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A new model for chromitite formation in ophiolites: Fluid immiscibility

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Abstract Although the involvement of hydrous fluids has been widely invoked in formation of podiform chromitites in ophiolites, there is lack of natural evidence to signify the role and mechanism of fluids. In this study, a new model for the genesis of podiform chromitite is proposed on basis of revisits of comprehensive petrological, mineralogical and geochemical results of the well-preserved Kızıldağ ophiolite and the well-characterized Luobusa chromite deposit. In this model, ascending magmas intruding oceanic lithospheric mantle would presumably form a series of small magma chambers continuously connected by conduits. Tiny chromite nuclei would collect fluids dispersed in such magmas to form nascent droplets. They tend to float upward in the magma chamber and would be easily transported upward by flowing magmas. Chromite-rich droplets would be enlarged via coalescence of dispersed droplets during mingling and circulation in the magma chamber and/or transport in magma conduits. Crystallization of the chromite-rich liquid droplets would proceed from the margin of the droplet inward, leaving liquid entrapped within grains as precursor of mineral inclusions. With preferential upward transportation, immiscible chromite-rich liquids would coalesce to a large pool in a magma chamber. Large volumes of chromite would crystallize *in situ*, forming podiform chromitite and resulting in fluid enrichment in the chamber. The fluids would penetrate and compositionally modify ambient dunite and harzburgite, leading to significant fractionations of elemental and isotopic compositions between melts and fluids from which dunite and chromitite respectively formed. Therefore, fluid immiscibility during basaltic magma ascent plays a vital role in chromitite formation.

Keywords Chromitite, Fluid immiscibility, Mineral inclusion, Ophiolite

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1. Introduction

Podiform chromitites in ophiolites are unique deposits that form in the mantle and are hosted mainly in mantle peridotites. Numerous hypotheses on the mechanism of chromitite formation have been proposed over the years, including hydrothermal activity (e.g., Fisher, 1929), fractional crystallization (e.g., Lago et al., 1982), partial melting (e.g., Bao et al., 1999), melt-rock interaction (e.g., Arai and Yurimoto, 1994; Zhou et al., 1994), and mantle plume (e.g., Xiong et al., 2015; Yang et al., 2015). However, individual hypotheses only explain partial features of ophiolitic chromitite deposits, resulting in many challenges to our understanding of their geology and geochemistry (González-Jiménez et al., 2014; Arai and Miura,

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2016; Chen and Yang, 2018; Su et al., 2018a). In particular, the discovery of exotic minerals in many ophiolites (e.g., ultra-high pressure, super-reduced and crustal phases) (Robinson et al., 2004, 2015; Yang et al., 2007, 2015; Xiong et al., 2016) has raised many problems with former models.

After reviewing the evidence supporting a hydrothermal model for chromitite formation, which has been abandoned for many years, we found that widespread serpentinization, as postulated in this hypothesis, is typical of most podiform chromitites (Fisher, 1929; Arai and Miura, 2016; Su et al., 2018a, 2020). In particular most chromitites are more highly serpentinized than the surrounding dunites and harzburgites, and the extent of alteration of silicate minerals correlates positively with the modal abundance of chromite in the rocks (Su et al., 2020). These features imply that such alteration is mostly "self-alteration" owing to high water contents in silicates when they formed, and the water originated from fluids that collected on chromite grain surfaces (Matveev and Ballhaus, 2002; Su et al., 2018a, 2020). On the other hand, many ophiolitic chromitites contain inclusions of hydrous silicates (mainly pargasitic amphibole and phlogopite), which also may form the interstitial matrix between chromite grains (e.g., Melcher et al., 1997; Jannessary et al., 2012; Su et al., 2020). Some solid inclusions are also accompanied by fluid or melt inclusions (Melcher et al., 1997; Sachan et al., 2007). However, it is still uncertain how fluids facilitate the chromite nucleation, growth, and then accumulation to form a chromitite. Matveev and Ballhaus (2002) observed that in immiscible basalt-water systems saturated with olivine and chromite, olivine crystals reside in the melt while chromite grains collect in the fluid phase. This physical fractionation is driven by the differential wetting of melt and fluid against silicate and oxide surfaces. This is an effective mechanism for the accumulation of large amounts of chromite accompanied by lesser amounts of olivine.

The experimental results mentioned above, together with geochemical fingerprints from microanalysis of minerals, call for an updating and a critical review of the genetic models for the origin of podiform chromitites in ophiolites. In this contribution, we investigated mineral inclusions in chromite and compiled bulk-rock platinum-group elements (PGEs) and Re-Os isotopes of the Kızıldağ ophiolitic rocks to further investigate the role of fluid immiscibility in chromitite formation. Published elemental and isotopic data of minerals from the Kızıldağ and Luobusa ophiolites are also revisited to supplement the new data, and a new fluid immiscibility model is proposed that takes into account the role of fluids in the genesis of podiform chromitite.

2. Mineral inclusion evidence of fluid immiscibility

The Kızıldağ ophiolite in southeastern Turkey preserves a complete ophiolitic sequence (Dilek and Delaloye, 1992; Dilek and Furnes, 2009) and contains tens of chromitite deposits (Chen et al., 2015, 2019). Podiform chromitites in this ophiolite are enveloped by dunites in host harzburgites. Their silicate matrices consist of olivine and/or clinopyroxene (Figure 1a; Chen et al., 2019; Su et al., 2020). Chromite grains in chromitites are highly variable in size ranging from ~2 cm to <0.1 mm. Large grains are mostly anhedral with well-defined grain boundaries, whereas smaller ones are commonly round (Figure 1a). Mineral inclusions are widespread in large chromite grains but rare in very small grains.

2.1 Morphology of inclusions

Inclusions range up to a maximum diameter of 0.2 mm but are mostly less than 50 μm. They generally have round to subhedral outlines, and relatively large inclusions invariably occur at or near the grain centers (Figure 1a). Some chromite grains contain several inclusions that are randomly distributed; a few grains contain linear and curved bands of inclusions, whereas others are free of inclusions (Figure 1a). Many irregular silicate inclusions are surrounded by a band of chromite (Figure 1b, 1c; Borisova et al., 2012). Some appear to fill negative crystals in chromite grains and apparent crystal faces of host chromite project into the silicate inclusion in some grains (Figure 1d).

Multiple mineral phases can occur in individual inclusions (Figure 1b–1l). Silicate minerals include clinopyroxene, orthopyroxene, olivine, phlogopite and amphibole, which are similar to those reported in chromite from other ophiolites (Melcher et al., 1997; Borisova et al., 2012; Zhou et al., 2014; Liu et al., 2018; Rollinson et al., 2018). They may coexist with each other as multi-phase inclusions (Figure 1c, 1e, 1f, 1g), and some silicate phases themselves contain inclusions of apatite (Figure 1d), fine-grained chromite (Figure 1h), or are associated with calcite (Figure 1i), sulfide and/or metal alloy (Figure 1j, 1k). Platinum group elements (PGEs) typically occur in the form of sulfides or alloys. Iridium-bearing PGE phases (IPGM) are mostly restricted to the interior parts of chromite grains (Figure 1j, 1k), whereas platinum-bearing PGE minerals (PPGM) are typically along grain margins (Figure 1l). These platinum group minerals are particularly abundant in clinopyroxene-bearing chromitites. Globules of native Au are also present in some chromite grains (Figure 1m); these are similar to Fe-rich immiscible globules in Si-rich liquids (Charlier and Grove, 2012).

