Reaction of orthopyroxene in peridotite xenoliths with alkali-basalt melt and its implication for genesis of alpine-type chromitite

SHOJI ARAI, NATSUE ABE
Department of Earth Sciences, Faculty of Science, Kanazawa University, Kakuma, Kanazawa 920-11, Japan

ABSTRACT
The Kawashimo alkali basalt of the southwest Japan arc has peridotite xenoliths with a wide lithological range, from lherzolite (Fo of olivine, 89; Cr' [=Cr/(Cr + Al) atomic ratio] of spinel 0.10) to harzburgite (Fo of olivine, 91; Cr' of spinel, 0.54). Reaction zones between orthopyroxene and alkali-basalt melt are low-pressure analogues of mantle-melt interaction products and consist of two subzones: a fine-grained inner subzone (adjacent to orthopyroxene) and a relatively coarse-grained outer subzone. In both xenolith types the reaction products are olivine + diopsidic clinopyroxene ± spinel ± glass, but the spinel concentrations are remarkably different around lherzolite from those around harzburgite. Cr-bearing spinel is concentrated only in the outer subzone on harzburgite orthopyroxene (Cr' > 0.14); the inner subzone on harzburgite orthopyroxene and both the inner and outer subzones on lherzolite orthopyroxene (Cr' = 0.05) are almost free of spinel. The remarkable enrichment of spinel in the outer subzone on the harzburgite orthopyroxene suggests a mechanism of spinel concentration, i.e., the origin of podiform chromitite is related to interaction between Cr-rich orthopyroxene and basaltic melt. This observation for the Kawashimo xenoliths is concordant with the near absence of podiform chromitite in lherzolitic mantle. Chromian spinel could be concentrated if a relatively silica-rich secondary melt, produced by interaction between pyroxene-undersaturated magma and harzburgite orthopyroxene, is mixed with a primitive magma in the upper mantle.

INTRODUCTION
Alpine-type podiform chromitites with dunite envelopes occur in harzburgitic upper mantle (e.g., Nicolas, 1989). The origin of the podiform chromitite is a subject of debate, and dissolution of orthopyroxene may play an important role in its formation within the upper mantle (e.g., Nicolas, 1989; Nicolas and Al Azri, 1991; Roberts, 1988, 1992). Arai (1992) and Arai and Yurimoto (1992, 1993, 1994) concluded that podiform chromitite is a product of melt-mantle interaction and related melt mixing. We describe the products of reaction between an alkali basaltic melt and orthopyroxenes in peridotite xenoliths from Kawashimo, southwest Japan, which support the interaction theory for the origin of alpine-type podiform chromitites (e.g., Arai and Yurimoto, 1994).

Orthopyroxene in peridotite xenoliths with a wide compositional range from Kawashimo has reacted with the host alkali basalt to form various products, depending on xenolith type and orthopyroxene composition. This phenomenon may be a low-pressure analogue of melt-mantle interaction. Their origin may contribute to understanding some aspects of alpine-type chromitite genesis by explaining why alpine-type chromitites occur only in harzburgitic mantle and not in lherzolitic mantle and by connecting the genesis of chromitites to the dissolution of mantle orthopyroxene and related melt mixing.

PETROGRAPHY
Geological background and host basalt
In the Kawashimo area, Shimane Prefecture, southwestern Japan, small amounts of alkali basalt occur (Iizumi et al., 1975). This is one of the dissected monogenetic volcanoes of Cenozoic age in southwestern Japan (e.g., Takamura, 1973; Iwamori, 1991), and the age is 6.7 Ma (whole-rock K-Ar method, Uto et al., 1986). The Kawashimo volcano is rather isolated, not belonging to any of the main volcanic clusters (Takamura, 1973; Iwamori, 1991). The host alkali olivine basalt contains up to 12 wt% of normative nepheline (Iizumi et al., 1975; Nagao and Sakaguchi, 1990). The Kawashimo basalt has intersertal texture; phenocrysts are olivine and clinopyroxene, and the groundmass is composed of clinopyroxene, olivine, titanomagnetite, plagioclase, and interstitial glass (Nagao and Sakaguchi, 1990). Olivine phenocrysts are nearly euhedral and <1 mm across.

