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# A New View on the Petrogenesis of the Oman Ophiolite Chromitites from Microanalyses of Chromite-hosted Inclusions

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To decipher the petrogenesis of chromitites from the Moho Transition Zone of the Cretaceous Oman ophiolite, we carried out detailed scanning electron microscope and electron microprobe investigations of ~500 silicate and chromite inclusions and their chromite hosts, and oxygen isotope measurements of seven chromite and olivine fractions from nodular, disseminated, and stratiform ore bodies and associated host dunites of the Magsad area, Southern Oman. The results, coupled with laboratory homogenization experiments, allow several multiphase and microcrystal types of the chromite-hosted inclusions to be distinguished. The multiphase inclusions are composed of micron-size (1-50 µm) silicates (with rare sulphides) entrapped in high cr-number  $\lceil 100Cr/(Cr+Al) \mid up \text{ to } 80 \rceil$  chromite. The high cr-number chromite coronas and inclusions are reduced (oxygen fugacity,  $f_{O2}$ , of  $\sim 3$  log units below the quartz-fayalite-magnetite buffer, QFM). The reduced chromites, which crystallized between 600 and 950°C at subsolidus conditions, were overgrown by more oxidized host chromite ( $f_{O2} \approx QFM$ ) in association with microcrystal inclusions of silicates (plagioclase Ange, clinopyroxene, and pargasite) that were formed between 950 and 1050°C at 200 MPa from a hydrous hybrid mid-ocean ridge basalt (MORB) melt. Chromium concentration profiles through the chromite coronas, inclusions, and host chromites indicate non-equilibrium fractional crystallization of the chromitite system at fast cooling rates (up to  $\sim 0.1^{\circ}C$  $a^{-1}$ ). Oxygen isotope compositions of the chromite grains imply involvement of a mantle protolith (e.g. serpentinite and serpentinized peridotite) altered by seawater-derived hydrothermal fluids in an oceanic setting. Our findings are consistent with a three-stage model of chromite formation involving (1) mantle protolith alteration by seawater-derived hydrothermal fluids yielding serpentinites and serpentinized harzburgites, which were probably the initial source of chromium, (2) subsolidus crystallization owing to prograde metamorphism, followed by (3) assimilation and fractional crystallization of chromite from water-saturated MORB. This study suggests that the metamorphic protolith assimilation occurring at the Moho level may dramatically affect MORB magma chemistry and lead to the formation of economic chromium deposits.

KEY WORDS: Oman ophiolite; chromitite; chromian spinel; MORB; inclusions; Moho Transition Zone; hydrothermal fluid; serpentinites; protolith; oxygen isotopes; AFC

#### INTRODUCTION

Chromian spinel in the mantle-crust transition zone (referred to here as the Moho Transition Zone or MTZ) plays an important role in the global budget of chromium in the Earth's lithosphere. The chemical composition of chromian spinel and chromite-hosted inclusions is variable, reflecting the wide range of physicochemical and geological conditions that can exist along the interface between the crust and upper mantle (e.g. Dick & Bullen, 1984; Roeder & Reynolds, 1991; Sack & Ghiorso, 1991; Kamenetsky, 1996; Borisova et al., 1997, 2002, 2008; Kamenetsky et al., 2001; Arai et al., 2006). Chromian spinel is a main economic Cr reserve on Earth and may form large chromitite ore bodies whose petrogenesis remains a subject for debate. The pioneering model of McDonald (1965) on the Bushveld chromitites invoked the formation of Cr-rich immiscible liquids, forming at temperatures above 1400°C and even as high as 2000°C (Jackson, 1966). However, this model cannot be applied to chromitites in ophiolites or layered intrusions where hydrous silicate minerals, crystallizing at much lower temperatures, are systematically found as inclusions in chromite (e.g. Lorand & Ceuleneer, 1989; Melcher et al., 1997; Li et al., 2005; Arai et al., 2006; Pagé et al., 2008; Rollinson, 2008). Other models were subsequently proposed to explain chromitite petrogenesis based on experimental data (e.g. Roeder & Reynolds, 1991), chromite-hosted inclusion data (e.g. Melcher et al., 1997; Schiano et al., 1997; Li et al., 2005; Spandler et al., 2005; Borisova et al., 2008), or both (e.g. Irvine, 1975; Matveev & Ballhaus, 2002). Most models invoke a magmatic system, based on experimental data on basaltic systems (e.g. Irvine, 1975; Murck & Campbell, 1986; Roeder & Reynolds, 1991; Matveev & Ballhaus, 2002). For example, Irvine (1975) suggested either crustal contamination or silicate melt mixing to stabilize chromite on the liquidus in such a system. Roeder & Reynolds (1991) suggested a highly reduced basaltic magma as the chromium source. Matveev & Ballhaus (2002) proposed a magmatic system saturated with an aqueous fluid phase with physical separation of chromite from olivine. These models consider either open-system interactions of olivine-saturated melts with felsic melts (Irvine, 1975) or incongruent dissolution of crustal rocks with the formation of chromite-saturated melts (Bédard et al., 2000). Hydrous magmas are indeed favourable for abundant chromite crystallization because the presence of water in a mafic melt widens the stability domain of spinel, especially under oxidizing conditions (Ford *et al.*, 1972; Feig *et al.*, 2006) and stabilizes chromite on the liquidus (Nicholson & Mathez, 1991). However, a major shortcoming of most previous models is the lack of a satisfactory explanation for the source of the Cr capable of accounting for the formation in a mid-oceanic ridge setting of huge chromitite ore bodies reaching tens of thousand cubic meters (e.g. Lorand & Ceuleneer, 1989).

Most researchers acknowledge the role of aqueous fluids or hydrous silicate melts in the petrogenesis of the Oman chromitites (Johan et al., 1983; Augé, 1987; Lorand & Ceuleneer, 1989; Leblanc & Ceuleneer, 1992; Schiano et al., 1997; Arai et al., 2004, 2006; Ahmed et al., 2006; Rollinson, 2008). The source of water and its involvement in the Maqsad MTZ chromitite petrogenesis is, however, controversial. Water might originate from either (1) hydrothermal fluid sources (Augé & Johan, 1988) or (2) dehydration of a subducting slab (Schiano et al., 1997; Ahmed et al., 2006; Rollinson, 2008) or (3) re-melting of hydrated lithosphere in a spreading-ridge setting in response to episodic emplacement of mantle diapirs at the MTZ (Benoit et al., 1999; Python et al., 2007).

Studies of inclusions trapped in chromian spinel crystals may provide key information on the petrogenesis of chromitite ore bodies. Chromian spinel is an ideal 'microcontainer' for inclusions owing to its resistance to alteration (e.g. Shimizu et al., 2001; Arai et al., 2006, 2011). In contrast to chromites disseminated in volcanic rocks (Kamenetsky, 1996; Borisova et al., 2001; Kamenetsky et al., 2001, 2002), chromian spinel forming chromitite ores contains abundant inclusions of fluid, hydrous and anhydrous silicates, sulphides, and platinum group minerals (Augé, 1987; Augé & Johan, 1988; Lorand & Ceuleneer, 1989; Melcher et al. 1997; Kamenetsky et al., 2001, 2002; Arai et al., 2004; Spandler et al., 2005; Ahmed et al., 2006; Borisova et al., 2008). Inclusions of hydrous silicate minerals have been found in chromian spinel from chromitites in different tectonic settings, ranging from subduction zones to spreading ridges, and in their fossil equivalents exposed in ophiolites (e.g. Lorand & Ceuleneer, 1989; Melcher et al., 1997; Arai et al., 2006; Rollinson, 2008). However, the origin of these hydrous silicate minerals and the role of aqueous fluids and/or hydrous melts in chromite petrogenesis remain unclear.

We carried out a systematic investigation by scanning electron microscope and electron microprobe of about 500 chromite-hosted inclusions and their host chromites as well as oxygen isotope measurements of chromite and olivine grain fractions from four nodular, disseminated, and stratiform chromitites and three associated host dunites located at different levels of the MTZ in the Oman

ophiolite, Maqsad area. We also performed homogenization experiments on the chromite-hosted inclusions, and analysed numerous elemental profiles through inclusion—host interfaces. The new data are evaluated with existing petrogenetic models and imply that metamorphic recrystallization of a mantle protolith altered by seawater-derived hydrothermal fluids is likely to be the key process responsible for the formation of chromitite ore in an oceanic MTZ setting.

# GEOLOGICAL BACKGROUND AND SAMPLES

#### The Maqsad area of the Oman ophiolite

The Oman ophiolite is an ~95-100 Ma fragment of the Tethyan oceanic lithosphere obducted onto Arabian continental lithosphere (Coleman, 1981; Tilton et al., 1981; Tippit et al., 1981). It was detached during an intra-oceanic thrusting event that occurred ~95 Myr ago; that is, soon after its igneous accretion (Ghent & Stout, 1981; Boudier et al., 1985, 1988; Montigny et al., 1988). The final emplacement onto the Oman margin was achieved during Maastrichtian times (~70 Ma) (Glennie et al., 1973: Coleman, 1981). The present exposure of the Oman ophiolite results from the recent (Miocene) uplift of the Oman range (Glennie et al., 1973). The detailed context of the petrogenesis and emplacement of the Oman ophiolite is still debated. It may have evolved in a mid-ocean ridge setting (e.g. Coleman, 1981) or in a marginal, possibly back-arc, setting (e.g. Pearce et al., 1981; Searle & Cox, 1999; Tamura & Arai, 2006).

#### Magsad mantle diapir

The Magsad area is located in the southeastern part of the Oman ophiolite (Fig. 1). Its structural and igneous evolution was conditioned by the emplacement of a mantle diapir at Moho level below a spreading axis (Jousselin et al., 1998; Rabinowicz & Ceuleneer, 2005). The Magsad mantle diapir is less than 10 km in cross-section but constitutes the central part of a much larger structure: a former spreading segment, about 80 km in length parallel to the paleo-spreading axis (which trends NW-SE). Abundant primitive melts percolated through the mantle peridotite in the diapir and are now manifested by troctolitic and gabbroic 'impregnations' and segregations (Python & Ceuleneer, 2003; and references therein). The parental melts of the Magsad troctolites and gabbros were similar to mid-ocean ridge basalt (MORB) as attested by the crystallization sequence and mineral composition (Kelemen et al., 1995; Python et al., 2008; and references therein). Their isotopic signature is typically that of present-day Indian MORB, pointing to a common mantle source (Benoit et al., 1999; and references therein).

The crustal section at the top of the Magsad diapir is made of flat-lying, slightly dipping to the SE, interlayered cumulates such as dunites, troctolites, olivine gabbros and gabbros, presenting variably developed modal graded bedding. The thickness of this gabbroic unit reaches about 2 km. The overlying sheeted dykes have a NW-SE azimuth. The regularity of the gabbro layering is locally perturbed by syn-magmatic normal faults (Abily et al., 2011). The petrological nature of MORB-derived segregations in the mantle peridotite that were 'processed' in the Magsad diapir contrasts with the more common situation observed in Oman where mantle dykes are essentially filled with pyroxenite and high-Mg gabbronorite (Python & Ceuleneer, 2003). The parental melts of the Oman pyroxenites and gabbronorites are interpreted to have been formed by low-pressure hydrous re-melting of the hydrated oceanic lithosphere in a mid-ocean ridge setting (Benoit et al., 1999; Clénet et al., 2010). Such pyroxenites and gabbronorites are absent from the Magsad diapir but occur as intrusions in the mantle peridotite and as layered lower crustal cumulates 10-15 km away from the Maqsad diapir. These pyroxenites and gabbronorites are possibly relics of shallow lithospheric melts that formed in the early stages of the opening of the Magsad basin, and that were eventually transported passively into an off-axis position by sea-floor spreading (Benoit et al., 1999; Clénet et al., 2010).

#### Signatures of hydrothermal activity

Evidence for deep and very hot (up to at least 900°C) hydrothermal activity is strong in the Maqsad area. It is manifested by veins (usually ridge-parallel) filled with hydrothermal diopside and anorthite (Python et al., 2007), peridotites transformed into assemblages of talc and carbonates, and igneous minerals (cumulates from the lower crust) partially transformed into amphibole and green spinel in the vicinity of syn-magmatic faults (Abily et al., 2011). These are the footprints of transient interaction processes between the hot basaltic melts percolating through the Magsad diapir and filling the magma chamber and hydrothermal fluids reaching the Moho level. More classical lower-temperature minerals and their mineral assemblages (serpentine, chlorite, tremolite, sulphide, sulphate, carbonate and zeolite) are also abundant in faults and cracks withi the Maqsad mantle and lower crustal sections (Abily et al., 2011; and references therein). This hydrothermal activity has led locally to the formation of small plagiogranitic pods (Amri et al., 1996, see also Koepke et al., 2007).