2.2 Chemical compositions of clinopyroxene inclusions

Clinopyroxene is the most common inclusion in the Kızıldağ chromitites, and it can coexist with any of other phases (Figure 1). Thus, its composition provides an effective means of infering the origin of mineral inclusions in chromite. The

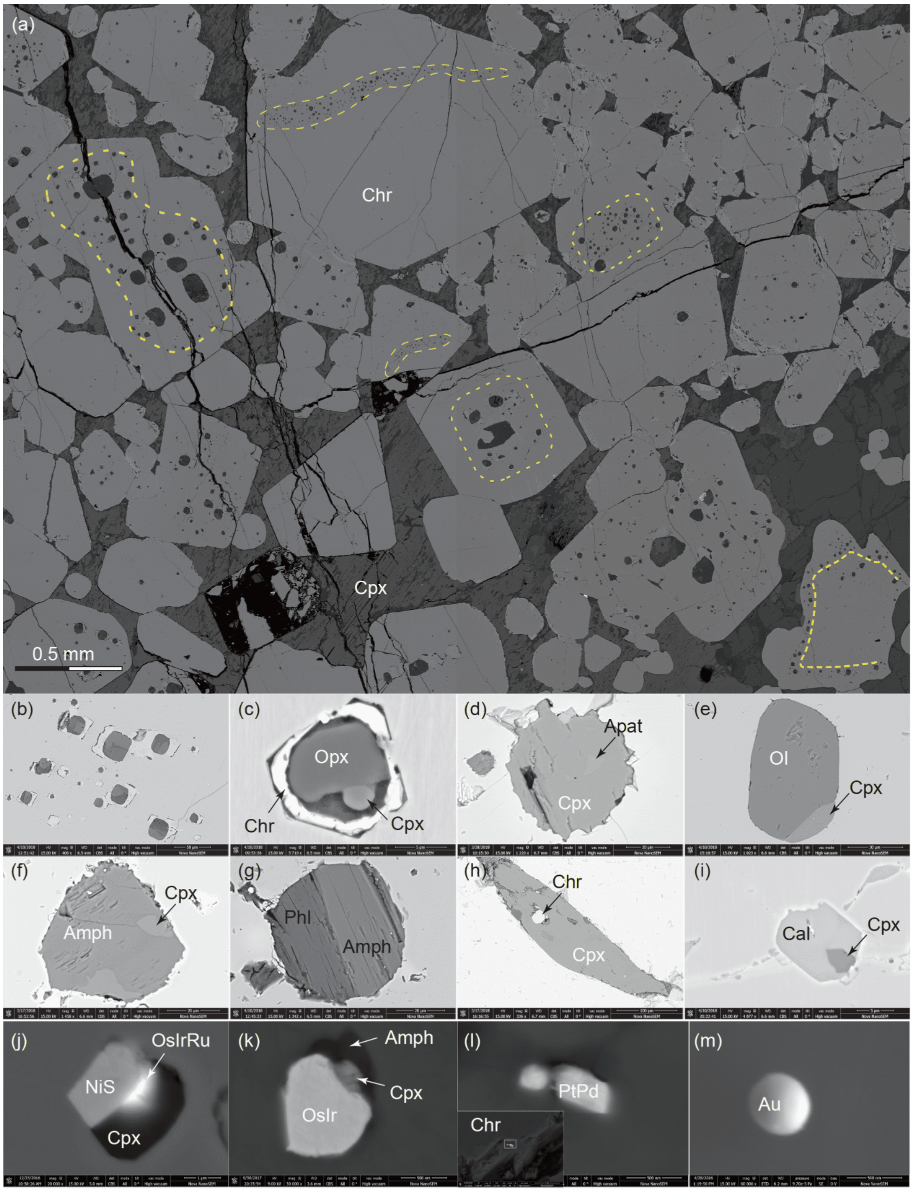

Figure 1 Mineral inclusions in chromite (Chr) in the Kızıldağ chromitites. (a) Sample KZ40-2: general occurrence and distribution of mineral inclusions; (b) KZ40-2: silicate inclusion surrounded by a band of high-Cr Chr; (c) TK57-13: association of clinopyroxene (Cpx) and orthopyroxene (Opx) surrounded by high-Cr Chr; (d) KZ14-27-2: Cpx inclusion enclosing apatite (Apat); (e) TK55-3: association of Cpx and olivine (Ol); (f) KZ15-25: association of Cpx and amphibole (Amph); (g) KZ40-2: association of phlogopite (Phl) and Amph; (h) KZ15-31: Cpx inclusion enclosing Chr; (i) TK57-11: association of Cpx and calcite (Cal); (j) KZ15-37: association of Os-Ir-Ru alloy, Ni sulfide and clinopyroxene; (k) KZ14-29: association of Os-Ir alloy, Cpx and Amph; (l) KZ14-27-1: Pt-Pd alloy occurring in the margin of Chr grain; (m) KZ15-30: globule native Au.

clinopyroxene inclusions analyzed in this study have variable Na_2O (0.16–0.68 wt.%), Al_2O_3 (mostly 0.70–2.03 wt.% but up to 4.25 wt.%) and Cr_2O_3 (1.14–2.12 wt.%) (Supplementary Table S1, http://link.springer.com). They are considerably richer in CaO (22.1–24.8 wt.%) and Cr_2O_3, and more depleted in TiO_2 (mostly 0.05–0.13 wt.% but up to 0.44 wt.%) and FeO (1.21–2.11 wt.%) with higher Mg# of 93.6–95.8 than clinopyroxenes from MORB and boninite (Figure 2). Instead, their compositional features are comparable to those of clinopyroxenes enclosing chromite in chromitites and those associated with chromite in dunites and harzburgites (Figure 2), which are thought to have crystallized from a melt-fluid mixture (Su et al., 2020).

3 Origin and formation of mineral inclusions

3.1 Trapped liquid during chromite growth? Nuclei of chromite crystallization? Or trapped liquid during late-stage chromite recrystallization?

Primary origin of fluid and/or melt inclusions in minerals is commonly regarded as captured liquid phases during crystal

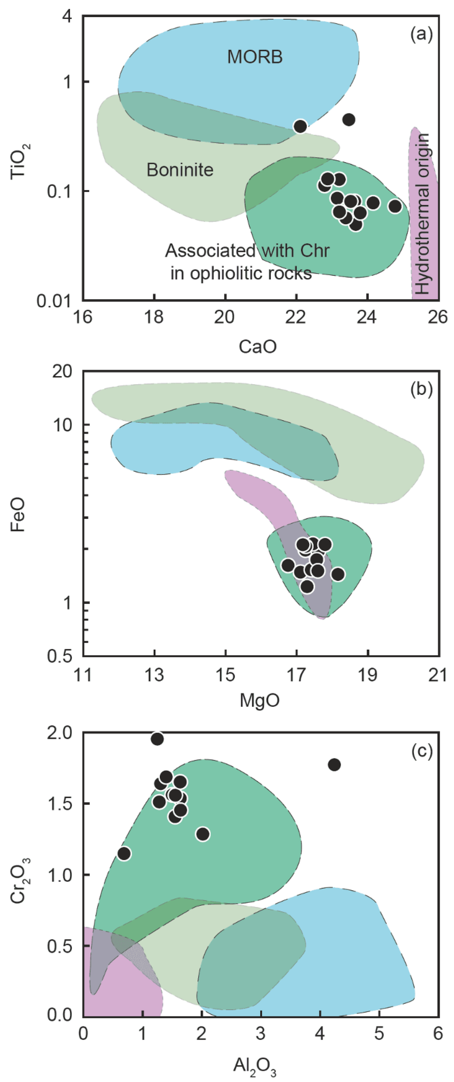

Figure 2 Compositions of clinopyroxene inclusions in chromite in the Kızıldağ chromitites. Fields of clinopyroxene associated with chromite in ophiolitic rocks, clinopyroxene in boninites and mid-ocean ridge basalts (MORBs), and hydrothermal clinopyroxene are from Su et al. (2020) and references therein.

growth. During chromite crystal growing from a nucleus, silicate melts could be trapped by dendrites and then conceivably crystallized polymineral silicate inclusions (Lorand and Ceuleneer, 1989; Liu et al., 2020). However, the large size and variety of the observed inclusions, their preferential distribution in the centers of chromite grains, and presence of border zones of small irregular inclusions around a main inclusion (Figure 1) present formidable objections to such an explanation for their formation (McDonald, 1965).

