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Research Article
Possible sub-arc origin of podiform chromitites

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Abstract The sub-arc mantle condition possibly favors the formation of podiform chromitites. The Cr/(Cr + Al) atomic ratio (= Cr#) of their chromian spinel frequently is higher than 0.7, which is comparable with the range for arc-related primitive magmas. This almost excludes the possibility of their sub-oceanic origin, because both oceanic peridotites and MORB have chromian spinel with the Cr# < 0.6. Precipitation of chromitite and associated dunite enhances a relative depletion of high-field strength elements (HFSE) to large-ion lithophile elements (LILE), one of chemical characteristics of arc magmas, for the involved magma. This cannot alter completely, however, the MORB to the arc-type magma, especially for Ti and Zr. The presence of chromitite xenoliths, similar both in texture and in chemistry to podiform chromitites of some ophiolitic complexes, in some Cenozoic alkali basalts from the southwest Japan arc indicates directly that the upper mantle beneath the Japan arcs has chromitites.

Key words: arc setting, mantle-melt interaction, podiform chromitites, replacive dunite.

INTRODUCTION

Chromian spinel (or chromite) is frequently concentrated as pod- or sheath-like bodies (podiform chromitite) (Thayer 1964) within upper mantle peridotites of ophiolites (cf. Nicolas 1989). Chromitites are expected to have specific geochemical characteristics because chromian spinel, the main constituent of the chromitites, itself has peculiar geochemical characteristics relative to other mantle minerals (cf. Kelemen et al. 1990). The tectonic setting of chromitite formation and the mechanism of chromian spinel concentration are still subjects of debate (e.g., Lago et al. 1982; Roberts 1988). Recently genesis of podiform chromitites by peridotite-melt interaction combined with magma mixing was discussed (Arai 1992; Arai & Yurimoto 1992, 1993, 1994; Zhou et al. 1994). Arai and Yurimoto (1993, 1994) especially proposed sub-arc settings for the precipitation of major podiform chromitite bodies. We intend to highlight the sub-arc setting for the formation of podiform chromitites with a review on geological and petrological characteristics and origin of podiform chromitites. The discussion may place some constraints on the origin and derivation of some ophiolite suites because of the frequent occurrence of podiform chromitites in their mantle member.

PODIFORM CHROMITITES: GEOLOGY, PETROGRAPHY AND MINERAL CHEMISTRY

Chromitites can be divided into two types of mode of occurrence. One, the layered type, occurs in mafic layered intrusions and the other, podiform type, in alpine-type peridotite masses or in ophiolitic complexes. The former type occurs as continuous layers associated with pyroxenites, anorthosites and peridotites. The latter, the podiform chromitite, is usually associated with dunite (e.g., Cassard et al. 1981). It occurs most characteristically as pod-like bodies with dunite envelopes within mantle harzburgite (e.g., Thayer 1964; Cassard et al. 1981). The podiform chromitite with a dunite envelope sometimes cuts deformation structures of surrounding harzburgite, indicating a younger generation of the former type (Cassard et al. 1981). Subsequent plastic deformation, if any, has made the initially discordant chromitite bodies concordant with the structure of surrounding peridotites (e.g., Nicolas 1989). The thickness

of the dunite envelope seems to be in proportion to the size of the core chromitite (Lago *et al.* 1982; Gervilla & Leblanc 1990).

The podiform chromitite has various textures; nodular, anti-nodular and orbicular textures are particular to the podiform chromitite, especially to undeformed types (e.g., Nicolas 1989). Volume per cent of chromian spinel is highly variable; chromitite is sometimes monomineralic (i.e., chromian spinel rock) and is gradual to dunite (e.g., Arai 1980). Olivine dominates other primary silicates associated with chromian spinel in the podiform chromitite. Pyroxenes and plagioclase are sometimes associated with chromian spinel (e.g., Augé 1987). Chromian spinel in podiform chromitites, especially in undeformed types, often has rounded inclusions of primary silicates (e.g., Talkington *et al.* 1986). Hydrous minerals, especially phlogopites and pargasites, commonly are found as an inclusion in spinel in chromitites (Johan *et al.* 1983; Johan 1986; Talkington *et al.* 1986; Lorand & Ceuleneer 1989; McElduff & Stumpfl 1991). Chromian spinel in podiform chromitite from the Tari–Misaka peridotite complex, southwestern Japan (Arai 1980), includes irregular aggregates of rutile and ilmenite which are possibly subsolidus exsolution products. This indicates Ti-saturation of chromian spinel at least at subsolidus conditions.