#### Magsad Moho Tranzition Zone (MTZ)

The transition between the layered gabbroic cumulates and the underlying mantle harzburgites is represented by an ~300 m thick dunitic transition zone. The dunitic rocks are particularly well developed above the center of the Maqsad mantle diapir (Fig. 2). Chromitite ore bodies,

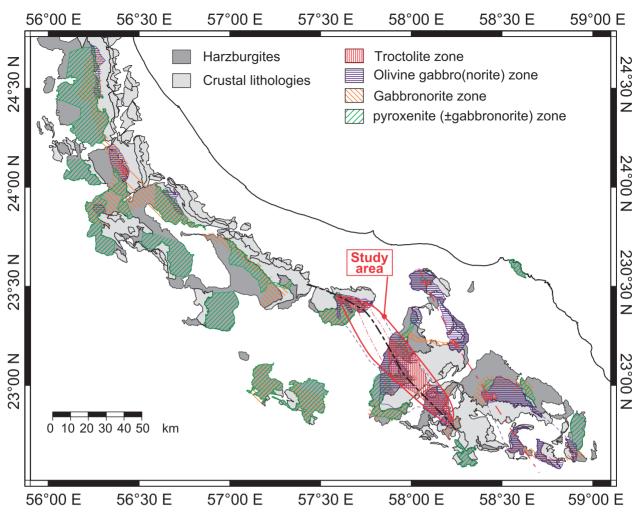


Fig. 1. Map of the Oman ophiolite showing the location of the Magsad study area. Troctolites are MORB cumulates developed above and within the Magsad diapir surface area (~1000 km<sup>2</sup>). There are numerous occurrence of evolved lithospheric cumulates (gabbronorites and pyroxenites) near the Maqsad area (marked by orange and green shading). Modified after Python & Ceuleneer (2003).

which are the focus of the present study, are abundant in the Maqsad dunitic transition zone (Leblanc & Ceuleneer, 1992). They were neither deformed nor transposed by mantle solid-state flow, unlike most of the chromitite ore bodies cropping out in the mantle harzburgites. This good preservation of the Magsad chromitite bodies offers a unique opportunity to study in detail the magmatic processes related to chromite ore genesis. Our study focuses on the undeformed chromitites, which are among the most spectacular manifestations of complex processes in the MTZ. The chromitite samples investigated come from three ore bodies located at various levels in the MTZ above the Magsad diapir (Fig. 2).

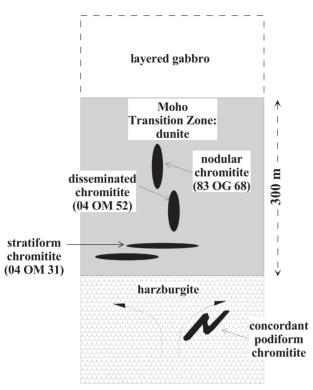
#### Host dunites

The host dunite samples are predominantly composed of olivine (>95% of olivine, Fo 87.5-90.5 mol %), scattered

chromian spinel (cr-number varies from 32 to 55) and interstitial diopside (Abily & Ceuleneer, in press). The investigated samples are weakly altered (≤30% serpentine) dunites (11TUF1: 23°6'16·86"N, 57°57'58·44"E, 883 m; 11TUF2: 23°6'15.96"N, 57°58'3.78"E, 898 m) diopside-bearing dunite (11TUF7: 23°6'9.54"N, 57°58'28. 26"E, 977 m) hosting the chromitites at the Maqsad MTZ. The dunite samples consist of partly serpentinized olivine (Fo 87–89 mol %), scattered chromite (cr-number = 50–54) and interstitial diopside (mg-number  $\sim$ 96).

#### Stratiform chromitite

Sample 04 OM 31 E is from a stratiform chromitite body at the base of the MTZ (23°07.055N, 57°56.618E, 950 m). This body is about 45 m thick and consists of interlayered horizons of massive ore (>90% chromite) up to 3 m in thickness and of disseminated ore. The massive ore is a



**Fig. 2.** Schematic geological cross-section of the Moho Transition Zone (MTZ) in the Maqsad area of the Oman ophiolite. Chromitite ore bodies are localized in the host dunite layer (~300 m thickness).

compact assemblage of euhedral to subhedral chromite grains  $100-200 \,\mu\mathrm{m}$  in size; the interstitial silicate minerals are olivine, diopside, pargasite and, rarely, enstatite. The disseminated ore exhibits antinodular textures (nodular aggregates of olivine grains embedded in a matrix of chromian spinel) or, more commonly, chain textures (subhedral single olivine grains with interstitial chromian spinel). These textures suggest that a partly consolidated dunitic host was invaded and partly disaggregated by a hydrated melt that precipitated chromian spinel ( $\pm$  other silicate minerals) (e.g. Bédard et al., 2007). The chromian spinel to olivine ratio exhibits gradual variations, defining graded bedding. This indicates that the stratiform chromitite formed a suspension at some stage of its evolution. Chromite grains contain silicate and chromite inclusions (Table 1).

### Disseminated chromitite

Sample 04 OM 52D from a disseminated chromitite of the median part of the dunitic MTZ (23°05.703N, 57°57.675E, 997 m) where irregular patches of interstitial chromian spinel (locally concentrated to form lenses of massive ore) are abundant and interpreted as former magmatic impregnations (Leblanc & Ceuleneer, 1992). The silicate minerals are olivine, clinopyroxene, pargasite, and plagioclase.

#### Nodular chromitite

Two samples of nodular chromitite [83 OG 68(1) and 83 OG 68(2)] come from an  $\sim 3$  m thick and  $\sim 35$  m high dyke located at the top of the MTZ (23°06.013N, 57°58.601E, 1225 m), several tens of meters below the layered gabbros. Troctolitic and gabbroic sills are present in the dunite that hosts the dyke. The dyke is vertical and strikes parallel to the paleo-ridge axis (NW-SE). The contact between the chromite ore filling the dyke and the host dunite is sharp. The texture of the ore is nodular. Chromitite nodules may reach 2 cm in size. They consist of sintered aggregates of minute (a few hundred micrometres) chromite grains containing silicate inclusions (Table 1). A nucleus rich in silicates (olivine, clinopyroxene, plagioclase) is often present in the core of the nodules. At the base of the dyke [83 OG 68(1)], the nodules are tightly packed and flattened. The size and abundance of the nodules decrease progressively upward, and the texture of the ore becomes disseminated [single chromian spinel grains embedded in a silicate matrix, 83 OG 68(2)] at the top of the dyke. This chromitite ore body is pervasively affected by hydrothermal alteration, primary magmatic minerals from the silicate matrix (olivine, clinopyroxene and plagioclase) being partly transformed into lowtemperature hydrous minerals such as serpentine, chlorite, prehnite and zeolites (Leblanc & Ceuleneer, 1992). Carbonates are also commonly found as alteration products.

#### Sample preparation and analyses

We selected samples that had escaped pervasive transformation of the primary silicate assemblage into low-temperature hydrothermal phases. The freshest samples still contain some minor secondary minerals (≤5%) such as tremolite, hydrogrossular, talc, chlorite, carbonate and serpentine (in dunites) and sulphides scattered between and inside the primary grains along cracks and replacing the primary silicate phases. A database of all the studied silicate and chromite phases, including the host chromite and minerals of the chromite-hosted inclusions (Table 1), is available in the Electronic Appendix (EA; available for downloading at http://www.petrology.oxfordjournals.org).

Different inclusion types were identified based on detailed backscattered electron images of about 200 inclusions in four samples of nodular, disseminated and stratiform chromitite using a scanning electron microscope [JEOL JSM-6360 LV at Geosciences Environment Toulouse (GET), France and JEOL JSM-6480LV with EDS INCA-Energy 350 at Geological Department of Moscow State University, Moscow, Russia]. Major and minor element concentrations in the minerals of the inclusions and their host spinel were determined by electron microprobe using a CAMECA SX50 microprobe (GET)

Table 1: Types of chromite-hosted inclusions of nodular, disseminated and stratiform chromitites of the Magsad MTZ (Oman ophiolite)

Туре	Shape	Mineralogical composition	Features of inclusion	Sample number	Figure	Participating melt or fluid
Multipl	hase assemblage					
1	Rounded or lens-shaped	$Cr-Na Parg \pm Enst \pm$ $Cpx \pm Sulph as$ $co-entrapped phases*$	Cr-Na Parg overgrowths on Enst; associated with Chr coronas	Nodular: 83 OG 68(2)	4b	Aqueous fluid
2	Rounded or octahedral shape	$Aspid \pm Enst \pm Cr ext{-Na}$ $Parg \pm Sulph$	Aspid is the predominant mineral in inclusion; Aspid overgrowths on Enst and Cr-Na Parg; associated with Chr coronas	Nodular: 83 OG 68(1) Disseminated: 04 OM 52D	4d, 5a	Aqueous fluid
2a	Octahedral shape	Aspid/Phlog/Cr-Na Parg ± Enst ± Sulph, rare Serp, altered spinel	Aspid/Phlog/Cr-Na Parg are associated with Chr coronas; predominant type in the stratiform chromitite 04 OM 31E	Disseminated: 04 OM 52D Stratiform: 04 OM 31E	4c, 5b and f	Aqueous fluid
Microc	rystal(s)		5W 51E			
3	Euhedral Anhedral	Enst + Cpx, Fo	Euhedral, anhedral as associated with Chr coronas	Nodular: 83 OG 68(2) Disseminated: 04 OM 52D	4e, 5e	Aqueous fluid
4	Anhedral	Cpx/Plag ± Cr-Na Parg	Microcrystals are isolated or associated; Trem as replacing Plag	Nodular: 83 OG 68(1) 83 OG 68(2) Disseminated: 04 OM 52D	4f	Hydrous hybrid MORB
5	Anhedral Euhedral	$Hgross \pm Cr ext{-Na} \; Parg$	Isolated crystals; Hgross as replacing Plag	Nodular: 83 OG 68(2)	4g	Hydrous hybrid MORB
6	Euhedral	Chr	Isolated primary crystals; frequent association with hydrous silicate micro-inclusions	Disseminated: 04 OM 52D	4h, 5c and d	Aqueous fluid

Aspid, aspidolite; Cpx, clinopyroxene (between augite and diopside composition); Plag, plagioclase; Chr, chromite with high cr-number (chromite phase visible with optical microscopy in type 2a and invisible in type 2 inclusions); Cr-Na Parg, Cr-Na pargasite; Enst, enstatite; Fo, forsterite; Hgross, hydrogrossular; Phlog, phlogopite (in stratiform chromitites); Sulph, sulphides; Trem, tremolite replacing plagioclase; Serp, serpentine (in stratiform chromitites). \*Fe-Ni and Os-Ru-Ir sulphide microphases (laurite-erlichmanite group) are identified in the type 1, 2 and 2a multiphase inclusions.

with SAMX automation and wavelength-dispersive spectrometry (WDS). Analyses were conducted using an accelerating voltage of 15 kV, a beam current of 10 nA for silicate minerals and 20 nA for chromian spinels, and a beam size of  $2 \mu m$ . The applied acquisition conditions are typical for standard electron microprobe analysis (e.g. Borisova et al., 2010), allowing low detection limits (300-700 ppm for most major and minor elements in chromite and ~1200 ppm for Ni) and high internal precision (RSD ≤3% for major Mg, Al, Cr and Fe, and ≤30% for minor Mn and Ti in chromite). The compositions are reported in Figs 3-6, Table 2 and the Electronic Appendix. The ferric iron content of the chromite was determined by assuming ideal stoichiometry,  $XY_2O_4$ , where  $X = (Fe^{2+}, Mg, Ni,$ Mn, Co, Zn) and  $Y = (Cr^{3+}, Fe^{3+}, Al)$ . Titanium is assumed to be present as an ulvöspinel component, and Cr as Cr<sup>3+</sup>. Iron is subdivided into ferrous and ferric to satisfy the condition  $n_Y = 2 \times n_X$ , where  $n_Y$  is the total number of trivalent cations and  $n_X$  is the total number of divalent cations per unit cell. Possible Cr2+ contents in chromite are negligible because only  $\operatorname{Cr}^{3+}$  is a major component stabilizing chromian spinel (Hanson & Jones, 1998).

