Conversion of low-pressure chromitites to ultrahigh-pressure chromitites by deep recycling: A good inference

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ARTICLE INFO

Article history:
Received 6 June 2013
Accepted 2 August 2013
Available online 28 August 2013
Editor: B. Marty

Keywords:
podiform chromitites
low-pressure cumulates
UHP minerals
mantle convection
deep recycling

ABSTRACT

Podiform chromitites have been interpreted as a peridotite/melt reaction product within the upper mantle (= low-P chromitites). Some of them, however, contain ultrahigh-pressure (UHP) minerals such as diamond and coesite (= UHP chromitites). The UHP chromitites can be produced by deep recycling of low-P chromitites via mantle convection. Carbon-rich UHP minerals were changed from fluidal C species (e.g., CO₂) metasomatically entrapped during the travel of chromitites within the mantle. Lamellae of coesite and other silicates observed in UHP chromite were possibly originated from globular inclusions of hydrous minerals and pyroxenes, which are common in low-P chromitites. Platinum-group element (PGE) sulfides, which commonly characterize the low-P chromitites, were converted to PGE metals or alloys by heating on their decompression during mantle convection. Peculiar igneous textures, e.g., nodular textures, characteristic of low-P chromitites can be preserved even after compression and subsequent decompression during recycling because of possible absence of reactions between olivine and chromite or their high-P polymorphs. The UHP chromitites can thus be an indicator of mantle convection; UHP minerals in chromite may support the two-layer convection model.

1. Introduction

There has been a consensus that podiform chromitites are formed through reaction between mantle peridotite (especially harzburgite) and melt, with subsequent magma/melt mixing at an uppermost mantle level (e.g., Arai and Yurimoto, 1994; Zhou et al., 1994; Arai, 1997). The podiform chromitites serve as a good indicator of peridotite–melt reaction in the upper mantle (e.g., Arai, 1997). However, ultrahigh-pressure (UHP) minerals including diamond have been recently found from two Tibetan ophiolites as well as from Ray-Iz massif, the Polar Urals (e.g., Robinson et al., 2004; Yang et al., 2007, 2011; Yamamoto et al., 2009; Xu et al., 2009), and this strongly requires us to revisit the origin(s) of podiform chromitites. Origin of UHP chromitites has been recently proposed but not been discussed in great detail (e.g., Robinson et al., 2004; Ruskov et al., 2010). The important point is that, as far as we know, the UHP podiform chromitites are basically similar in petrography and mineral chemistry to “ordinary” podiform chromitites. The UHP chromitite mainly comprises chromite (chromian spinel) and olivine, and some of them show nodular textures (e.g., Zhou et al., 1996; Yamamoto et al., 2009), which characterize igneous low-P chromitites (e.g., Nicolas, 1989). Arai (2010) proposed a possibility of deep recycling origin for the UHP chromitites. Here I would like to discuss the origin of the UHP podiform chromitites in more detail and more extensively based on mineralogical characteristics, although the discussion below may be speculative at present. This work will promote re-examination and more systematic descriptions of UHP chromitites and related peridotites.

