. However, Li isotope systematics of olivine may provide clues about the tectonic setting of the infiltrating melts. High-temperature partial melting is thought to induce negligible Li isotope fractionation (e.g., Tomascak et al., 1999; Ionov and Seitz, 2008) and Jeffcoate et al. (2007) estimated that the $\delta^7\text{Li}$ value of magmas generated by equilibrium melting would be $< 0.5\text{‰}$ different from their source. In addition, most studies have shown that Li isotopes do not fractionate during fractional crystallization of silicate magmas (e.g., Tomascak et al., 1999; Teng et al., 2006). Many studies also demonstrated that diffusion is an important mechanism controlling Li abundances and isotopic distribution (e.g., Su et al., 2014; Tomascak et al., 2016). Lithium

concentrations and isotopes do not show core-to-rim zoning in individual olivine grains in most samples of the Orhaneli and Harmancık ophiolites (Table S2), and chromite contains little or no Li (e.g., Jeffcoate et al., 2007; Chen et al., 2019). Thus, the Li isotopic compositions of olivine have not been affected by inter-mineral diffusion. Therefore, the Li isotopic compositions of olivines in the Orhaneli and Harmancık dunites record the history of melt-rock interaction.

Compared to typical mantle peridotites with $\delta^7\text{Li}$ values of 2-6‰ and 1.0-1.8 ppm Li (Seitz and Woodland, 2000; Su et al., 2014), the olivines from the Orhaneli dunites show a similar range of Li concentrations (0.9-1.5 ppm), but a slightly larger range of $\delta^7\text{Li}$ values (+4.0 to +11.0‰) (Table S1; Figs. 7, 8), offset to higher values. As the samples are relatively homogeneous (1s 0.8-1.7‰ based on multiple olivine analyses in each sample) (Fig. 7) and the olivines are unzoned, these samples likely reached Li isotope equilibrium during rock-melt interaction, and therefore could reflect the composition of the infiltrating melt. Average $\delta^7\text{Li}$ per sample shows a more restricted range from +4.8 to +8.7‰ with 1.1-1.3 ppm Li, suggesting reaction with relatively homogeneous melt batches.

The Orhaneli chromitites have somewhat higher $\delta^7\text{Li}$ values (average $\delta^7\text{Li}$ per sample +6.0 to +10.6‰ with 1.0-1.3 ppm), but the two samples with highest $\delta^7\text{Li}$ shows considerable heterogeneity (based on multiple olivine analyses in each sample) of > 4-7‰ even though individual olivines are unzoned. Excluding these samples, the range of Orhaneli chromitites is +6.0 to +8.2‰, an even smaller range than the dunites. These Li isotopic characteristics could be attributed to infiltrating melts in a

subduction zone setting. Dehydration of altered oceanic crusts during subduction can induce that the Li isotope fractionation generates isotopically heavy-Li fluids and light-Li slab residues (e.g., Elliott et al., 2004; Penniston-Dorland et al., 2017), but the Li isotopic range of arc lavas (-1 to +12‰) reflects the heterogeneity of the altered oceanic plate and overlying sediments (Tomascak et al., 2002; Elliott et al., 2004). Mixing of various slab components and re-equilibration with Li already present in the mantle wedge results in arc lavas with $\delta^7\text{Li}$ values that only slightly extend beyond that of MORB. The dominance of $\delta^7\text{Li}$ values in the Orhaneli mantle-crust transition zone that extends well beyond the MORB/mantle peridotite range point to a ubiquitous subducting slab component present in the infiltrating melts. The survival of these signatures suggests that the source of the interacting agent was rather shallow, as Li isotopic signatures will re-equilibrate with ambient mantle at short length and timescales (Halama et al., 2009). This is consistent with a subduction initiation.