The large size of the chromite crystals and aggregates makes them ideal targets for high-precision analyses by

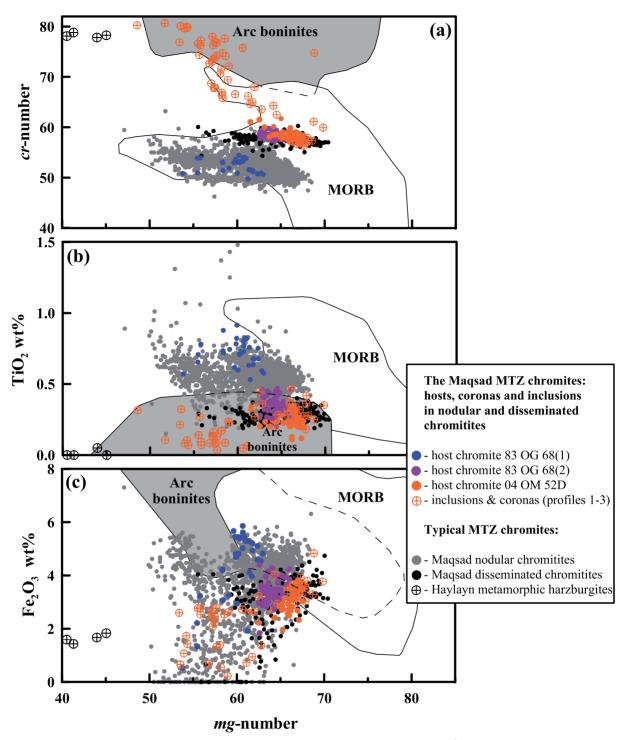


Fig. 3. (a-c) Cr-number [100Cr/(Cr+Al)], TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> contents vs mg-number [100 Mg/(Mg+Fe<sup>2+</sup>)] of the host chromite, chromite coronas and inclusions in nodular and disseminated chromitites of the Maqsad MTZ of the Oman ophiolite. Chromite data are summarized in Table 2 and the Electronic Appendix. The data for 'Haylayn metamorphic harzburgites' correspond to chromites from the serpentinized peridotites of the Haylayn area (G. Ceuleneer, unpublished data). The typical Maqsad MTZ chromite compositions are according to G. Ceuleneer (unpublished data). The 'MORB' field corresponds to chromite compositions from http://www.petdb.org (Lehner *et al.*, 2000) and data summarized by Kamenetsky *et al.* (2001, 2002); 'Arc boninites' are chromite compositions from Sigurdsson *et al.* (1993) and Kamenetsky *et al.* (2001, 2002) and the chromite database of Barnes & Roeder (2001). (d-f) Cr-number [100Cr/(Cr+Al)], TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> contents vs mg-number [100 Mg/(Mg+Fe<sup>2+</sup>)] of the host chromite and chromite coronas in the Maqsad stratiform chromitites of the Oman ophiolite. The 'MORB' field and 'Arc boninitic series' or 'Arc boninites' field are shown for comparison. All data sources are as in (a-c).

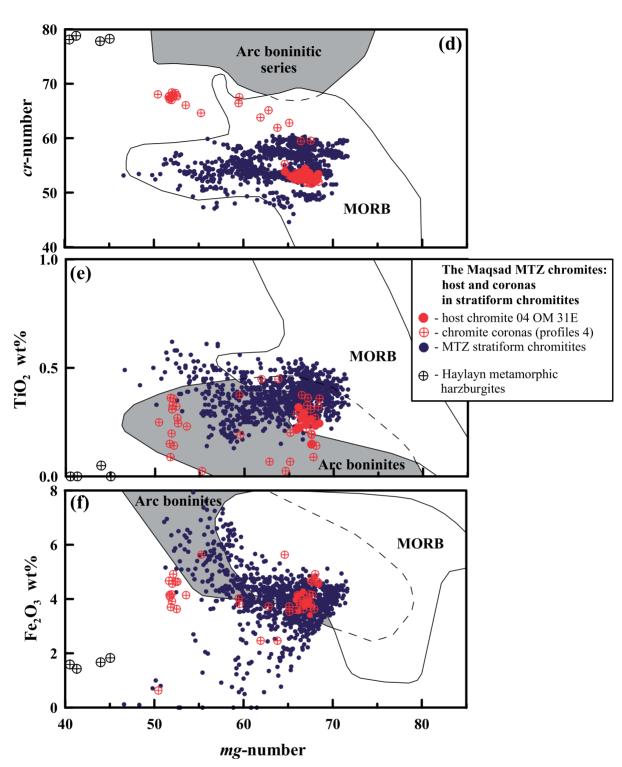


Fig. 3. (Continued)

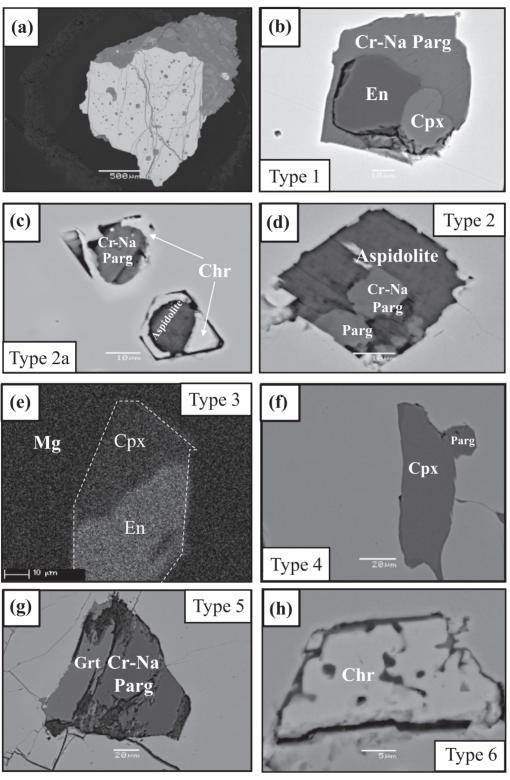


Fig. 4. Backscattered electron (BSE) images and X-ray map (using wavelength-dispersive spectroscopy; WDS) of chromite-hosted inclusions in chromitites of the Maqsad MTZ. Cr–Na Parg, Cr–Na pargasite; Aspidolite is Na phlogopite; En, enstatite; Cpx, clinopyroxene; Grt, hydrogrossular; Chr, high cr-number chromite coronas and inclusion. (a) BSE image showing the distribution of multiphase and microcrystal inclusions in the entire host chromite grain [83 OG 68(2) nodular chromitite]; (b) type 1 multiphase inclusion containing enstatite, clinopyroxene and Cr–Na pargasite [83 OG 68(2) nodular chromitite]; (c) type 2a coexisting inclusions consisting of single-phase Cr–Na pargasite and aspidolite enveloped by high cr-number chromite coronas (04 OM 31E stratiform chromitite); (d) type 2 multiphase inclusion containing Cr–Na pargasite and aspidolite [83 OG 68(1) nodular chromitite]; (e) type 3 inclusion Mg X-ray map (K $\alpha$ ) of enstatite and clinopyroxene [83 OG 68(2) nodular chromitite]; (f) type 4 microcrystal inclusion containing clinopyroxene and pargasite (04 OM 52D disseminated chromitite); (g) type 5 microcrystal inclusion with hydrogrossular (Grt) and Cr–Na pargasite [83 OG 68(2) nodular chromitite]; (h) type 6 microcrystal inclusion of high cr-number chromite (04 OM 52D disseminated chromitite).

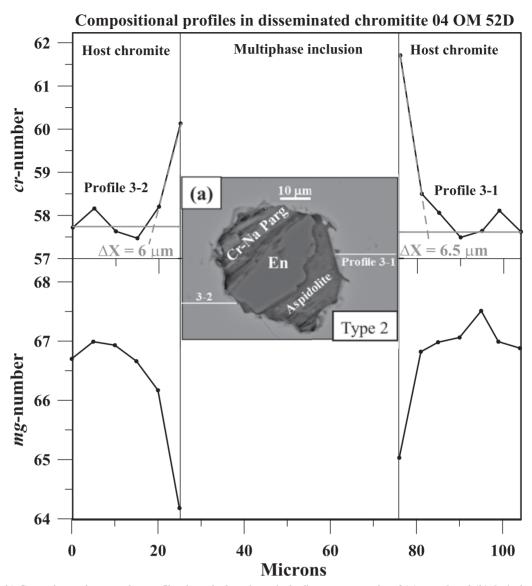


Fig. 5. (a, b) Cr-number and mg-number profiles through chromian spinel adjacent to examples of (a) type 2 and (b) 2a inclusions in the Maqsad MTZ disseminated and stratiform chromitites.  $\Delta X$  is the measured length of the profile of the type 2 inclusion [see equation (l) in the main text] and is obtained by finding the intersection between the estimate of the cr-number in the core of the grain and the tangent to the concentration profile near the corona–host interface (shown by the grey lines). Data are given in Electronic Appendix. (c, d) BSE image of an example of a chromite inclusion in host chromite of the disseminated chromitie 04 OM 52D. (c) Cr-number, mg-number and (d)  $Fe^{2+}/Fe^{3+}$  in chromian spinel and melt calculated for profile A–B through the type 6 inclusion. Data are given in the Electronic Appendix.  $\Delta X$  is the length measured on the profiles of type 6 inclusion [see equation (l) in the main text] and is obtained by finding the intersection between the estimate of the cr-number in the core of the grain and the tangent to the concentration profile near the inclusion–host interface (shown by the grey lines). (e) BSE image of olivine (Fo<sub>95</sub>) in a type 3 inclusion overgrown by the high cr-number chromite phase (Chr) and the host chromite in the disseminated chromitite 04 OM 52D. The transition zone between the olivine grain (Fo<sub>94-95</sub>; CaO up to 0·03 wt % and Cr<sub>2</sub>O<sub>3</sub>=0·01 wt % at olivine grain center) is enriched in Cr (up to Cr<sub>2</sub>O<sub>3</sub>=0·1-0·3 wt %) at the contact with the high cr-number chromite. Cr2O3 (wt%) and mg-number in chromian spinel (and Fo mol%, in olivine inclusion) are illustrated for profile A–B. Data are given in the Electronic Appendix. (f) BSE image of an example of altered spinel (cr-number  $\sim$ 30) and pargasite in a type 2a inclusion overgrown by the high cr-number chromite phase and the host chromite in the disseminated chromitite 04 OM 52D. Cr-number and mg-number in spinels are illustrated for profile A–B. Data are given in the Electronic Appendix.

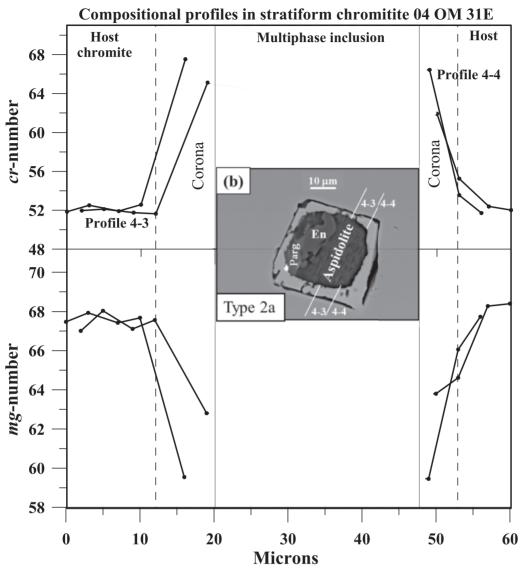
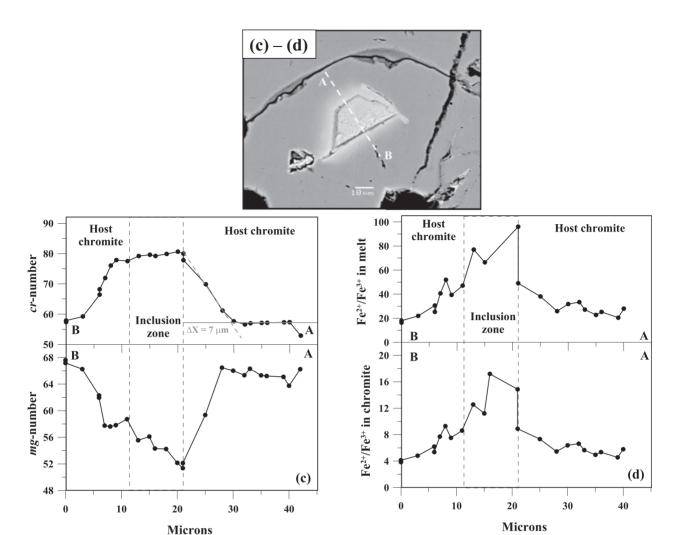


Fig. 5. (Continued)

laser fluorination for oxygen isotopes (Bindeman, 2008). Grain fractions of four chromite samples, treated in diluted HCl, rinsed with H<sub>2</sub>O and dried, were selected for oxygen isotope analysis. To separate the primary olivine grains from the secondary serpentine, olivine fractions from three dunite samples were treated chemically at GET according to the leaching method of Snow *et al.* (1994). Three leaches were made on each crushed dunite sample, using leaching solution of 6·2 N HCl, 5% HF. The first leach was cold for 5 min, the second was in an ultrasonic bath for 10 min, and the third was in the ultrasonic bath for 10 min followed by 10 min at 125°C. The samples were then dried and the fresh olivine cores were selected for laser fluorination analysis at the University of Oregon

(USA). Samples were heated with an infrared laser  $(9.6 \, \mu m, \, CO_2)$  in the presence of purified  $BrF_5$  to release oxygen. The generated  $O_2$  gas was purified in a series of cryogenic traps held at liquid nitrogen temperature, and then a mercury diffusion pump was used to remove any remaining traces of  $BrF_5$ . Oxygen was converted to  $CO_2$  gas by reacting with graphite at high T (1450°C), the yields were measured, and  $CO_2$  was analyzed by isotope ratio mass spectrometry (IRMS) in a dual inlet mode. Four to seven garnet standards ( $\delta^{18}O=6.52\%$ , University of Oregon garnet from Gore Mt, NY, USA named as "UOG garnet") were analyzed together with the samples during each of seven analytical sessions. Day-to-day  $\delta^{18}O$  variability of standards ranged from 0.1 to 0.3‰ lighter



**Fig. 5.** (Continued)

than their reference values and the measurements of unknowns were adjusted accordingly. The precision on standards is better than 0.1% of  $1\sigma$  standard deviation.