2. Low-pressure magmatic origin of podiform chromitites: some lines of evidence

The podiform chromitites, enveloped by dunite (e.g., Cassard et al., 1981), are commonly found within mantle peridotites, mainly harzburgite (e.g., Arai, 1997) in ophiolites or mantle-derived peridotite complexes (Fig. 1a). They form a kind of cumulates filling melt conduits within the residual mantle peridotite (e.g., Cassard et al., 1981; Lago et al., 1982). Origin of the podiform chromitites with dunite envelope can be explained by harzburgite–melt reaction and subsequent melt mixing (e.g., Noller and Carter, 1986; Arai and Yurimoto, 1994; Zhou et al., 1994): the dunite envelope is essentially similar to a replacive dunite (Quick, 1981; Kelemen et al., 1990; Arai and Yurimoto, 1994). This process includes incongruent decomposition of orthopyroxene, and is effective at low-P conditions (cf. Kushiro, 1969).
Chromite in chromitites sometimes contains minute inclusions of Na-rich pargasite, Na-phlogopite and pyroxenes (e.g., Augé, 1987; Lorand and Ceuleneer, 1989; Borisova et al., 2012) (Fig. 1b, c). Their globular shape (Fig. 1b, c) indicates their initial entrapment as melt by spinel (e.g., Borisova et al., 2012). They sometimes show concentric distribution within spinel grains, indicating their primary nature (Roedder, 1984) (Fig. 1b). Pargasite, one of the main constituents of the inclusions (Fig. 1c), shows a low-P (< ca. 3 GPa) stability field (e.g., Niida and Green, 1999; Frost, 2006). The presence of low-P hydrous minerals in the primary inclusions in spinel (Fig. 1b, c) indicates a shallow upper mantle origin for concerned chromitites (e.g., Borisova et al., 2012), which is consistent with the above inference.

Typical low-P chromitites may be represented by so-called discordant chromitites, which are relatively young and, if flattened, can become so-called concordant chromitites together with surrounding peridotites via mantle flow beneath a spreading center (Cassard et al., 1981; Lago et al., 1982). Cassard et al. (1981) concluded that peculiar igneous textures, e.g., nodular, anti-nodular and orbital, were only found in the discordant chromitites, but got unclear via deformation (cf. Nicolas, 1989). The minute mineral inclusions possibly disappeared with the progress of deformation too (Cassard et al., 1981). The situation is, however, not so simple with concordant and discordant chromitites (Ahmed and Arai, 2002) from the northern Oman ophiolite; the two types are essentially different in terms of chemical and petrographical characteristics (Miura et al., 2012). That is, the discordant chromitite is not simply a deformed equivalent to the discordant one (Ahmed and Arai, 2002; Miura et al., 2012).

3. Characteristic of UHP chromitites

The geological context of UHP chromitites has not been described in great detail and is not clearly known, but, as far as we know from the literature, they show features on the outcrop similar to those of ordinary low-P chromitites. The chromitites from Luobusa, Tibet (e.g., Zhou et al., 1996; Xu et al., 2011), some of which show UHP features (e.g., Robinson et al., 2004; Yang et al., 2007; Yamamoto et al., 2009; Xu et al., 2009), seem to share the same geological features to those of low-P origin, e.g., those from Oman ophiolite (e.g., Miura et al., 2012) (Fig. 1a). UHP chromitites are enveloped by dunite, within harzburgitic mantle peridotite (e.g., Zhou et al., 1996, 2005; Yamamoto et al., 2009). A concordant attitude to surround harzburgite is expected for UHP chromitites but not clearly shown (cf. Zhou et al., 1996) (Fig. 1a).

Diamond and other UHP minerals have been found as inclusions in chromite in podiform chromitites from Tibetan ophiolites (e.g., Robinson et al., 2004; Yang et al., 2007, 2011; Yamamoto et al., 2009; Dobrzhinetskaya et al., 2009; Xu et al., 2009) (Table 1). They include native elements (e.g., diamond), alloys (e.g., PGE and Ni-Fe-Cr-C), Fe-silicides, carbide (moissanite), oxides (e.g., Si-rich rutile) and nitrides (TiN and c-BN) (Table 1). In addition, even the former presence of much higher-P minerals was suggested, although they had been broken down. Yamamoto et al. (2009) suggested a precursor UHP CF (calcium ferrite)-type chromite that is decomposed to low-P chromite containing silicate exsolutions. Yang et al. (2007) considered the precursor stishovite for the blade-shaped coesite. Robinson et al. (2004) suggested the presence of ringwoodite as a precursor of now altered Mg-Fe silicate with an octahedral shape.

Robinson et al. (2004) referred to a possibility of a xenocrystal origin for UHP minerals; they were accidentally trapped as xenocrysts by chromite in magmatic formation of podiform chromitites in the upper mantle. Yamamoto et al. (2009), however, found exsolution of coesite and pyroxenes in chromite from
some Luobusa chromitites, suggesting a UHP formation of chromitite and precluding the possibility of xenocrystal origin for the UHP minerals.