The Cr# of chromian spinel in podiform chromitities ranges from 0.4 to 0.9 and is most frequently from 0.7 to 0.8 (Fig. 1). It is interesting that rocks from ocean floor rarely have chromian spinel with the Cr# higher than 0.7 (e.g., Dick & Bullen 1984; Arai 1994b). Both primitive volcanics and peridotites from arc settings, on the other hand, frequently have Cr-rich spinel with the Cr# higher than 0.7 (e.g., Dick & Bullen 1984; Arai 1994a, 1994b). Chromian spinel in the podiform chromitite is very similar in composition, both in the Cr# and in some trace element contents, to that in its dunite envelope (Fig. 2) (Arai & Yurimoto 1994). Both are sometimes different in composition, especially in the Ti content, from that in the wall harzburgite; the Cr# of the former is almost similar to or higher than the ratio of the latter (Fig. 2) (Arai & Yuri-
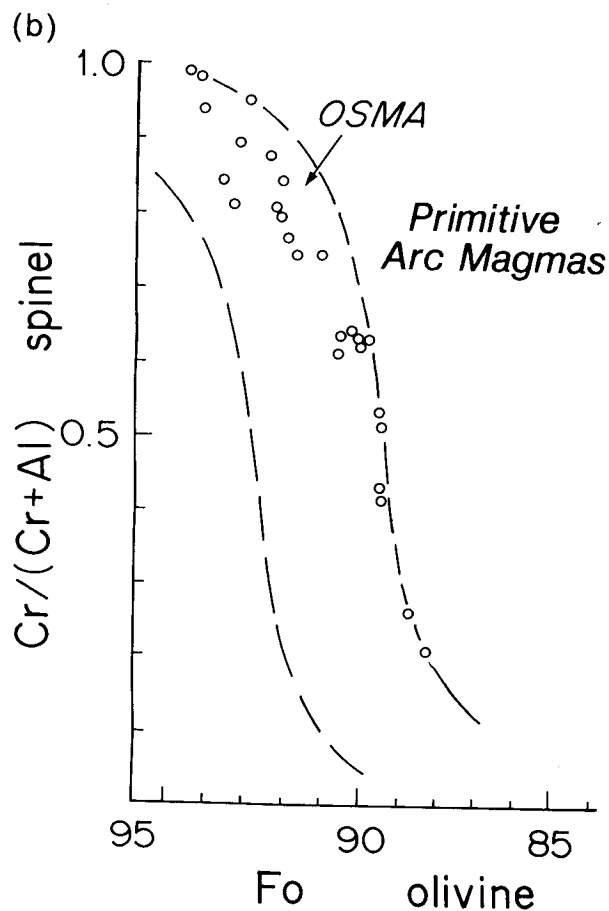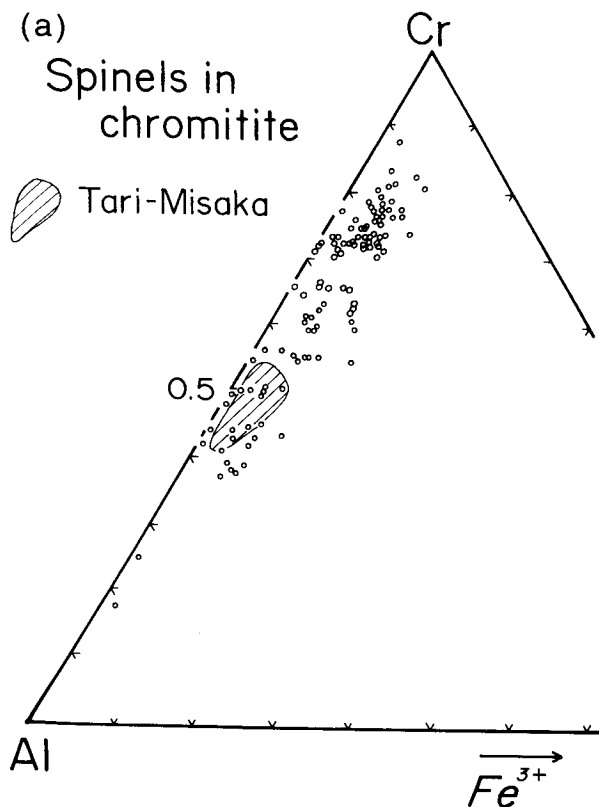