Homogenization experiments on selected inclusions were conducted at the University of Tasmania (Hobart, Australia) to study the silicate inclusion transformations upon heating. Hand-picked chromite grains from the nodular chromitite sample (83 OG 68-1) were placed in a platinum container and heated in a vertical furnace at  $1300 \pm 5^{\circ}$ C for 3 min under high-purity argon gas flow. These conditions were found to be suitable for complete melting of the multiphase inclusions entrapped in chromite. Heating was followed by quenching in water. Then the grains were hand-picked and mounted in epoxy and polished to expose the inclusions to the surface. Silicate glasses (silicate inclusions were converted to homogeneous melt at  $1300^{\circ}$ C) in more than 60 experimentally homogenized inclusions were analysed at standard conditions (e.g. Kamenetsky *et al.*,

2001) for major elements using a Cameca SX-50 microprobe (University of Tasmania, Australia).

#### RESULTS

#### Chromite host, coronas, and inclusions

The compositions of the host chromian spinel (up to 70–80% of the chromite volume) are reported in Figs 3 and 5, Table 2, and the Electronic Appendix. The chromites in nodular sample 83 OG 68(l) have mg-numbers (54–63), cr-numbers (50–54),  $\text{TiO}_2$  (0·6–0·9 wt %) and  $\text{Fe}_2\text{O}_3$  (0·2–6·0 wt %) contents typical of the Maqsad MTZ nodular chromitites. Host chromian spinel in both disseminated and stratiform samples (04 OM 52D and 04 OM 31E) is also typical of the high mg-number chromites of the Maqsad MTZ. The association of chromite (cr-number = 50–62; mg-number = 54–68) with olivine (Fo<sub>88–91</sub>) from the dunite hosting the

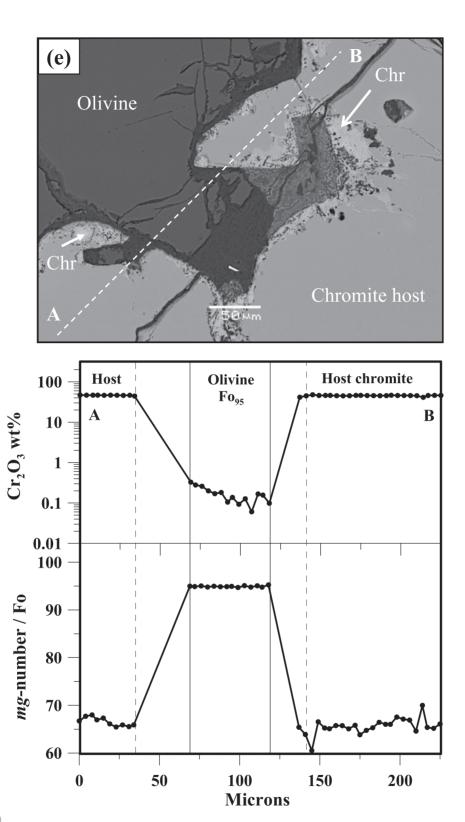


Fig. 5. (Continued)

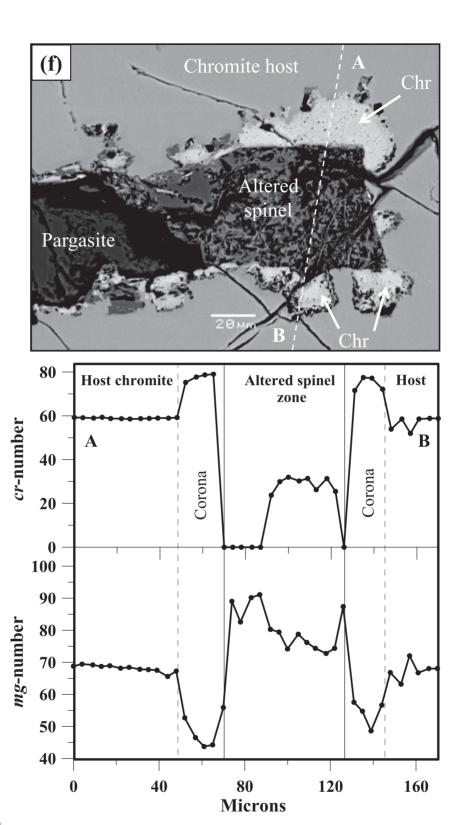
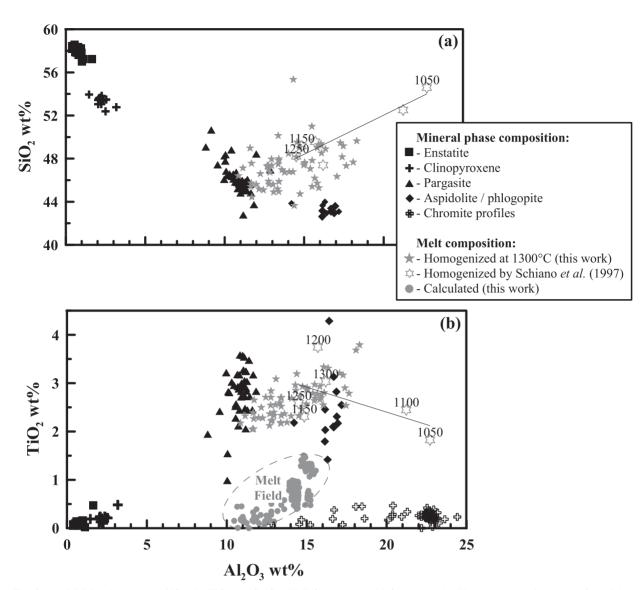


Fig. 5. (Continued)



**Fig. 6.** (a–d) Major elements: (a) SiO<sub>2</sub>, (b) TiO<sub>2</sub>, (c) Cr<sub>2</sub>O<sub>3</sub>, (d) FeO contents vs Al<sub>2</sub>O<sub>3</sub> contents in silicate and chromite phases of multiphase and microcrystal inclusions from the Maqsad MTZ nodular [83 OG 68(l,2)], disseminated (04 OM 52D) and stratiform (04 OM 31E) chromitites. Grey stars indicate the glass compositions of experimentally homogenized inclusions at 1300°C (this study). Lines show the compositional trends for melts obtained in homogenization experiments at 1050–1400°C (open stars with corresponding homogenization temperature; Schiano *et al.*, 1997). Chromite profiles' indicate TiO<sub>2</sub> FeO and Al<sub>2</sub>O<sub>3</sub> contents in chromites adjacent to the multiphase inclusions. The high concentrations of FeO (up to 14 wt %) and Cr<sub>2</sub>O<sub>3</sub> (1–3 wt %) in the experimentally homogenized inclusions are probably controlled by a strong diffusive Fe input from the adjacent chromite during the laboratory experiment and the initially high Cr contents in hydrous silicate minerals, respectively (see Electronic Appendix). The hydrous minerals and experimental melt compositions are recalculated on a water-free basis. In (b) the 'Melt Field' indicates the calculated TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> contents in equilibrium melts based on the compositions of the host chromite and chromite coronas and inclusions (as well as the equilibrium chromite—melt partitioning; see text). TiO<sub>2 melt</sub> contents (<2 wt %) calculated based on the composition of the type 4 clinopyroxenes [and using experimental  $K_d^{\text{Cpx/melt}}$  clinopyroxene—mafic melt partition coefficients from 0·27 to 0·43 of Dunn (1987), Hart & Dunn (1993) and Skulski *et al.* (1994); and TiO<sub>2Cpx</sub> = 0·2·0·5 wt %] are lower than those measured in the homogenized glasses. The type 1, 2, 4 and 5 pargasite gives TiO<sub>2 melt</sub> <1·2 wt % [as calculated based on the experimental  $K_d^{\text{Chromite}}$  and TiO<sub>2Parg</sub> = 15–3·5 wt %], which is lower compared with the homogenized glasses. The type 2 phlogopite mafic melt partition coefficient range 0·98–1·77 for phlogopite of Adam & G

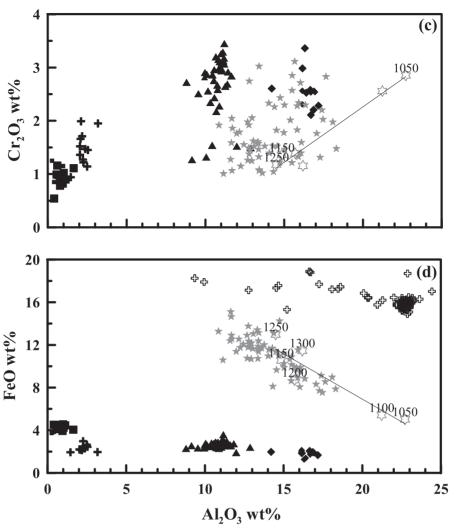


Fig. 6. (Continued)

Maqsad chromitites corresponds to the MORB field in the olivine–spinel mantle array (Arai *et al.*, 2011; and references therein). It should be noted that the mg- and cr-numbers in the host chromite of the Maqsad MTZ chromitites are typical of MORB (Fig. 3), whereas the  ${\rm TiO_2}$  and  ${\rm Fe_2O_3}$  contents plot in the intermediate field between those of the typical MORB and the hydrothermally altered harzburgites.

Typical compositional profiles through chromite coronas and inclusions (up to 10-15% of the chromite volume) are shown in Fig. 5. The chromite coronas in nodular, disseminated and stratiform chromitites have high cr-numbers (68–80) and low mg-numbers (50–58). A similar range of high cr-numbers (73–80) and low mg-numbers (54–60) is observed in the chromite inclusions (Type 6) in the host chromite of the disseminated chromitites (Table 2 and Electronic Appendix). The similar idiomorphic and compositional features of the high

cr-number chromite coronas and inclusions (Figs 3-5) suggest that they were formed in a common process. High cr-numbers and low TiO2 contents in the chromite coronas and inclusions resemble those of arc boninites (Fig. 3). In contrast, the Magsad MTZ chromite coronas and inclusions have much lower Fe2O3 contents than those of chromites from typical arc boninites and MORB. The Maqsad high cr-number chromites are also different from the chromites described in 'anomalous' MORB-related plutonic rocks from Ocean Drilling Program (ODP) Holes 735B (Southwest Indian Ridge) and 895 (Hess Deep) (Arai & Takemoto, 2007; Kamenetsky & Gurenko, 2007), which have higher TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> contents. It should be noted that the extremely low TiO2 and Fe2O3 contents in the Maqsad high cr-number chromites approach those of chromites in the Haylayn hydrothermally altered harzburgites of the Oman ophiolite (Fig. 3).