Mineral inclusions in chromite grains may represent nuclei around which chromite crystallization occurred. If this were the case, they should consist exclusively of olivine or clinopyroxene as these are the only silicate minerals crystallizing nearly contemporaneously with chromite. All the other mineral inclusions in chromite should have theoretically crystallized later than chromite but they do not form interstitial grains in the chromitites (Figure 1). Textural relationships of inclusions in the chromite grains indicate that the silicates crystallized later than the enclosing chromite. Marginal irregularity of inclusions was governed by the negative crystal outline of chromite. Inclusions acting as nuclei for chromite crystallization are presumably monomineralic and possess rudimentary crystal outlines (McDonald, 1965; Liu et al., 2020). However, inclusions in the chromite grains from the ophiolitic chromitites are typically polymineralic and subangular to spherical. Thus, it is unlikely that these inclusions could have acted as nuclei for chromite crystallization.

Recrystallization of chromite during post-magmatic hydrothermal activity may trap liquids that could crystallize to form inclusions (Lorand and Ceuleneer, 1989; Melcher et al., 1997; Johan et al., 2017). Such inclusions would most likely distribute at the margins of chromite grains, and may be connected to or optically continuous with similar interstitial materials surrounding the grains (McDonald, 1965). Inclusions of this type would normally be monomineralic. Thus, the multi-phase and centrally-located inclusions studied here were not formed in this manner.

3.2 Formation of mineral inclusions by fluid immiscibility

In immiscible basalt-water systems, chromite and olivine can be physically fractionated into fluid and melt phases, respectively (Ballhaus, 1998; Matveev and Ballhaus, 2002). Chromite and fluid could have occurred as droplets in which crystallization proceeded from the margin of the droplet inward. Nucleation could probably be initiated by contamination of the surface of the droplet by crystallites or small crystals suspended in the magmas as depicted by McDonald (1965). The crystallites and mineral crystals are mostly olivine which can crystallize under various *P*-*T* conditions and share a eutectic with chromite. Such olivine crystallites would be attracted to the fluids with the greatest dielectric constant (McDonald, 1965) and enclosed by growing chromite. This can explain why olivine commonly occurs as single-phase inclusions in chromite (Figure 1e; Zhou et al., 2014; Liu et al., 2018).

With nucleation initiation, dendrites of chromite (Prichard et al., 2015) would have grown on the surfaces of the droplets and probably continued growing until a solid zone had developed around the droplet. The remaining chromite-rich liquid would thus have been isolated from the silicate melt by a solid shell of chromite (McDonald, 1965). As the remaining liquid continued to crystallize, silica would have been progressively enriched until its concentration reached a level sufficient to develop a new immiscible droplet. The silica-rich melts persisted until nearly all the chromite had crystallized as evidenced by the concentration of inclusions in the cores of the chromite grains (Figure 1a). Before the enclosed silica-rich melts crystallized, they may also have altered the chromite host, generating a narrow rind of new chromite surrounding the inclusions, which are featured by greater reflectivity than the enclosing chromite (Figure 1b, 1c; Borisova et al., 2012). Simultaneous crystallization of both phases may have produced clusters of small, irregular-shaped silicate inclusions around the main central one (Figure 1a) (McDonald, 1965). As the silicate liquid gradually crystallized, trace amounts of chromite separated from it to form inclusions in the silicate minerals (Figure 1h). Immiscible liquid may have filled interstices of dendrites, forming marginally and randomly distributed inclusions in the chromite (Figure 1a).

With variable rates of nucleation on the droplet surfaces, crystallization may have proceeded irregularly in some droplets and form uneven outer crystalline shells with variable thickness. Crystallization under such conditions could separate the entrapped silicate-rich liquid into several parts and lead to subsequent formation of several independent silicate inclusions (Figure 1a, 1b). Also, initial marginal crystallization may not have favored full development of crystal shell. Liquid within the incompletely crystallized chromite shell could escape across crystal indentations of the droplet into outer silicate melts, and silicate melts may also have traversed across the indentations into the enlarging space in the droplet. Such mixing of fluid and melt may account for the crystallization of clinopyroxene associated with other phases (e.g., apatite, amphibole, olivine, orthopyroxene, etc.) in inclusions (Figure 1c–1f, 1i–1k) and also explain clinopyroxene partially enclosing chromite (Figure 1a). Interstitial clinopyroxene could have also formed from mixing of the fluids on chromite surfaces and the melts from which olivine crystallized (Su et al., 2020). These observations suggest that the two occurrences of clinopyroxene essentially resulted from the same mechanism. This inference is supported by the identical compositions of the clinopyroxene, which plot near to hydrothermal clinopyroxene (Figure 2), suggesting large amounts of H_2O were involved in their formation. This is consistent with the measured H_2O contents (up to 801 ppm (1 ppm=1 μg g^{-1})) of interstitial clinopyroxene in the Kızıldağ chromitites (Su et al., 2020).

4 Bulk-rock PGE and Re-Os isotope evidence of fluid immiscibility

The PGEs are highly siderophile elements and thus fractionate along with Fe into the fluid phase in immiscible melt-fluid systems, producing PGE-Fe alloy nuggets as demonstrated experimentally (Matveev and Ballhaus, 2002). In nature, PGE-Fe alloys also preferentially occur in hydrous magmatic systems such as Alaskan-type complexes (e.g., Garuti et al., 2003). Also, PGE alloy inclusions are common in chromite in ophiolitic chromitites (Figure 1j–1m). Due to high partition coefficients in sulfide, PGEs may occur both as sulfide solid solution and as alloys associated with sulfides (e.g., Figure 1j; Lorand and Ceuleneer, 1989; Uysal et al., 2009; Saka et al., 2019).

In the Kızıldağ ophiolite, chromitites show overall higher ∑PGE concentrations than dunites (Figure 3), which is compatible with the preferential accumulation of PGE inclusions in the chromitites. Clinopyroxene-bearing chromitites with high H_2O in the clinopyroxene have much higher PGE concentrations than clinopyroxene-free ones (Chen et al., 2020; Su et al., 2020; Supplementary Table S2) (Figure 3), suggesting that immiscible fluids have a great capacity for transferring PGE. Additional extreme PPGE concentration differences between the two chromitite types (Figure 3) and Pt-Pd inclusions in chromite rims (Figure 1l) indicate higher mobility of PPGE in fluids than IPGE. Thus, we suggest that PGE fractionation between chromitites is largely controlled by the range of fluid immiscibility in magmas. However, all but one of the Kızıldağ chromitites have uniform Os isotopic ratios (Figure 3; Supplementary Table S2), implying that radiogenic isotopes were not fractionated and that the parental magmas of the chromitites originated from mantle sources with similar Os isotopic compositions.