Xenoliths
The basalt has many ultramafic xenoliths, up to 5 cm across, and megacrysts (Iizumi et al., 1975), which have been described by Nagao and Sakaguchi (1990). According to these authors, the relative abundance (volume ratio) of rock species in the Kawashimo xenolith suite is
Fig. 1. Photomicrographs of Kawashimo peridotite xenoliths using plane-polarized transmitted light (a and c) and plane-polarized reflected light (b and d). Scale bar is 0.2 mm. (a and b) Products of reaction between alkali basalt (bottom) and orthopyroxene in harzburgite. Note the spinel concentration in the outer reaction subzone. (c and d) Reaction zone between alkali basalt (right) and orthopyroxene in lherzolite. Note that spinel is almost absent.

Fig. 2. Schematic illustration of the reaction zones around orthopyroxene.

<table>
<thead>
<tr>
<th>Opx-melt interaction products</th>
</tr>
</thead>
<tbody>
<tr>
<td>olivine + diopside + glass</td>
</tr>
<tr>
<td>olivine + diopside + spinel + glass</td>
</tr>
</tbody>
</table>

Harzburgite xenolith  Lherzolite xenolith

Alkali Basalt

lherzolite 11%, harzburgite 17%, dunite 12%, wehrlite 2%, clinopyroxenite 21%, websterite 8%, and orthopyroxenite 30%. The predominance of pyroxenite, especially orthopyroxenite, is noteworthy. The samples of peridotite are strongly deformed and have porphyroclastic textures. Chromian spinel, which is scarce in harzburgite, is usually round. Clinopyroxene content is variable, from almost nil in harzburgite to more than 20 vol% in lherzolite (Nagao and Sakaguchi, 1990). The clinopyroxene grains are characteristically round.

**Reaction products of orthopyroxene**

Orthopyroxene in all kinds of xenoliths and megacrysts is intensely reacted where in contact with host alkali-basalt melt, resulting in a corona texture (Fig. 1). The reaction zone is composed of two subzones, inner (i.e., adjacent to orthopyroxene) and outer (adjacent to melt), as first described by Iizumi et al. (1975). The two subzones are basically composed of olivine + diopsidic clinopyroxene ± spinel ± glass; the inner zone is remarkably finer grained than the outer. However, the reaction zones differ in the concentration of spinel, depending on the type of xenolith and on the composition of orthopyroxene (Fig. 1).
Spinel is concentrated only in the outer subzone on harzburgite orthopyroxene (Figs. 1 and 2). The color of the spinel varies outward from deep brown to opaque in the reaction zone on harzburgite orthopyroxene; the inner subzone is almost spinel free (Figs. 1 and 2). Within the xenolith, orthopyroxene that is not in direct contact with the host basalt locally is partially decomposed to form olivine + diopside + glass, free of spinel (Figs. 1 and 2). In lherzolite and pyroxenite (orthopyroxenite and websterite), in contrast, both the inner and outer reaction subzones on orthopyroxene grains are almost free of spinel (Figs. 1 and 2). Reaction products differ depending on lithology or mineral compositions, and this is true of all xenoliths examined from Kawashimo (eight harzburgite, 11 lherzolite, and 12 pyroxenite samples).

The most important point is that spinel concentration in the reaction products is controlled by the composition of orthopyroxene; chromian spinel is concentrated in the reaction zone (outer subzone) only on harzburgite orthopyroxene and only where it was in contact with alkali-basalt melt (Figs. 1 and 2).

The interaction between alkali basalt and orthopyroxene is a dynamic disequilibrium process, possibly depending on orthopyroxene composition, rate of supply of undersaturated melt, and other parameters (e.g., Daines and Kohlstedt, 1994). This is supported by the strong outward variations of mineral compositions in the reaction zones (e.g., Fig. 3). The reaction front is planar without any distinct melt fingers or scallopings (Fig. 1), probably because the reactant is essentially a single

Fig. 3. Cr-Al-Fe$^{3+}$ ratios of spinels. Outward variation in composition of spinels (solid circles) in the reaction zones around orthopyroxene in harzburgite (open diamonds) is shown by arrow. Fe$^{3+}$ content was calculated assuming spinel stoichiometry after subtracting ulvöspinel component (Fe$_2$TiO$_4$). Note that chromian spinel in the inner part of the reaction zones can be much higher in Cr' (up to 0.8) than both harzburgite and alkali basalt spinels (0.35–0.54 and ca. 0.5, respectively).