Compared to Orhaneli, olivine from the Harmancık dunites shows much larger $\delta^7\text{Li}$ variations of -2.5‰ up to +20.3‰, but also larger sample heterogeneity, with only one sample having a ranging of $\delta^7\text{Li}$ of < 3‰ (Figs. 7, 8). The Harmancık dunites were considerably more altered than the Orhaneli dunites, but the olivine grains selected for Li isotope analyses were fresh and unzoned, and hence the influences of alteration (such as serpentinization) on $\delta^7\text{Li}$ values between different grains are likely to be small (e.g., Lundstrom et al., 2005). The larger range of $\delta^7\text{Li}$ values in the Harmancık dunite may indicate the infiltrating melts with a wider range of $\delta^7\text{Li}$ values, especially given that the slab-derived fluids and melts have a broad

range of compositions and are highly variable from one location to another (Elliott et al., 2004; Yao et al., 2018). However, the heterogeneous distribution of $\delta^7\text{Li}$ in individual samples from the Harmancık dunites and the negative correlation between $\delta^7\text{Li}$ values and Li concentrations is indicative of incomplete diffusive equilibration between olivines and infiltrating melts (Fig. 8) (e.g., Jeffcoate et al., 2007; Penniston-Dorland et al., 2017), which is consistent with the studies of olivine Li isotope of dunite from Trinity ophiolite (Lundstrom et al., 2005) and Luobusa ophiolite (Su et al., 2016). Many studies have demonstrated that ^6Li diffuses about 2-3% faster than ^7Li through melts and minerals (e.g., Lundstrom et al., 2005; Teng et al., 2006). As Li diffuses from percolating melt into olivine, the $\delta^7\text{Li}$ of olivine will become lower at first, but will then increase to higher values until $\delta^7\text{Li}$ equilibrates with that of the infiltrating melt, due to equilibrium partitioning (Lundstrom et al., 2005). During this process, temperature and time are the fundamental parameters that control the efficiency of the isotopic exchange (Tomascak et al., 2016). We, therefore, estimated the equilibration temperatures of the Harmancık and Orhaneli dunites and chromitites based on the Al (Coogan et al., 2014) and Mg-Fe exchange (Ballhaus et al., 1991) between olivine and chromite (Table 1). The Al-in-olivine thermometry results (Coogan et al., 2014) show that the temperature range for Harmancık dunites (933-979°C) is similar to that of the Orhaneli suite (960-993°C), while Mg-Fe exchange temperatures (Ballhaus et al., 1991) are considerably lower: 714-778°C for Orhaneli dunites and 663-755°C for Harmancık dunites. This suggests no significant difference in temperature between Harmancık and Orhaneli ophiolites, so this cannot

explain the heterogeneity of the Harmancık samples. The main another factor of diffusion is time. Richter et al. (2014) found that very large lithium isotopic fractionations persisted after the lithium concentration had become effectively homogenized during diffusion process, suggesting that it still takes longer for the isotopic composition to become uniform compared to the time it takes for diffusion to homogenize the total lithium concentration. Thus, if infiltration of melts into the rocks occurred shortly before obduction and exhumation, Li isotopes would not fully equilibrate, and isotope heterogeneity would be preserved during relatively rapid cooling. Heterogeneities in the Harmancık samples could indicate rapid cooling was essential to preserve the observed isotope heterogeneities.

In summary, excluding two heterogeneous samples (Fig. 7), the Li isotope signatures of olivine in dunites and chromitites from the Orhaneli ophiolite are likely primary features inherited from their parental melts, with all olivines falling between $\delta^7\text{Li}$ values of +5‰ and +9‰, which is within the range of arc lavas but isotopically heavier than MORB (Fig. 7) (Chan et al., 2002; Tomascak et al., 2002), suggesting an affinity with arc magmatism. The olivine Li isotopic compositions of Harmancık mantle-crust transition zone chromitites are similar to those from Orhaneli, but still, likely have diffusional heterogeneities due to incomplete equilibration between infiltrating melt and olivine. Nevertheless, their average compositions (+6 to +11‰) does suggest a melt source similar to the one that crystallized Orhaneli chromitites.