The Kızıldağ harzburgites have lower ∑PGE and IPGE concentrations than the chromitites (Chen et al., 2020; Supplementary Table S2), which is consistent with their

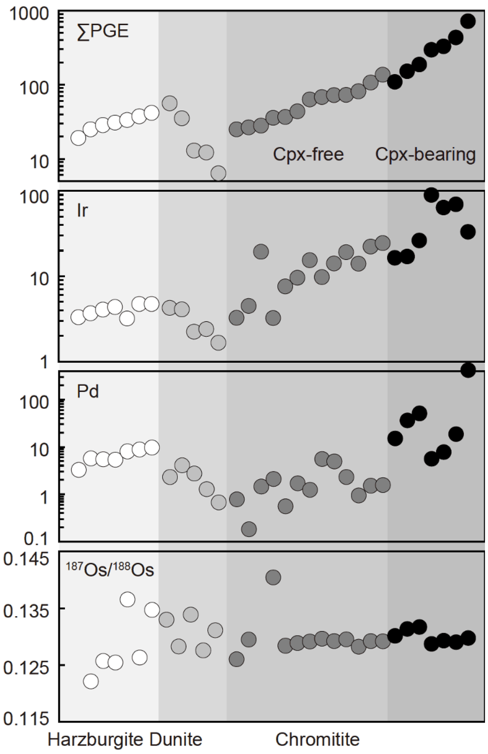

Figure 3 Bulk-rock PGE concentrations (ppb) and Os isotopes of harzburgite, dunite and chromitite from the Kızıldağ ophiolite (data available in Supplementary Table S2) (1 ppb=1 ng g^{-1}).

formation by partial melting (Chen et al., 2015, 2019). Lower ∑PGE and IPGE concentrations in the Kızıldağ dunites relative to the harzburgites and chromitites (Figure 3) suggest that fluid immiscibility could result in greater degree of PGE fractionation than partial melting. Fractionation by fluid immiscibility between melts and fluids is also suggested by larger $^{187}Os/^{188}Os$ variations in the dunites than in chromitites. However, neither process alone can account for the higher PPGE concentrations in the harzburgites than in most chromitites and the moderate PPGE concentrations in the dunites. These discrepancies are interpreted in Section 5 as the result of progressive penetration of evolving fluids released from chromite-rich droplets, which enhances the variability of $^{187}Os/^{188}Os$ ratios of the harzburgites (Figure 3). Such fluid penetration may also contribute to the observed light rare earth element enrichments observed in many ophiolitic dunites and harzburgites (e.g., Zhou et al., 2005; Xiong et al., 2015; Saka et al., 2019).

5 Revisiting and re-interpreting olivine and chromite compositions

5.1 Extreme compositions and abrupt changes in major and trace element contents

Our current understanding of the genesis of podiform chromitites is based mainly on comparisons of major and trace element compositions of chromite with those in volcanic lavas (e.g., Kamenetsky et al., 2001; Pagé and Barnes, 2009; Zhou et al., 2014) and seemingly gradual, smooth variations of major elements of major constituent minerals in individual harzburgite-dunite-chromitite transects (Zhou et al., 1996; Su et al., 2016). Olivine and clinopyroxene in chromitites are very magnesian (e.g., Figures 4 and 5a; Melcher et al., 1997; Xiong et al., 2015; Xiao et al., 2016; Liu et al., 2018; Rollinson et al., 2018), which distinguish them from those in volcanic rocks (Su et al., 2018a). Many authors attribute these features to melt-harzburgite interaction and subsequent sub-solidus elemental diffusion between silicates and chromite (e.g., Zhou et al., 1996; Melcher et al., 1997; Pagé and Barnes, 2009; Xiao et al., 2016). However, we suggest that this interpretation needs to be reconsidered. For example, mantle-derived melts are theoretically more enriched in Fe than the residual peridotites and thus their reaction with mantle peridotites would lower the Mg#s of minerals in the peridotites, an observation that has been widely confirmed by studies of mantle peridotite xenoliths (e.g., Menzies and Hawkesworth, 1987; Xiao et al., 2010). Sub-solidus diffusion cannot explain extreme olivine compositions and restricted chromite compositions in chromite-poor dunite and disseminated chromitite, where olivine and chromite are expected to be least and most affected, respectively (Figure 5a).

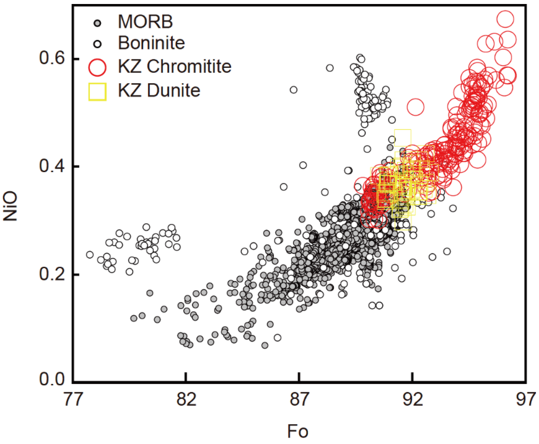

Figure 4 Correlation diagrams of Fo vs. NiO for olivine in dunite and chromitite from the Kızıldağ ophiolite (Chen et al., 2015, 2019) with comparisons of those in boninites and MORBs (GEOROC: http://georoc.mpch-mainz.gwdg.de/georoc/Start.asp).

Indeed, a detailed examination of lithological contacts and bands in compositional profiles of chromitites and peridotites (Figure 5a) reveals abrupt changes in FeO content and Mg# of olivine and chromite, as well as variations of Li in olivine and Na_2O in clinopyroxene. Moreover, variations of trace elements of chromite abruptly jump at the contacts between chromitite, dunite and harzburgite (Figure 5b; Su et al., 2019). Kamenetsky et al. (2001) revealed that Fe-Mg exchange between olivine and chromite is considered to be minimal <5% Mg#, and the decrease in chromite Mg# is still a reflection of fractional crystallization. In addition, the observed decrease in Mg# (increase in Fe^{2+}) in chromite as Fo contents decrease is most likely controlled by spinel-liquid equilibria (Smith and Leeman, 2005). Thus these abrupt compositional changes cannot be explained by either melt-rock interaction or sub-solidus diffusion. Instead, relatively restricted ranges of the element contents and related ratios in individual lithologies (Figure 5) suggest distinct changes in the compositions of the parental magmas of chromitites and dunites.

5.2 Anomalous Li and Fe isotopes

During preliminary studies of the samples reported here, we did not consider that bulk-rock Os isotopes or Li and Fe isotopic compositions of olivine and chromite were important features that would help to explain the processes involved in their formation (Chen et al., 2015; Su et al., 2016; Xiao et al., 2016; Zhang et al., 2017). However, Li isotopic compositions of olivine are distinctly different in dunite and chromitite (Figure 5a). The high δ^7Li values in dunite were originally interpreted as typical features of arc-like magmas related to dehydration of a subducting slab, whereas the light Li isotopic compositions in chromitite were suggested to have originated from partial melting of a subducted slab after

