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Invited review article

Chromitites in ophiolites: How, where, when, why? Part II. The crystallization of chromitites

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ABSTRACT

A review of previous work relevant to the formation of concentrations of chromite in peridotites from ophiolitic (s.l.) sequences highlights some of the key problems in understanding the complex processes involved. This review forms the basis for chromitite-genesis models that integrate new geochemical data with petrologic, field and microstructural observations, and for a re-interpretation of previous data and concepts. The geochemical data include major- and trace-element contents of chromite and coexisting phases and especially the nature and Os-isotope compositions of platinum-group minerals (PGM) and base-metal sulfides (BMS); the PGM data in particular provide new insights into chromitite formation.

Differences in the morphology, structural relationships, and geochemical signatures of chromitites allow the recognition of three distinct types. Type I is the most abundant and is distinguished by bulk-rock enrichment in Os, Ir and Ru relative to Rh, Pt, and Pd; it shows no consistent spatial location within the ophiolite “stratigraphy”. The second type (Type IIA) is generally confined to the shallower zones of the oceanic lithosphere (mainly as concordant layers, bands and seams, but also as discordant pods or irregular bodies), and is significantly enriched in the incompatible platinum-group elements (PGE) with generally higher total PGE contents than Type I. The third type (Type IIB) shows the same spatial distributions and PGE patterns as Type IIA but has a more limited range of Cr# and a wider range of Mg# that overlap with the compositional range of chromites from layered mafic intrusions.

Reaction of melts with peridotite wall-rocks results in the extraction of pyroxene into the melts, forming anastomosing dunitic melt channels in the mantle sections of ophiolites. The Os-isotope heterogeneity in PGMs within single chromitite samples, as described in Part I, provides clear evidence that melt mingling take place on very small scales. This suggests that ophiolitic chromitites are generated through the disequilibrium precipitation of chromite, forced by small-scale mingling of melts that had different SiO₂ contents, reflecting derivation from different source rocks, different degrees of partial melting and/or wall-rock reaction. Progressive reaction, crystallization and mixing of melts within the channel system assures the presence of a spectrum of melts at any one time, making the system self-sustaining; each new injection of mafic melt would find more evolved melts with which to react, producing more chromite. Chromite is carried to its final deposition by migration of the chromite-bearing melts, or fluids derived from them. This explains the general association of chromitite with the dunitic portions of ophiolitic mantle; dunite margins around chromite segregations represent the original host rock intruded by chromitite-forming fluids.

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1. Introduction

Ophiolites are fragments of the oceanic (*s.l.*) crust and upper mantle, tectonically emplaced on land. Some contain chromitites, rocks consisting mainly of Cr- and Al-rich spinel; these occur usually in the upper-mantle part of the ophiolite pseudosection, or near the crust–mantle boundary, and less commonly in the lowermost oceanic crust. They are economically important as source of chromium, and scientifically important because they encapsulate information on the nature of ancient upper mantle, young oceanic mantle, processes of melt formation and percolation in the mantle, and large-scale geodynamic mechanisms (Ahmed and Arai, 2002; Arai, 1997; Borisova et al., 2012; Gervilla et al., 2005; Kapsiotis, 2013; Melcher et al., 1997; Pagé and Barnes, 2009; Proenza et al., 1999; Rollinson, 2008; Uysal et al., 2005, 2009; Zaccarini et al., 2011). Unraveling the layers of information held within these rocks, using new geochemical and microstructural observations, can contribute to a better understanding of the “Lithosphere and Beyond”, the aim of this volume.

The origin of chromitites has been the subject of many frontline studies and remains a hotly debated topic with diverse and passionately defended hypotheses. It is not possible to refer to every paper available on the topic; we have cited those most relevant to the scope of this study and which form a basis for its concepts. These detailed and thoughtful previous works provide a robust platform for the formulation of new ideas from new data.

In this study, as in Part I (González-Jiménez et al., in this volume), we accept the definitions of Dilek and Furnes (2011), distinguishing six main types of ophiolite in terms of their environment origin or emplacement: Continental margin, Mid-ocean-ridge, Plume, Suprasubduction-zone, Volcanic-arc and Accretionary. Thus some chromitites from ultramafic massifs, which were not considered as ophiolites by previous authors, are included in this scheme. Unless otherwise specified, we will use the generic term “fluid” to cover a range of media from silicate melts, through to hydrous solutions; in the mantle conditions under consideration these form a continuum.

Chromitites are found worldwide in ophiolites of all ages. The sheer volume of Cr contained in a large deposit requires precipitation from melt/fluids that have integrated significant volumes of the mantle (e.g., González-Jiménez et al., 2013a; Leblanc and Ceuleneer, 1992); this makes chromitites a potential resource to probe and uncover the geochemical differentiation processes in the deeper Earth. The composition of chromites and the chemistry and isotopic signatures of their mineral inclusions can provide clues to the mechanisms of mass transfer between the layers that make up the solid Earth, and the types of

transporting fluids that make them possible (González-Jiménez et al., 2011a,b, 2012, 2013a; Malitch, 2004; Melcher et al., 1997; Pagé and Barnes, 2009; Prichard et al., 2008; Shi et al., 2007, 2012; Tsuru et al., 2000; Walker et al., 2002). However, there are many uncertainties about their genesis. Among the unresolved questions are: (1) how can chromium, a minor element in mantle peridotites and their derived partial melts, be concentrated to produce large bodies of massive chromite?; (2) how does the chromite nucleate and grow, and then accumulate to form a chromitite?; and (3) what factors control the size of individual chromitite bodies?

Forensic-type studies of individual chromitite bodies in isolation have led to a profusion of genetic models. These can be grouped into three broad categories. (1) *Fractional crystallization* of basaltic melts in magma chambers or conduits in the upper mantle or near the crust–mantle boundary (Dickey, 1975; Greenbaum, 1977; Lago et al., 1982; Leblanc and Ceuleneer, 1992; Leblanc and Nicolas, 1992). Variants of this model include changing the composition of the melt by an external process such as melt–rock reaction (Edwards et al., 2000; Zhou et al., 1994) or assimilation of pre-existing mafic rocks (Arai et al., 2004; Bédard and Hébert, 1998; Borisova et al., 2012; González-Jiménez et al., 2013a; Proenza et al., 1999). (2) *Mixing or mingling of melts within dunite channels* (Arai, 1997; Arai and Abe, 1995; Arai and Yurimoto, 1994; Gervilla et al., 2005; González-Jiménez et al., 2011b; Paktunc, 1990; Shi et al., 2012; Zhou et al., 1994, 2001b). (3) *Separation of volatile-rich fluid phases* from small fractions of evolving hydrous-silicate melts (Gervilla et al., 2002; González-Jiménez et al., 2011a) with an important role for oxygen fugacity (Melcher et al., 1997; Proenza et al., 1999).

During the last decade, experimental studies have simulated the crystallization and accumulation of chromite under conditions broadly relevant to the formation of chromitites in the ophiolitic mantle. Ballhaus (1998) studied the fractionation of chromite between conjugate siliceous and fayalitic melts in experiments at 1 atm and 1150 °C, by oversaturating the system $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--FeO--K}_2\text{O}$ with FeCr_2O_4 . He observed that melts with different Si-contents and viscosities do not mix, but mingle as droplets of one melt in the other. Chromite only nucleates in the less siliceous melt, mimicking the observed morphology of the droplets of the more siliceous melt, and resulting in nodular and orbicular microstructures. Based on these results, Ballhaus presented a numerical model for the generation of podiform chromitites. Using a picritic melt (~2 GPa, 1295 °C) and a boninitic melt (~0.5 GPa, 1275 °C), he demonstrated that melt-mixing is an effective way to precipitate chromitites in the uppermost part of the oceanic mantle in supra-subduction zone settings. In subsequent experiments Matveev and Ballhaus (2002) oversaturated

the system with water. They 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, as is typical of ophiolitic chromitites.

Another major development has been the refinement of laser-ablation ICPMS techniques for *in situ* microanalysis, which can now provide constraints on the trace-element contents of chromite and coexisting phases (González-Jiménez et al., 2011a, 2013a,b; Pagé and Barnes, 2009), and the Os-isotope compositions of platinum-group minerals and base-metal sulfides (Ahmed et al., 2006; González-Jiménez et al., 2011a,b, in this volume; Malitch, 2004; Malitch et al., 2003; Marchesi et al., 2011; Pearson et al., 2002; Shi et al., 2007).

The experimental results mentioned above, together with the geochronological insights and geochemical fingerprints from microanalysis of minerals, call for an updating and a critical review of the genetic models for the origin of chromitites in ophiolites. We combine these results with new field observations in this paper, which is Part II of a review of ophiolitic chromitites (Part I is González-Jiménez et al., in this volume). This approach provides a new knowledge base for a lithosphere-scale understanding of the origin of these chromitites.

2. Classifications of chromitites in ophiolites

Numerous schemes for classifying chromitites have been proposed, in an attempt to highlight aspects of their occurrence that might be useful in deciphering their genesis. One group categorizes the bodies depending on their position in the ophiolite pseudo-stratigraphy: mantle, transitional or crustal. Another group of classification schemes uses structural criteria. For example, Cassard et al. (1981) classified the chromitites in ophiolites from New Caledonia and Oman, using the morphology of chromite bodies and their structural relationships with the enclosing peridotites. They defined three categories: (1) discordant chromitites, corresponding to subvertical dikes that can also appear to be lenticular, flaring conduits and pods, and may be connected by inferred conduits; (2) concordant chromitites, with tubular, lanceolate, fusiform or boudinaged shapes, flattened and elongated parallel to the foliation and lineation of the peridotites; (3) subconcordant deposits, which are partially conformable with the foliation in the host rock and may occur as synfoliation isoclinal folds. The term “podiform” has also been used for ophiolite-hosted chromitites regardless of the morphological distinctions (see Stowe, 1994; references therein). A third type of classification scheme is based on chromite chemistry. For example, Leblanc and Violette (1983), Hock et al. (1986) and Nicolas and Azri (1991) classified “podiform-type” chromitites into two main types: those with high Cr# (≥ 0.6) and those with high Al (Cr# < 0.6).

A remarkable development in the study of ophiolites has been the discovery of ultrahigh-pressure mineral assemblages in ophiolitic chromitites from Tibet, and more recently from the Urals, Myanmar and Oman (Dobrzhinetskaya et al., 2009; Robinson et al., 2004; Yamamoto et al., 2009; Yang et al., 2007; submitted for publication). The assemblages include diamond, coesite, stishovite and moissanite (e.g., Dobrzhinetskaya et al., 2009; Trumbull et al., 2009) and chromites that appear to have inverted from the CF (calcium ferrite) structure (Yamamoto et al., 2009), implying depths > 400 km. The UHP minerals are accompanied by a remarkable assemblage of highly-reduced phases including native elements (e.g., diamond), alloys (e.g., Os–Ir and Ni–Fe–Cr–C), Fe-silicides, carbide (moissanite), oxides (e.g., Si-rich rutile) and nitrides (TiN and C–BN). The REE patterns of the diamonds show negative anomalies in Eu, Sm and Yb, consistent with highly reducing conditions (Yang et al., submitted for publication). Robinson et al. (2004) suggested that the Tibetan chromitites crystallized near the top of the Transition Zone, and somehow were brought

to shallow levels and emplaced into mantle peridotites. However, the geochemistry of the chromitites is typical of SSZ ophiolitic chromitites (McGowan et al., in prep.) and their host rocks may be as old as Archean (Shi et al., 2012).

It therefore seems more likely that these ophiolites were developed from thinned continental lithospheric mantle, and then subducted to extreme depths; the natural buoyancy of ancient SCLM would enable their rapid exhumation when compression was replaced by extension. Arai (2010) has proposed this mechanism, and suggested a classification that distinguishes between high-pressure (*concordant*) recycled chromitites and low-pressure (*discordant*) podiform chromitites. This distinction is based on structural criteria, but also depends on the presence of inclusions of HP/UHP minerals in chromite. He showed that the nodular chromitites, which have been considered to be low-pressure igneous features (Cassard et al., 1981), are also found at Luobusa chromitites (Yamamoto et al., 2009; Zhou et al., 1996) but are cut by fractures filled with olivine. Arai (2010) interpreted these nodular chromitites as a distinct type produced during their travels through the deep mantle. According to descriptions of the Luobusa chromitites, their chromian spinels are completely free from minute primary inclusions of hydrous minerals and pyroxenes (e.g. Miura et al., 2012; Yamamoto et al., 2009), which is one of characteristics of discordant chromitites (Cassard et al., 1981). This is consistent with UHP formation or metamorphism of the chromitites under conditions where hydrous minerals were unstable. However, this classification is not applicable to chromitites found in the uppermost Moho Transition Zone and that have not been subducted, or to those in ophiolitic lower-crustal cumulates. These are concordant with the host-rock structures, but clearly have crystallized at low pressure and do not record any evidence for HP/UHP conditions.