Table 2: The Magsad MTZ chromite inclusions and their host chromite compositions

Label:	04 OM 52Di-incl-3	04 OM 52Di-incl-4	04 OM 52Di-incl-5	04 OM 52Di-incl-8	04 OM 52Di-incl-15	04 OM 52Di-incl-16	04 OM 52Di-incl-18	04 OM 52Di-incl-19	04 OM 52Di-incl-20
Analysis number:	50	51	52	59	85	86	88	91	92
TiO <sub>2</sub>	0.09	0.09	0.05	0.08	0.09	0.14	0.14	D.L.	0.13
$Al_2O_3$	11.29	11.52	12-22	10-26	11.78	13.50	11.59	10.82	11.56
Cr <sub>2</sub> O <sub>3</sub>	58-26	57-32	56.93	59.70	56-36	54-37	56-43	57-09	56.85
FeO <sub>tot</sub>	17:38	17-88	17:34	17-52	18-54	18-14	18-48	17-97	18.00
MnO	0.24	0.36	0.36	0.23	0.23	0.27	0.32	0.15	0.32
MgO	11.98	11.87	12.87	10.88	11.37	11·83	11.21	11.84	11·84
NiO	0.08	0.011	D.L.	0.02	0.12	0.13	0.09	0.08	D.L.
Sum	99-51	99-34	100-33	98-71	98-61	98-66	98.53	98-69	98.86
FeO*	15-11	15-67	14.89	16-55	16.05	15.83	15.99	15-81	15.50
Fe <sub>2</sub> O <sub>3</sub>	2.53	2.46	2.72	1.07	2.77	2.57	2.77	2.41	2.78
$\mathrm{Fe^{2+}/Fe_{spinel}^{3+}}$	6.63	7.08	6.09	_	6.45	6.84	6.42	7.30	6.20
Fe <sup>2+</sup> /Fe <sup>3+</sup> <sub>melt</sub>	33-42	36-41	29.89	_	32.25	34-81	32.08	37-91	30.64
Al <sub>2</sub> O <sub>3 melt</sub>	10.88	10-97	11.24	10-46	11.07	11.71	11.00	10-69	10.99
TiO <sub>2 melt</sub>	0.17	0.17	0.10	0.15	0.17	0.23	0.23	<0.03	0.22
$100 \mathrm{Mg/(Mg + Fe^{2+})}$	58-57	57-45	60-63	53.94	55-80	57·12	55.53	57·17	57-65
100Cr/(Cr + AI)	77-59	76.96	75.77	79-62	76·25	72:99	76-57	77-97	76.74
Label:	04 OM	04 OM	04 OM	04 OM	04 OM				
	52Di-host-1	52Di-host-2	52Di-host-3	52Di-host-4	52Di-host-5	52Di-host-6	52Di-host-8	52Di-host-9	52Di-host-10
Analysis number:	53	54	57	58	65	66	89	90	96
TiO <sub>2</sub>	0.21	0.18	0.23	0.21	0.13	0.08	0.18	0.29	0.19
$Al_2O_3$	22.59	22.57	22-43	22.70	20.22	22.78	22.60	22.48	22.37
Cr <sub>2</sub> O <sub>3</sub>	45-68	45.46	45-64	46-13	48-62	45.06	45-14	44-63	45·11
FeO*	12.65	12·11	12·19	12.28	12.75	12.89	12.49	12.01	12.01
Fe <sub>2</sub> O <sub>3</sub>	2.93	3.63	3.69	3.67	3.33	3.07	3.75	3.95	3.60
MgO	14.75	15.01	15-13	15-37	14-43	14-40	11.68	15.03	15.05
Fe <sup>2+</sup> /Fe <sup>3+</sup> <sub>spinel</sub>	4.79	3.71	3.67	3.72	4.26	4.66	3.71	3.38	3.71
Fe <sup>2+</sup> /Fe <sup>3+</sup> <sub>melt</sub>	21.85	15-65	15-41	15.71	18-73	21.08	15-62	13-83	15-64
100 Mg/(Mg + Fe <sup>2+</sup> )	67·52	68-84	68-86	69-06	66-86	66-57	67-83	69-04	69.08
100Cr/(Cr + AI)	57.58	57-47	57.73	57·70	61.74	57-03	57-27	57·13	57.50

<sup>\*</sup>FeO, Fe<sub>2</sub>O<sub>3</sub>, Fe<sup>2+</sup>/Fe<sup>3+</sup> in spinel are calculated according to spinel stoichiometry; Al<sub>2</sub>O<sub>3</sub> and Fe<sup>2+</sup>/Fe<sup>3+</sup> in melt are calculated after Maurel & Maurel (1982a, 1982b), 1982c). TiO<sub>2</sub> in melt is calculated after Kamenetsky et~al. (2001) and Rollinson (2008) using the equation for 'Arc'. SiO<sub>2</sub> contents are below 0.5 wt %. D.L., values below detection limit.

### Chromite-hosted inclusion types and mineral associations

The Maqsad MTZ chromite-hosted multiphase and microcrystal inclusions consist of silicate, sulphide and chromite of  $1-50\,\mu m$  in size. Silicates make up to 20% of the host chromite grain surface (Fig. 4a). Six main types and one sub-type of inclusion are distinguished based on inclusion shape (rounded to octahedral, anhedral to euhedral), mineral assemblages and composition; they

are summarized in Table 1 and illustrated in Figs 4b-h and 5a-f.

#### Type 1, 2 and 2a multiphase inclusions

Type 1, 2 and 2a multiphase inclusions are composed of hydrous and anhydrous silicates and minor sulphides, and are always associated with high cr-number coronas (Table 1). Type 1 contains abundant Cr-Na pargasite, and types 2 and 2a contain aspidolite (Na phlogopite). In type

l, 2 and 2a inclusions, Cr—Na pargasite surrounds enstatite located in the inclusion core and is associated with aspidolite; it is occasionally co-entrapped with clinopyroxene (Fig. 4b—d). Subtype 2a inclusions are distinguished from the main type 2 by euhedral coronas of high cr-number chromite overgrowing pargasite, aspidolite or phlogopite (Fig. 4c). The chromite-hosted micas have variable Na<sub>2</sub>O and K<sub>2</sub>O contents ranging from aspidolite to phlogopite (phlogopite occurs only in the type 2a inclusions of the stratiform chromitite; Electronic Appendix). Rare inclusions of an altered spinel and serpentine assemblage are also associated with high cr-number coronas (Fig. 5f, Table 1).

#### Type 3, 4, 5 and 6 microcrystal inclusions

Type 3, 5 and 6 inclusions are euhedral microcrystals of silicates and high cr-number chromite. Type 3 inclusions contain an association of clinopyroxene with enstatite [limited by a single crystal in nodular chromitite, sample 83 OG 68(2); Fig. 4e] associated with the host chromite. In contrast, the high cr-number chromite phases are found adjacent to type 3 forsterite grains (Fig. 5e), suggesting that the olivine is associated with the high cr-number chromite rather than with the host chromite. In addition, type 4 anhedral inclusions associated with the host chromite contain clinopyroxene and bytownite partially transformed into secondary phases (Table 1), sometimes associated with Cr-Na pargasite (Fig. 4f). In addition, anhedral type 5 inclusions, also associated with the host chromite, are composed of hydrogarnet and occur alone or in association with Cr-Na pargasite (Fig. 4g). Type 6 inclusions are euhedral microcrystals of high cr-number chromite (Figs 4h and 5c, d). Their euhedral shape indicates a primary origin and an early entrapment into the host chromite.

#### Silicate mineral composition

The compositions of Cr-Na pargasite, aspidolite, phlogopite, olivine, clinopyroxene and enstatite are summarized in Fig. 6 and the complete dataset is provided in the Electronic Appendix. The composition of the chromitehosted plagioclase (An<sub>86</sub>) is in the range of that in orthopyroxene-rich, high-Mg gabbronorites depleted in incompatible trace elements drilled from the Mid-Atlantic Ridge at Deep Sea Drilling Project (DSDP) Site 334 (Nonnotte et al., 2005), of those from the periphery of the Magsad diapir (Benoit et al., 1999), and of those of the Magsad mantle plagiogranites (Amri et al., 1996). In contrast, the chromite-hosted Fe-Mg silicates have higher mg-numbers (90–97) and  $Cr_2O_3$  (0·5–4 wt %) than (1) those from the troctolitic and gabbroic cumulates, occurring in the crustal section of the Maqsad area and filling former melt channels and dykes in the Magsad mantle diapir (e.g. Python & Ceuleneer, 2003), (2) those from the Magsad mantle plagiogranites (Amri et al., 1996), and (3) those from the DSDP Site 334 gabbronorites (Nonnotte *et al.*, 2005). The Maqsad MTZ clinopyroxenes (varying from augite to diopside in composition), Cr–Na pargasite, and micas are variable in  $TiO_2$  (typically 0.2-0.5 wt %, 1.5-3.5 wt %, and 1.7-4.0 wt %, respectively, Fig. 6).

### Composition of homogenized inclusions

The glasses obtained from the homogenization experiments at  $1300 \pm 5^{\circ}$ C show large variations in the concentrations of major elements, especially Al<sub>2</sub>O<sub>3</sub> (10–18 wt %),  $SiO_2$  (44–56 wt %) and CaO (4–10 wt %) (Fig. 6; Electronic Appendix). These compositions are similar to those of 'polymineral' solid inclusions from the chromitite dyke homogenized at 1300°C by Schiano et al. (1997). In the latter study, the inclusions were homogenized at 1050–1400°C. They show that compositional trends in all homogenized inclusions are controlled by incongruent melting with formation of olivine at 1150-1200°C. Intra-inclusion homogeneity of the quenched glasses was observed by Schiano et al. (1997) only at >1300°C. The average TiO<sub>2melt</sub>, Al<sub>2</sub>O<sub>3melt</sub>, FeO<sub>melt</sub> and MgO<sub>melt</sub> contents in the homogenized inclusions are  $2.6 \pm 0.4$  wt %,  $14 \pm 2$  wt %,  $11 \cdot 1 \pm 1 \cdot 8$  wt %, and  $10 \cdot 5 \pm 2 \cdot 1$  wt %, respectively, whereas the corresponding host chromite contains average TiO<sub>2Chr</sub>, Al<sub>2</sub>O<sub>3Chr</sub>, FeO<sub>Chr</sub> and MgO<sub>Chr</sub> contents of  $0.4 \pm 0.05$  wt %,  $23 \pm 1$  wt %,  $12 \pm 0.7$  wt %, and  $15.4 \pm 0.5$  wt %, respectively (for  $\sim 60$  pairs of the homogenized inclusion-host chromite, see Electronic Appendix). The corresponding partition coefficients  $(K_{\rm d}^{\rm Chr/melt})$  between the host chromite and the melts homogenized at 1300°C are:  $K_{\rm d~Ti} = 0.15 \pm 0.03$ ;  $K_{\rm d~Al} = 1.7 \pm$ 0.2 and  $K_{\rm d-Fe/Mg} = ({\rm FeO_{Chr}MgO_{melt}})/({\rm FeO_{melt}MgO_{Chr}})$  $=0.7\pm0.1$  (see Electronic Appendix). The partition coefficient  $K_{\rm d}^{\rm Chr/melt}$  for Ti is far from the equilibrium chromite-melt partitioning summarized by Kamenetsky et al. (2001), which is  $\sim 0.8$  at TiO<sub>2Chr</sub> = 0.4 wt %. In contrast,  $Al_2O_{3melt}$  contents (average  $14\pm 2\,wt$  %) and FeO/  $MgO_{melt}$  ratios (average  $1\cdot1\pm0\cdot1$ ) in the homogenized melts are in accord with equilibrium with the host chromite (Electronic Appendix). The high concentrations of FeO (up to 14 wt %) in the homogenized inclusions heated to 1300°C would require a strong diffusive Fe input from the chromite coronas or host during the experiment (e.g. Kamenetsky et al., 2001; Danyushevsky et al., 2002). The elevated  $Cr_2O_3$  contents (average  $1.8 \pm 0.5$  wt %) in the quenched glasses are probably due to the initial high Cr<sub>2</sub>O<sub>3</sub> contents in the hydrous silicate minerals and additional chromite dissolution in the melt (e.g. Murck & Campbell, 1986).

# Oxygen isotope signatures of chromites and olivines from the Maqsad MTZ

We performed the first measurements of the oxygen isotope composition of chromite and associated olivine grains in the MTZ of the Oman ophiolite. The  $\delta^{18}$ O values of

chromite grains (Maqsad chromitites) vary from 3·2 to 3·7‰ (Table 4). The  $\delta^{18}O$  values of single olivine grains in the associated Maqsad dunites vary from 5·2 to 5·8‰, which is similar to and slightly higher than the 5·18  $\pm$  0·28% reported for olivines from mantle peridotites (Mattey *et al.*, 1994), perhaps reflecting protolith seawater alteration at low temperatures.

