Chemistry of chromian spinel in volcanic rocks as a potential guide to magma chemistry

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Abstract

Chromian spinel in volcanic rocks is a potential discriminant for magma chemistry. The TiO_2 content of spinel, compared at similar $Fe^{3+}/(Cr + Al + Fe^{3+})$ ratios, can distinguish island arc basalts from intraplate basalts. MORB spinels are low in this ratio and are intermediate for the TiO_2 level at comparable Fe^{3+} ratios. Spinels from back-arc basin basalts, although similar in TiO_2/Fe^{3+} ratio, are more enriched in Fe^{3+} than the MORB spinels. Spinels in the oceanic plateau basalts are distinctly lower in TiO_2 than other intraplate basalt spinels and even slightly lower in TiO_2 than the MORB spinels. The data were successfully applied to estimate the kind of the magma from which spinel-bearing cumulates, especially dunites, were formed. Original magma chemistry of altered or metamorphosed volcanics in which spinels survive can also be estimated by the chemistry of relict spinel alone. It is possible to estimate the magma type of source volcanics for detrital spinel particles of volcanic derivation.

KEYWORDS: chromian spinel, TiO_2 content, MORB, island-arc basalt and andesite, intraplate basalt, magma chemistry.

Introduction

CHROMIAN spinel is an important petrogenetic indicator in ultramafic to mafic rocks because it contains several cations as major and minor constituents. The ratios can change subtly according to physico-chemical conditions (e.g. Irvine, 1965, 1967). It is well known that chromian spinel chemistry plays an important role in classifying mantle-derived peridotites in terms of origin and tectonic setting (Dick and Bullen, 1984; Arai, 1990*a*). Chromian spinel sometimes memorizes equilibrium temperatures in olivine-bearing rocks (Irvine, 1967; Jackson, 1969; Evans and Frost, 1975; Fabries, 1979). It also serves as a speedometer to show a cooling rate of olivine-bearing rocks (e.g. Ozawa, 1985). More recently Ozawa (1989) demonstrated that chromian spinel can be a stress indicator in peridotitic and other rocks. Chromian spinel in mantle-derived peridotites could also be an oxygen barometer of the upper mantle (e.g. Mattioli and Wood, 1986; Wood and Virgo, 1989).

Chromian spinel can contain the cations, Mg^{2+}, Fe^{2+}, Fe^{3+}, Cr^{3+}, Al^{3+} and Ti^{4+}, and its composition is sensitive to changes in the chemistry of the surrounding magma (e.g. Rimsaite, 1971). Chromian spinel, therefore, has the potential to indicate the chemical character of the mother magam. In this paper I summarize the compositions of chromian spinel in volcanic rocks and define its compositional range in mid-oceanic ridge basalts, arc basalts and andesites, and intraplate basalts.

If the chemistry of chromian spinel is a successful indictor of its mother magma, original chemistry of altered or metamorphosed volcanic rocks might be estimated from relict chromian spinel. It might also be used to estimate a provenance and parentage of detrital chromian spinel grains.

In this investigation cationic ratios were calculated, assuming spinel stoichiometry. All Ti was combined with Fe as the ulvöspinel component (Fe_2TiO_4).

Compositional change of chromian spinel during magmatic differentiation

Chromian spinel commonly occurs as phenocrysts (or microphenocrysts) or as inclusions in the other phenocryst minerals, especially in olivine, of basaltic to andesitic rocks. Compositional changes of chromian spinel in volcanic rocks and cumulates can be detected if they are

Mineralogical Magazine, June 1992, Vol. 56, pp. 173–184

monitored by the Fo content of coexisting olivine. In general, Ti content and Fe^{3+}# [= $Fe^{3+}/(Cr + Al + Fe^{3+})$ atomic ratio] of chromian spinel increase with a decrease of the Fo content of coexisting olivine (Fig. 1; Arai and Takahashi, 1987). The Cr# [= Cr/(Cr + Al) atomic ratio] of chromian spinel increases or decreases or is unaffected with a decrease of the Fo content of olivine (Fig. 2). Note that the compositional variation of chromian spinel is due to an apparent differentiation process of magmas, which may integrate crystallization differentiation, magma mixing (Sakuyama, 1978), disequilibrium crystallization of spinel (Thy, 1983), assimilation etc.