Classifications based only on structural criteria and chromite major-element compositions are limited, because they do not recognize the distinctive geochemistry and mineralogy of different chromitites, especially their marked differences in platinum-group element (PGE) abundances and patterns. Considering those markers, we suggest a new threefold classification of the chromitites in ophiolite complexes; this classification may serve as a supplement (not a replacement) to existing schemes, offering new insights.

Type I is the most common and is found at most levels in the ophiolite pseudo-stratigraphy of the oceanic lithosphere. It occurs in a range of geometries traditionally referred to as pods, boudins, conduits, pencils, lanceolate or fusiform, leaf or disk, tubular, veins, dikes, stockworks, irregular, swarms or schlieren. These bodies may be concordant or discordant with foliation in their host rocks. Their *distinguishing feature* is the higher concentration of the refractory IPGE (Ir-group PGE): Os, Ir, Ru relative to the PPGE (Pt-group PGE): Rh, Pt, Pd, regardless of their bulk-rock PGE contents (usually between 0.001 and 1 times C1-chondrite; Fig. 2a–b). Chromite in Type I shows a wide (almost continuous) variation in Cr# but little variation in Mg#, overlapping the compositional fields defined for the ophiolitic chromitites (Barnes and Roeder, 2001; Irvine, 1967; Leblanc and Nicolas, 1992; Fig. 1). A vertical compositional zoning is observed in Type I chromitites in the ophiolites of Mayari-Baracoa in Cuba (Gervilla et al., 2005; Proenza et al., 1999) and in Oman (Ahmed and Arai, 2002; Rollinson, 2008). Those with high Cr (Cr# ≥ 0.6) are generally below the Moho in the ophiolite stratigraphy, and those with high Al (Cr# < 0.6) are generally located in the crust–mantle transition zone close to the contact between upper-mantle peridotites and lower-crustal gabbros and cumulates. High-Cr and high-Al chromitites may coexist within the same horizon in the mantle, as in Poum in New Caledonia (Leblanc, 1995), Mount Lightning in the Australian Coolac Belt (Graham et al., 1996), Dobromirski in the Bulgarian Rhodopes (González-Jiménez et al., submitted for publication), and Santa Elena in Costa Rica (Zaccarini et al., 2011).

Type II chromitites are less abundant and are distinguished from Type I by enrichment in the PPGE relative to the IPGE, with bulk-rock PGE

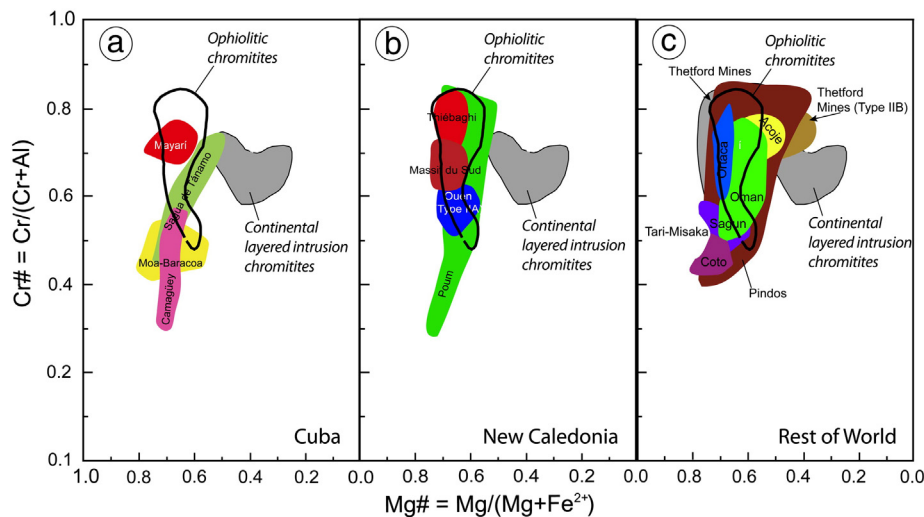


Fig. 1. Chromite composition: Cr# (Cr/Cr + Al atomic ratio) versus Mg# (Mg/Mg + Fe²⁺ atomic ratio) of chromite. Fields of chromite in chromitites of the “ophiolitic-type” and “layered mafic intrusions-type” (Barnes and Roeder, 2001) are included for comparison. (a–b). Chromitites within the ophiolitic belts of Cuba (González-Jiménez et al., 2011b; Henares et al., 2010; Proenza et al., 1999) and New Caledonia (González-Jiménez et al., 2011a; Leblanc, 1987). (c) Composition of chromite from chromitites of ophiolites of Thetford Mines in Canada (Gauthier et al., 1990), Acoje and Coto in the Philippines (Leblanc and Violette, 1983; Zhou et al., 2000), Sagun Zone (Matsumoto et al., 1997) and Tari-Misaka (Arai and Yurimoto, 1994) in Japan, Ortaca in Turkey (Uysal et al., 2005), and Pindos in Greece (Kapsiotis et al., 2009).

contents usually higher than in Type I (Fig. 2c–d). They are pods, or more commonly layers that extend over significant distances concordant with (and sometimes alternating with) host rocks of the crust–mantle transition zone, the lower crust, or arc roots. Some Type II chromitites are irregular bodies or stockworks hosted in dunite bodies (discordant or not) within crustal cumulate rocks. Examples of those in the crust–mantle transition zone or the lower crust of the oceanic lithosphere are: Cliff in the Shetland Ophiolite in Scotland (Prichard et al., 1986); Leka in Norway (Pedersen et al., 1993); Acoje block of the Zambales Ophiolites in the Philippines (Bacuta et al., 1990); Vourinos Ophiolite in Greece (Konstantopoulou and Economou-Eliopoulos, 1991; Tarkian et al., 1996); Great Serpentine Belt in New South Wales (Yang and Seccombe, 1993); Tropoja and Shebenik Ophiolites in Albania (Burgath, 1999; Burgath et al., 2003; Kocks et al., 2007; Neziraj, 1992; Stribny et al., 2000); Pirogues and Ouen Island in New Caledonia (Augé and Maurizot, 1995; Augé et al., 1998; González-Jiménez et al., 2011a). An example of those in arc roots is Cabo Ortegal in NE Iberia (Moreno et al., 2001). Examples of those in dunite bodies (discordant or not) within crustal cumulate rocks are the Cr-3 type chromitites of Pagé et al. (2003) in the Thetford Mines ophiolite in Canada, and the CR11 chromitites of Grieco et al. (2006) in Nurali, Russia.

Type II can be further divided into Types IIA and IIB on the basis of chromite composition. Type IIA chromitites have trends of Cr# vs Mg# that overlap the compositional field of Type I (i.e., wide variation in Cr# from high-Al to high-Cr but little variation in Mg#) (Fig. 1). Type IIB chromitites have a more limited range in Cr# but a wider range of Mg#, overlapping the compositional range of chromite in layered mafic intrusions (Barnes and Roeder, 2001; Irvine, 1967; Leblanc and Nicolas, 1992; Fig. 1).

3. Which types of ophiolites host chromitites?

Leblanc and Nicolas (1992) discussed the genetic link between our Type I chromitites and *lherzolite-type* and *harzburgite-type* ophiolites, as defined by Ishiwatari (1985) and Boudier and Nicolas (1985). In their model, *lherzolite-type* ophiolites form beneath spreading centers with very low spreading velocity, with sufficiently low degrees of melting that the necessary chromium is not sufficiently extracted; therefore these are not likely to host chromitites. They suggested that chromitites

are restricted to *harzburgite-type* ophiolites that formed in oceanic-ridge settings with intermediate spreading rates. This allowed higher degrees of melting of the upper mantle, more favorable to the production of melts enriched in Cr, and generation of a depleted harzburgitic residue. This model explicitly regards all ophiolites as originating at mid-ocean ridges, and assumes that the host magmas of the chromitites are produced by melting within the observed mantle section. Thus the precipitation of chromitites is a consequence of changes in temperature and fO_2 taking place along the mantle–crust transition beneath the spreading center (Nicolas and Azri, 1991), and Leblanc and Nicolas (1992) linked to the spreading rates of the oceanic ridge.

Many of these ideas are not consistent with the new Re–Os isotopic data, which show that the peridotitic parts of some ophiolites are much older than the formation of the ophiolite sequence, including the chromitites (Ahmed et al., 2006; Alard et al., 2005; Frei et al., 2006; Gervilla et al., 2005; González-Jiménez et al., 2012, 2013a; Marchesi et al., 2011; O'Driscoll et al., 2012; Shi et al., 2007, 2012; Snow et al., 2000; Tsuru et al., 2000; Walker et al., 2002). The Os model-age data commonly suggest that these peridotites may be fragments of the sub-continental lithospheric mantle (SCLM), unroofed and thinned during the extension accompanying the development of new ocean basins (González-Jiménez et al., 2013a; Hassler and Shimizu, 1998; Rampone et al., 2005; Shi et al., 2007) or relict buoyant domains stranded in oceanic basins during rifting (O'Reilly et al., 2009). Their major-element depletion in these cases significantly predates the formation of the oceanic lithosphere and is unrelated to the production of the observed basalts which were sourced by partial melting of more fertile domains at deeper levels.

Arai (1997) reviewed the model of Leblanc and Nicolas (1992) and considered the petrological characteristics of both *lherzolite-* and *harzburgite-type* ophiolites. He concluded that the largest chromitite bodies are hosted by moderately refractory harzburgites containing spinels with Cr# between 0.4 and 0.6. In contrast, fertile lherzolites (Cr#_{sp} < 0.3) or highly refractory harzburgites (Cr#_{sp} > 0.7) contain rare, and usually small, chromitites. Arai inferred that melting of pyroxenes is the key to the formation of the chromitites, invoking mantle–melt reaction and subsequent mixing of melts as previously suggested by Arai and Abe (1995), Arai and Yurimoto (1994) and Zhou et al. (1994, 1996). He suggested that the most favorable setting for the formation of large-scale chromitites (our Type I) is beneath island arcs