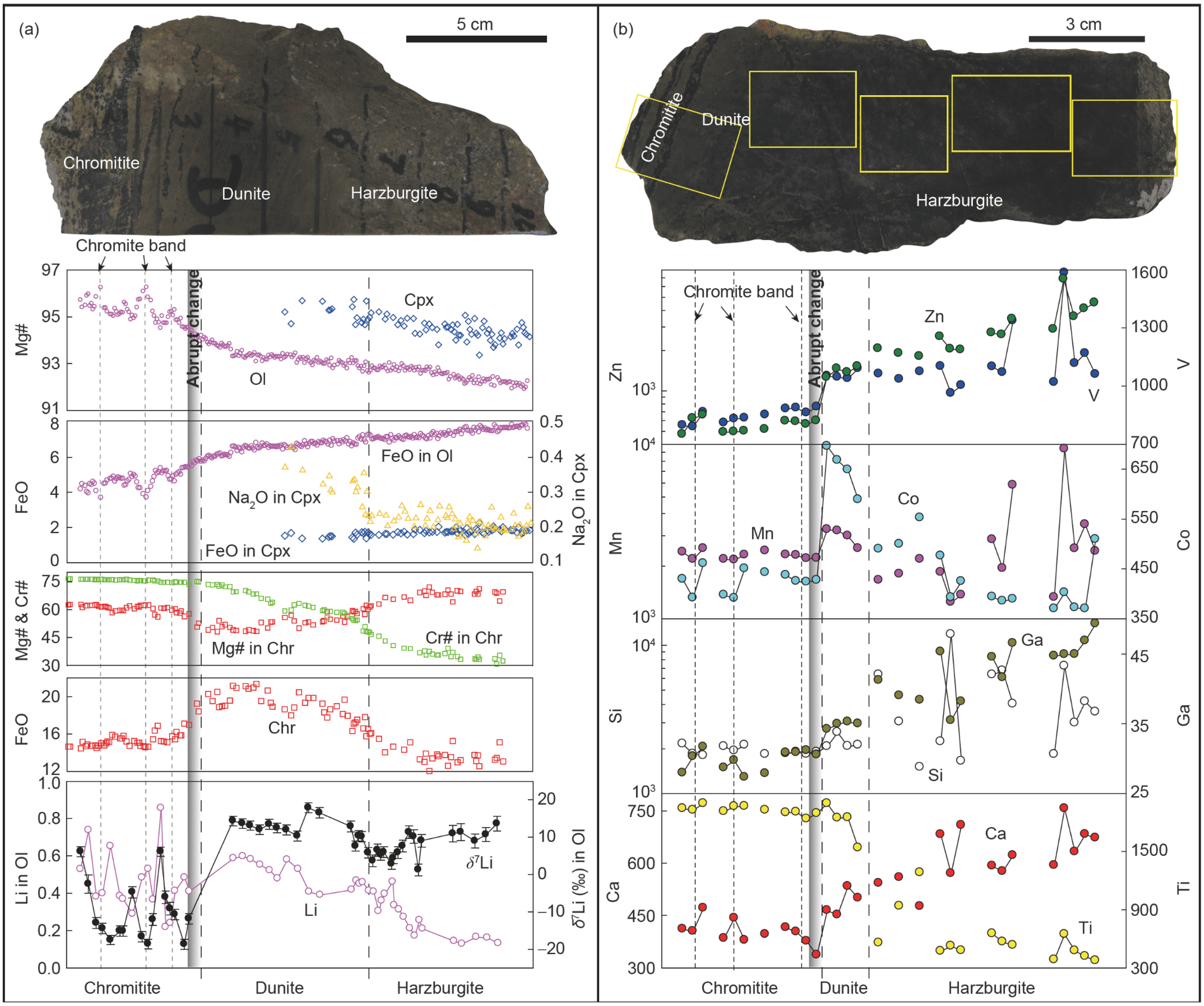

Figure 5 Hand specimen photograph of two transect chromitite-dunite-harzburgite samples from the Luobusa ophiolite and their chemical variations of olivine and chromite (data from Su et al., 2016, 2019).

high degrees of dehydration (Su et al., 2016). These interpretations turned out to be unconvincing because such events would not produce the centimeter-scale variations observed in hand specimens. In contrast, the observed variations of Li isotopes are totally compatible with the mineral and bulk elemental variations and Os isotopes mentioned above. This further confirms that none of the previously considered hypotheses could reasonably account for the anomalous geochemical characteristics of podiform chromitite.

To date, reported Fe isotope data on minerals from mantle sequences of ophiolites are all anomalous (Chen et al., 2015; Xiao et al., 2016; Zhang et al., 2017). Both olivine and chromite in chromitite and dunite have large Fe isotopic variations with higher δ^{56}Fe values in olivine than in coexisting chromite (Figure 6), which is contrary to theoretical predictions (Roskosz et al., 2015) and the previous empirical results (e.g., Zhao et al., 2012; Macris et al., 2015). This inter-mineral fractionation seems to result from Fe-Mg exchange, in which the light Fe isotope diffuses from olivine to chromite more rapidly than the heavy isotope (Xiao et al., 2016; Zhang et al., 2017; Su et al., 2018a). This diffusion process can explain the elevated δ^{56}Fe values of olivine in chromitite and lower δ^{56}Fe values of chromite in dunite because olivine is a trace phase in chromitite and chromite in dunite; in contrast, the anomalously low δ^{56}Fe values of chromite in chromitite cannot be explained by this process because chromite is abundant in chromitite and has high Fe contents, making it immune to Fe-Mg exchange, and another process should be involved. Furthermore, the Kızıldağ harzburgites and some harzburgite samples from the Luobusa ophiolite show the same Fe isotopic fractionation between olivine and chromite (Figure 6). These harzburgites are considered to have formed by partial melting followed by metasomatism and presumably have δ^{56}Fe values of chro-

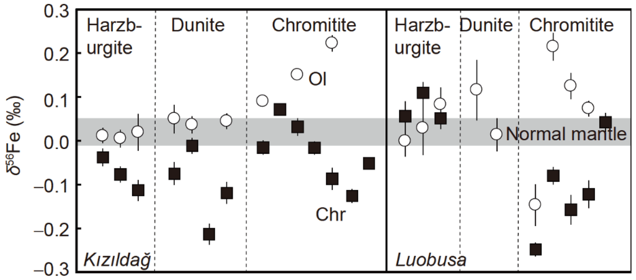

Figure 6 Fe isotopic ratios of olivine and chromite in harzburgite, dunite and chromitite from the Kızıldağ (Chen et al., 2015) and Luobusa (Xiao et al., 2016) ophiolites.

mite > olivine as is the case in mantle xenoliths (e.g., Zhao et al., 2012; Macris et al., 2015). Hence, if chromite in ophiolitic harzburgites primarily has heavier Fe isotopic compositions than olivine, the observed value (δ^{56}Fe chromite < olivine) is a different signature and should have been controlled by the presence of fluids.

5.3 New interpretations from fluid immiscibility

Exsolution of fluids from basaltic melts would produce two systems showing compositional fractionation (Irvine, 1977; Matveev and Ballhaus, 2002). The two phases would be separated by a well-defined interface, which would tend to be an isothermal surface if no solidification was taking place and if the crystals showed isotropic thermal conduction (McDonald, 1965; Matveev and Ballhaus, 2002). Chemical compositions in each system would be relatively homogeneous. Thus, chromite in chromitite crystallized from the fluids and olivine in dunite from the melts would be homogeneous in both major and trace element compositions. The fluid-melt interface in such a system would be a precursor of the chromitite-dunite contact across which there would be abrupt elemental changes (Figure 5). However, isotopic compositions of the fluid and melt phases might be sensitively modified with progressive solidification.

The common occurrence of olivine inclusions in chromite and the rarity of chromite inclusions in olivine (Figure 1a, 1e; Liu et al., 2018) indicate earlier crystallization of olivine than chromite, thus dunite envelopes should have formed prior to podiform chromitite. As a consequence, suspended olivine in the melts and later in dunite would be modified by fluids associated with the chromite-rich droplets. Olivine crystallites accidentally intruded into or entrapped by the droplets to form inclusions in chromite should have been hydrated by fluids in the droplets (Johan et al., 2017). Hydration reactions or so-called fluid-olivine reactions, working in a mechanism similar to serpentinization, would leach fluid-mobile elements such as Fe and Li from olivine (Su et al., 2018b). With crystallization of chromite from the droplets, H_2O would become enriched in the remaining liquid of a single droplet because chromite crystals cannot structurally accommodate water. Such fluids, if released from the droplets, could further hydrate surrounding olivine crystals located between droplets. The fluids path could extend to ambient dunite or even harzburgite surrounding the immiscible chromite-rich pool depending on the amount of fluids and size of the pool.