To be interesting, the nodular texture has been preserved in some of the Luobusa chromitites (Zhou et al., 1996; Yamamoto et al., 2009), which are seemingly concordant to the surrounding peridotite (although not referred to clearly in the literature). According to the descriptions of the Luobusa chromitites, their chromites are completely free from the minute primary inclusions of hydrous and other minerals (e.g., Zhou et al., 1996; Yamamoto et al., 2009; Miura et al., 2012), of which presence is one of the characteristics of discordant chromitites (Cassard et al., 1981) (Fig. 1).

Platinum-group minerals (PGMs) are only PGE-bearing alloys in the Luobusa and Donggjiao chromitites (Bai et al., 2000; Shi et al., 2007); this is in contrast to predominance (or common presence) of laurite and other PGE sulfides and arsenides in ordinary podiform chromitites (e.g., Ahmed and Arai, 2002, 2003). Bulk-rock IPGE (Ir-group PGE)/PGPE (Pt-group PGE) ratio is relatively high in the Luobusa chromitites (Zhou et al., 1996; Bai et al., 2000) as discussed below.

4. Discussion: Possible conversion of low-pressure chromitites to UHP chromitites through mantle recycling

4.1. Possibility of direct UHP magmatic formation of chromitite

One possibility of UHP origin is their direct magmatic formation at UHP condition (cf. Ruskov et al., 2010). The primary magmatic UHP chromitite with associated rocks, if any, is strictly required to be converted to the set of chromitite + dunite envelope + harzburgite host (Fig. 1a), when decompressed. It is, however, difficult to picture the decomposition-induced conversion of the UPH primary chromitite-dunite (ringwoodite rock?) pair to exactly the same thing, by coincidence, commonly formed by low-P magmatism. On the other hand, it is much easier to recycle the low-P chromitite-dunite-harzburgite set (Fig. 1a) through the mantle, because the basic structure and texture of chromitite and associated peridotites can be restored when reappearing at the upper mantle after recycling as discussed below.

4.2. Recycling origin of UHP chromitite

Deep recycling of low-P magmatic chromitites formed at the upper mantle well explains several key features of the UHP chromitites as discussed below in detail. The depth for recycling is a matter of debate; subducted slab may be stagnated as megagahit around the transition zone and further subsided down to the core–mantle boundary (e.g., Ringwood, 1975, 1991). The megagahit is expected to contain chromitite pods, because the low-P igneous chromitite is one of the members of oceanic lithosphere (Arai and Matsukage, 1998; Abe, 2011). Some of subducted materials, on the other hand, have been known to be recycled only through the upper mantle without further sinking (e.g., Morishita et al., 2003).

The recycling of chromitite does not mean recycling of a whole crust–mantle slice that will reappear as a “recycled ophiolite”, if any. Any of crustal sequences of ophiolites of which mantle section contain UHP chromitites are not representative of recycled materials. Mantle rocks, which contain recycled materials, have been partially melted to form magmatic crustal rocks in ophiolites or oceanic lithosphere. Constituents of subducted lithosphere are possibly disintegrated during sinking, and may be mixed individually with ambient mantle peridotite to various extents (e.g., Allègre and Turcotte, 1986). This is consistent with the findings of crustal zircons from podiform chromitites (Savelieva et al., 2006, 2007; Yamamoto et al., 2013), which suggests disintegration and partial digestion of subducted crustal materials. These examples suggest that zircons as relics of recycled crustal materials were restored in the mantle and participated in magmatic formation of podiform chromitites at the shallow mantle (Yamamoto et al., 2013). It is noteworthy that this is not at all the case for the UHP chromitites, which have been formed together with surrounding peridotites in the upper mantle and recycled together as a rock suite (chromite + peridotites) within the mantle. They reappeared as the chromitites (+ surrounding peridotites) that have experienced UHP condition to show UHP mineral features, still preserving basic textural features established at low pressures. The density of the bulk rock suite (chromitite + peridotites) can be low enough, depending on their proportions, to be recycled. Depending on the melting condition, some of the mantle rocks, e.g., very old peridotites recovered from a current mid-ocean ridge (Gakkel ridge) (Liu et al., 2008), did not participate in partial melting beneath a spreading ridge. The UHP chromitites and surrounding peridotites could survive magmatism beneath a ridge, and can be incorporated in newly formed residual and cumulative rocks of the upper mantle.