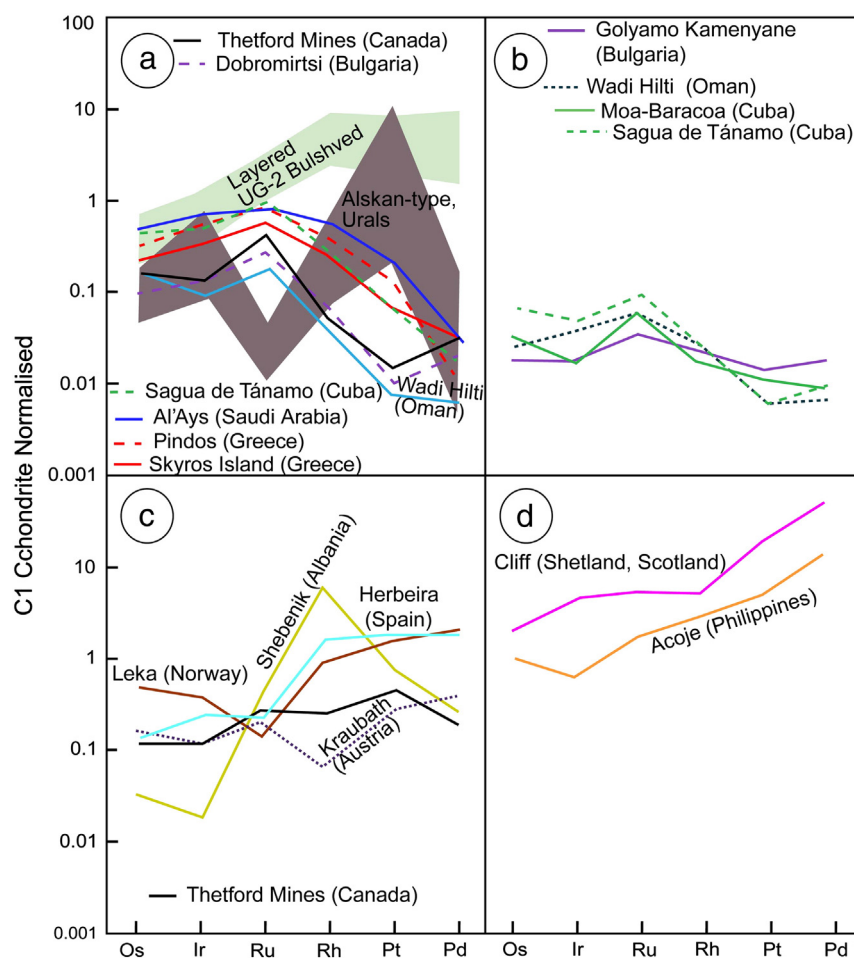


Fig. 2. Chondrite-normalised (Naldrett and Duke, 1980) patterns of platinum-group-elements in chromites from ophiolites (average) and comparison with the chromitites hosted in Alaskan-type complexes (Garuti et al., 2003, 2005) of the Urals and Bushveld (UG2) Layered Complex (Naldrett et al., 2011). (a) High-Cr Type I chromitites, (b) high-Al Type I chromitites, (c) Type IIA and Type IIB chromitites, (d) Type II chromitite containing high proportions of interstitial sulfides. Data sources for Type I chromitites: Thetford Mines, Canada (Gauthier et al., 1990); Wadi-Hilti, Oman (Ahmed and Arai, 2002); Al'Ays, Saudi Arabia (Prichard et al., 2008); Pindos, Greece (Economou-Eliopoulos, 1993; Economou-Eliopoulos and Vandonios, 1995); Skyros Island, Greece (Economou, 1983); Moa-Baracoa, Cuba (Gervilla et al., 2005; Proenza et al., 1999); Sagua de Tánamo, Cuba (Gervilla et al., 2005; González-Jiménez et al., 2011b; Proenza et al., 1999); Dobromirski, Bulgaria (González-Jiménez et al., submitted for publication; Tarkian et al., 1991); Golyamo Kamenyane, Bulgaria (Gervilla, unpublished data). Data sources for Type II chromitites: Thetford Mines, Canada (Gauthier et al., 1990); Leka, Norway (Pedersen et al., 1993); Kraubath, Austria (Malitch et al., 2003); Shebenik, Albania (Kocks et al., 2007); Herbeira, Spain (Moreno et al., 2001); Cliff, Scotland (Prichard et al., 1986); Potosí, Cuba (Proenza et al., 2001); Acoje, Philippines (Bacuta et al., 1990).

on oceanic lithosphere formed at oceanic ridges or in back-arc basins with high extension rates. The mantle section beneath these arcs consists mainly of moderately refractory harzburgites containing spinels with $\text{Cr}\# = 0.4\text{--}0.6$ and orthopyroxene with high ($\text{Cr}_2\text{O}_3 + \text{Al}_2\text{O}_3$).

Our own review of the literature shows that suprasubduction-zone (SSZ) ophiolites (as defined by Dilek and Furnes, 2011) are the main host for chromitites, providing support for the interpretations of Arai (1997). Chromitites are particularly common in ophiolites that have developed in back-arc basins, or in back-arc basins that have evolved from fore-arc settings or *vice versa*. These are ophiolites with the geochemical character of island arcs but in which the oceanic crust originated in the zones of extension (fore-arc, intra-arc or back-arc basin) developed during subduction processes. Other ophiolite types, such as Continental Margin (or ocean–continent transition), Mid-ocean ridges, Volcanic-arc, or Plume (Dilek and Furnes, 2011) may host rare chromitites.

In suprasubduction-zone ophiolites that have preserved evidence of an evolution or transition from back-arc to fore-arc environments or *vice versa* (i.e., MORB-island arc tholeiite–boninite sequence of igneous activity), chromitites may occur as giant bodies several hundred meters long. Examples include Donskoi in the Kempirsai Ophiolite, Kazakhstan (1500×200 m; Melcher et al., 1994, 1997); Masinloc in the Coto

ophiolites, Philippines ($600 \times 300 \times 80$ m; Dickey, 1975); and Mercedita in the Moa-Baracoa district of eastern Cuba ($600 \times 250 \times 20$ m; Proenza et al., 1998a,b, 1999). The mantle sections of these ophiolites consist of harzburgite with subordinate lherzolite, but the largest chromitite bodies are always hosted in the harzburgites (highly depleted in the case of high-Cr ores as in Kempirsai, or moderately depleted in the case of high-Al types as in Moa-Baracoa).

Suprasubduction-zone ophiolites that have only preserved oceanic lithosphere formed in the back-arc or fore-arc basin carry small chromitites, rarely over 50×5 m in maximum dimensions, regardless of the degree of depletion in their host harzburgite. Examples include the chromitites of the Appalachians ophiolites like Thetford Mines or the Advocate Complex (Corrivaux and Laflamme, 1990; Escayola et al., 2011; Gauthier et al., 1990; Laurent and Kacira, 1987; Pagé and Barnes, 2009; Pagé et al., 2003), and Shetland (Prichard and Lord, 1993; Prichard et al., 1986; Tarkian and Prichard, 1987). In the massif of Poum, in the New Caledonia ophiolite, high-Cr and high-Al chromitites hosted in harzburgite and lherzolite, respectively, are closely associated along a transform fault (Leblanc, 1995). Malpas et al. (1997) suggested that they were formed in a fore-arc environment where hot asthenosphere rose along transform faults during the initiation of subduction.

Where subcontinental lithospheric mantle has been exhumed by the opening of a back-arc basin above the suprasubduction zone (e.g. Ronda-Ojén in southern Spain; Gervilla et al., 2002; González-Jiménez et al., 2013a; Gutierrez-Narbona et al., 2003) or by rifting of a continental margin (e.g. Nurali in the Urals; Grieco et al., 2006), chromitites are scarce and usually smaller than 10×1 m.

Ophiolites related to continental margins such as Harzburgite Peak in the Yukon (Escayola et al., 2012), and thus were not affected by fluids related to a suprasubduction zone, also enclose small Type II chromitites (<1 m \times <10 cm). The Yukon chromitites contain up to 2600 ppb total PGE, with enrichment in PPGE over IPGE. The chromite is high-Cr (Cr# ~ 0.45) with moderate Mg# (~ 0.6) and relatively high TiO_2 (0.4–0.6 wt.%).

Small chromitites are also typical of the lherzolitic or highly-refractory harzburgitic mantle in modern (e.g. East Pacific Rise in the Hess Deep; Arai and Matsukage, 1996) or fossil mid-ocean ridge (MOR) settings or in the roots of volcanic arcs (e.g. Cabo Ortegal in northwestern Spain; Monterrubio, 1991; Moreno et al., 1999, 2001). The Loma Peguera chromitites ($<10 \times 1$ m; Proenza et al., 2007) are hosted in suboceanic upper mantle affected by a mantle plume (plume-type ophiolite of Dilek and Furnes, 2011).

4. Significant characteristics of ophiolitic chromitites

4.1. Spatial relationships between chromitites and peridotites

Most chromitites found in the deep mantle or Moho Transition Zone sections of ophiolites have dunite envelopes of variable thickness (some centimeters to several meters) that separate them from the host harzburgite or lherzolite. There is no consistent correlation between the size of the chromitite body and the thickness of the dunite envelope. Small to mid-size chromitites can be found in thick dunite bodies while large chromitite bodies commonly have very thin dunite envelopes, or none at all (Fig. 3). However, the profile chromitite–dunite–harzburgite/lherzolite commonly is preserved with either gradational or sharp contacts between the rock types. Some chromitites show clear evidence of intrusion into their host peridotites or contain isolated islands (or lenses) of dunite and/or harzburgite/lherzolite (Fig. 4a). Other chromitites are in direct contact with the mantle harzburgite or lherzolite with no dunite envelope (Fig. 4b). Mafic rocks such as gabbros (or troctolites) and pyroxenites may also be included within the chromitites or cut them (Fig. 3), particularly near the mantle–crust transition.

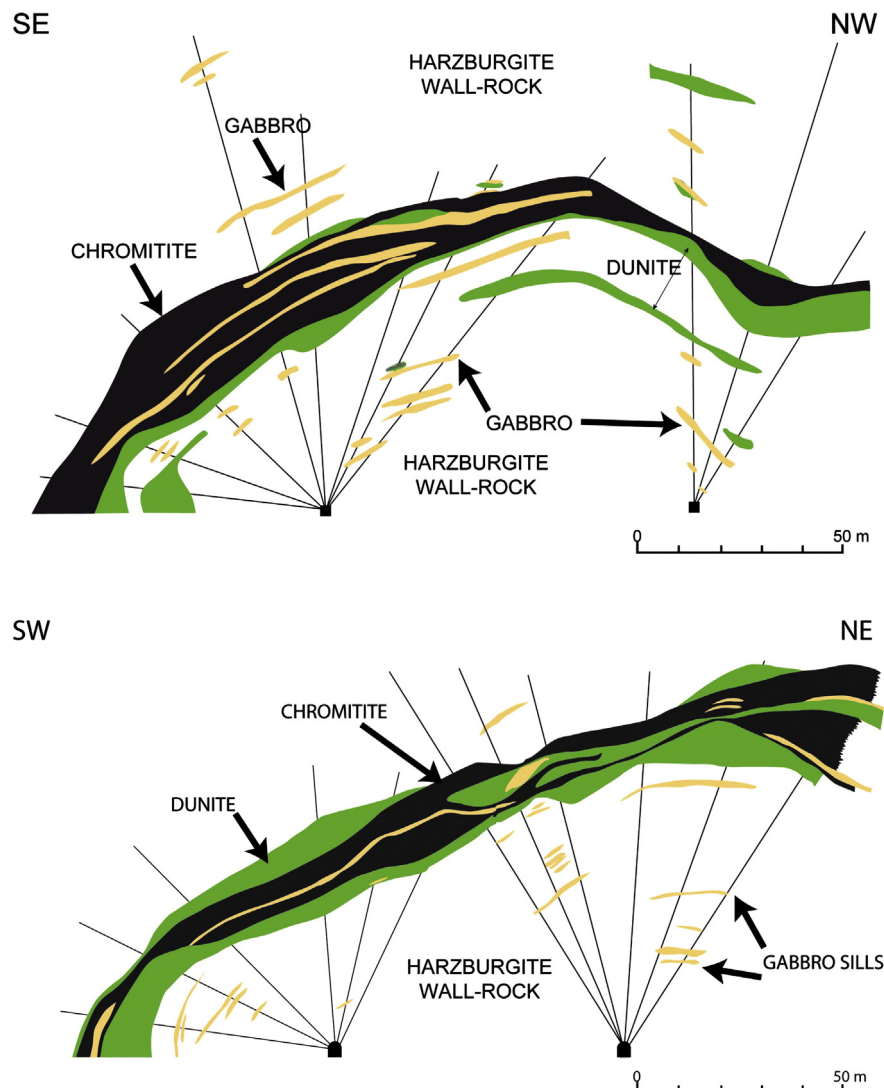


Fig. 3. Vertical profile (Proenza et al., 1999) through the high-Al chromitite of Mercedita, located in the mantle–crust transition of the Mayarí-Baracoa ophiolite, eastern Cuba. The relationships between chromitite, dunite, gabbros and harzburgite were interpreted from holes drilled upward from the roof of the mine's galleries.