#### **DISCUSSION**

# Was a silicate melt involved in the Maqsad Moho Transition Zone petrogenesis?

In this section we use the composition of the Magsad MTZ chromites, together with the new data from this study and published experiments on the homogenization of the chromite-hosted multiphase inclusions, to better constrain the origin of the chromite-hosted inclusions. The known sensitivity of the Cr/Al ratio in chromian spinel to water activity and the composition of the original melt (Irvine, 1975; Onuma & Tohara, 1981; Dick & Bullen, 1984; Roeder & Reynolds, 1991) can be used to better constrain these parameters during chromite crystallization. Calculations of the melt composition using the analysed chromite compositions and reported experimental chromite-melt partitioning coefficients (Maurel & Maurel, 1982a, 1982b, 1982c; Kamenetsky et al., 2001; see Table 2 and Electronic Appendix) imply that the melts in equilibrium with the host chromite of the nodular, disseminated, and stratiform chromitites had high Al<sub>2</sub>O<sub>3 melt</sub> (~14·5 wt % on average) and  $TiO_{2 \text{ melt}}$  (0.8 wt %) contents,  $FeO/MgO_{melt}$  of  $\sim 1$ , and high mg-numbers (~65), consistent with primitive tholeiitic MORB-like compositions (Fig. 6b; Electronic Appendix). The calculated melts in equilibrium with the high cr-number chromite coronas and inclusions had lower  $Al_2O_3$  melt (10–11 wt %) and  $TiO_2$  melt ( $\leq$ 0·3 wt %) contents, but similar mg-numbers of ~65 (Table 2). The TiO<sub>2 melt</sub> contents are much lower than those measured in the homogenized glasses (2-4 wt %, Fig. 6b). Moreover, the temperature stability domain of amphibole and micas and associated chromites below 1050°C (see discussion below; Table 3) indicates that the observed homogenization temperature of 1300°C for the multiphase inclusions is much higher than the true temperature of the Magsad MTZ chromitite crystallization. Therefore, neither host chromite, high cr-number inclusions and coronas, nor silicate minerals in the multiphase inclusions could have crystallized from the experimentally produced melts. The large inter-inclusion compositional variation of the melts can be explained only by heterogeneous entrapment of silicates (i.e. variable proportions of enstatite, pargasite, aspidolite and/or phlogopite). The euhedral shapes of the high cr-number coronas and inclusions and their predominance over the silicate phase in the multiphase inclusions (Figs 4c and 5b) indicate that the high cr-number chromite crystallized early, either as microcrystals (Figs 4h and 5c, d) or as chromite overgrowths on the silicate crystals or their assemblages (Fig. 5e and f) rather than as a daughter phase from the homogenized melt as previously suggested by Schiano *et al.* (1997) and Borisova *et al.* (2008).

In the framework of an entirely magmatic scenario, non-equilibrium (fractional) crystallization of the host chromite accounts for the preservation of early-stage phases (high cr-number chromite). However, our homogenization experiments provide no evidence either for entrapment of a melt phase or for a melt-crystal reaction (e.g. incongruent reaction with melt formation), which could be responsible for the Magsad chromite crystallization. We did not find any geological evidence for a close association of the Magsad chromitites with pyroxenites or anorthosites. Therefore, a chromitite origin by incongruent dissolution of pyroxene or feldspar into an olivine + chromite-saturated melt (Bédard & Hébert, 1998; Bédard et al., 2000) is also unlikely for the Magsad MTZ chromitites. Because the experimentally homogenized melts are well explained by heterogeneous trapping of silicates, the Magsad MTZ chromites could not have crystallized from an arc boninite melt, in contrast to the suggestion of Schiano et al. (1997).

# Constraints on T-P- $\alpha_{H2O}$ conditions of the Magsad MTZ chromitite crystallization

The mineral assemblages of the chromite-hosted inclusions, together with available experimental and geological data on mineral phase equilibrium, provide new constraints on the chromite crystallization sequence and the  $T-P-\alpha_{\rm H2O}$  conditions during chromitite crystallization (Table 3).

### High cr-number chromite corona and inclusion crystallization

The first group of constraints stems from the multiphase inclusions (Types 1, 2 and 2a) and euhedral type 3 inclusions associated with the high cr-number chromite coronas. The high mg-numbers of the chromite-hosted Fe-Mg silicates are consistent with high water activity ( $\alpha_{H2O} = 1$ ) in the crystallizing melt (e.g. Koepke et al., 2009) or its crystallization directly from a high-temperature aqueous fluid (e.g. Python et al., 2007). Phase-equilibria experiments (e.g. Presnall, 1995; Feig et al., 2006) indicate that, in the presence of an H<sub>2</sub>O or H<sub>2</sub>O-CO<sub>2</sub> phase, pargasitic amphibole forms from a silicate melt or fluid between 700 and  $1000^{\circ}$ C and P > 50 MPa. Above  $900-1000^{\circ}$ C, chromian pargasite transforms into olivine, chromite and a melt (Johan & Le Bel, 1978), although pargasite may be stable at higher T in the presence of high F and Cl contents (e.g. Presnall, 1995). It is well known that a miscibility gap exists in the aspidolite-phlogopite solid solution at 200 MPa and 700°C (e.g. Costa et al., 2001, and references therein). Thus, where aspidolite (Na end-member),

Table 3:  $T-P-f_{O2}$  conditions and model stages responsible for the Magsad MTZ chromitite petrogenesis

Model stages:	Serpentinized mantle protolith	Prograde metamorphism	Assimilation by MORB
Stage number:	Ī	II	III
Altered spinel	+	-	_
Serpentine assemblage	+	_	_
High cr-number chromite	_	+	_
Forsterite	_	+	_
Phlogopite	_	+	_
Aspidolite	_	+	_
Clinopyroxene	_	+	+
Enstatite*	_	+	+
Cr-Na pargasite	_	+	+
Plagioclase	_	_	+
Host chromite	_	_	+
Inclusion types:	2a	1, 2, 2a, 3, 6	4, 5
Pressure† (MPa):	200?	200	200
Temperature† (°C):	≤600	600-950 (±10)	950-1050 (±10)
Redox conditions; (log $f_{\rm O2}$ , bars)	_	-14 to $-12$	-11
Oxygen buffer:	_	QFM - 2·7 to QFM at 600-950°C	QFM - 0·4 at $1000 \pm 15^{\circ}\text{C}$
Olivine-chromite assemblage‡	_	The Maqsad MTZ type 3 inclusion ( $Fo_{95-96}$ ) and incongruent olivine ( $Fo_{85-91}$ )§ + High cr-number chromite coronas and inclusions	Olivine (Fo <sub>88-91</sub> ) from the Maqsad MTZ dunites + Host chromite from the Maqsad MTZ chromitites

<sup>\*</sup>Rare presence of enstatite in chromitite matrix.

§Composition of incongruent olivine appearing during homogenization experiment on polymineralic inclusions is after Schiano et al. (1997).

Composition of olivine Fo88-91 from the Maqsad MTZ dunites, which are the host rocks for the investigated MTZ chromitites, is according to Abily & Ceuleneer (in press).

+ indicates presence of the phase or assemblage

phlogopite (K end-member) and Cr-Na pargasite are all present in type 2a chromite-hosted inclusions (Figs 4c and 5b), all phases could have crystallized from a hydrothermal fluid at temperatures as low as 700°C and pressures of 200 MPa. The association of clinopyroxene with enstatite and pargasite found in one inclusion of type 1 (Fig. 4b) and in type 3 (Fig. 4e) suggests that these phases crystallized simultaneously and were entrapped near the two-pyroxene closure temperature of 860-900°C (obtained according to Wells, 1977). It should be noted that the Magsad MTZ chromite-hosted Cr-Na pargasite and aspidolite contain high Na2O and Cl concentrations reaching 6 and 0.4 wt %, respectively. Therefore, the assemblage of type 1-3 inclusions with high cr-number

Table 4: Oxygen isotope composition  $\delta^{18}O$  (‰) of the Magsad MTZ chromitites and host dunites

Host dunites	Olivines*	Chromitites	Chromites
11 TUF1 11 TUF2 11 TUF7	$5.8 \pm 0.1$ $5.4 \pm 0.1$ $5.2 \pm 0.1$	83 0G 68 (1) 83 0G 68 (2) 04 OM 52D	$3.2 \pm 0.1$ $3.8 \pm 0.1$ $3.6 \pm 0.1$
		04 OM 31E	$3.5\pm0.1$

<sup>\*</sup>Oxygen isotope composition of the mineral fractions measured at the University of Oregon (USA).

<sup>†</sup>Temperatures were estimated based on the available experimental data on silicate mineral phase equilibrium (see text). The pressure of 200 MPa used for the calculation (see below) is based on the thickness of the geological sequence of the

<sup>‡</sup>Oxygen fugacity and closure temperature for the olivine-chromite assemblages were calculated following O'Neill & Wall (1987) and Ballhaus et al. (1991) at 200 MPa. The log units of fO<sub>2</sub> are relative to the quartz-fayalite-magnetite (QFM) oxygen buffer.

chromite (Tables 1 and 3) may have crystallized in the presence of an aqueous NaCl-bearing fluid. Our estimates of closure temperature for olivine inclusions and high cr-number chromite fix the lowest temperature of the high cr-number chromite crystallization at  $600-630^{\circ}$ C [obtained using equations of O'Neill & Wall (1987) and Ballhaus *et al.* (1990, 1991) at 200 MPa, Table 3]. Thus, a T of  $600-950^{\circ}$ C and P of  $\sim 200$  MPa for high cr-number chromite crystallization corresponds to subsolidus conditions for a hydrous mafic melt (similar to primitive MORB; Feig *et al.*, 2006) and implies metamorphic recrystallization in the presence of an NaCl-bearing fluid.

#### Host chromite crystallization

The second group of constraints stems from anhedral type 4 and 5 inclusions. The ore bodies were emplaced and crystallized at the base of the oceanic crust whose stratigraphic thickness does not exceed 6 km. This places a major geological constraint for the maximum lithostatic pressure of crystallization of 200 MPa. Moreover, there is abundant crystallization of MORB-type tholeiites along the low-pressure olivine-plagioclase cotectic (troctolitic cumulates) evolving to the olivine-plagioclase-clinopyroxene cotectic as temperature decreases (olivine gabbro cumulates) in impregnations, sills, and dykes adjacent to the chromitite ore bodies (Korenaga & Kelemen, 1997, and references therein). This provides further evidence for low-pressure conditions in the Magsad MTZ. Type 4 and 5 inclusions, containing plagioclase (An<sub>86</sub>) in association with anhedral pargasite (Fig. 4f and g), could be at equilibrium at 800-1120°C and 200-300 MPa according to the geothermometer of Holland & Blundy (1994). To avoid complete destabilization of the chromite-hosted pargasite, the chromite crystallization should occur in the pargasite stability field (below 1070°C; Muntener et al., 2001). Indeed, Feig et al. (2006) demonstrated that H<sub>2</sub>O-saturated MORB melts crystallize pargasite below 1020°C in equilibrium with chromite at pressures of ~500 MPa. Thus, our findings of the same assemblage of chromite with pargasite, clinopyroxene and plagioclase at lower pressures (200 MPa) in the Magsad MTZ offer two possibilities: (1) pargasite crystallization from a fluid-saturated (~5 wt % H<sub>2</sub>O at ~200 MPa) mafic melt ('magmatic' scenario), or (2) direct pargasite precipitation from an aqueous fluid or recrystallization from another silicate mineral in the presence of fluid ('subsolidus scenario'). We prefer the first hypothesis for the host chromite crystallization because, in the case of a water-saturated MORB system at 200 MPa, hydrous MORB melt is present above 950°C (Berndt et al., 2005; Feig et al., 2006), and the host chromite shows compositions similar to MORB chromites (Fig. 3). However, the second 'subsolidus scenario' cannot be completely excluded. Thus, the host chromite may crystallize at 950-1050°C from a water-saturated hybrid MORB melt (see discussion below). Therefore, P of  $200 \pm 50$  MPa

and T from 600 to  $1050^{\circ}$ C are likely to be the range of conditions of the Maqsad MTZ chromite formation in a water-bearing system.