Scowen *et al.* (1991) demonstrated that chromian spinel even totally enclosed in olivine could change its solidus composition by diffusion through olivine in slowly cooling magmas. The chemistry of chromian spinel is also dependent on the cooling rate, even if the magma chemistry is

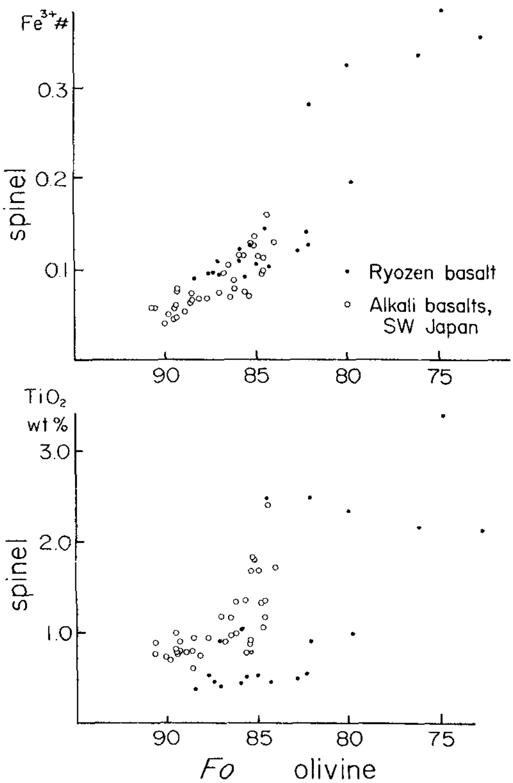

FIG. 1. Relationships between Fo of olivine and Fe^{3+}# and TiO_2 wt.% of coexisting chromian spinel. Ryozen basalt is a Mg-rich arc tholeiite of Miocene age in northeast Japan arc (e.g. Shuto *et al.*, 1985). Fe^{3+}#, $Fe^{3+}/(Cr + Al + Fe^{3+})$ atomic ratio. Data source: Ryozen, Arai (unpublished); Alkali basalts (Arai, 1990*b*).

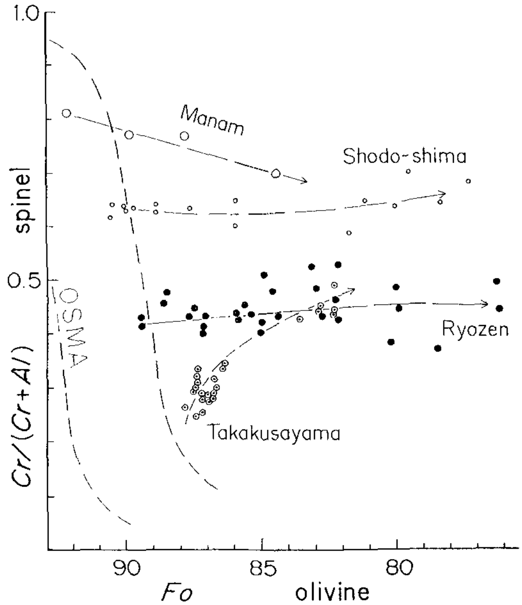

FIG. 2. Relationships between Fo of olivine and Cr# of coexisting chromian spinel in some volcanic rocks. OSMA, olivine-spinel mantle array (Arai, 1987, 1990*a*), in which mantle-derived spinel peridotites are plotted. Manam data are after Johnson *et al.* (1985). Shodo-shima basalt is Miocene high-Mg tholeiite associated with high-Mg Setouchi andesites (Tatsumi and Ishizaka, 1981). Tekakusayama alkali basalt, central Japan is Miocene in age (Hattori, 1986).

the same (e.g. Ozawa, 1985; Scowen *et al.*, 1991). The Ti content of spinel is, however, a reliable indicator of magma chemistry because the diffusivity of Ti^{4+} in olivine is relatively low (Scowen *et al.*, 1991).

Chemical characteristics of chromian spinel in Mg-rich magmas

In this article three main groups, arc magmas (basalts and andesites), ocean-floor basalts (MORB) and intraplate basalts, are considered. The three groups of magmas can be distinguished to some extent from each other by Ti contents (e.g. Fig. 6 of Glassley, 1974, and Fig. 2.4 of Wilson, 1989); the contents increase from island-arc magmas to intraplate basalts via MORB on a particular FeO/MgO ratio (Glassley, 1974). This indicates a potential usefulness of the TiO_2 content of chromian spinel for distinguishing between these three magma groups.

High-magnesian andesites and boninites are included in the arc magmas in a broad sense in the paper. Calc-alkaline andesites produced by magma mixing sometimes contain chromian spinels (e.g. Sakuyama, 1978). These are possibly inherited from the basalt end component of mixing (Sakuyama, 1978). Some back-arc basin basalts have an intermediate character between arc tholeiites and MORB (e.g. Sato and Tohara, 1985), and so are discussed separately. The oceanic plateau basalts (Tokuyama and Batiza, 1981) are also discussed separately from other intraplate basalts; they are depleted in incompatible elements compared to other intraplate basalts.