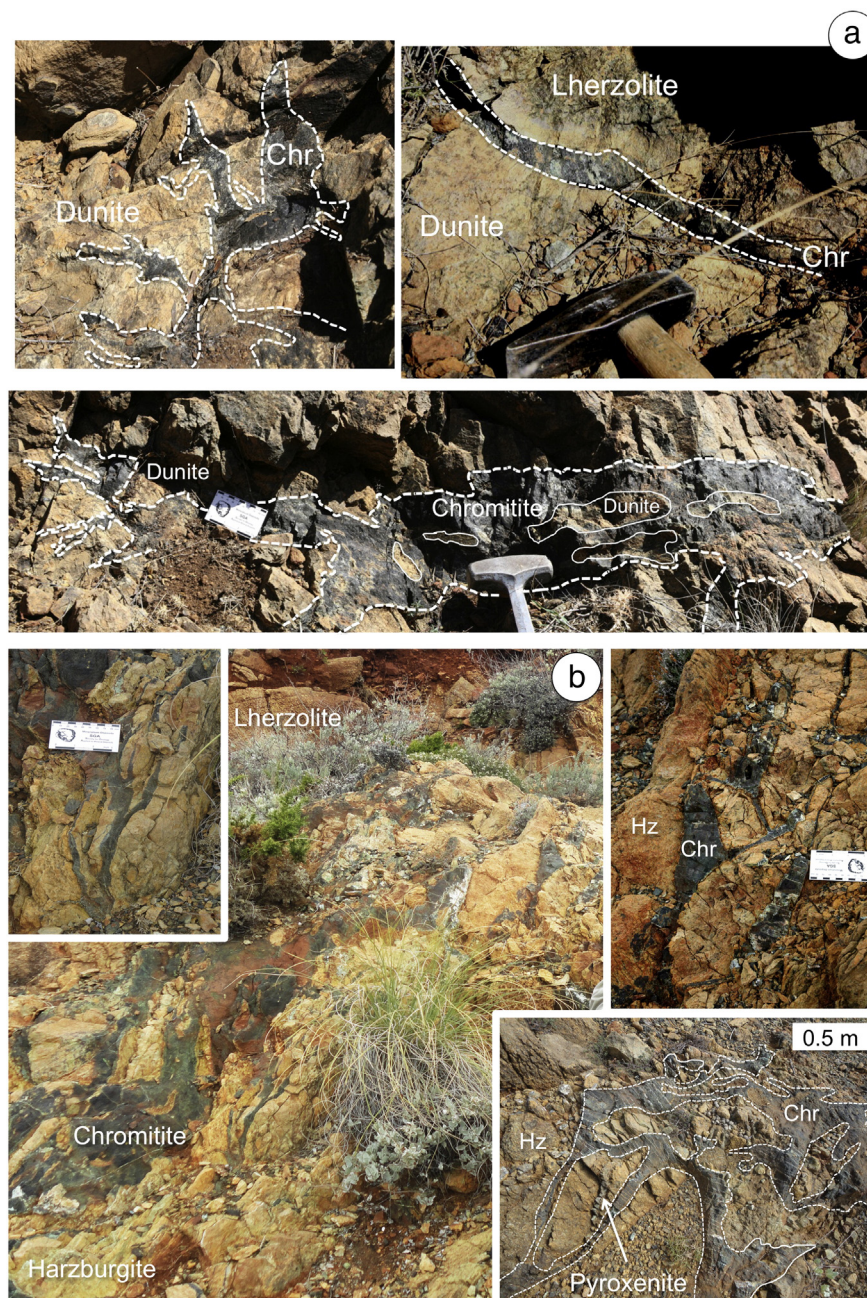


Fig. 4. Field images of the Type I chromitites hosted in the upper mantle section of the ultramafic massif of the Serranía de Ronda, southern Spain. (a) Chromitite pod in the Arroyo de los Caballos in Ojén, showing irregular ends and islands of dunite. (b) Stockwork of chromitite intruding harzburgite/lherzolite hosting some dunite and dykes of orthopyroxenites. Note that the contact between chromitite and the peridotites usually is sharp with the chromitite isolating angular blocks of the peridotites. In contrast, the contact between chromitite and the orthopyroxenite is gradational.

All these spatial relationships between chromitites, peridotites and mafic rocks can be seen in the ophiolite of Mayarí-Baracoa in eastern Cuba, where Proenza et al. (1998a,b, 1999), Gervilla et al. (2005) and González-Jiménez et al. (2011b) showed that the Type I chromitites found in the deepest part of the mantle section and the Moho Transition Zone always have dunite envelopes, but of variable thickness. The contact between chromitite and dunite may be a zone of disseminated ore; less commonly, it is sharp. In some bodies, such as the high-Al chromitite of Mercedita, chromitite is in direct contact with the host harzburgite (Fig. 3).

In the Mayarí-Baracoa ophiolite there is a close association of gabbros and high-Al chromitites, and Proenza et al. (1998b, 1999, 2002) have shown that chromitite invaded and replaced a first

generation of concordant gabbro in dunite, whereas a second generation of later gabbroic dykes cuts these types of chromitites. This feature is also common in other high-Al chromitites of the Mayarí-Baracoa ophiolite and other deposits of high-Al chromite like those from Camagüey in central Cuba (Henares et al., 2010), the Australian Coolac Belt (Graham et al., 1996) and Sartohay, China (Zhou et al., 2001b). Bédard and Hébert (1998) also found a close link between high-Cr chromitites and pyroxenite layers in the Moho Transition Zone of the North Arm Mountain Massif (Bay of Islands ophiolite in Canada). Dykes of high-Cr pyroxenites also cut high-Cr chromitites in the Mayarí-Baracoa ophiolite (Proenza et al., 1999). González-Jiménez et al. (2013a) described chromitites containing slices of pyroxenite ± dunite dykes, cutting the harzburgite

and lherzolite of the Ojen massif. High-Cr chromitites are associated with Cr-rich pyroxenites whereas high-Al chromitites replaced Al-rich clinopyroxenites and/or dunites (Fig. 4a).

Type I chromitites containing lenses of dunite without mafic rocks are also common in the Lycian ophiolites of southwestern Turkey (Fig. 5) as well as in the Ronda massif, southern Spain (Fig. 4b). In the Arroyo de la Cala locality in Ronda, veins of massive chromitite form a stockwork within dunite, showing the injection of the chromitite parental melt into already solid rock (Gervilla et al., 2002). In the same area, thick bodies of dunite may contain no chromitites. Similarly, Type II chromitites form stockworks or breccia fillings in metasomatic dunite in the uppermost part of the “crustal” sequence of the Thetford Mines ophiolite (the upper discordant type or Cr-3 chromitite in the nomenclature of Pagé et al., 2003 in Pagé and Barnes, 2009).

4.2. Primary magmatic microstructures of chromite

4.2.1. Chromite microstructures in chromitites

Chromitites may show a wide range of primary microstructures, and some of these carry important information on the processes of crystallization. The microstructures of chromitites can be classified into three groups: (1) massive (>80% chromite), (2) semi-massive (80–30%) and (3) disseminated (<30%), all of which may grade into one another. Specific varieties include nodular, orbicular and antinodular types, found only in ophiolitic chromitites, as well as banded, vein, net, breccia and schlieren microstructures (Figs. 6 and 7). A given chromitite body may show only one type of microstructure, but most display several types;

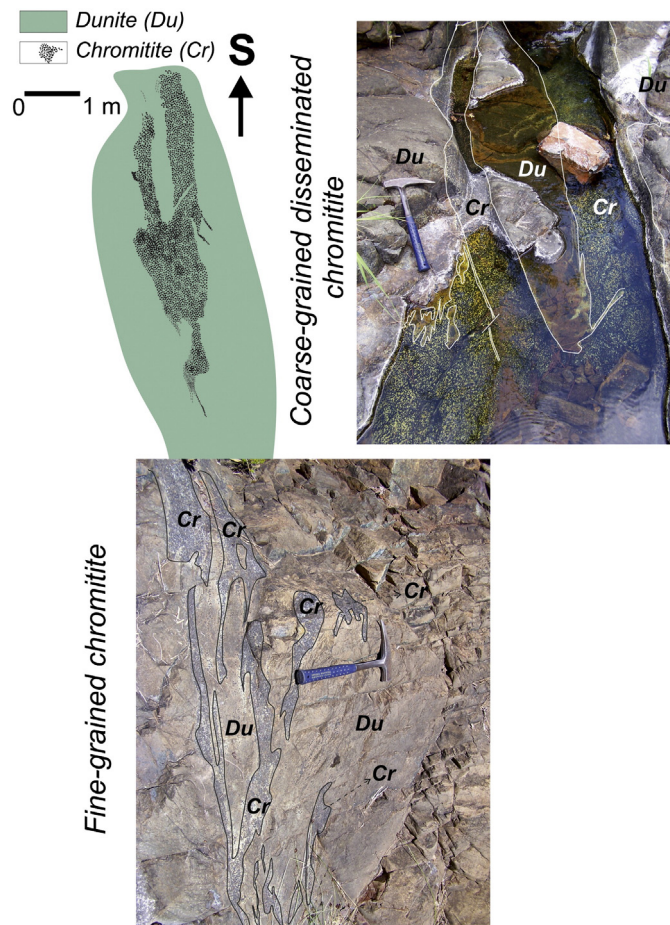


Fig. 5. Field images (and interpretation) of the Inbasi chromitite isolating lenses of upper mantle dunite; Lycian ophiolites, southwestern Turkey.

typical zoned bodies have massive chromitite in the center and semi-massive and/or disseminated types at their rims (Fig. 6a–d).

Massive chromitites (Fig. 6a–b) show two main types of structure (Leblanc and Nicolas, 1992): (1) a “compact” type with little scarce intergranular space, made up of large equidimensional grains of chromite that may show curved faces and/or triple junctions; and (2) anhedral grains of chromite separated by an olivine matrix. Chromite grains in *semi-massive* and *disseminated* chromitites (Fig. 6c–d) show the whole range of morphology but are predominantly euhedral against matrix olivine, and less frequently subhedral to anhedral. In some cases the grains are dendritic or skeletal and may show corrosion along their edges with embayments penetrating to the core of the crystal, and solution cavities on crystal faces (Leblanc and Nicolas, 1992; references therein).

Nodular chromitites consist of spherical or ovoid masses of chromite in a matrix of olivine (Fig. 6d–j) or olivine ± plagioclase when the chromitite has assimilated a mafic rock (Fig. 6k). The size of the individual chromite nodules is variable but most do not exceed a few centimeters in length; often they show flattening, mutual indentation, stretching, cracking and dismembering (Leblanc and Nicolas, 1992 and references therein). In many cases, the nodules are isolated or aligned (Fig. 6f–g), or coalesce to form massive chromitite (Fig. 6h–j). In chromitites associated with mafic rocks the nodules nucleate on plagioclase crystals (Fig. 6k; Henares et al., 2010). In *antinodular* chromitites the chromitite surrounds relatively larger ovoid masses of olivine (± chromite) (Fig. 6l).

Orbicular structures have ellipsoidal or rounded cores of dunite, enclosed by shells of chromite. The orbicules are usually set in a dunite matrix, which contains chemically similar euhedral chromite grains. The orbicular textures may grade to nodular as the dunite cores become smaller and the chromite shells thicker (see Fig. 3i–ii in Zhou et al., 2001a).

Schlieren chromitites are irregular lensoid disseminations of chromite in a dunite matrix (Fig. 6n). The grains of chromite may show a wide range of morphology from skeletal to euhedral.

Banded chromitites consist of alternating layers or chains of chromite and dunite (Fig. 7a–c). These structures are traditionally interpreted as a product of settling of chromite in a dunitic magma, as in the chromitite horizons of layered igneous complexes. However, they can also represent stringers or veins of chromite grains or massive chromitite, forming anastomosing chains and coalescing laterally (Fig. 7a–c). These entwined stringers of chromite or veins of massive chromitite may surround lenses or patches of olivine forming a *network* texture (Fig. 7a–b), or may cut through a dunite broken up into angular fragments, giving rise to a breccia of dunite in chromitite (Fig. 7a). Conversely, veinlets of dunite or mafic rocks (e.g. gabbros; Proenza et al., 2001) may cut the chromitite, producing *brecciated chromitites*, with angular or subangular pieces of massive chromitite in a dunitic or gabbroic matrix (Fig. 6m).

4.2.2. Chromite morphology in host peridotite

Leblanc (1980) observed that in the New Caledonia ophiolite the transition from harzburgite to dunite is accompanied by a change in the morphology of the chromite, from small/vermicular (low-Cr#) to large/euhedral (high-Cr#). Matsumoto and Arai (2001) quantified these changes using the “degree of roundness” (DR#), defined as $\text{area}/(\text{round-length})^2$ normalized to the value of a circle ($1/4\pi = 0.0796$). Therefore, DR# is 0.785 for a perfect square and 0.0604 for an equilateral triangle. The values of DR# are consistent with microscopic observations on the chromite of the Sagun zone in Japan: 1.0–0.6 for euhedral, 0.64–0.4 for subhedral, and <0.4 for anhedral (<0.2 for vermicular) chromite. In the ultramafic massifs of the Sagun zone, the chromite displays similar morphologies in both dunite (DR# >0.4, euhedral to subhedral) and harzburgite (DR# <0.5). However, a suite of samples collected within 200 m of the largest chromitite body shows a gradual transition between dunite (DR# >0.4) and harzburgite

(mostly <0.4). Harzburgite also contains euhedral grains with extraordinarily high DR# = 0.7–0.9. About 400 m away from the ore body the contact between dunite and harzburgite is sharp; the dunite also has euhedral to subhedral chromite with DR# >0.4 but the harzburgite has chromite with DR# mostly <0.7 (anhedral to subhedral).