### Constraints on redox conditions and mantle source

The major challenge in understanding chromitite formation is to identify a mechanism that concentrates Cr given that it has a low solubility in basaltic melts (Roeder & Reynolds, 1991) and aqueous fluids at redox conditions corresponding to the quartz-fayalite-magnetite buffer (QFM) (see below). Our data suggest that the Maqsad MTZ chromitites crystallized in the presence of an aqueous fluid and/or a hydrous melt sharing many characteristics with MORB. Because MORB magmas are generally dry (e.g. Danyushevsky et al., 1996; Asimov & Langmuir, 2003), these conditions require an external source of water. The strong decrease in Fe<sup>2+</sup>/Fe<sup>3+</sup> in the profiles from chromite inclusions to the host chromite (Fig. 5d) indicates a sharp change in temperature and/or oxygen fugacity upon the chromite crystallization  $[f_{\Omega^2}]$  is calculated based on the olivine-chromite equilibrium of O'Neill & Wall (1987) and Ballhaus et al. (1990, 1991) at 200 MPa, Table 3]. Initially high  $Fe^{2+}/Fe^{3+}$  ratios (up to  $\sim$ 16) are similar to those of chromite from the Oman metamorphic harzburgites  $(Fe^{2+}/Fe^{3+}=12-16)$ , whereas  $Fe^{2+}/Fe^{3+}$ values of 3-5 are typical magmatic values (e.g. Kamenetsky et al., 2001). Three independent arguments provide evidence for reducing conditions during the early stages of the chromite crystallization in the presence of a high-temperature fluid: (1) extremely high Fe<sup>2+</sup>/Fe<sup>3+</sup> ratios in early (high cr-number) chromite (Table 2, Fig. 5d); (2) elevated Cr contents (probably in the form of  $Cr^{2+}$ ) in the silicate-phase inclusions (Fig. 6); (3) low oxygen fugacity inferred from the olivine-chromite equilibrium. The reducing conditions (from QFM - 2.7 to QFM at 600-1000°C, Table 3) evidenced for the chromite crystallization strongly support the derivation of the chromite grains from serpentinized oceanic lithospheric mantle rather than from more oxidized fluids from the subducting slab, at least in the Maqsad area of the Oman ophiolite. Only serpentinized oceanic mantle can provide highly reducing fluids as evidenced by native iron in the serpentinized peridotites from the Maqsad area (Lorand, 1987). Methane-rich fluids are observed as olivine-hosted inclusions in hydrated harzburgite (Sachan et al., 2007). The initial stages of dehydration of methane-bearing serpentinized mantle could result in the liberation of such aqueous CH<sub>4</sub>-bearing fluids. Highly reduced C-O-H fluids have been documented in chromite-hosted inclusions in the Kempirsai ophiolites from the mantle-crust transition zone (Melcher et al., 1997), and highly reducing conditions have also been inferred for the Thetford Mines ophiolite (Pagé et al., 2008). Our estimates of the redox conditions of the chromite-hosted fluid, based on the

Kempirsai fluid inclusion data (Melcher et al., 1997) using the SUPCRT thermodynamic database (Sverjensky et al., 1997), yield oxygen fugacity between QFM - 5 and QFM -2 at  $1000^{\circ}$ C and 200 MPa. The  $Cr_{2}O_{3}$  (0.8–2.0 wt %) and  $100 \,\mathrm{Mg/(Mg + Fe^{2+})}$  (92–96) values in the Maqsad MTZ type 2 and 3 pyroxenes and forsterite inclusions are much higher than those typical of the Magsad harzburgites (<0.8 wt % and ~91, respectively; G. Ceuleneer, unpublished data), suggesting that these phases are not xenocrysts derived from water-poor harzburgitic mantle. The Magsad MTZ assemblage of high cr-number chromite (low Fe<sub>2</sub>O<sub>3</sub>) with forsterite (Fo<sub>95-96</sub>), pyroxene (mg-number = 92-94), and pargasite (mg-number = 90-94) inclusions (Tables 2 and 3; Electronic Appendix) suggests their origin to be from a highly refractory mantle source, probably hydrated harzburgite.

# Constraints on Cr mobility in high-temperature fluids

The hydrous silicates of the chromite-hosted inclusions are either magmatic or high-temperature hydrothermal phases as indicated by their high TiO<sub>2</sub> (≥0.5 wt %) and  $Cr_2O_3$  ( $\geq 1.5$  wt %) concentrations, because both  $Ti^{4+}$ and Cr3+ are generally not mobile in low- to moderatetemperature aqueous fluids (≤450°C; e.g. Crerar et al., 1985). In addition, high T and reducing conditions favour lower oxidation states of multivalent elements (Fe and Cr), which are far more soluble. Thus, the high Cr content (up to 4 wt % Cr2O3) in the Maqsad MTZ chromite-hosted silicates (Fig. 6c) might be due to abundant Cr<sup>2+</sup> in the fluid-melt system. By analogy with Fe<sup>2+</sup>, Cr<sup>2+</sup> and its Cl complexes are expected to be far more soluble than Cr<sup>3+</sup> species (e.g. Crerar et al., 1985; Pokrovski et al., 2003). Equilibrium calculations using thermodynamic data for Cr hydroxide complexes from the SUPCRT database (Shock et al., 1997, http://geopig.asu .edu/index.html#) also indicate that the stability field of Cr<sup>2+</sup> species in aqueous solution under the redox conditions of the QFM buffer widens with increasing temperature. The elevated Cr/Al ratios in boninitic melts and hydrothermal fluids may thus reflect high concentrations of Cr<sup>2+</sup> in the form of chloride complexes in aqueous fluid under reducing conditions that significantly enhance the solubility of Cr3+-bearing minerals, whereas the solubility of Al<sup>3+</sup>- and Ti<sup>4+</sup>-bearing solid phases is unaffected by the redox potential. In addition, dissolved silica may also influence Cr-Al-Ti fractionation during fluid-rock interaction. The high silica contents, evident from silicate inclusions, may promote formation of soluble metal-silicate complexes as demonstrated by experimental studies for Al, Ti and similar metals (Fe, Ga) both in moderate T-P hydrothermal solutions (Pokrovski et al., 2002; and references therein) and in high T-P subduction-zone fluids (Manning et al., 2008; and references therein). Such complexes may significantly enhance Cr transport by hydrothermal fluids. Such fluids may be responsible for the metamorphic recrystallization at subsolidus conditions of mineral phases rich in Cr.

An alternative or additional form of chromium transport and accumulation at subsolidus conditions may be so-called 'crystallosols' containing finely crystallized chromian spinel (Pushkarev *et al.*, 2007). The discovery in our work of micrometre-size multiphase silicates and associated high cr-number chromites in the Maqsad chromities may represent such micron-size 'crystallosols'. This substance, when assimilated by the oxidized MORB melt, may trigger the host chromite crystallization.

# Constraints on the Maqsad chromitite cooling rate from elemental diffusion profiles

The Magsad MTZ chromite-hosted Fe-Mg silicates (forsterite, pyroxene, amphibole and mica) of type 1-5 inclusions with elevated mg-numbers (90-97) have high MgO (>16 wt %) and low FeO (<5 wt %) contents (Fig. 6d, Electronic Appendix) compared with the lower MgO (12-15 wt %) and higher FeO (15-20 wt %) of the host chromites. This was previously explained by subsolidus Fe-Mg exchange between the Fe-Mg silicates and host chromite (e.g. silicate enrichment in Mg and depletion in Fe after entrapment owing to diffusive re-equilibration; Johan & Le Bel, 1978; Johan et al., 1983). However, this is unlikely for the following reasons: (1) the profiles through the host-chromites to silicate inclusions show no evidence for Fe-Mg exchange between the chromite and silicates (e.g. no forsterite content variation is observed in the  $>100 \,\mu m$  olivine associated with high cr-number chromite and host chromite, Fig. 5e); (2) the cooling rates (see below) are fast enough to inhibit diffusion across the silicate-chromite interface; (3) the Fe-Mg silicate mineral compositions do not show any dependence on the inclusion size (e.g. all silicates are systematically and homogeneously depleted in FeO, which is below 5 wt %; Fig. 6d). All these observations suggest originally high MgO and low FeO contents and high mg-numbers in the Maqsad MTZ chromite-hosted silicates.

We estimated closure temperatures for diffusive Fe–Mg exchange between the Maqsad MTZ host chromite and the Maqsad MTZ olivine of the host dunite to be  $1000 \pm 15^{\circ}$ C at 200 MPa (see Table 3). This is much higher than the closure temperature of 68l  $\pm 44^{\circ}$ C proposed for slowly cooling ophiolitic peridotites (Kamenetsky *et al.*, 2001). The chromitite cooling rates may be estimated from the elemental profiles through the chromite-hosted inclusions (Fig. 5) using the diffusion models of Ganguly *et al.* (1994) and Béjina *et al.* (2009). The available data on Cr diffusion in magnesiochromite (Suzuki *et al.*, 2008; and references therein) were used to estimate the cooling rate (*s*)

from Cr concentration profiles using the following equation (Ganguly et al., 1994; Béjina et al., 2009):

$$s = 4[D_{(T_0)}RT_0^2]/(Ex_c^2)$$
 (1)

where  $D_{(T_0)}$  is the Cr diffusion coefficient in magnesiochromite (cm<sup>2</sup> s<sup>-1</sup>) at  $T_{cv}$   $x_c = 2(Dt)^{0.5} = 0.564\Delta X$ , where  $\Delta X$  is measured on the profiles of type 2 and 6 inclusions (Fig. 5a, c) and  $x_c$  is the characteristic distance ( $\mu$ m) of diffusion, R is the ideal gas constant (8.3144 J mol<sup>-1</sup> K<sup>-1</sup>),  $T_0$ is the maximum temperature of crystallization (1273-1323 K), and E is the activation energy ( $J \text{ mol}^{-1}$ ) of Cr diffusion in magnesiochromite (cm<sup>2</sup> s<sup>-1</sup>). In equation (1),  $x_c$  is the only parameter that is extracted from the concentration profiles. On all the Cr concentration profiles analysed, we found  $x_c$  to be between 4 and 10  $\mu$ m. Using these values, equation (1) gives a rough estimate for s between 0.003 and 0.2°C a<sup>-1</sup>. The uncertainties of the estimations have been discussed by Béjina et al. (2009). A more precise determination of s would require the use of a multicomponent diffusion approach, but diffusion coefficients of most elements in chromites are lacking at present. Our calculated values approach the highest values reported for mid-ocean ridge crust (~0·01°C a<sup>-1</sup>, Schmitt et al., 2011). Moreover, our values are close to the highest values reported for the Oman lower oceanic crust (~l°C a<sup>-1</sup>, VanTongeren et al., 2008). The high cooling rates inferred in our study strongly support the involvement of an aqueous fluid that was cooler than the chromite-bearing system. The preservation of both the Magsad chromitite textures (e.g. Leblanc & Ceuleneer, 1992) and the sharp zonation of the Maqsad chromite grains provides a further support for rapid cooling in the MTZ. The fast cooling rates can be explained by active hydrothermal circulation at the Moho level of the oceanic lithosphere.

### Moho Transition Zone chromitite petrogenesis: 'magmatic' versus 'subsolidus' model

To unravel the complexity of the MTZ chromitite petrogenesis and the role of differentiation processes we discuss below all the new data obtained in this study in the light of existing models of chromitite origin in ophiolite massifs.

### 'Magmatic' versus 'subsolidus' scenarios

Two main types of petrogenetic model for chromitite petrogenesis exist. The most popular 'magmatic' model suggests massive chromite crystallization from chromite-saturated magmas (e.g. Augé, 1987). This and similar models require oversaturation in chromium in a hydrous silicate melt owing to a sharp temperature drop or oxidation of the magmatic system in 'minichambers' (Lago et al., 1982) or crustal assimilation by the olivine-saturated melt (Irvine, 1975). Entrapment of silicate melt into chromite is advocated by all these models (Lorand &

Ceuleneer, 1989; Leblanc & Ceuleneer, 1992; Schiano et al., 1997). We found two types of evidence for the possible presence of a melt in our system. (1) The host chromite composition is consistent with its crystallization from a MORB melt. (2) The type 4 and 5 plagioclase-pargasite inclusions are in an assemblage with the host chromite and were formed at temperatures within the stability domain of hydrous MORB melts (950-1050°C at 200 MPa, Table 3). The inclusions were possibly entrapped in the host chromite during magmatic crystallization (in case of water-saturated MORB melt at 200 MPa, Feig et al., 2006). Far above 1100°C, an efficient process of re-equilibration of the high cr-number chromite with the residual melt may occur by cationic diffusion (Scowen et al., 1991). However, the maximum temperature of 1050°C (Table 3) estimated here makes such a process for spinel-melt re-equilibration inefficient. In fact, the preservation of high cr-number chromite inclusions indicates extremely sluggish rates of spinel dissolution (Brearley & Scarfe, 1986) and the lack of equilibration in a mafic melt owing to fast cooling and efficient fractional separation of chromite. The fast cooling inferred in this study helps to explain the preservation of the chromite-hosted hydrous silicates (phlogopite, aspidolite, pargasite). However, the Magsad chromite-hosted inclusions themselves provide evidence for subsolidus conditions rather than for a molten or partially molten system, which would support the second group of models discussed below.