Fig. 1 (a) Summary of trivalent-cation ratio of chromian spinels in alpine-type podiform chromitites. (b) Relationships between Fo olivine and Cr# of spinel in relatively primitive arc magmas (basalts and high-Mg andesites). Refractory olivine-spinel pairs which plot within the olivine-spinel mantle array (OSMA; Arai 1987, = the region of mantle peridotites) are selected. See Arai (1994b) for data source. Additional data are from Ninomiya (1992). Note that the data are selected for Tertiary to recent rocks which are derived from arc settings without doubt.
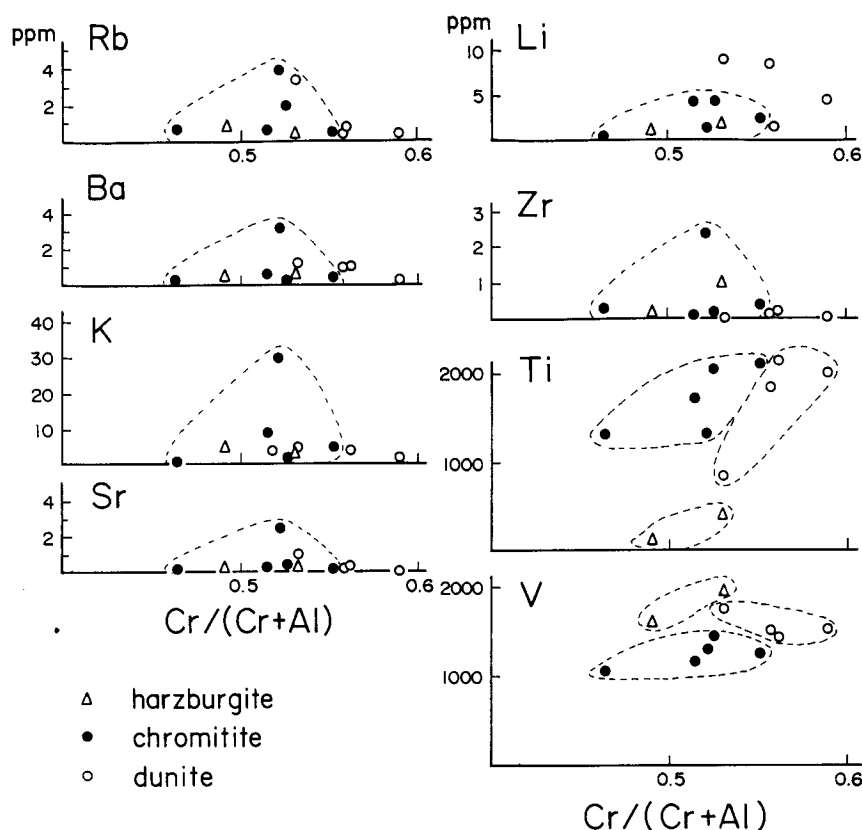
Fig. 2   Trace-element contents of chromian spinels from the Tari-Misaka complex (source, Arai & Yurimoto 1994). The Cr# was determined by an energy-dispersive microprobe, and trace-element contents were determined by an ion probe at the University of Tsukuba (Yurimoto *et al.* 1989).