4.3. Geochemistry of chromite

4.3.1. Major elements of chromite in chromitites and enclosing peridotites

Fig. 8 shows the Cr# of chromite in Type I chromitites and their host peridotites in selected ophiolites. In the high-Cr chromitites, the chromite has the same Cr# as the accessory chromite of the host dunite, or higher, whereas the chromite of the enclosing harzburgite

has lower Cr#. In contrast, in the high-Al bodies, the chromite of the dunite envelope has Cr# similar to, or higher than the chromite of the chromitites, but lower Cr# than the chromite of the surrounding harzburgite.

In some high-Cr bodies, such as those in the Mayarí-Baracoa ophiolite (eastern Cuba), the increase in Cr# in chromite of the host harzburgite towards dunite and chromite is generally coupled with an increase in TiO₂. This trend is distinct from that observed in the high-Al bodies, where accessory chromite in dunite has higher TiO₂ than that in chromitites and the surrounding harzburgite (Fig. 8). Interestingly, Proenza et al. (1999) reported that in such ophiolites, dunite hosting high-Cr chromitites has more magnesian olivine but lower REE contents (HREE <0.01 times chondrites) than dunite hosting high-Al chromitites (HREE >0.01).

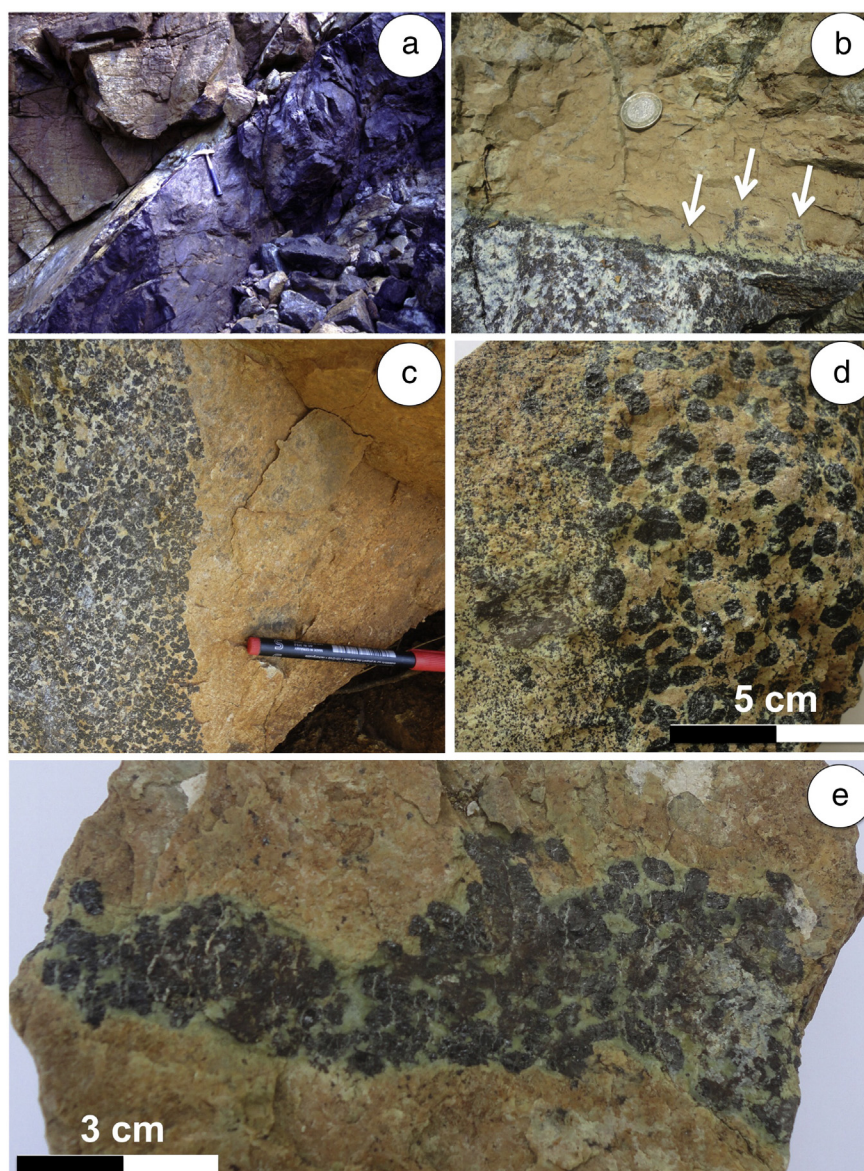


Fig. 6. Photographs of chromite microstructures in ophiolitic chromitites. (a) and (b) massive chromitites in contact with host dunite. Arrows in (b) indicate small chromitite veins penetrating into dunite. (c) Sharp contact between a nodular chromitites and dunite. (d) A late dyke of nodular chromitite cuts pre-existing dunite with disseminated chromite. (e) A vein of nodular chromitite intrudes a chromite-free dunite. (f) Aligned nodules of chromite in olivine-matrix are surrounded by stringers of chromite, marking a former melt-film network. (g) Chromite-free dunite containing nodules of chromite interconnected by thin veins of chromite; this texture is an example of the displacement of melt/fluids oversaturated in chromite through an interconnected network of melt pockets. (h), (i) and (j) represent different stages of agglomeration of nodules to produce massive chromitites. (k) Nodular chromitite with a troctolite matrix composed of plagioclase and olivine. Note that the cores of chromite nodules are rich in plagioclase inclusions. (l) Antinodular chromitite showing rounded patches of dunite with disseminated chromite. (m) Breccia of chromitite produced by intrusion of a late pegmatitic gabbro. (n) Schlieren of chromite in dunite. Photographs (a), (k) and (m) are from the Mayarí-Baracoa ophiolite, Cuba; (n) Dobromiristi ophiolite, Central Rhodope, Bulgaria; (j) and (f) Coolac Serpentine Belt, Australia; (b), (c), (d), (e), (g), (h), (i), and (l) Lycian ophiolite, southwestern Turkey.

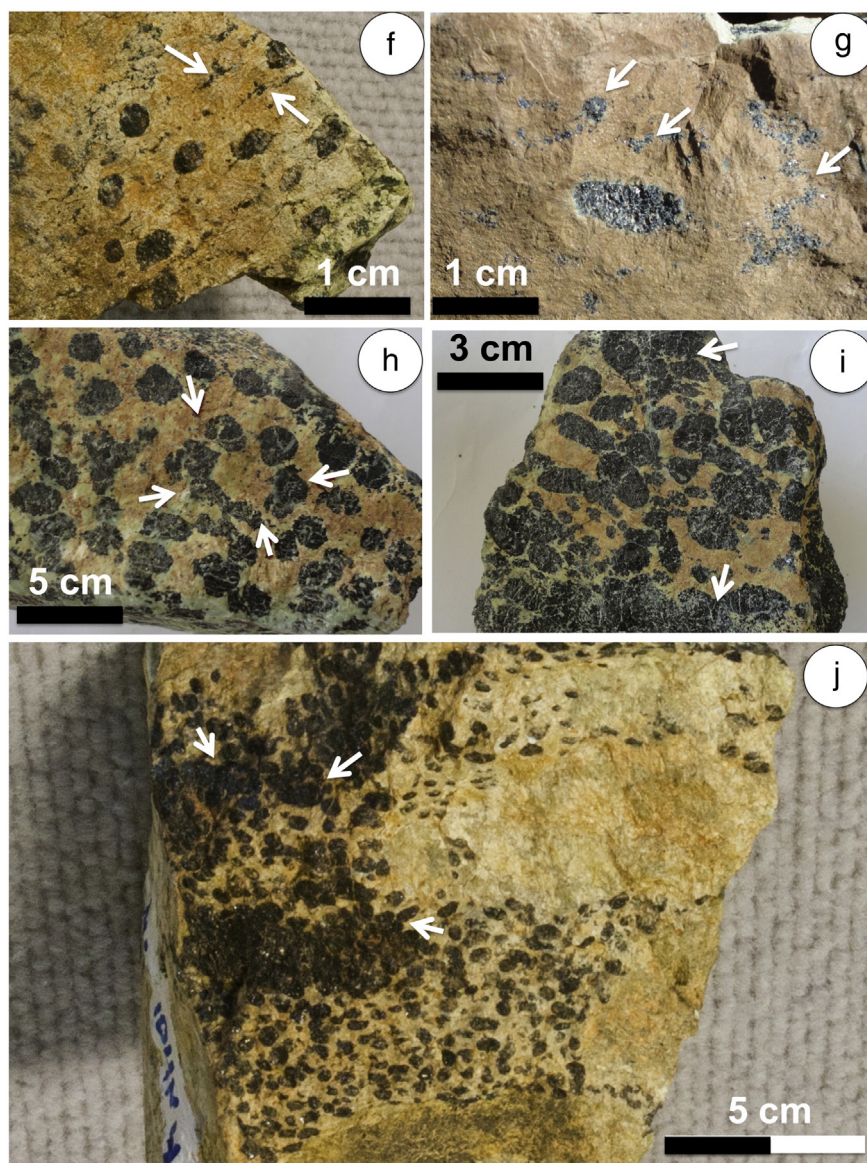


Fig. 6. (continued).

Proenza et al. (1999) found that in the high-Al chromitites enclosing gabbro lenses in the Mayarí-Baracoa ophiolite, chromite shows a progressive decrease of Cr and TiO_2 and an increase in Al, moving away from the contact with gabbro. They interpreted this trend as evidence that precipitation of high-Al chromitite was controlled by breakdown of plagioclase (from gabbro), as for other high-Al chromitites such as those of Coto in the Philippines (Leblanc and Violette, 1983) or North Arm Mountain in Canada (Bédard and Hébert, 1998). Proenza et al. (1999) also observed that chromite composition varies in the opposite way near the contact between chromite and the late, crosscutting pegmatite gabbro. The Al-enrichment with Cr-depletion in the nearby chromite can be interpreted as a consequence of late intrusion of residual basaltic melts with very low Ca/Al, produced during the latest stages of formation of the high-Al chromitite body (Henares et al., 2010; Proenza et al., 1999; Zhou et al., 2001b).

4.3.2. In-situ trace- and minor elements: a key to parental melts?

Pagé and Barnes (2009), in an attempt to determine the type of melts that produced the chromitites of Thetford Mines ophiolite, used in-situ laser ablation ICP-MS analysis to analyse a suite of

minor and trace elements (Ti, Ga, Ni, Zn, Co, V, Sc) in chromite. To facilitate comparisons they normalized the data to the composition of chromite from a mid-ocean ridge basalt (MORB) (Fig. 9). Similar patterns were observed in chromite from upper mantle chromitites and boninite lavas at the top of the ophiolite sequence, suggesting that high-Cr chromitites crystallized from melts of boninitic affinity that were en route from the upper mantle to the crust.