The second group of models suggests chromite crystallization at subsolidus conditions based on the stability field of the pargasite inclusions, which is below 1070°C (e.g. Muntener et al., 2001). These models state that 'the presence of sodium-rich hydrous phases indicates a high Na activity in the system and implies a temperature limit corresponding to the maximum thermal stability of pargasite' (Augé & Johan, 1988). Our investigation of the Magsad chromitite inclusions provides several lines of evidence in favour of such subsolidus petrogenesis (below 950°C). (1) In our case we have no evidence for a silicate melt in the chromitite system, as the multiphase inclusions are low-temperature silicates heterogeneously entrapped by the growing chromite rather than crystallized as daughter phases from an entrapped melt. (2) Because 'coronas' are typical textures of 'metamorphic crystallization' and rarely for magmatic systems (Deer et al., 1997), the presence of high cr-number chromite crystallized below 950°C probably indicates an early metamorphic stage of the chromite growth. (3) It helps explain the very good preservation of an association of hydrous minerals such as aspidolite and phlogopite (which are not stable above 700°C) and pargasite (which is not stable above 1050°C). Such preservation of multiphase inclusions would indicate subsolidus rather than magmatic conditions to avoid the complete destabilization and/or melting of entrapped in

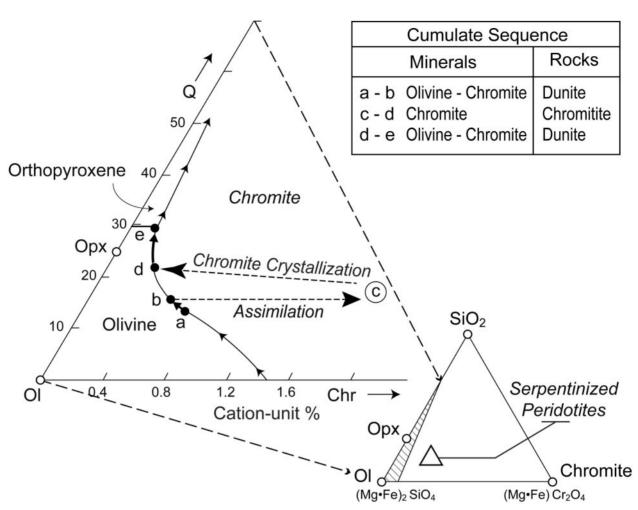


Fig. 7. Phase diagram model of Irvine (1975) applied to the petrogenetic model of the Maqsad MTZ chromitites formed through assimilation of a metamorphic mantle protolith by olivine-saturated MORB and fractional crystallization. The assimilation (b-c) is shown as a distinct process from the crystallization (a-b, c-d, and d-e). In reality, however, chromite could crystallize while the metamorphic protolith was being continuously assimilated. The composition of the serpentinized harzburgites corresponds to those of Li & Lee (2006).

chromite aspidolite and pargasite phases. Figure 5e and f demonstrates textural relationships between silicate phases, high cr-number and host chromites that are not typical for magmatic systems. It can be seen that the high-Mg silicate and altered spinel phases were overgrown by high cr-number chromites similar to some hydrothermal or metamorphic systems.

### Three-stage model for the Magsad MTZ chromitite petrogenesis

Some of our data are consistent with the magmatic processes, whereas others support the subsolidus models described above. We believe that both types of model can be reconciled within a single scenario involving three stages: (1) retrograde metamorphism (serpentinization) of a mantle protolith that was the primary source of chromium and water; (2) prograde metamorphism of this

serpentinized protolith (or serpentinite dehydration); (3) magmatic assimilation by MORB (Table 3; Figs 7 and 8).

Although the first stage is generally poorly preserved, it is evidenced by rare inclusions of serpentine and altered spinel in stratiform and disseminated chromitites (Fig. 5f; Tables 1 and 3), which are typical of serpentinized peridotites formed by hydration of the upper mantle at ≤600°C (e.g. Li & Lee, 2006). Moreover, serpentinites and serpentinized harzburgites are enriched in chromium with concentrations higher than 3000 ppm Cr (Li & Lee, 2006) and, therefore, may constitute an abundant chromium source. Thus, deep harzburgites serpentinized as a result of interaction with seawater-derived hydrothermal fluids may be a potential source for the MTZ chromitites.

The second stage is prograde metamorphic recrystallization of this hydrous mantle protolith as recorded by the multiphase type 1, 2 and 2a and microcrystal type 3

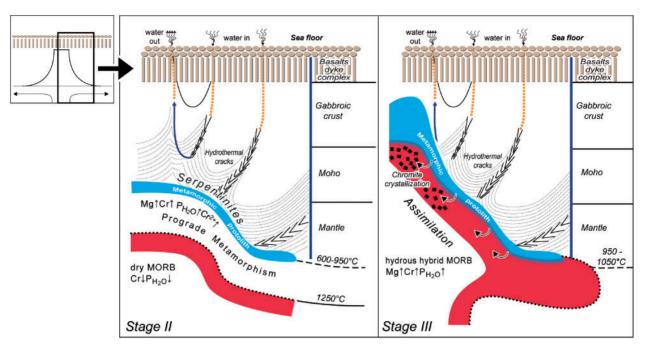


Fig. 8. Three-stage model of chromitite formation through assimilation of a metamorphic mantle protolith by MORB. Stages correspond to those in Table 3. Stage I is not shown in the figure. Stage II: during the uprise of an asthenospheric diapir, the overlying lithosphere is heated and serpentinized peridotite experiences prograde metamorphism. Reduced hydrothermal fluids (probably rich in  $Cr^{2+}$ ) and the high Mg–Cr silicate minerals of the multiphase and microcrystal inclusions are generated in the thermal field of mantle upwelling above  $600^{\circ}$ C. Stage III: the metamorphic phases generated during stage II are assimilated by primitive MORB melts (initially poor in Cr and  $H_2O$ ) and oxidized). The resultant hydrous hybrid MORB melt (enriched in Mg, Cr and  $H_2O$ ) becomes oversaturated in chromite, leading to abundant chromite and chromite—olivine fractional crystallization in the MTZ. The process is responsible for the petrogenesis of the MTZ chromitites and dunites. The cooling was rapid owing to hydrothermal fluid circulation. After Benoit *et al.* (1999), Bosch *et al.* (2004) and Python *et al.* (2007).

and 6 inclusions (Table 3). High-Mg and -Cr silicate minerals in multiphase inclusions, pyroxenes and forsterite microcrystals in equilibrium with high cr-number chromite may be formed during this stage as a result of dehydration of the high-Mg and -Cr serpentinized protolith upon prograde metamorphism above 600°C. For example, the forsterite microcrystals may represent the dehydrated serpentine assemblage (e.g. Khedr & Arai, 2012). The Magsad diapir (Fig. 8) channelled a large amount of rising MORB magma that produces the heat source in the contact aureole and the wall-rock serpentine dehydration during the second stage metamorphism. In addition to the mineral composition and inclusion data discussed above, our analyses of the oxygen isotope composition of the chromite ore bodies also support this scenario. The  $\delta^{18}$ O values measured in the chromites (3·2–3·8‰) are consistent with the involvement of hydrothermal fluids derived either from seawater directly or from prograde dehydration of the protolith, which was originally altered by seawater-derived hydrothermal fluids during the initial stage (e.g. Alt et al., 1996; Fruh-Green et al., 2003). Indeed, calculation of the isotope composition of the aqueous fluid using the equilibrium  $\Delta^{18}$ O values for the fractionation between chromite and water at 1000°C (Zheng, 1991) and the measured  $\delta^{18}O$  of chromite (3·2-3·8‰) yields a

δ<sup>18</sup>O<sub>H2O</sub> value of 7·9–8·5‰ for the aqueous fluid, typical for Cretaceous seawater-derived hydrothermal fluids associated with the Oman ophiolites (Gregory & Taylor, 1981).

The third stage, illustrated in Figs 7 and 8, occurred in the presence of a hydrous hybrid MORB melt as recorded by crystallization of the host chromite and late anhedral type 4 and 5 inclusions. The petrogenesis of the MTZ chromitites and host dunites during this stage is in accordance with Irvine's (1975) model applied to illustrate our model of assimilation of the metamorphic protolith into a MORB melt (Fig. 7). The resultant hydrous, hybrid MORB melt (enriched in Cr and H2O) becames oversaturated in chromite, leading to abundant fractional crystallization of chromite in the MTZ. At this stage, the chromite grains could crystallize while the metamorphic protolith was being continuously assimilated. Cooling was rapid owing to the involvement of hydrothermal fluids and fractional crystallization was efficient. The observed textures of the MTZ chromitites suggest a melt- or fluid-saturated medium during the third stage and cumulative, possibly, convective control on the distribution of the minerals inside the crystallizing dykes (see Leblanc & Ceuleneer, 1992). Once formed, the host chromite crystals may be accumulated gravitationally in an ore body owing to their high density (~4500 kg m<sup>-3</sup>; e.g. Mungall &

Naldrett, 2008) and may be sintered (Hulbert & von Gruenewaldt, 1985). The latter process may explain the absence of entrapped basaltic glass in the host chromite. Our oxygen isotope data also provide independent support for the third magmatic stage. The measured  $\delta^{18}$ O values in chromite (3·2-3·8‰) in the Magsad chromitites (Table 4) and associated olivine (5·2–5·8‰ in the Magsad dunites) vield an average chromite-olivine oxygen isotopic fractionation ( $\Delta^{18}$ O) value of -2.0%. This small fractionation is consistent with equilibrium isotope fractionation at high temperatures of 1050°C, calculated using a combination of available  $\delta^{18}$ O fractionation in the pairs chromitewater (Zheng, 1991), basalt-water and olivine-basalt (Zhao & Zheng, 2003). If the total range of  $\Delta^{18}$ O (olivine-spinel) = 1.4-2.6% that we observe between chromitites and associated dunite is considered, this would correspond to temperatures higher that 600°C. This indicates that although the involved protolith had a high δ<sup>18</sup>O, perhaps because of alteration by seawater during the first stage at lower temperature, the later prograde metamorphism and magmatic stages variably equilibrated olivine and chromite with respect to their  $\delta^{18}$ O values.

The proposed model for MTZ chromitite genesis extends our knowledge of physicochemical processes occurring during MORB transport at Moho-level depths. The metamorphic mantle protolith would supply H<sub>2</sub>O, S, Cl and Na to the primitive MORB melts (Bédard et al., 2000; and references therein). The saturation of the MORB melts with a C-O-H-Cl-S fluid would have played a key role in the MTZ chromitite formation. The presence of a deep metamorphic source and its impact on the MORB melt chemistry is thus consistent with the growing evidence for (1) oceanic lithosphere assimilation by MORB, and the petrogenesis of evolved lithospheric magmas in the mid-ocean ridges (e.g. Nonnotte et al., 2005; Kamenetsky & Gurenko, 2007) and in geodynamically similar regions such as Iceland (Bindeman et al., 2012), (2) abundance of MORB enriched in C-O-H fluids (e.g. Javoy & Pineau, 1991), and (3) ubiquity of chromitite ores found in the Moho Transition Zone of ophiolite massifs over the world.

### CONCLUSIONS

The results of systematic analyses, carried out in this study, of chromite-hosted inclusions as well as oxygen isotopes of chromite grain fractions from nodular, disseminated and stratiform chromitites and associated host dunites that are located at different levels of the MTZ in the Oman ophiolite (Maqsad area) are consistent with a three-stage model of the chromitite petrogenesis in which most of the Maqsad MTZ chromitites crystallized at temperatures between 600°C and 1050°C and pressures of 200 MPa. In the first stage, a mantle protolith altered by seawater-derived hydrothermal fluids yielded serpentinites

and serpentinized harzburgites, which were probably the main source of chromium for chromitite ore at the Moho level and explain the systematically high Mg/Fe ratios of the silicate minerals found in the ophiolite chromitites. The presence of such hydrous mantle protolith thus eliminates the existing controversy on the source of Cr and H<sub>2</sub>O and its role in the chromitite petrogenesis. The second stage involved subsolidus (metamorphic) crystallization at 600–950°C. It was followed by a third stage of assimilation and fractional crystallization of chromite from watersaturated MORB at 950-1050°C in the oceanic ridge setting. The assimilation of this protolith at Moho-level depths dramatically affected the MORB magma chemistry and favored Cr concentration into economic ores. Our model is supported by the growing evidence for oceanic lithosphere assimilation by MORB, abundance of hydrous MORB enriched in C-O-H fluids and ubiquity of chromitite ore deposits in the Moho Transition Zone observed in ophiolite massifs world-wide.

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#### SUPPLEMENTARY DATA

Supplementary data for this paper are available at *Journal* of Petrology online.

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