The estimated Al_2O_3 and TiO_2 contents of the parental magmas of chromitites in the two ophiolites are similar to the signatures of boninitic melts. Given that boninitic

magmas have been widely found in preserved fore-arcs related to subduction initiation (e.g., [Reagan et al., 2017](#); [Stern et al., 2012](#)), this suggests that the Orhaneli and Harmancık ophiolites possibly originated in a subduction initiation setting, which gives additional support to studies suggesting that these settings represent an ideal environment for forming ophiolites with economically viable chromitite deposits ([Johnson, 2012](#)).

7 Conclusions

This study presents in-situ trace elements and Li isotopic compositions of olivine in dunites and chromitites from the Orhaneli and Harmancık mantle-crust transition zone. The following conclusions can be drawn:

1. Compared to olivine from cumulate dunites, the olivine in the Orhaneli and Harmancık dunites is distinct by higher Ni, lower Mn concentrations and extreme depletion of incompatible trace elements (Ti, Zr and HREE), which are consistent with the formation of dunites driven by interaction of peridotite with depleted melts.
2. The relatively uniform Li isotopic compositions (+4 to +11‰) of olivines from Orhaneli dunites indicate these samples reached Li isotope equilibrium, and suggest a reaction driven by relatively homogeneous melt batches with a subduction component, whereas the large $\delta^7\text{Li}$ variations (-2.5 to +20.3‰) in olivine from Harmancık dunites reflect incomplete diffusive equilibration during the melt percolation through these dunites.

3. The formation of chromitites in the mantle-crust transition zone of the two ophiolites was likely triggered by the magma mixing. The calculated Al_2O_3 (9.8-11.4 wt.%) and TiO_2 (0.22-0.38 wt.%) contents of the parental magmas of chromitites demonstrate a boninite-like geochemical affinity, i.e., a subduction initiation setting, which is in good agreement with the Li isotopic compositions of their olivines.
4. In contrast to the dunites, the higher Fo contents of olivine in the chromitites could be caused by the Mg-Fe exchange between olivine and chromite. The lower Sc, V, Co and Zn concentrations of olivine in the chromitites are controlled by the modal abundances of chromite.

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Figure Captions:

Fig. 1 (a) Map showing distribution of the continental blocks, major sutures and related ophiolites in the Eastern Mediterranean region (modified after [Chen et al., 2018](#)). (b) Simplified geological map of the Orhaneli and Harmancık ophiolites (after [Uysal et al., 2015](#)). Red stars in (b) are the sampling locations. IASZ: Izmir-Ankara Suture Zone; ITSZ: Inner-Tauride Suture Zone; BZSZ: Bitlis-Zagros Suture Zone.

Fig. 2 Photographs of field sites with numbered sampling locations and hand specimens of dunites and chromitites from the Orhaneli mantle-crust transition zone.

(a) Banded chromitites that occur by the rhythmic layering of chromitite and dunite.

(b) Banded chromitite. (c) Disseminated chromitite.

Fig. 3 Back scattered electron images of thin sections of dunites and chromitites from the Orhaneli (a)-(c) (sample Ol-1, 2-2 and 4-2) and Harmancık (d) (sample 71.5 m) ophiolites.

Fig. 4 Plots of (a) MnO vs. Fo of olivine, (b) NiO vs. Fo of olivine, (c) Cr# of chromite vs. Fo, and (d) Cr# vs. TiO₂ of chromite in dunites from the Orhaneli and Harmancık ophiolites. The gray and pink fields represent literature olivine/chromite composition ranges of cumulate dunites and dunites formed by peridotite-melt interaction, respectively. The cumulate dunite field is defined using data from Santos et al. (2002), Song et al. (2007), Arai et al. (2012) and Seo et al. (2013). The replacive dunite field is defined using data from Suhr et al. (2003), Piccardo et al. (2007), Ackerman et al. (2009), Mazzuchelli et al. (2009), Oh et al. (2012), Sanfilippo et al. (2014, 2017).

Fig. 5 Elemental (Fo, Ni, Mn, Li, Co, Zn, Sc and V) and isotopic ($\delta^7\text{Li}$) variations of olivine compositions in the Orhaneli profile (a) and Harmancık drill hole (b). Olivine grains from dunites are shown as blue circles, whereas pink circles are olivine grains from chromitites. Scanned photographs of dunites and chromitites are shown to clearly describe the effect of chromite proportion on olivine trace element

compositions.