González-Jiménez et al. (2011a, submitted for publication) have presented LA-ICP-MS analyses of chromite in chromitites from ophiolites, komatiites and layered intrusions. These results show that the patterns of minor- and trace elements (Ga, Ti, Ni, Zn, Co, Mn, V, Sc) in chromite from ophiolitic chromitites are clearly distinct from those in other environments (Fig. 9). Chromite from high-Cr chromitites in ophiolites is similar to chromite in boninite lavas, whereas chromite from high-Al chromitites has MORB-like affinity. However, this approach is not sufficiently precise to distinguish between high-Cr chromitites from fore-arc (Thetford Mines ophiolite, Canada) or back-arc (Sagua de Tánamo in the Mayarí-Baracoa ophiolite, Cuba) environments. Similarly, there is no clear distinction between chromitites precipitated from back-arc basin basalts and the MORB-like melts that produced the high-Al chromitites in the ophiolites of Acoje (Philippines) and Sagua

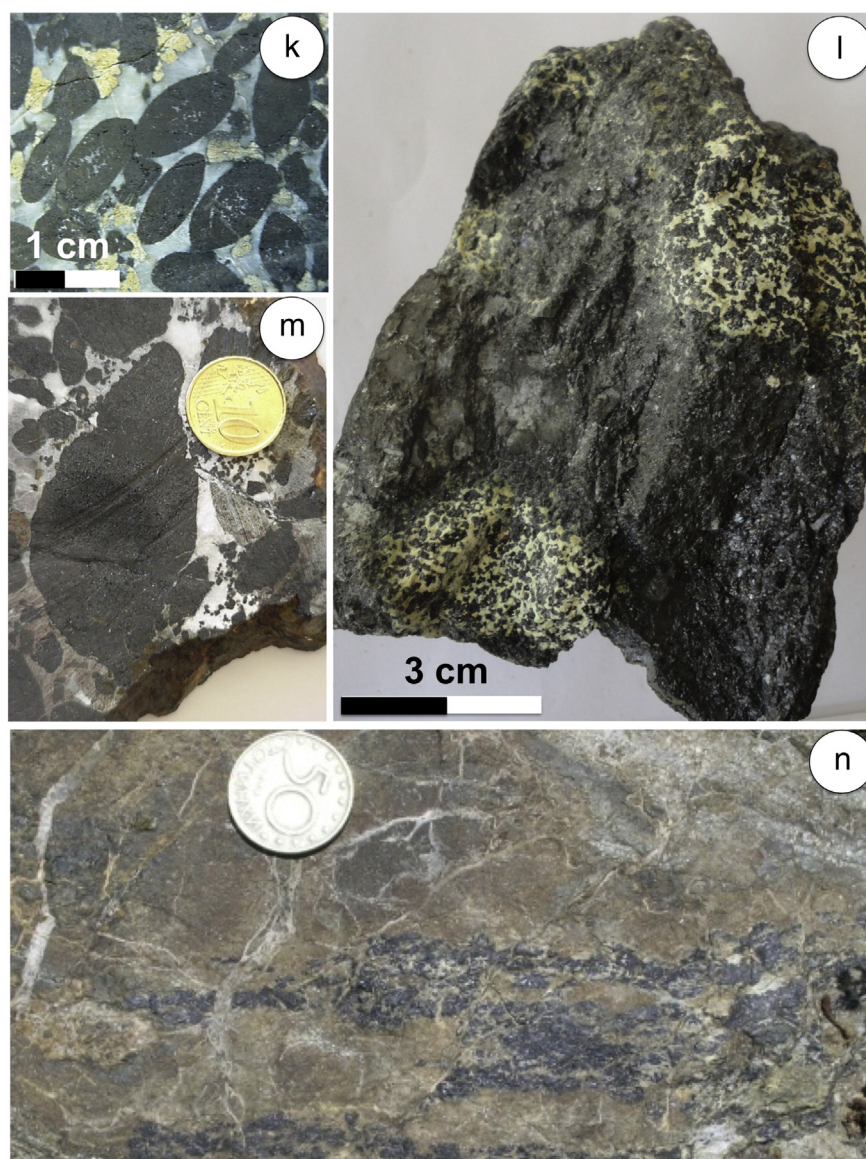


Fig. 6. (continued).

de Tánamo. This could reflect: (1) that the number of cases studied is insufficient for a proper comparison, or (2) the precipitation of chromitites from hybrid melts representing a range of arc-type melts.

5. Hydrous silicate, fluid and melt inclusions in chromitites: evidence for a water-rich fluid phase

Many ophiolitic chromitites contain inclusions of hydrous silicates (mainly pargasitic amphibole and phlogopite), which also may form the interstitial matrix between chromite grains (Augé, 1987; Gervilla et al., 2005; Graham et al., 1996; Gutierrez-Narbona et al., 2003; Johan, 1986; Johan and Lebel, 1978; Johan et al., 1983; Lorand and Ceuleneer, 1989; McElduff and Stumpfl, 1991; Melcher et al., 1997; Peng et al., 1995). The solid inclusions may be accompanied by fluid or melt inclusions (Melcher et al., 1997). Inclusions of hydrous silicates and fluid/melt inclusions both typically show negative-crystal forms with cubic symmetry imposed by the chromite host; they are commonly located along chromite growth faces (Leblanc and Ceuleneer, 1992) or in trails cross-cutting the chromite (Melcher et al., 1997). Most authors agree on a role for volatile-rich melts in the

formation of chromitites, but disagree about the nature and origins of the fluids.

Johan and Lebel (1978), Johan et al. (1983), Johan (1986) interpreted the hydrous inclusions as evidence for the unmixing of a basaltic melt and a fluid containing water and other volatile components. They suggested that podiform chromitites are hydrothermal in origin, in the sense that chromium was transported to the depositional site by a hydrous fluid phase (see below). Watkinson and Mainwaring (1980) and Lorand and Ceuleneer (1989) suggested that the hydrous silicates reflect the contamination of the basaltic melt with an exotic fluid phase during the crystallization of chromite. Lorand and Ceuleneer (1989) showed that the inclusions olivine and pyroxene record the effects of reaction with the volatile-rich fluid and suggested that pargasitic amphibole and phlogopite are the products of a reaction at lower temperatures than those prevailing during their entrapment by the chromite. Schiano et al. (1997) experimentally homogenized hydrous silicate inclusions (rich in sodic amphibole and phlogopite-rich) inclusions in chromite from the Oman ophiolite; these are interpreted as inclusions of the primary melt. They also showed significant differences in the inventory of trace elements between hydrous silicates included in chromite and those in the interstitial matrix. Dunlop

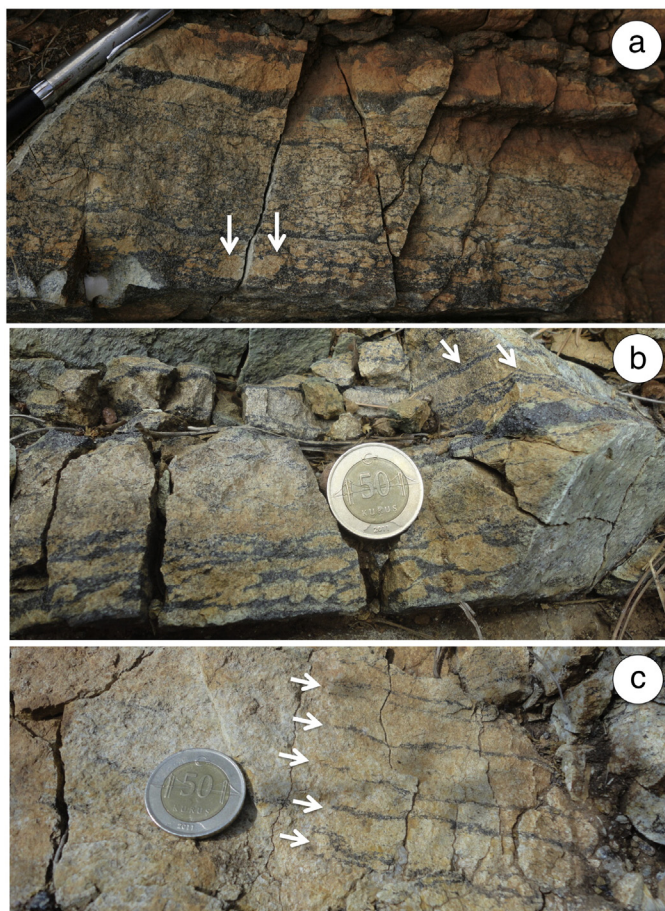


Fig. 7. Photographs of an outcrop of banded chromitites in dunite from the Antalya ophiolite, southwestern Turkey. (a), (b) and (c) are taken along the lateral extension of the outcrop; the images show multiple veins of massive chromitite coalescing into single chromitite veins to give rise to an apparent “layering”. In (a) the arrows indicate the presence of an angular block of dunite, whereas (b) and (c) show the apparent layering produced by the coalescence of several veins of chromitite.

and Fouillac (1986) analysed H and O isotopes in the fluid inclusions in chromite of chromitites from the Oman ophiolite and argued that an alkaline aqueous fluid was involved in the formation of the included OH-bearing silicates; this fluid may have migrated from the subducted slab and re-equilibrated with the overlying mantle wedge.

6. How does a chromitite body form? An integrated model

In Supplementary Appendix 1 we present short review of ideas and critically discuss the models proposed in the literature for the crystallization of chromitites. From those discussions it is clear that under appropriate fO_2 the crystallization of chromite in the upper mantle is promoted when the solubility of Cr decreases in a basaltic (arc-type) melt as a result of increases in Si, due to reaction with other more siliceous melts or rocks (either Si-rich mafic rocks or peridotites). Hydration of the melts also plays an important role in the extraction, transport, and later precipitation of chromium.

6.1. Pre-existing dunite channel networks: a necessary pathway for the hybridization of melts

Estimates by Leblanc and Ceuleneer (1992) for the 35×5 m dyke of massive chromitite at Maqad showed that the concentration of Cr in such a body required 300 to 400 times its mass in parental liquid. This implies that each chromitite body integrates melts formed by partial melting of very large volumes of mantle peridotite (up to

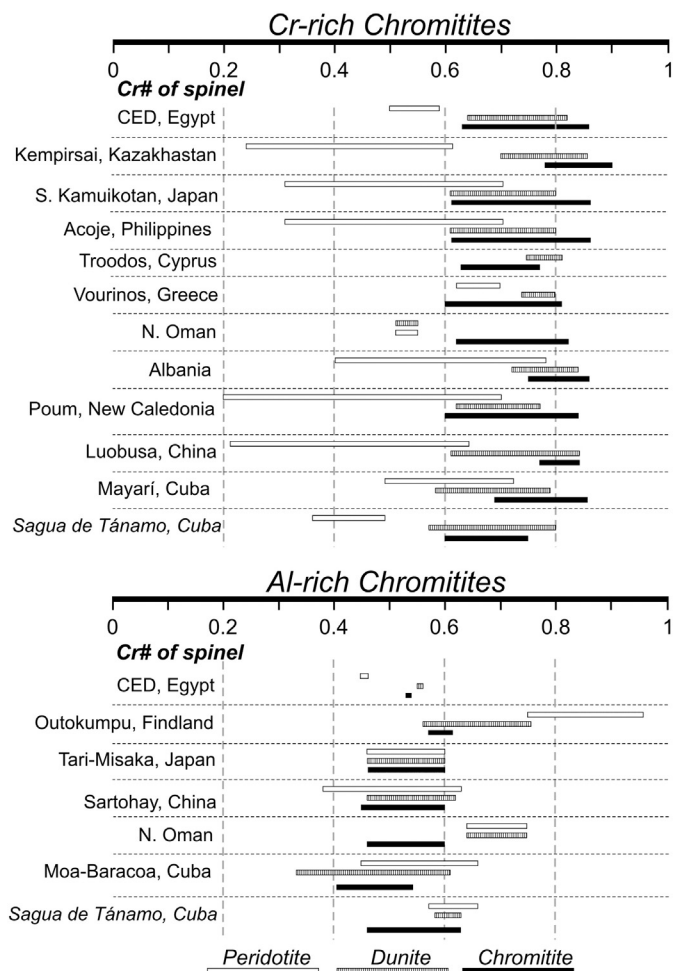


Fig. 8. Comparison of Cr# in chromian spinel from chromitites and enclosing host rocks in Type I high-Cr and high-Al chromitites of some ophiolites (González-Jiménez et al., 2011b).

$\sim 30 \times 10^3$ m³ for the 5×0.3 m high-Cr chromitite of the Ojén massif; González-Jiménez et al., 2013a). These calculations suggest that the formation of a chromitite body requires a continual flow and extraction of melts from the mantle, which would leave behind highly residual peridotites. However, not all chromitite-bearing peridotites are highly depleted, and chromitites with different Cr/(Cr + Al) can be hosted in geochemically similar peridotites (Fig. 8). In addition, if the parental melts of chromitites were produced by melt–rock reaction, it could be expected that with increasing melt/rock ratio and a higher degree of reaction with the host peridotite, larger chromitite bodies would be enclosed by thicker dunite envelopes and the “transitional lithologies” of Matsumoto and Arai (2001). However, many of the biggest chromitite bodies in ophiolites have thin dunite envelopes, or none. Moreover, many chromitites have clearly intruded their host peridotites (Figs. 3, 4a–b, 5) and/or are not in chemical equilibrium with them (Fig. 8; Proenza et al., 1999). This argues against the two rock types being strictly coeval such as suggested in the melt–rock reaction models (Arai, 1997; Arai and Abe, 1995; Arai and Yurimoto, 1994; Matsumoto and Arai, 2001; Zhou et al., 1994, 1996). Instead, the dunites may represent high-permeability pathways necessary for the transport and later emplacement of the parental melts of the chromitite.