Δ   harzburgite
•   chromitite
○   dunite

moto 1994). The Ti content of spinel is up to one order higher in the chromitite pod-dunite envelope than in harzburgite (Fig. 2) (Arai & Yurimoto 1994). The Zr content in chromitite spinel is generally very low (< 0.5 ppm) (Table 1). Chromian spinel from some podiform chromitites is poorer in some HFSE (e.g., Zr) and richer in V and some LILE (e.g., Rb) than N-type MORB (Fig. 3). Ion microprobe analysis of the exsolved Ti-rich aggregate in chromian spinel from the Tari-Misaka chromitite indicates that Ti and Zr are much more concentrated (e.g., 41 ppm in rutile and 67 ppm in ilmenite for Zr) than in the host spinel (less than 3 ppm for Zr; Fig. 2).

ORIGIN OF PODIFORM CHROMITITES

Recently the podiform chromitites have been interpreted to be conduit-filling cumulates initially penetrating mantle peridotites, especially harzburgites (Lago *et al.* 1982). Arai and Yurimoto (1992, 1993, 1994) interpreted that the podiform chromitites from the Tari-Misaka peridotite complex, southwestern Japan, are the products of interaction between harzburgite and melt at low pressures. The Tari-Misaka podiform chromitites (Arai 1980), have low-Cr# [= Cr/(Cr + Al) atomic ratio] (c. 0.5) spinel compared with the majority of the podiform chromitites (Fig. 1). In the Tari-Misaka

Table 1 Trace element contents (ppm) and Cr# of chromian spinel in massive olivine-poor chromitites from Tari-Misaka, Troodos and northern Oman. The trace element contents were determined by ion probe at the University of Tsukuba (Yurimoto *et al.* 1989). The Cr# was determined by an energy-dispersive microprobe at Kanazawa University.

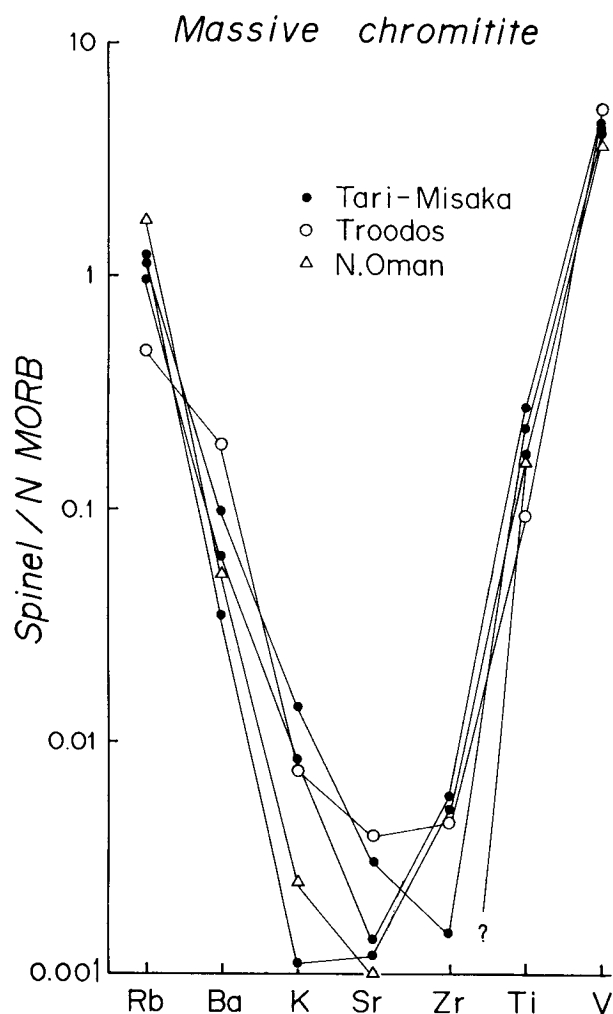|	Na	K	Rb	Sr	Ba	Ti	Zr	V	Cr#
Tari-Misaka									
Chubu-1	23.6	5.10	0.53	0.13	0.39	2103	0.43	1232	0.552
W55-1	2.3	0.65	0.68	0.11	0.22	1297	0.30	1076	0.562
W7-1	63.4	8.54	0.63	0.27	0.61	1712	0.11	1186	0.575
Troodos									
CY-MC	12.9	4.50	0.21	0.35	1.18	706	0.33	1383	0.687
Northern Oman									
OM-E4	4.4	1.51	0.97	0.09	0.27	1212	0.00	989	0.751

Fig. 3 Abundances of some trace elements normalized by N-MORB in chromian spinel from massive chromitites from Tari-Misaka, Troodos and northern Oman.