4.3. Diamond genesis

Very minute diamond inclusions in PGM (Os–Ir alloy) totally included by chromite in a Luobusa chromitite (Yang et al., 2007) can be formed by reduction of CO2 fluids obtained during the travel of low-P chromitites in the mantle due to the downward decrease of fO2 in the mantle (e.g., Ballhaus, 1995; Frost and McCammon, 2008) (Fig. 2). Inclusions of fluidal carbon species are so common in minerals from mantle-derived peridotites (e.g., Roedder, 1965). Diamonds, if any, can be oxidized easily during upwelling of recycled chromitites, but can survive modification especially when encapsulated in PGM that are further included by chromite (e.g., Yang et al., 2007).

The simple recycling of low-P chromitites that we know is, however, possibly difficult to produce coarse euhedral diamonds enclosed by chromite in UHP chromitites (e.g., Xu et al., 2009;
4.4. Fate of silicate mineral inclusions in chromite

The primary low-P silicate inclusions in chromite in chromitites mainly comprise Na-rich pargasite, pyroxenes and Na-phlogopite (e.g., Augé, 1987; Borisova et al., 2012). The hydrous minerals will be partially melted or broken down when compressed and/or heated during recycling although there have been no experimental results on such Na-rich systems. Depending on P–T path of recycling, they may be ultimately broken down or partially melted to expel fluid/melt outside and leave pyroxenes, especially diopside, (or their high-P polymorphs) (cf. Hollaway, 1973) because the bulk silicate inclusions in spinel are possibly rich in pargasite components (e.g., Augé, 1987; Borisova et al., 2012) (Fig. 1c). The residual pyroxene components will be dissolved in chromite (or in its high-P polymorph(s)), and will reappear as pyroxene lamellae exsolved in chromite (Yamamoto et al., 2009) when decompressed en route to the surface (Fig. 2). Silicate exsolutions in chromite from UHP chromitites (Yamamoto et al., 2009) are thus representative of refractory silicate components ultimately derived from the globular inclusions of hydrous and other silicate minerals, which initially formed magmatically at the uppermost mantle (Fig. 1). This is consistent with our careful observation that chromeite grains in UHP chromitites are totally free from the primary globular inclusions of hydrous and other silicates (Miura et al., 2012).

4.5. Platinum-group elements (PGE) and platinum-group minerals (PGM)

The UHP Luobusa chromitites are characterized by relatively low PGE levels as well as a high IPGE/PPGE ratio (Zhou et al., 1996) (Fig. 3). As stated above, the absence of PGE sulfides (and arsenides) is one of the characteristics of the Luobusa chromitites; only alloys have been found as PGM in them (Bai et al., 2000). These characteristics can be explained by heating of originally low-P chromitites in recycling. Primary igneous PGE sulfides in low-P chromitites are expected to be decomposed to PGE alloys and melts (or fluids), which are S-rich and possibly show a low IPGE/PPGE ratio (e.g., Andrews and Brenan, 2002; Peregoedova et al., 2004). Loss of these fluidal phase(s) outside, which possibly occurs, can give rise to lowering of total PGE levels as well as an increase of IPGE/PPGE ratio of the bulk chromitite. This process leaves only PGE alloys as PGM, which is characteristic of the Luobusa UHP chromitites (Zhou et al., 1996; Bai et al., 2000) (Fig. 3).