The biggest documented chromitite pods are 200 to 300 m in thick—the Masinloc ore body in the Coto ophiolite, Philippines (Dickey, 1975), Donskoi in the Kempirsai massif, southern Urals, Kazakhstan (Melcher et al., 1994), and Mercedita in the Moa-Baracoa district of eastern Cuba (Proenza et al., 1998a,b, 1999)—which suggests that the

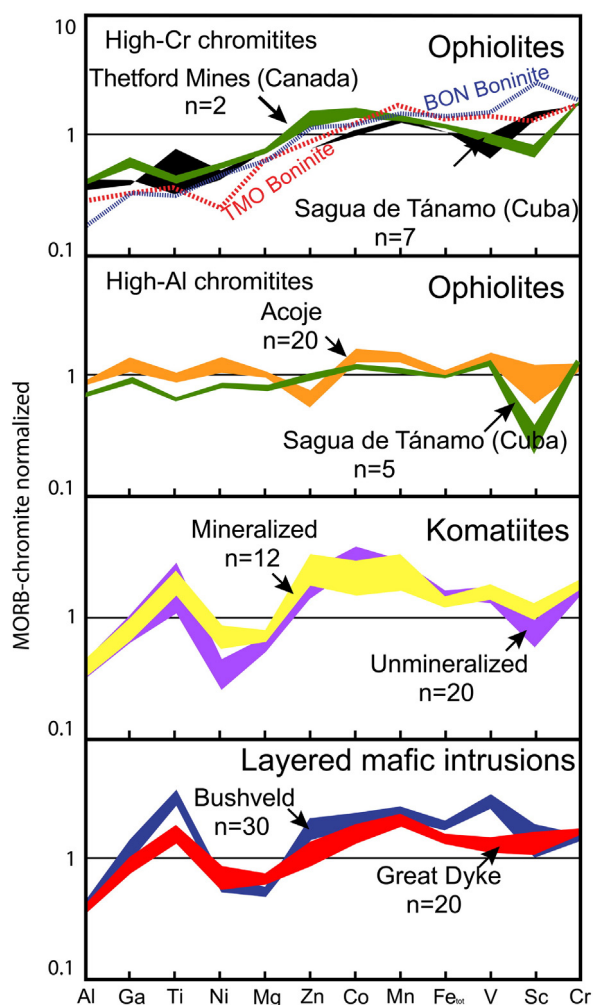


Fig. 9. Profiles of major, minor and trace elements in chromite from chromitites from different tectonic settings normalized to composition of chromite in MORB (Pagé and Barnes, 2009). Data for chromitites of the fore-arc ophiolite of Thetford Mines and boninite lavas (TMO: Thetford Mines ophiolites and BON: Bonin Island) are also from Pagé and Barnes (2009). Data for chromitites of back-arc ophiolites of Cuba and Philippines, and from komatiites and layered mafic intrusions are from González-Jiménez et al. (submitted for publication). Note that only data for chromite from massive chromitite (>80 vol.% chromite) samples are plotted.

width of the dunite through which their parental melt(s) moved was a few hundred meters. How do these thick dunite bodies form in the uppermost part of the mantle?

Beneath and close to spreading centers, such as those in fore-arc, intra-arc or back-arc basins developed above suprasubduction zones, peridotite-derived melts are adiabatically drained mainly through high-porosity, and high-permeability (dunite) dissolution channels (Fig. 10; Braun and Kelemen, 2002; Hewitt, 2010; Kelemen, 1990; Kelemen and Dick, 1995; Kelemen et al., 1995a,b, 1997, 1999, 2000; Quick, 1981; Spiegelman et al., 2001; Suhr et al., 2003). Low-silica olivine-saturated melts, accumulated in shear zones (Kelemen, 1990; Kelemen and Dick, 1995; Whittaker and Watkinson, 1984) or mantle heterogeneities (Hewitt, 2010; Katz and Weatherley, 2012) react with the mantle peridotite, stripping out pyroxene until the solid residuum is entirely olivine (Kelemen, 1990; Kelemen and Dick, 1995; Kelemen et al., 1995b; Quick, 1981). In channels generated in this way there is inward diffusive flux of heat, which powers melting within the channels and suppresses melting on their flanks (Katz and Weatherley, 2012). Therefore, the channels become high-porosity, high-permeability pathways for the rapid ascent of melts. The precipitation of olivine selvages from melts in contact with the peridotites

gradually eliminates permeability and prevents further infiltration of melts into the country peridotite, concentrating fluid flow into the central part of the channels (Daines and Kohlstedt, 1993; Kogiso et al., 2004). Where the melt/rock ratio is very high, focused porous flow of melt may increase the porosity and permeability of the porous channels in dunite, thus evolving into melt-filled conduits with impermeable walls. Subsequent melts that travel through these melt-filled channels are chemically isolated from the surrounding mantle peridotite, and can preserve the major- and trace-element compositions and isotopic signature(s) inherited by the melts from their sources at depth (Kogiso et al., 2004; Spiegelman and Kelemen, 2003).

Numerical models, tested on natural outcrops of dunite in the mantle peridotites of the Ingalls and Oman ophiolites, predict that these dissolution channels become increasingly organized into a coalescing network, in which many small conduits feed fewer large ones (Braun and Kelemen, 2002; Hewitt, 2010; Katz and Weatherley, 2012; Kelemen et al., 1995a,b). During deformation associated with mantle spreading, these dunite channels are uprooted and become single dunite pods that may still be discordant or become (sub)-concordant with the foliation of mantle peridotite (Fig. 10). In addition, gabbro bodies can be formed in the cooler upper parts of the dunite channels, from MORB- or back-arc basin basalt-type melts, before the arrival of chromite parental melts. This mechanism would explain the frequent layered structure of gabbro sills in some chromitites near the mantle–crust transition (e.g. Mayarí-Baracoa ophiolite; Proenza et al., 1999). An interconnected network of channels provides an ideal framework to produce chromitites by mixing of melts of different provenance and/or melts of the same type with different levels of SiO_2 (Spiegelman and Kelemen, 2003). This can explain why chromitites in many ophiolites occur associated with horizons rich in dunites (\pm gabbro) in the deep mantle and near the mantle–crust transition. The formation of a chromitite body, its size and the type of chromitite microstructures could reflect focused melt flow within these high-porosity and high-permeability networks of channels (Leblanc and Ceuleneer, 1992) at different melt/rock ratios.

6.2. Origin of chromitite microstructures

6.2.1. Stage 1. Melt percolation at low melt/rock ratio: the formation of disseminated chromitites

The high abundance of olivine in dunite favors the movement of basaltic melts because they have low wetting angles with olivine grain boundaries, which facilitates the formation of continuous 3-dimensional film-like networks (O'Reilly and Griffin, 2012; Toramaru and Fuji, 1986). The low interfacial energy drives fluid penetration into a low-porosity rock such as dunite, even in the absence of a pressure gradient (Watson and Brenan, 1987; Watson et al., 1990). The melts that are displaced by this mechanism may cause pervasive metasomatism over large areas, as observed in the Lherz and Ronda-Ojén massifs (Bodinier et al., 1990, 2004; Le Roux et al., 2007; Lenoir et al., 2001; Van der Wal and Vissers, 1993). In these exposed peridotite massifs, the pervasive infiltration along grain boundaries is ascribed to small fractions of melt generated by low degrees of partial melting ($\sim 6\%$ in the Ronda massif; Lenoir et al., 2001). Movement of such melts by grain-boundary infiltration is achieved if: (1) there is a continuous supply of melt from depth, (2) the temperature of the peridotite is close to the solidus, and (3) crystallization is slower than viscous relaxation, which allows “decompacting” of the mantle peridotites to maintain porosity (Rabinowicz and Toplis, 2009; Yoshino et al., 2007).

If interconnected film-like networks exist in two (or more) different porous dunite channels, and they transport melts with different SiO_2 contents, the mixing of these melts at the intersections between channels would promote the formation of “hybrid” melts that could precipitate chromite throughout the entire percolated system. Chromite is thus preferentially concentrated along grain-boundaries in the olivine matrix, mimicking the former interconnected film-like network

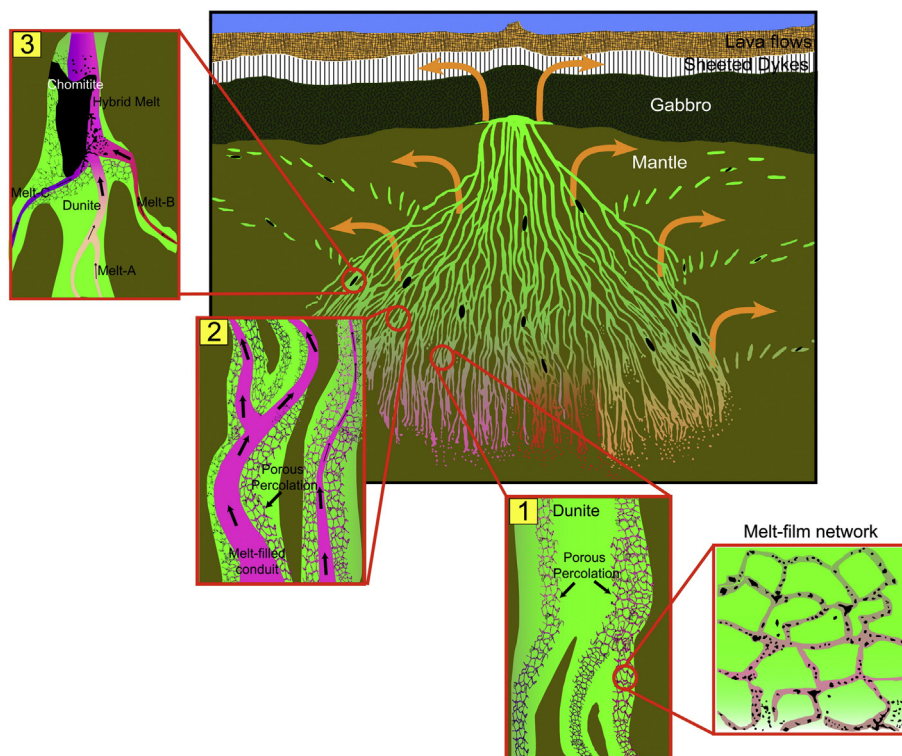


Fig. 10. Formation of ophiolitic chromitites according to the new mechanism of crystallization proposed in this work. A network of dunite channels drains melts ascending from different sources (marked with different colours) in the heterogeneous deeper mantle (modified from Kelemen, 2004). (1) Ascending melts move mainly by porous percolation through a melt-film network; in the zone of intersection between dunite channels mixing of basaltic melts with different SiO₂ promotes precipitation of chromite. The image is not to scale, as grains of olivine are generally from <0.5 mm to a few centimeters. (2) Focused flow of melt produces melt-filled channels in dunite allowing the chemical isolation and rapid ascent of the melts. (3) Chemically isolated melts drained through different channels in the dunite meet and mix to produce hybrid melts able to precipitate volumes of chromitite. The size of the dunite network and the chromitite bodies can vary from a few metres to many kilometers.

(Fig. 6f), and resulting in more or less *homogeneously disseminated chromitite* in dunite. In the framework of this model, some of the concentrations and stringers of pyroxenes in the dunite would also represent former pathways for the passage of magma through the dunite, rather than residua produced by reaction between migrating melts and mantle harzburgite. The reaction of the migrating olivine- and chromite-saturated melts with these pre-existing pyroxenes would also contribute to the precipitation of chromite; it is analogous at a small scale to the assimilation of Si-rich rocks suggested by Bédard and Hébert (1998), Arai et al. (2004) and González-Jiménez et al. (in press).

However, it could be argued that the crystallization of small amounts of chromite should make the rock impermeable to porous flow, as pyroxene does. Although no experimental data are available on the surface energy of chromite or on the dihedral angles between chromite and melt, chromite grains precipitated via percolation display rounded habits (Leblanc, 1980; Matsumoto and Arai, 2001). Chromite with relatively low dihedral angles ($DR\# < 0.4$) has low surface anisotropy and thus allows the creation and maintenance of an interconnected, intergranular melt film during the formation of the chromitites.

If melts percolate through a dunite that is rich in pyroxene and/or euhedral chromite ($DR\# \geq 0.6$), and/or is at temperature below its solidus, the peridotite's permeability is much lower. This limits porous infiltration along grain boundaries, hindering the formation of an interconnected film-like network and promoting the segregation of melt-rich lenses and their subsequent migration to develop a network of interconnected melt-pockets. As a result, heterogeneous melt percolation in the zone of intersection between "porous" dunite channels, producing *antinodular* chromitites. An excellent example of the sequence of formation of antinodular chromitites from disseminated chromitites is shown in Fig. 6l. Other evidence for the migration of

melts oversaturated with chromite into a network of interconnected melt-pockets (but in a chromite-free dunite) is shown in Fig. 6g. These globules (nodules) probably correspond to former melt-pockets interconnected by thin stringers of chromitite, which mark the former melt-like network.