relatively immobile in subsolidus element redistribution with olivine, and the magma involved in chromitite formation is different from that for harzburgite formation. In terms of trace-element chemistry of spinel the dunite is almost identical to the chromitite (Fig. 2), indicating that the fractional crystallization did not work on the formation of the chromitite and its dunite envelope. The dunite is not a simple residue from the surrounding harzburgite because its spinel is not depleted in incompatible elements relative to the harzburgite spinel (Fig. 2). The dunite envelope is most likely of rejuvenating origin instead, i.e., an interaction product between melt and harzburgite essentially identical to so-called discordant or rejuvenating dunite (Kelemen 1990). For example, in the Oen peridotite, Spain, dunite delicately mantles irregular-shaped chromitite pod, cutting the structure of surrounding peridotite (Gervilla & Leblanc 1990), which indicates the rejuvenating origin for the dunite. Melts fed into harzburgite interact preferentially with its orthopyroxene with simultaneous precipitation of olivine (plus chromian spinel) (Kelemen 1990). The relatively silica-rich melt thus formed (Fisk 1986), favorably at low pressures, could be mixed with subsequently fed more primitive melt to precipitate only chromian spinel because the mixed melt is brought into the chromite primary field (Irvine 1977; Arai 1992; Arai & Yurimoto 1994; Zhou et al. 1994). The mixed melt is expected to have low abundance both in LILE (large-ionlithophile elements) and in HFSE (high-field strength elements), because the harzburgite orthopyroxene (15 volume % on average) has very low abundance of these elements relative to, for example, N-type MORB (Table 2). The most important point is that the melt is relatively enriched in Cr, because of the high Cr content of harzburgite orthopyroxene (Roberts 1988) (Table 2), and thus it has high potential to precipitate chromian spinel. Thanks to this replen-

complex Cr# of chromian spinels are almost identical to between chromitite, dunite envelope and harzburgite host (Arai 1980). Their Ti and V contents are, however, clearly different between the chromitite and the harzburgite (Fig. 2), being consistent with the chromite-dike hypothesis (Lago et al. 1982; Nicolas 1989). Ti and V in spinel are

Table 2 Crystal (or rock)/melt distribution coefficients (by weight) and contents (ppm) in orthopyroxene and N-MORB for selected elements. Ol, olivine; Sp, chromian spinel; Chr, chromitite (0.7 Ol + 0.3 Sp). Orthopyroxene form the Tari-Misaka complex was analyzed by SIMS (Yurimoto et al. 1989). $D^{Ol-Melt}$ and $D^{Sp-Melt}$ are from Yurimoto et al. (1984, 1987) except for V (Kelemen et al. 1990). Data for N-MORB are from Sun and Mcdonough (1989) except for V (Walker 1991).

	$D^{Ol-Melt}$	$D^{Sp-Melt}$	$D^{Chr-Melt}$	Tari-Misaka Opx (ppm)	N-MORB (ppm)
K	2.5×10^{-3}	3.7×10^{-5}	7.8×10^{-4}	73	600
Sr	1.1×10^{-2}	6.9×10^{-4}	3.7×10^{-3}	0.52	90
Zr	7.0×10^{-3}	7.0×10^{-2}	5.1×10^{-2}	0.12	74
Ti	6.9×10^{-3}	4.0×10^{-1}	2.85×10^{-1}	38	7600
V	3.0×10^{-2}	3.9	2.75	97	267
Cr	5.9×10^{-1}	2.77×10^4	1.94×10^4	3640	290

ishment of Cr the mixed magmas continue to have an ability to produce chromitites.

The low-pressure origin of podiform chromitites is supported by their distribution within ophiolites; podiform chromitites are mostly concentrated in the transition zone, the shallowest part of the upper mantle section (e.g., Nicolas 1989). Chromian spinel is likely to be concentrated to form podiform chromitites for the same reason as that for layered chromitites in stratiform intrusions (Irvine 1977), i.e., by mixing of the two kinds of melts (Arai & Yurimoto 1994), silica-rich and primitive ones, in conduits (Lago et al. 1982) or in magma pockets (Paktunc 1990) within the upper mantle.

Origin of the whole transition-zone dunite is controversial. Nicolas and Prinzhofer (1983) favor a residual origin based on the structural analysis. Although the detailed mineralogical data have not been available, it may be partly of rejuvenating (or interactive) origin and partly of cumulus origin (cf. Quick 1981; Quick & Gregory 1995).