There is a small but clear difference in PGE distribution pattern between the Luobusa UHP chromitites (Zhou et al., 1996) and some discordant chromitites from Oman and other ophiolites (Fig. 3). The latter show a clear trough at Ir, which is absent in the former (Fig. 3). This is possibly due to a preference of Ir relative to other PGE for alloys in equilibrium with S-rich melt (Andrews and Brenan, 2002). If we assume decomposition of a PGE sulfide into an alloy + S-rich melt during recycling, the PGE alloy is expected to show an abundance of Ir relative to other PGE (Andrews and
The conclusion of Cassard et al. (1981) and Nicolas (1989) is that it is difficult to observe in the field, especially in the Oman ophiolite, despite discordant chromitite to the concordant one being the result of magmatic processes. The process of textural conversion from the nodular, anti-nodular, and orbicular textures, such as nodular, anti-nodular, and orbicular textures, are preserved even during conversion of discordant chromitites to concordant ones, i.e., during transportation of the discordant chromitites off the spreading center, beneath which they were formed in magmatic processes. The process of textural conversion from the discordant chromitites to the concordant one is, however, difficult to observe in the field, especially in the Oman ophiolite, despite the conclusion of Cassard et al. (1981) and Nicolas (1989).

The initial igneous textures have been basically preserved even during deep recycling down to the transition zone mantle, if any, because of the possible absence of reactions between olivine (and its high-P polymorphs) and chromite (and its high-P polymorph) (Fig. 4). For example, chromitites can be converted to a mixture of ringwoodite (or wadsleyite) (e.g., Ringwood, 1991) and CF (calcium ferrite) type chromite (e.g., Chen et al., 2003) with compression, and the ringwoodite–chromite rocks (cf. Robinson et al., 2004) will revert to ordinary chromitites on decompression (Fig. 4). The enveloping dunite may be more ductile than chromitites and easily deformed, and is expected to act as a lubricant to prevent enclosed chromitites from strong deformation during mantle convection, if any. The nodular textures of some UHP chromitites from Luobusa (Zhou et al., 1996; Yamamoto et al., 2009) have been basically preserved from the initial magmatic ones (Fig. 4). Behavior of chromitites brought to the lower mantle is further unclear. If UHP chromite (or its UHP decomposed equivalents) will not be reacted or solved with ferropericlase and Mg-perovskite, decomposed from ringwoodite (e.g., Wood, 2000; Stachel et al., 2005), some of the primary igneous textures can be preserved when reappearing near the surface. Ferropericlase, however, does contain appreciable amount of Cr (cf. Odake et al., 2008), and we need UHP phase relations in appropriate systems, such as Mg$_2$SiO$_4$–MgCr$_2$O$_4$–SiO$_2$.

If deep recycling occurred, the primary igneous textures may have been destroyed through possibly strong physical and chemical modification. Cassard et al. (1981) argued that the peculiar igneous textures, such as nodular, anti-nodular, and orbicular textures, are destroyed even during conversion of discordant chromitites to concordant ones, i.e., during transportation of the discordant chromitites off the spreading center, beneath which they were formed in magmatic processes. The process of textural conversion from the discordant chromitite to the concordant one is, however, difficult to observe in the field, especially in the Oman ophiolite, despite the conclusion of Cassard et al. (1981) and Nicolas (1989).

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Some of the UHP minerals such as diamond and moissanite in chromitites are C-bearing (cf. Robinson et al., 2004), and the UHP chromitites play an important role in global C cycle. Age determination and analysis of P-T trajectory of the UHP chromitites (cf. Yamamoto et al., 2009) are potentially important for our understanding of mantle dynamics; the UHP podiform chromitite can be an indicator of mantle dynamics (Fig. 4). The UHP chromitites can be present beneath the mid-ocean ridge, and available through ultra-deep mantle drilling on the ocean floor. They can be one of important targets for the coming MoHole project.

Acknowledgements

I thank Y. Tatsumi, P.T. Robinson, S. Yamamoto, A.H. Ahmed, S.K. Mondal and M. Miura for their discussions. A.H. Ahmed kindly provided me with unpublished data on some of bulk PGE contents of Oman chromitites. M. Miura helped me to prepare some revision. reviewer for their critical comments, which greatly helped me in preparing some revision.

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