Fig. 4. Schematic phase diagrams showing spinel concentration. (a) Approximate pseudoquaternary liquidus phase diagram estimated from Irvine (1977) and Fig. 712 of Levin et al. (1964). (b) Cr-rich section of a. (c) Al-rich section of a. Note that the curvature of the boundary between olivine and spinel primary fields may be very different between high Cr' and low Cr' systems.
orthopyroxene crystal instead of a mixture of olivine and pyroxenes (e.g., Daines and Kohlstedt, 1994). As described above, variability among interaction products depends mainly on orthopyroxene composition, and the presence or absence of spinel concentration may be maintained despite some disequilibrium during the interaction. The reaction between alkali-basalt melt and orthopyroxene in peridotite xenoliths is generally observed and well known. The phenomenon is, however, not restricted to alkali-basalt melt, i.e., melt that is strongly Si undersaturated; a similar reaction has been observed between orthopyroxene in xenolithic peridotites and subalkalic, high-alumina arc basalt from the Megatavolcano in the northeast Japan arc (Katsui et al., 1979; Aoki and Fujimaki, 1982).

MINERAL CHEMISTRY

Xenoliths

Selected microprobe analyses of minerals are listed in Table 1. There are three kinds of peridotites in terms of mineral chemistry: refractory harzburgite, fertile harzburgite, and lherzolite (Fig. 3; Table 1). Olivine shows inter- and intragrain chemical homogeneity, Fo$_{88}$ (Fo$_{90.5-91.3}$) in harzburgite and Fo$_{90}$ (Fo$_{86.5-89.1}$) in lherzolite. Orthopyroxene has Mg' [=Mg/(Mg + Fe$_{eq}$) atomic ratio] similar to that of olivine, ranging from 0.913 to 0.917 in harzburgite and from 0.887 to 0.890 in lherzolite. Average Al$_2$O$_3$ and Cr$_2$O$_3$ contents of orthopyroxene are 3.2 and 1.1 wt%, respectively, in refractory harzburgite and 6.7 and 0.60 wt%, respectively, in lherzolite. Cr' is quite different in orthopyroxene: 0.20 in refractory harzburgite, 0.14 in fertile harzburgite, and 0.056 in lherzolite (Table 1). Clinopyroxene in lherzolite has relatively low Mg' content, ca. 0.87, and high Al$_2$O$_3$ content, ca. 7.8 wt%. Na$_2$O contents are <1 wt%; these are intermediate for clinopyroxene from Japan arc mantle peridotites (Arai, 1994). Cr' of spinel in refractory harzburgite is ca. 0.54 (Table 1), near the refractory end for spinel in peridotites beneath the Japan arcs (Arai, 1994) (Fig. 3). Lherzolite has chemically homogeneous Al-rich spinel, Cr' of ~0.1 (Table 1; Fig. 3).

Host alkali basalt

The Fo content of phenocrystic olivine varies from 74.0 to 80.4 but is generally around 75.0 (Table 1). Olivine contains spinel inclusions with various compositions, from Ti-rich chromian spinel to Al-, Cr-, and Mg-bearing titanomagnetite (Table 1; Fig. 3). The least titaniferous spinel inclusion has about 2 wt% of TiO$_2$ and Cr' of ~0.5, near the refractory end of the spinel compositional range in Cenozoic alkali basalts from southwest Japan (Arai, 1990).

Reaction products of orthopyroxene in xenoliths

The minerals changed in composition, depending on their position in the reaction zones; they were enriched outward in incompatible elements such as Fe, Al, and Ti. Olivine is variable in composition, from Fo$_{88}$ to Fo$_{90}$ outward (Table 1). Clinopyroxene is relatively Al-poor and Cr-rich, containing 0.87–3.5 wt% of Al$_2$O$_3$ and 1.1–1.3 wt% of Cr$_2$O$_3$ in most cases. Spinel grains in the outer reaction zone on harzburgite orthopyroxene are highly variable in composition, from Ti-bearing chromian spinel to Ti,Fe$^{4+}$-rich chromian spinel. Ti contents and Fe$^{3+}$