Fig. 6 (a) Primitive mantle-normalized pattern of olivine in the dunites from Orhaneli and Harmancık ophiolites. Plots of (b) Ni (ppm) vs. Mn (ppm), (c) Co (ppm) vs. Mn (ppm) of olivine in the dunites from the two ophiolites. Primitive mantle values are from Anders and Ebihara (1982). Compositions of lower crust data in (a) are from Sanfilippo et al. (2014, 2017) and Rampone et al. (2016). The compositions of olivine phenocrysts in MORB are from Sobolev et al. (2007).

Fig. 7 Li isotopic compositions of olivines in dunite and chromitites from the Orhaneli and Harmancık ophiolites. The $\delta^7\text{Li}$ range of MORB is from Tomascak et al. (2008), and the $\delta^7\text{Li}$ range of arc lava is from Tomascak et al. (2002) and Chan et al. (2002).

Fig. 8 Diagram of $\delta^7\text{Li}$ vs. Li of olivine in the Orhaneli and Harmancık dunites. The arrow is the trend of Li diffusion during melt-rock interaction (after Lundstrom et al. (2005)).

Fig. 9 A petrologic model for chromitite formation in the Orhaneli and Harmancık ophiolites in the simplified system olivine (Ol) - quartz (Q) - chromite (Chr). The trends in the phase diagrams are after Zhou et al. (1994) and Zhang et al. (2017).

Fig. 10 (a) TiO_2 vs. Al_2O_3 (after Kamenetsky et al., 2001 and Derbyshire et al., 2013),

879 (b) Cr# vs. TiO_2 (after [Pearce et al., 2000](#)) of chromite in the chromitites and (c) TiO_2
880 vs. Al_2O_3 (after [Peighambari et al., 2016](#)) of parental melts for the Orhaneli and
881 Harmancık chromitites. FMM: fertile MORB mantle. The subscripts b and I represent
882 boninite and island arc tholeiite, respectively. BON: boninite; IAT: island arc tholeiite;
883 MORB: mid-ocean ridge basalt. Data of grey hexagons, triangles and circles
884 representing lherzolite, harzburgite and dunite, respectively, are from [Uysal et al.](#)
885 [\(2014\)](#).

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Table 1. Equilibrium temperature estimates for dunite and chromitite samples from the Orhaneli and Harmancık ophiolites

		T(Al-ol) ^a	T Ballhaus (°C) ^b
Orhaneli ophiolite			
90 m	Dunite	967	714
90 m	Dunite	960	724
80 m	Dunite	993	760
70 m	Dunite	974	778
25 m	Dunite	965	720
5 m	Dunite	973	754
average		972	742
60 m	Chromitite	977	754
50 m	Chromitite	982	828
40 m	Chromitite	971	779
30 m	Chromitite	973	863
20 m	Chromitite	969	840
10 m	Chromitite	982	839
0 m	Chromitite	973	940
average		975	835
Harmancık ophiolite			
63.4 m	Dunite	960	755
65.6 m	Dunite	979	719
66.6 m	Dunite	964	750
67.1 m	Dunite	937	691
68.5 m	Dunite	953	663
69.2 m	Dunite	966	682
70.1 m	Dunite	933	690
73.4 m	Dunite	972	724
average		958	709
65.9 m	Chromitite	985	767
70.8 m	Chromitite	984	858
71.5 m	Chromitite	1009	744
72.8 m	Chromitite	991	624
average		992	748

Supplementary material/Appendix (Files for online publication only)

[Click here to download Supplementary material/Appendix \(Files for online publication only\): Data Repository.docx](#)

Conflicts of Interest Statement

Manuscript title: **Formation processes of dunites and chromitites in Orhaneli and Harmancık ophiolites (NW Turkey): evidence from in-situ Li isotopes and trace elements in olivine**

The authors whose names are listed immediately below certify that they have **No** affiliations with or involvement in any organization or entity with any financial interest (Such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationship, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

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