DISCUSSION: POSSIBLE SUB-ARC ORIGIN OF PODIFORM CHROMITITES

Low pressure, high water-vapor pressure, high temperature and compressional stress may be necessary for favorable upper mantle conditions for the formation of the podiform chromitites. Low pressure (Boyd et al. 1964) and/or high P_{H2O} (Kushiro et al. 1968) conditions may be favorable for the selective dissolution of orthopyroxene in peridotites to produce the dunite and the silica- and Cr-rich melt which is mixed with a primitive melt to precipitate chromian spinel as discussed above (e.g., Arai & Yurimoto 1994). Ambient high-temperature conditions are of great advantage to promote the melt-peridotite interaction. Lithospheric compression may make an uprising melt stagnant, which should also promote interaction with peridotite wall. All these conditions are likely to be simultaneously available only at the arc setting.

Chemical composition, especially the Cr# (= Cr/(Cr + Al) atomic ratio), of chromian spinel may give a strong constraint on the setting for the chromitite genesis. Chromian spinel from podiform chromitites has relatively high Cr#, from 0.4 to 0.9, mostly around 0.7–0.8 (Fig. 1). This range of Cr# for the chromitite spinel is almost identical to that for chromian spinel coexisting with Mg-rich olivine in arc and related (forearc, arc proper and

backarc) magmas (Fig. 1), indicating that the magma in equilibrium with podiform chromitites could be a primitive arc magma in terms of Fo (of olivine)–Cr# (of spinel) relationship (cf. Arai 1990; Arai 1994a). This conclusion is further confirmed if petrological data from ophiolite and other complexes derived from arcs (e.g., DeBari & Coleman 1989) are taken into consideration. Origin of the main podiform chromitite bodies beneath mid-oceanic ridges can be excluded because neither ocean floor peridotites nor MORB have high-Cr# (>0.6) spinels (Dick & Bullen 1984; Arai 1994b) (Fig. 1).

Chromitites are actually present in the arc mantle (Arai & Abe 1994). The southwest Japan arc has many young (Miocene to recent) monogenetic volcanoes which had erupted alkali basalts with ultramafic xenoliths derived from the arc mantle (Takahashi 1978; Aoki 1987). Alkali basalts from Takashima (Ishibashi 1970; Kobayashi & Arai 1981) and Kurose (Arai & Hirai 1983) in the southwest Japan arc do contain chromitite xenoliths (Arai 1978; Arai & Abe 1994). They sometimes have a nodular texture, which is characteristic of the undeformed alpine-type podiform chromitite (Nicolas 1989). The Cr# of chromian spinel in the nodular-textured chromitite xenoliths from Takashima is around 0.8, quite similar to the ratio in the commonest alpine-type podiform chromitite (Arai & Abe 1994; Fig. 1a). The extreme rarity of chromitites as the mantle-derived xenolith is evident (Thayer 1970), which may be due both to their low abundance within the mantle and to the low possibility of rising of mantle xenolith-bearing magmas through the arc mantle. The high density of chromitite may be responsible partly for the rarity (Thayer 1970). Dunite xenoliths are very common on the Japan island arcs. The Cr# of chromian spinel coexisting with Mg-rich (> Fo_{89}) olivine in the dunite xenoliths ranges from 0.2 to 0.8 (mean >0.5), which is again similar to the Cr# range of chromian spinel coexisting with Mg-rich olivine in arc magmas (Fig. 1). The dunites as well as the chromitites from the upper mantle of the Japan arcs can thus be in equilbrium with primitive arc magmas.

The magma in equilibrium with the pair of podiform chromitite and dunite envelope is expected to have geochemical characteristics of the arc magma (i.e., the depletions of HFSE relative to LILE). Chromian spinel and olivine have strong preference of HFSE relative to LILE on partitioning with basaltic melts (Yurimoto & Sueno 1984, 1987; Kelemen et al. 1990; Table 1). Precipitation

of chromian spinel and olivine thus enhances the depletions of HFSE relative to LILE for the derivative melts.