### Table 1. Selected microprobe analyses of minerals

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Harzburgite (HA-1)</th>
<th>Harzburgite (KWS-9)</th>
<th>Lherzolite (LZ-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>56.54</td>
<td>51.15</td>
<td>51.15</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.05</td>
<td>0.16</td>
<td>0.78</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>2.93</td>
<td>2.52</td>
<td>3.52</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>1.09</td>
<td>4.37</td>
<td>1.20</td>
</tr>
<tr>
<td>FeO</td>
<td>5.31</td>
<td>14.77</td>
<td>5.19</td>
</tr>
<tr>
<td>MnO</td>
<td>0.11</td>
<td>0.22</td>
<td>0.24</td>
</tr>
<tr>
<td>NiO</td>
<td>0.12</td>
<td>0.23</td>
<td>0.24</td>
</tr>
<tr>
<td>MgO</td>
<td>32.53</td>
<td>16.05</td>
<td>16.05</td>
</tr>
<tr>
<td>CaO</td>
<td>1.99</td>
<td>0.17</td>
<td>21.13</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.13</td>
</tr>
<tr>
<td>Total</td>
<td>100.72</td>
<td>101.15</td>
<td>99.56</td>
</tr>
</tbody>
</table>

**Note:** opx = orthopyroxene, sp = spinel, cpx = clinopyroxene, and n.d. = not detected. Mg' = Mg/(Mg + Fe$_{eq}$) atomic ratio, except for spinel [Mg/(Mg + Fe$^{3+}$) after subtracting all Ti as ulvöspinel, Fe$_{tot}$,T]. Cr' = Cr/(Cr + Al) atomic ratio. Cr, Al, and Fe$^{3+}$ in spinel were calculated assuming spinel stoichiometry. Fo = Fo component of coexisting olivine.
Fig. 5. Correlation of orthopyroxene–alkali-basalt interaction products with mantle-melt interaction products. During the melt-mantle interaction, the podiform chromitite with dunite envelope could be formed in the harzburgitic mantle (a), whereas dunite (or wehrlite) with a harzburgitic aureole may be formed in the lherzolitic mantle (b). The products of mantle-melt interaction, a and b, are analogous, respectively, to the products of xenolith-alkali basalt, c and d. Reconstructed from descriptions by Quick (1981a, 1981b), Nicolas (1989), and Takahashi (1992).

**DISCUSSION**

**Origin of spinel concentration in orthopyroxene-melt reaction zones**

The inner and the outer zones around orthopyroxene can be interpreted as a reaction zone and a melt-mixing zone, respectively (Figs. 1 and 2). In the reaction zone, reaction occurred between orthopyroxene and melt: orthopyroxene + alkali-basalt melt = olivine + clinopyroxene + Si-enriched melt. Alternatively, but less likely, this zone could be an incongruent melting zone where orthopyroxene simply decomposed into olivine (+ clinopyroxene) + Si-enriched melt (Figs. 1 and 2). In the melt-mixing zone, the relatively Si-rich secondary melt is mixed with the surrounding, more primitive alkali basalitic melt.

It is noteworthy that spinel concentration occurs only in the melt-mixing zone and only on harzburgite orthopyroxene, which has higher Cr', >0.14 (Figs. 1 and 2). It is probable that spinel cannot be precipitated by decomposition of orthopyroxene but can be precipitated from the hybrid melt (secondary Si-enriched melt + primitive alkali basalitic melt), which entered the primary liquidus volume of spinel, as suggested by Irvine (1977) for the origin of layered chromitites (Fig. 4b). Spinel is not precipitated from the hybrid melt on the lherzolite (low Cr') orthopyroxene possibly because of a difference in the curvature of the boundary surface between spinel and olivine phase volumes. The curvature depends on the Cr/(Cr + Al) ratio of the system (Fig. 4). In the low Cr' system, the
1046  ARAI AND ABE: REACTION OF ORTHOPYROXENE AND BASALT MELT

Fig. 6. Cr-Al-Fe$^{3+}$ ratios of spinels in podiform chromitite and the host harzburgite from four peridotite (or ophiolite) complexes (Sarugawa, Tari-Misaka, Northern Oman, and Troodos). Data from Arai (unpublished) and Arai and Yurimoto (1994). The Sarugawa (or Iwanai-dake) complex (Arai, 1978; Katoh and Nakagawa, 1986) and the Tari-Misaka complex (Arai, 1980; Arai and Yurimoto, 1994) are located, respectively, at Hokkaido, northern Japan, and at Tottori Prefecture, southwestern Japan. Note that the peridotite with podiform chromitite is harzburgite with high-Cr<sup>+</sup> (>0.4) spinel, and that the Cr<sup>+</sup> of spinel between chromitite and harzburgite wall rock is similar to that between spinel in orthopyroxene reaction product (the least fractionated part) and the harzburgite xenolith in Figure 3.