The fluid-olivine reaction would induce Fe depletion in olivine and thus both Fo and δ^{56}Fe would increase (Figures 4, 5a and 6), whereas Li depletion in olivine would lead to decreasing δ^{7}Li (Figure 5a) because the light Fe isotopes and heavy ^{7}Li are preferentially leached (Zhang et al., 2017; Su et al., 2018b). Such effects should be quite prominent in chromitite and dunite but less remarkable in harzburgite as the fluid contents diminish. Simultaneously, the reaction would promote chromite crystallization from the compositionally varying fluids with increasing Fe contents and light Fe isotopes, producing variably low-δ^{56}Fe chromite (Figure 6). However, olivine most likely preserves primary Mg isotopic compositions (Xiao et al., 2016; Su et al., 2018b) because Mg would be retained in olivine during hydration reactions.

6. Fluid immiscibility model for podiform chromitite formation and potential implications

Many investigators have concluded that separation of immiscible oxide phases from silicate melts is important for the origin of magnetite and ilmenite deposits (e.g., Charlier and Grove, 2012; Liu et al., 2014). From above discussions it is clear that fingerprints of fluid activities are widespread in podiform chromitites, and we thus propose a fluid immiscibility model as follows.

Stage 1: Crystallization of olivine and tiny chromite nuclei

Ascending magmas intruding oceanic lithospheric mantle would presumably form a series of small magma chambers continuously connected by conduits (Figure 7). Olivine is typically the first phase crystallizing from magmas at depth, although tiny chromite grains could form contemporaneously. Owing to the affinity of water-rich fluids to oxide surfaces (Matveev and Ballhaus, 2002), chromite grains would collect fluids dispersed in the magmas and form water-rich droplets (Figure 7), which is the first and critical step for the development of fluid immiscibility. Because the fluid droplets have lower densities than olivine, they tend to float upward in the magma chambers and could be easily transported upward by flowing magmas, leaving cumulus olivine behind that form podiform dunites at depth. Podiform dunites commonly occur in the lower mantle sequences of ophiolites and are typically fine-grained and free of chromite (Figure 7). The chromite nuclei formed at this stage are probably the inclusion-free, small chromite grains that make up podiform chromitites (Figure 1a).

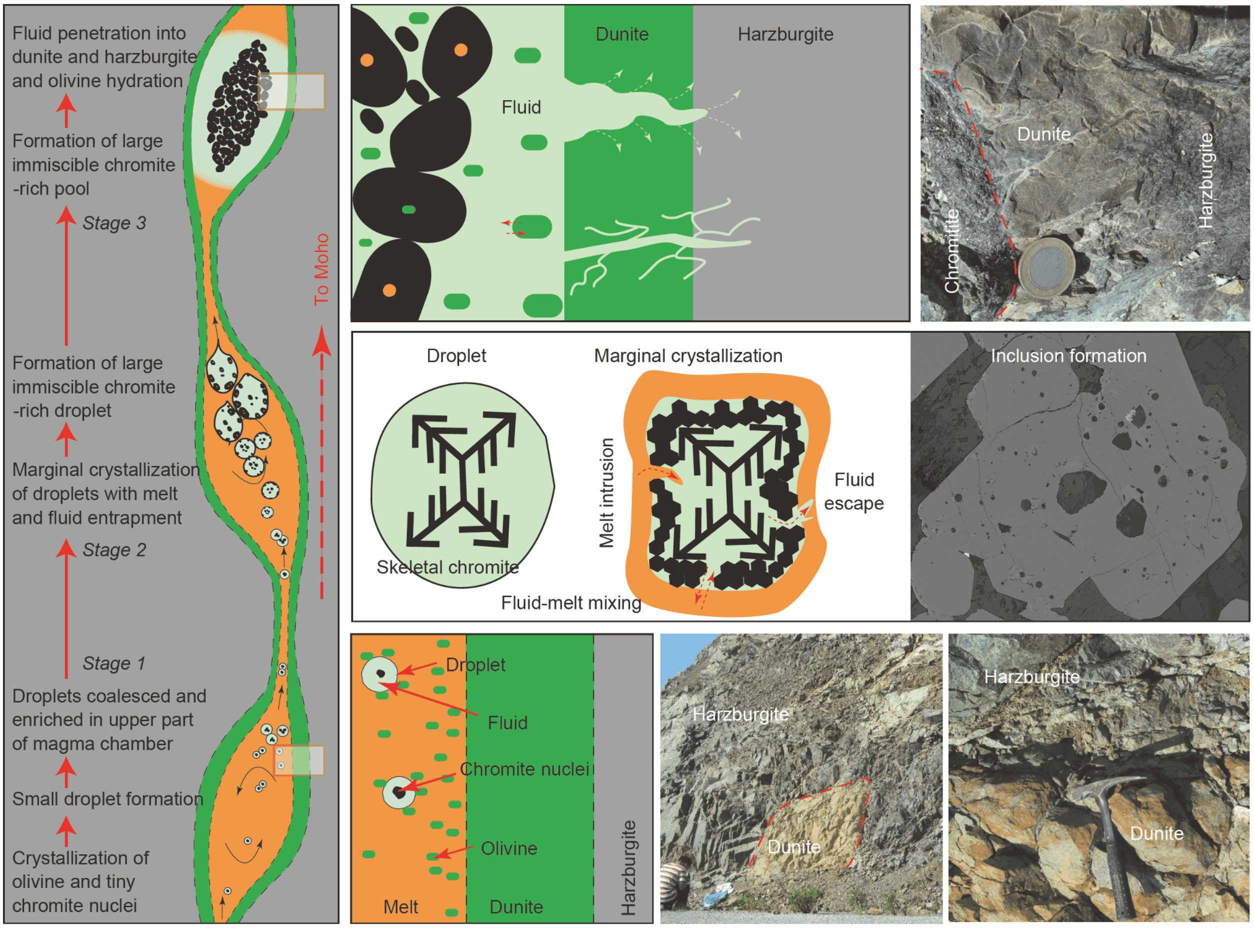

Figure 7 Fluid immiscibility model for podiform chromitite formation. See details in main text.

Stage 2: Formation of large immiscible chromite-rich droplets and fluid/melt entrapment

Chromite-rich fluid droplets would be enlarged via coalescence of dispersed droplets during mingling and circulation in the magma chambers and/or transportation in magma conduits (Figure 7). Crystallization of the chromite-rich liquid droplets would proceed from the margins of the droplets inward, leaving liquid entrapped within the newly-formed chromite grains (Figure 7). Because chromite is isometric, dendrites mostly have orthogonal outlines (Prichard et al., 2015). Dendritic growth and filling of dendrites would probably continue until a solid shell developed around the surfaces of the droplets (Liu et al., 2020). Defects in the marginal dendrites may allow mixing by outward escaping fluids and inward flowing melts (Figure 7), thus producing the observed varieties of inclusions (Figure 1; Melcher et al., 1997; Zhou et al., 2014; Liu et al., 2018, 2020). With solidification of droplets, the newly crystallizing chromite grains would continuously collect ambient fluids to promote larger-scale fluid immiscibility in the magma chambers. Meanwhile, olivine grains crystallizing from the melts would be preferentially attached to the fluid-melt interfaces (Matveev and Ballhaus, 2002), and likely form the commonly observed dunite envelopes around podiform chromitites.