The crystallization of chromite by these mechanisms requires that each type of melt preserves the geochemical characteristics inherited from its source until mixing occurs. This is only possible if melts can "outrun" the kinetics of the melt-rock reaction, thus limiting diffusive equilibration between the melt and its surroundings. Estimates for some dunite-dominated mantle suites indicate that at low melt/rock ratios, melt segregation can still be more rapid than diffusive equilibration, particularly if there is an interconnected network of melt-like film and/or veins (Becker et al., 2001; Kelemen et al., 1999; Kogiso et al., 2004). This would be consistent with the observation that in the Ojén lherzolite massif the ¹⁸⁷Os/¹⁸⁸Os of the peridotite remained mostly unmodified during the melting, melt transport/pooling and melt-rock reaction processes responsible for the formation of the small chromitites and their accessory Os-bearing phases (González-Jiménez et al., in press).

6.2.2. Stage 2. High melt/rock ratio: a self-sustaining system allows the "infinite" formation of massive chromitites

As the increasing melt mass produces focused porous flow of melt, increasing the porosity and permeability of the porous channels in dunite, they evolve into melt-filled conduits or tubes with impermeable walls; these conduits are high-speed pathways for the rapid ascent of melts. Melts of different provenance can mix at the intersections between melt-filled channels, producing hybrid melts that can precipitate chromite. The availability of these different physical pathways avoids the problem of mixing distinct melts in a single conduit (Arai, 1997; Arai and Abe, 1995; Arai and Yurimoto, 1994; Lago et al., 1982;

Leblanc and Ceuleneer, 1992; Zhou et al., 1994, 1996), where the earlier melt generally leaves a crystalline product, isolated from mixing with the later melts (Edwards, 1995).

If melts with different physico-chemical properties (contrasting SiO_2 , viscosity, density, temperature and degree of polymerization) move along the channels with different flux regimes, and meet at the intersections, these melts will mix. SiO_2 -rich melts are more polymerized than less siliceous melts. When they meet the more polymerized melt(s) will be entrained in the denser melt as micro-plumes driven by density and velocity contrast (Campbell and Turner, 1986a, b; Campbell et al., 1983; Naldrett and Gruenewaldt, 1989). The experiments of Ballhaus (1998) show that this inhibits (or at least delays) mixing as melts mingle as droplets; chromite crystallization mimics the former melt fractions with contrasting SiO_2 , forming nodular and orbicular chromitites (Fig. 6e). In a dynamic environment, grains and nodules of chromite can coalesce to form larger nodules or aggregates and ultimately more massive chromitites (Fig. 6h–j).

The formation of large nodules of chromite and massive chromitites obstructs the original melt-feeder channels, creating a “body” of chromite Leblanc and Ceuleneer (1992). The melt flow is then displaced towards the margins of this body as an aureole that infiltrates the host dunite by porous flow (Fig. 10). This would move the system back to the initial stage to produce disseminated as well as antinodular chromitites. At this stage, if the supply of melt is stopped and the system cools, the melts freeze and semi-massive and disseminated textures are preserved, as is observed in the outer parts of many chromitite bodies. The cooling rate thus controls the final meso-scale structure of the chromitite.

In contrast, if the influx of melts continues and becomes focused, under increasingly higher melt/rock ratios, the drainage network would become unstable. The collapse/coalescence of multiple single channels (with/without chromitites) may produce larger single ones. In this scenario, pooled and incoming melts can partially assimilate the crystal mush of chromitite and olivine (\pm pyroxene \pm hydrous silicate) matrix. This instability promotes a positive feedback mechanism in which melts with different Si-contents are produced and react, contributing to the almost continuous precipitation of chromite. Fractional crystallization of some melts in the system olivine–quartz–chromite leaves a residue of small fractions of a relatively silica-rich (orthopyroxene-saturated) component (Fig. 1 in Supplementary Appendix 1; Irvine, 1977). Ballhaus (1998) reproduced this Si-rich component (in the form of trydimite) in his melt-mixing experiments. Such a Si-rich remnant would also act as reservoir for the continual contamination of Si-poor melts, thus contributing to the self-sustainability of the system. The normal zoning observed in many laurite inclusions in chromite grains of chromitites is consistent with such fractional crystallization of small volumes of melt in the channels (González-Jiménez et al., 2009).

There is no clear outcrop-based evidence for the anastomosing network of channels figured here, but dunite islands are common within masses of chromitite (Figs. 3 and 5). These could represent incompletely assimilated relics of the walls between melt channels, analogous to the morphology of drainage networks formed via erosion and deposition of sediments. The dikes or veins of nodular chromite common seen within the dunites (Fig. 6e) could represent former single conduits or fractures (O'Reilly and Griffin, 2010), fed by upstream-coalescing melt-filled channels in pre-existing dunite, where mixing/mingling of melts took place. Some of these dykes or veins cut zones of dunite with disseminated chromitites (Fig. 6d), supporting the sequence of increasing melt/rock ratio and formation of melt-filled channels after pervasive percolation at low melt/rock ratios.

Chromite readily re-equilibrates with surrounding melts, so the composition of chromite itself does not normally record evidence of its crystallization from multiple batches of melts, involving processes of crystallization–dissolution–crystallization and grain agglomeration. However, individual chromite grains (and massive samples) often

contain several generations of inclusions of platinum-group minerals (and Ni–Cu–Fe sulfides) that record crystallization in a dynamic open system, dominated by short-term variations in T – $f\text{O}_2$ – $f\text{S}_2$ relationships (and the activity of As). These grains commonly coexist millimeters apart, or form composite aggregates, but show a wide dispersion of $^{187}\text{Os}/^{188}\text{Os}$ (Ahmed et al., 2006; González-Jiménez et al., 2012, in press; Marchesi et al., 2011) as well as intra-grain zoning of Os-isotope ratios (González-Jiménez et al., 2012; González-Jiménez et al., in this volume). These chemical and isotopic heterogeneities are evidence of growth from multiple isotopically-distinct magmas that mixed during the growth of the platinum-group minerals and Ni–Cu–Fe sulfides. The complex internal chemical and isotopic zoning of these minute mineral grains suggests multiple events of crystallization/dissolution associated with their physical displacement from one melt to another. These observations are consistent with the proposed mechanism for the crystallization of chromite by mixing/mingling of batches of melts that were moving upward within a network of coalescing/anastomosing melt-filled channels. Such a framework of melt-filled conduits also allows pre-existing “residual” platinum-group minerals and Ni–Cu–Fe sulfides to be physically entrained from the peridotite wall-rock into the chromitite-forming system, thus contributing to the wide range of $^{187}\text{Os}/^{188}\text{Os}$ observed in the chromitites (González-Jiménez et al., in this volume).

6.2.3. Stage 3. Low melt/rock ratio: expulsion of chromite-rich fluid phase into veins or channels

Chromite veins form stockworks or filling breccias, as observed in peripheral parts of large chromitite bodies of the Antalya ophiolite in southern Turkey (Fig. 7a–c) and the Dobromirski Ultramafic Massif (González-Jiménez et al., submitted for publication), suggesting that they represent fractures that were filled by chromite-bearing fluids. Crack propagation is a well-known mechanism for the almost instantaneous movement of fluid in the mantle (O'Reilly and Griffin, 2010, 2012); it can occur when there is fluid overpressure or where crystallization in pore spaces in sub-solidus matrices is more rapid than the viscous relaxation of the rock. The latter situation initiates diverging, random porous flow ponding of melt beneath a permeability barrier, increasing melt pressure until it produces hydrofracturing (Braun and Kelemen, 2002). Another possibility is that a relatively high concentration of volatiles in the silicate melts promoted the unmixing of a fluid-rich phase that could penetrate through the cooler dunite by hydraulic overpressure (Kirby et al., 1987; Maaløe, 2003; O'Reilly and Griffin, 2010). Either of these two mechanisms or their combination would promote changes in pressures of hydrofracturing, thus producing transitions from anastomosing networks of veins to “layers” as observed in Antalya (Fig. 7a–c). The localization of these “fractures” filled with chromite in the peripheral parts of the bodies suggests that this is a late process associated with small fractions of escaping residual melts after the system is relatively cool. As noted above, this is not a mechanism for the “crystallization” but a process that accumulates the crystallized product.

Similar relationships are seen, at a larger scale, in the chromitites of the Arroyo de la Cala in the Ronda massif, in southern Spain (Fig. 4b), where chromite forms networks that isolate subangular blocks of peridotite. These observations suggest that hydrofracturing is an effective way to concentrate chromite at a range of scales, especially in relatively cold peridotitic wall-rock.

Interestingly, some of the Type II chromitites that apparently have been deposited from a water-rich fluid phase are anomalously enriched in PGE, especially in PPGE (up to 11 ppm Pt + Pd in the case of Ouen Island). This suggests that the segregation of water-rich fluid from relatively evolved melts effectively concentrates not only chromite but also incompatible elements such as the PGE; Matveev and Ballhaus (2002) and Ballhaus et al. (2006) have experimentally verified this idea. The unmixing of silicate melt and a H_2O -rich fraction may also enhance the segregation of sulfide melt(s)

(Ballhaus and Stumpfl, 1986; Ferrario and Garuti, 1990; Melcher et al., 1997). Because sulfide melts wet the surfaces of oxides better than silicate liquids, the immiscible sulfide melt(s) would tend to concentrate with a dense phase like chromian spinel in the spinel-laden H₂O-rich pools (Barnes in Augé et al., 2005; Holzeid, 2010). Immiscible segregation of sulfide melt(s) would also produce a further concentration of available PGE, especially PPGE (Ballhaus et al., 2001; Lorand et al., 2010; Makovicky et al., 1986), giving rise to assemblages containing PGE-rich base-metal sulfides, found within chromite grains or in the intercumulus silicate matrix (González-Jiménez et al., in this volume). Significant amounts of base-metal sulfides are associated with the strong enrichment of PPGE in Type II chromitites such as those found at Cliff in the ophiolite of Shetland ophiolite (Prichard and Lord, 1993; Prichard et al., 1986), and the Great Serpentine Belt in Australia (Yang and Seccombe, 1993).

7. Conclusions

1. Three types of chromitites in ophiolite complexes can be defined using integrated field and new PGE data. *Type I* includes chromitites that, independently of their morphology, host rock and spatial localization in the ophiolite sequence, show bulk-rock enrichment in Os, Ir and Ru (i.e. IPGE) relative to Rh, Pt, and Pd (i.e. PPGE). *Type II* includes chromitites that also may show a range of morphologies and are usually localized in the shallower zones of the oceanic lithosphere; their common feature is a significant enrichment in the incompatible PPGEs, and they generally show higher total PGE contents than *Type I*. *Type II* chromitites can be further divided into two sub-types on the basis of chromite composition: *Type IIA* shows trends of Cr# vs Mg# that overlap the compositional field of *Type I*, whereas *Type IIB* show a more limited range in Cr# but a wider range of Mg#, overlapping the compositional range of chromite in layered mafic intrusions.
2. Ophiolitic chromitites occur mainly in dunite-rich parts of the peridotites. Interconnected 3-dimensional networks of film-like channels are formed in the dunite by melt infiltration (and/or crack propagation), providing an ideal setting for producing chromitites by mixing of basaltic melts of different provenance and degrees of fractionation. The formation of a chromite body, its size and type of chromite microstructures could reflect focused melt flow within these high-porosity and high-permeability networks of channels at different melt/rock ratios, and a range of temperature contrast between melts and the host peridotites.
3. *Type I* chromite is a consequence of mixing/mingling of mafic melts of different provenance and SiO₂ contents at the intersection between melt-filled dunitic channels in a suprasubduction-zone setting. The melt/rock controls the amount of crystallizing chromite and the chromite microstructures. Disseminated chromitites form at low melt/rock ratios, and massive chromitites at high melt/rock ratios; nodular, orbicular and antinodular chromitites reflect episodic variations in this ratio.
4. The *Type II* chromitites owe their generation to water oversaturation in small volumes of evolving silicate melts. The segregation of fluid-rich phases favors concentration of the incompatible PPGE. Some of the *Type II* chromitites form in hydrofractures penetrating peridotites that were filled with chromite-bearing fluids.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.lithos.2013.09.008>.

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