The basalt-xenolith interaction described in this study occurred at low pressures. However, essentially the same process is expected to occur widely within the shallow upper mantle. The high-pressure melt, alkaline or subalkaline, that becomes undersaturated with pyroxenes with a decrease in pressure, should react with pyroxenes if it comes in contact with peridotites at lower pressures (e.g., Quick, 1981b; Daines and Kohlstedt, 1994). Therefore, the interaction between the alkali basal and orthopyroxene in peridotite xenoliths from Kawashimo may mimic the interaction between a magma and peridotite with a wide lithological variation in the shallow upper mantle.

Arai (1992), Arai and Yurimoto (1992, 1993, 1994), and Zhou et al. (1994) proposed that the alpine-type (or podiform) chromitites are formed by a combined process, that is, an interaction between melt of deeper origin and harzburgite wall rock, with associated magma mixing. The reaction products between the Kawashimo alkali basal and orthopyroxene in peridotite xenoliths are similar to the alpine-type chromitites and may support an interaction origin for the latter.

The observations on the concentration of chromian spinel in the Kawashimo xenoliths are germane to the mode of occurrence of alpine-type podiform chromitites (Figs. 1, 2, and 5). The spinel-enriched outer subzones on harzburgite orthopyroxenes are analogous to the podiform chromitites, whereas the spinel-poor inner subzones are analogous to dunite envelopes (Figs. 1, 2, and 5). The near absence of podiform chromitite in lherzolite mantle (Fig. 5) is compatible with the absence of spinel concentration in the reaction zones of orthopyroxene in the Kawashimo lherzolite xenoliths (Figs. 1 and 2). The near absence or rarity of chromitite associated with dunite in some peridotite massifs, e.g., Trinity (Quick, 1981a, 1981b; Noller and Carter, 1986) and Horoman (Takahashi, 1992), may be due to lack of either high-Cr<sup>+</sup> orthopyroxene in wall-rock peridotite or magma mixing in the conduits within the peridotite. The relative abundance of diopsidic clinopyroxene in the reaction zones between alkali basal and orthopyroxene is due in part to saturation of olivine and diopside for the alkali basaltic melt (e.g., Arai et al., 1994).

Cr<sup>+</sup> of chromian spinel in podiform chromitite is similar to or higher than that of host harzburgite (Fig. 6). A similar relationship is observed between the orthopyroxene-melt interaction products and the harzburgite xenoliths from Kawashimo (Fig. 3). The relatively high Cr<sup>+</sup> of podiform chromitite may be due to a possibly high Cr<sup>+</sup> of the Si-enriched hybrid melt inherited from high-Cr<sup>+</sup> orthopyroxene in harzburgites.

In conclusion, the observations and interpretations of the spinel concentrations in the orthopyroxene-melt reaction zones in the Kawashimo xenoliths can be applied to the generation of podiform chromitites. Chromian spinels can be concentrated by mantle-melt interaction (1) if the wall-rock peridotite, especially the orthopyroxene, is sufficiently high in Cr<sup>+</sup> and (2) if secondary Si- and Cr-enriched melts that are formed by decomposition of orthopyroxene are well mixed with more primitive melts.

Implications for origin of alpine-type chromitites

Alpine-type chromitites occur as pipes or lenses with dunite envelopes almost exclusively within harzburgite (e.g., Nicolas, 1989) (Figs. 5 and 6). They are very rare in lherzolite (Nicolas and Al Azri, 1991; Roberts, 1992) (Figs. 5 and 6). Leblanc and Timagoult (1989) and Gervilla and Leblanc (1990) reported podiform chromitites from lherzolitic massifs from Betic Cordillera, but they are very small (see Fig. 6 of Gervilla and Leblanc, 1990).

The basalt-xenolith interaction described in this study
ACKNOWLEDGMENTS

We are grateful to H. Hirai, who collected all the samples and prepared all the thin sections used in this study. Discussions with A. Nicolas, F. Boudey, C. Ballhaus, J. Pearce, and R. Hébert at IAVCEI assembly in Canberra were very useful to us in preparing the manuscript. Critical comments by G. Sen, D. Smith, and C. Hearn helped to improve the manuscript. K. Nakamura assisted us with preparation of some of the figures.

REFERENCES CITED


MANUSCRIPT RECEIVED DECEMBER 23, 1994
MANUSCRIPT ACCEPTED MAY 10, 1995