Stage 3: Formation of podiform chromitite and fluid penetration

With preferential upward transportation, immiscible chromite-rich liquids would coalesce to a large pool occupying most of the space in a magma chamber (Figure 7). Such a process would also probably be related to decompression because podiform chromitite occurs invariably close to the petrological Moho in ophiolites (e.g., Zhou et al., 2014), which is consistent with experimental pressure conditions of the immiscible basalt-water system (Matveev and Ballhaus, 2002). Large volumes of chromite would crystallize *in situ*, resulting in fluid enrichment in the chamber. It is essential that the surface tension of the fluid wetting the dispersed chromite grains be sufficient to minimize disintegration of aggregated chromite (Matveev and Ballhaus, 2002; Johan et al., 2017). This would favor transformation of the chromitite into its final podiform shape during solidification.

Extensive fluid penetration would take place in the surrounding peridotites at this stage (Figure 7). Olivine in the fluid pool would interact with the fluids and lose Fe into them, after which the fluids would progressively infiltrate the ambient dunites and nearby harzburgites to produce the observed smooth borders. The degree of modification of the olivine and orthopyroxene in the dunite and harzburgite would depend on the volume of fluids available and the distance to the fluid source (Figure 7). The richer in Fe the fluids become, the more chromite could crystallize and settle in chromitite, dunite and harzburgite. The chromite-clinopyroxene association in ophiolitic peridotites is thought to be a product of such fluid penetration (Su et al., 2019, 2020). The compositional modifications along penetrating path of the fluids would be as shown in the above sections (Figure 5). Such processes could also have occurred at Stage 2 on a small scale.

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References

Arai S, Miura M. 2016. Formation and modification of chromitites in the mantle. Lithos, 264: 277–295

Arai S, Yurimoto H. 1994. Podiform chromitites of the Tari-Misaka ultramafic complex, southwestern Japan, as mantle-melt interaction products. Econ Geol, 89: 1279–1288

Ballhaus C. 1998. Origin of podiform chromite deposits by magma mingling. Earth Planet Sci Lett, 156: 185–193

Bao P S, Wang X B, Peng G Y, Chen F Y. 1999. Chromite Deposit in China (in Chinese). Beijing: Science Press

Borisova A Y, Ceuleneer G, Kamenetsky V S, Arai S, Béjina F, Abily B, Bindeman I N, Polvé M, De Parseval P, Aigouy T, Pokrovski G S. 2012. A new view on the petrogenesis of the Oman ophiolite chromitites from microanalyses of chrome-hosted inclusions. J Petrol, 53: 2411–2440

Charlier B, Grove T L. 2012. Experiments on liquid immiscibility along tholeiitic liquid lines of descent. Contrib Mineral Petrol, 164: 27–44

Chen C, Su B X, Uysal I, Avcı E, Zhang P F, Xiao Y, He Y S. 2015. Iron isotopic constraints on the origin of peridotite and chromitite in the Kızıldağ ophiolite, southern Turkey. Chem Geol, 417: 115–124

Chen C, Su B X, Xiao Y, Pang K N, Robinson P T, Uysal I, Lin W, Qin K Z, Avcı E, Kapsiotis A. 2019. Intermediate chromitite in Kızıldağ ophiolite (SE Turkey) formed during subduction initiation in Neo-Tethys. Ore Geol Rev, 104: 88–100

Chen C, Su B X, Xiao Y, Uysal İ, Lin W, Chu Y, Jing J J, Sakyi P A. 2020. Highly siderophile elements and Os isotope constraints on the genesis of peridotites from the Kızıldağ ophiolite, southern Turkey. Lithos, 368-369: 105583

Chen Y, Yang J. 2018. Formation of podiform chromitite deposits: Review and prospects (in Chinese with English abstract). Earth Sci, 43: 991–1010

Dilek Y, Delaloye M. 1992. Structure of the Kızıldağ ophiolite, a slow-spread Cretaceous ridge segment north of the Arabian promontory. Geology, 20: 19–22

Dilek Y, Furnes H. 2009. Structure and geochemistry of Tethyan ophiolites and their petrogenesis in subduction rollback systems. Lithos, 113: 1–20

Fisher L W. 1929. Origin of chromite deposits. Econ Geol, 24: 691–721

Garuti G, Pushkarev E V, Zaccarini F, Cabella R, Anikina E. 2003. Chromite composition and platinum-group mineral assemblage in the Uktus Uralian-Alaskan-type complex (Central Urals, Russia). Miner Deposita, 38: 312–326

González-Jiménez J M, Griffin W L, Proenza J A, Gervilla F, O'Reilly S Y, Akbulut M, Pearson N J, Arai S. 2014. Chromitites in ophiolites: How, where, when, why? Part II. The crystallization of chromitites. Lithos, 189: 140–158

Irvine T N. 1977. Chromite crystallization in the join Mg_2SiO_4-$CaMgSi_2O_6$-$CaAl_2Si_2O_8$-$MgCr_2O_4$-SiO_2. Carnegie Institution of Washington Yearbook, 76: 465–472

Jannessary M R, Melcher F, Lodziak J, Meisel T C. 2012. Review of platinum-group element distribution and mineralogy in chromitite ores from southern Iran. Ore Geol Rev, 48: 278–305

Johan Z, Martin R F, Ettler V. 2017. Fluids are bound to be involved in the formation of ophiolitic chromite deposits. Euro J Mineral, 29: 543–555

Kamenetsky V S, Crawford A J, Meffre S. 2001. Factors controlling chemistry of magmatic spinel: An empirical study of associated olivine, Cr-spinel and melt inclusions from primitive rocks. J Petrol, 42: 655–671

Lago B L, Rabinowicz M, Nicolas A. 1982. Podiform chromite ore bodies: A genetic model. J Petrol, 23: 103–125

Liu P P, Zhou M F, Chen W T, Boone M, Cnudde V. 2014. Using multiphase solid inclusions to constrain the origin of the baima Fe-Ti-(V) oxide deposit, SW China. J Petrol, 55: 951–976

Liu X, Su B X, Bai Y, Chen C, Xiao Y, Liang Z, Yang S H, Peng Q S, Su B C, Liu B. 2018. Ca-enrichment characteristics of parental magmas of chromitite in ophiolite: Inference from mineral inclusions (in Chinese with English abstract). Earth Sci, 43: 1038–1050

Liu X, Su B X, Bai Y, Robinson P T, Tang X, Xiao Y, Xue D S, Cui M M. 2020. Genesis of “silicate exsolution lamellae” in chromite of the Stillwater Complex: A challenge to the high-pressure crystallization of ophiolitic chromitite. Lithos, 378–379, 105796

Lorand J P, Ceuleneer G. 1989. Silicate and base-metal sulfide inclusions in chromites from the Maqsad area (Oman ophiolite, Gulf of Oman): A model for entrapment. Lithos, 22: 173–190

Macris C A, Manning C E, Young E D. 2015. Crystal chemical constraints on inter-mineral Fe isotope fractionation and implications for Fe isotope disequilibrium in San Carlos mantle xenoliths. Geochim Cosmochim Acta, 154: 168–185

Matveev S, Ballhaus C. 2002. Role of water in the origin of podiform chromitite deposits. Earth Planet Sci Lett, 203: 235–243

McDonald J A. 1965. Liquid immiscibility as one factor in chromitite seam formation in the Bushveld Igneous Complex. Econ Geol, 60: 1674–1685