Kelemen *et al.* (1990) pointed out the possibility that a MORB can be altered to have one characteristic of the arc magma, that is, relative abundance of LILE to some HFSE (e.g., Zr and Ti), through the interaction with mantle peridotites, especially with chromian spinel and olivine. Some geochemical characteristics (Fig. 3), however, possibly indicate that the precipitation of chromian spinel and associated olivine alone can not effectively change the N-MORB into some arc magma. Chromian spinel in podiform chromitites is not distinctively high in the HFSE (e.g., Ti and Zr)/ LILE ratio relative to MORB (Fig. 3) even if the composition of exsolved rutile-ilmenite is considered as in the case of the Tari–Misaka chromitite (Arai 1980; Arai & Yurimoto 1994). The exsolved Ti-rich phases in spinel are very small in relative volume ($\leqslant$ 1%), and their Zr (one of HFSE) content is not so high (41 ppm for rutile and 67 ppm for ilmenite) to enhance effectively the content in the homogenized high-temperature spinel.

CONCLUSIONS

Most of the podiform (alpine-type) chromitites may be formed in the upper mantle or in the mantle-crust transition zone at the arc setting. The Cr# of chromian spinel in podiform chromitites is mostly from 0.7 to 0.8; the range is almost identical to that for chromian spinel in primitive arc and related magmas. The majority of podiform chromitites may be precipitated from primitive arc magmas (Fig. 4). The precipitation of chromian spinel and olivine (chromitite and dunite) can enhance, although not so effectively, the arc magma characteristics (i.e., the depletions of HFSE relative to LILE), for the involved magma (Fig. 4). Ubiquity of dunites and the presence of chromitites in the upper mantle beneath the Japan arcs strongly indicate that their precipitation actually occurs beneath the arcs. Chromitites, sometimes with the orbicular texture, are found as xenoliths in the southwest Japan arc.

ACKNOWLEDGEMENTS

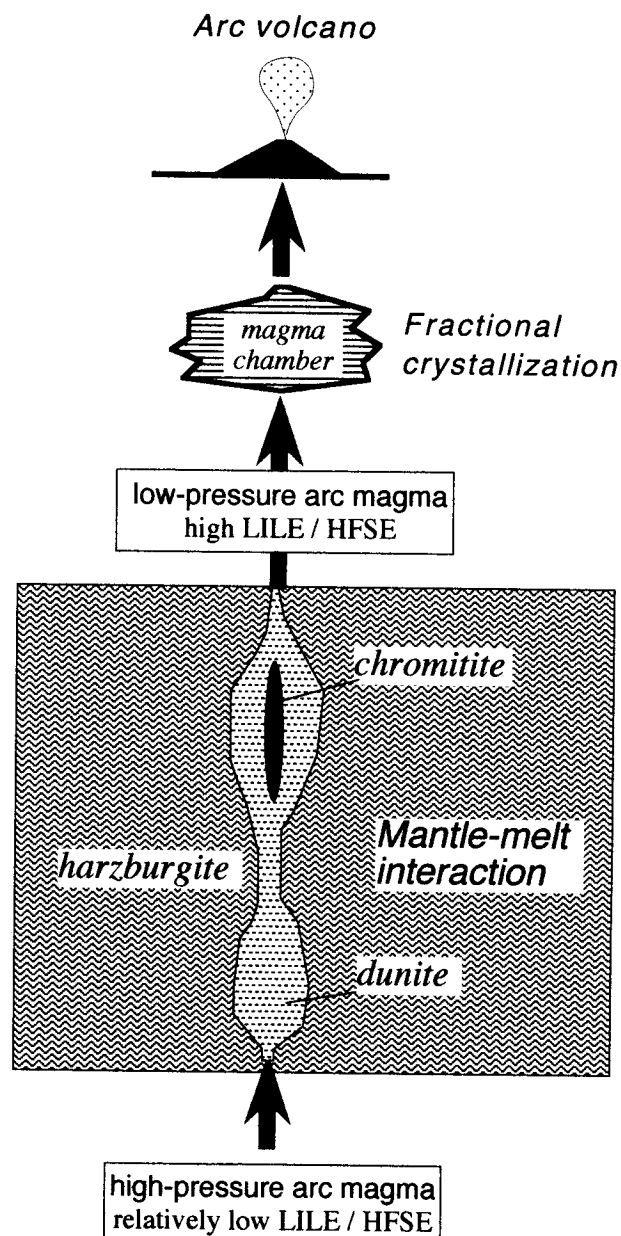**Fig. 4** Schematic diagram to illustrate a possible setting of podiform chromitite combined with evolution of the arc magma.

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