Melcher F, Grum W, Simon G, Thalhammer T V, Stumpfl E F. 1997. Petrogenesis of the ophiolitic giant chromite deposits of Kempirsai, Kazakhstan: A study of solid and fluid inclusions in chromite. J Petrol, 38: 1419–1458

Menzies M A, Hawkesworth C J. 1987. Mantle Metasomatism. London: Academic Press

Pagé P, Barnes S J. 2009. Using trace elements in chromites to constrain the origin of podiform chromitites in the Thetford Mines ophiolite, Quebec, Canada. Econ Geol, 104: 997–1018

Prichard H M, Barnes S J, Godel B, Reddy S M, Vukmanovic Z, Halfpenny A, Neary C R, Fisher P C. 2015. The structure of and origin of nodular chromite from the Troodos ophiolite, Cyprus, revealed using high-resolution X-ray computed tomography and electron backscatter diffraction. Lithos, 218-219: 87–98

Robinson P T, Bai W J, Malpas J, Yang J S, Zhou M F, Fang Q S, Hu X F, Cameron S, Staudigel H. 2004. Ultra-high pressure minerals in the Luobusa ophiolite, Tibet, and their tectonic implications. Geol Soc London Spec Publ, 226: 247–271

Robinson P T, Trumbull R B, Schmitt A, Yang J S, Li J W, Zhou M F, Erzinger J, Dare S, Xiong F. 2015. The origin and significance of crustal minerals in ophiolitic chromitites and peridotites. Gondwana Res, 27: 486–506

Rollinson H, Mameri L, Barry T. 2018. Polymineralic inclusions in mantle chromitites from the Oman ophiolite indicate a highly magnesian parental melt. Lithos, 310-311: 381–391

Roskosz M, Sio C K I, Dauphas N, Bi W, Tissot F L H, Hu M Y, Zhao J, Alp E E. 2015. Spinel-olivine-pyroxene equilibrium iron isotopic fractionation and applications to natural peridotites. Geochim Cosmochim Acta, 169: 184–199

Sachan H K, Mukherjee B K, Bodnar R J. 2007. Preservation of methane generated during serpentinization of upper mantle rocks: Evidence from fluid inclusions in the Nidar ophiolite, Indus suture zone, Ladakh (India). Earth Planet Sci Lett, 257: 47–59

Saka S, Uysal I, Kapsiotis A, Bağcı U, Ersoy E Y, Su B X, Seitz H M, Hegner E. 2019. Petrological characteristics and geochemical compositions of the Neotethyan Mersin ophiolite (southern Turkey): Processes of melt depletion, refertilization, chromitite formation and oceanic crust generation. J Asian Earth Sci, 176: 281–299

Smith D R, Leeman W P. 2005. Chromian spinel-olivine phase chemistry and the origin of primitive basalts of the southern Washington Cascades. J Volcanol Geotherm Res, 140: 49–66

Su B X, Bai Y, Chen C, Liu X, Xiao Y, Tang D M, Liang Z, Cui M M, Peng Q S. 2018a. Petrological and mineralogical investigations on hydrous property of parental magmas of chromite deposits (in Chinese with English abstract). Bull Mineral Petrol Geochem, 37: 1035–1046

Su B X, Chen C, Pang K N, Sakyi P A, Uysal I, Avci E, Liu X, Zhang P F. 2018b. Melt penetration in oceanic lithosphere: Li isotope records from the Pozantı-Karsantı ophiolite in southern Turkey. J Petrol, 59: 191–205

Su B X, Zhou M F, Jing J J, Robinson P T, Chen C, Xiao Y, Liu X, Shi R D, Lenaz D, Hu Y. 2019. Distinctive melt activity and chromite mineralization in Luobusa and Purang ophiolites, southern Tibet: Constraints from trace element compositions of chromite and olivine. Sci Bull, 64: 108–121

Su B X, Zhou M F, Robinson P T. 2016. Extremely large fractionation of Li isotopes in a chromitite-bearing mantle sequence. Sci Rep, 6: 22370

Su B X, Robinson P T, Chen C, Xiao Y, Melcher F, Bai Y, Gu X Y, Uysal I, Lenaz D. 2020. The occurrence, origin, and fate of water in chromitites in ophiolites. Am Miner, 105: 894–903

Uysal I, Tarkian M, Sadiklar M B, Zaccarini F, Meisel T, Garuti G, Heidrich S. 2009. Petrology of Al- and Cr-rich ophiolitic chromitites from the Muğla, SW Turkey: Implications from composition of chromite, solid inclusions of platinum-group mineral, silicate, and base-metal mineral, and Os-isotope geochemistry. Contrib Mineral Petrol, 158: 659–674

Xiao Y, Teng F Z, Su B X, Hu Y, Zhou M F, Zhu B, Shi R D, Huang Q S, Gong X H, He Y S. 2016. Iron and magnesium isotopic constraints on the origin of chemical heterogeneity in podiform chromitite from the Luobusa ophiolite, Tibet. Geochem Geophys Geosyst, 17: 940–953

Xiao Y, Zhang H F, Fan W M, Ying J F, Zhang J, Zhao X M, Su B X. 2010. Evolution of lithospheric mantle beneath the Tan-Lu fault zone, eastern North China Craton: Evidence from petrology and geochemistry of peridotite xenoliths. Lithos, 117: 229–246

Xiong F, Yang J, Robinson P T, Xu X, Liu Z, Li Y, Li J, Chen S. 2015. Origin of podiform chromitite, a new model based on the Luobusa ophiolite, Tibet. Gondwana Res, 27: 525–542

Xiong F H, Yang J S, Robinson P T, Xu X Z, Ba D Z, Li Y, Zhang Z M, Rong H. 2016. Diamonds and other exotic minerals recovered from peridotites of the Dangqiong ophiolite, western Yarlung-Zangbo suture zone, Tibet. Acta Geol Sin, 90: 425–439

Yang J S, Dobrzhinetskaya L, Bai W J, Fang Q S, Robinson P T, Zhang J, Green H W. 2007. Diamond- and coesite-bearing chromitites from the Luobusa ophiolite, Tibet. Geology, 35: 875–878

Yang J S, Robinson P T, Dilek Y. 2015. Diamond-bearing ophiolites and their geological occurrence. Episodes, 38: 344–364

Zhang P F, Zhou M F, Su B X, Uysal I, Robinson P T, Avcı E, He Y S. 2017. Iron isotopic fractionation and origin of chromitites in the paleo-Moho transition zone of the Kop ophiolite, NE Turkey. Lithos, 268-271: 65–75

Zhao X, Zhang H, Zhu X, Tang S, Yan B. 2012. Iron isotope evidence for multistage melt-peridotite interactions in the lithospheric mantle of eastern China. Chem Geol, 292-293: 127–139

Zhou M F, Robinson P T, Bai W J. 1994. Formation of podiform chromitites by melt/rock interaction in the upper mantle. Mineral Deposita, 29: 98–101

Zhou M F, Robinson P T, Malpas J, Edwards S J, Qi L. 2005. REE and PGE geochemical constraints on the formation of dunites in the Luobusa ophiolite, southern Tibet. J Petrol, 46: 615–639

Zhou M F, Robinson P T, Malpas J, Li Z. 1996. Podiform Chromitites in the Luobusa Ophiolite (Southern Tibet): Implications for melt-rock interaction and chromite segregation in the upper mantle. J Petrol, 37: 3–21

Zhou M F, Robinson P T, Su B X, Gao J F, Li J W, Yang J S, Malpas J. 2014. Compositions of chromite, associated minerals, and parental magmas of podiform chromite deposits: The role of slab contamination of asthenospheric melts in suprasubduction zone environments. Gondwana Res, 26: 262–283

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