(*1*) *Olivine–spinel compositional relationships*. As is shown in Fig. 3, the Fo of spinel-bearing olivine is frequently low in arc magmas relative to MORB and intraplate basalts (especially alkali basalts). MORB and intraplate alkali basalts usually plot within or very near the olivine–spinel mantle array (Arai, 1987, 1990*a*) in the Fo–Cr# plane (Fig. 3). This is consistent with the tendency for arc magmas to be more frationated (i.e. lower in MgO/total FeO) than intraplate alkali basalts, which often carry mantle-derived peridotite xenoliths, and MORB.

High-magnesian andesites, boninites and some high-Mg tholeiites have distinctly higher Fo and Cr# than other kinds of magmas (Fig. 3). Intraplate alkali basalts (mostly from the southwest Japan arc) have Cr# < 0.6 (Arai, 1990*b*) (Fig. 3C). Oceanic plateau basalts and back-arc basin basalts are very similar to intraplate basalts (oceanic hot-spot basalts and flood basalts) and to MORB, respectively (Fig. 3ACD).

(*2*) *Cr#–TiO_2 relationships*. Chromian spinels from arc magmas have a wide spread of Cr# (Fig. 3). Boninites, high-magnesian andesites and high-Mg tholeiites have spinels with extremely high-Cr# (>0.8) (Fig. 3; Arai, 1990*a*). Chromian spinels in Quaternary subalkalic arc magmas from northeast Japan arc show an inter-volcano variation of the Cr#, from 0.2 to 0.7 (Fig. 3). It is noteworthy that the range of the Cr# of spinel in arc magmas is much extended towards low Cr# than that of Dick and Bullen (1984).

As Fe^{3+}# of spinel is strongly dependent on the degree of differentiation of the host magma (e.g. Arai and Takahashi, 1987), the TiO_2 content should be compared for spinels with comparable Fe^{3+}#. In Fig. 4 spinels from the intraplate basalts are clearly distinguished from other ones by their high Ti contents. Spinels from boninites and high-Mg andesites are also discriminated from other spinels by their higher Cr and lower Ti contents. The commonest spinels in the MORB are, however, indistinguishable from those in the arc magmas and those in back-arc basin basalts in terms of the Cr#–TiO_2 relationship (Fig. 4). The oceanic plateau basalt spinels are distinctly lower in TiO_2 than other intraplate tholeiites, in spite of the similarity in Cr# (Fig. 4).

Distinction of chromian spinels in three primary magma clans; a discussion

The similar TiO_2 content of chromian spinels in MORB and arc magmas (Fig. 4) may be partly ascribed to the difference of the degree of differentiation between the two magmas. The Ti content of spinels was compared at similar Fe^{3+} contents. Fig. 5 shows the Cr#–TiO_2 relationships of spinels contoured by the Fe^{3+} ratio for three basalt clans. Comparison of spinels with the comparable Fe^{3+}#, e.g. 0.1, shows that the TiO_2 content of spinel increases from arc magmas through MORB to intraplate basalts. This is consistent with the relative TiO_2 abundance of the magmas (Glassley, 1974). It is noteworthy that the Fe^{3+}# of the MORB spinels is very low (Fig. 5A), which is partly due to the less fractionated character of the MORB relative to other magmas. Fig. 6 shows TiO_2–Fe^{3+}# relationships for spinels with Cr# of 0.3 to 0.6. It is clearly demonstrated that spinels in the intraplate basalts can be discriminated clearly from those in the arc magmas (Fig. 6). Spinels in an arc-related alkaline basalt from Rishiri volcano (Arai and Takahashi, 1987; Arai, 1990*b*), the nearest continental volcano of the Kurile arc (Katsui *et al.*, 1978; Kobayashi, 1987), occupy a high-Ti portion of the arc-magma region on the TiO_2–Fe^{3+}# diagram (Fig. 6). The MORB spinels are intermediate, although not so clearly, between the arc-magma and intraplate-basalt spinels in their TiO_2 content. Low Fe^{3+}# is a characteristic of MORB spinels (Figs. 5 and 6). Spinels in the oceanic plateau basalts (Tokuyama and Batiza, 1981) plot in a distinctively lower-Ti area than other intraplate basalt spinels in Fig. 6. They differ from MORB spinels in their higher Cr# and Fe^{3+}# and are slightly higher in TiO_2 content than the main group of the arc-magma spinels (Figs. 3 and 6). The Ontong–Java Plateau spinel (Stoeser, 1975) is exceptional; it is rather similar in chemistry to the ordinary intraplate basalt spinels (Figs. 3 and 6). Spinels in back-arc basin basalts are intermediate in TiO_2 content; they are similar to the MORB spinels in this sense but extend more towards a high-Fe^{3+}# region (Fig. 6).

Some applications

The results of the preceding discussion can be applied to assessment of origin of spinel-bearing

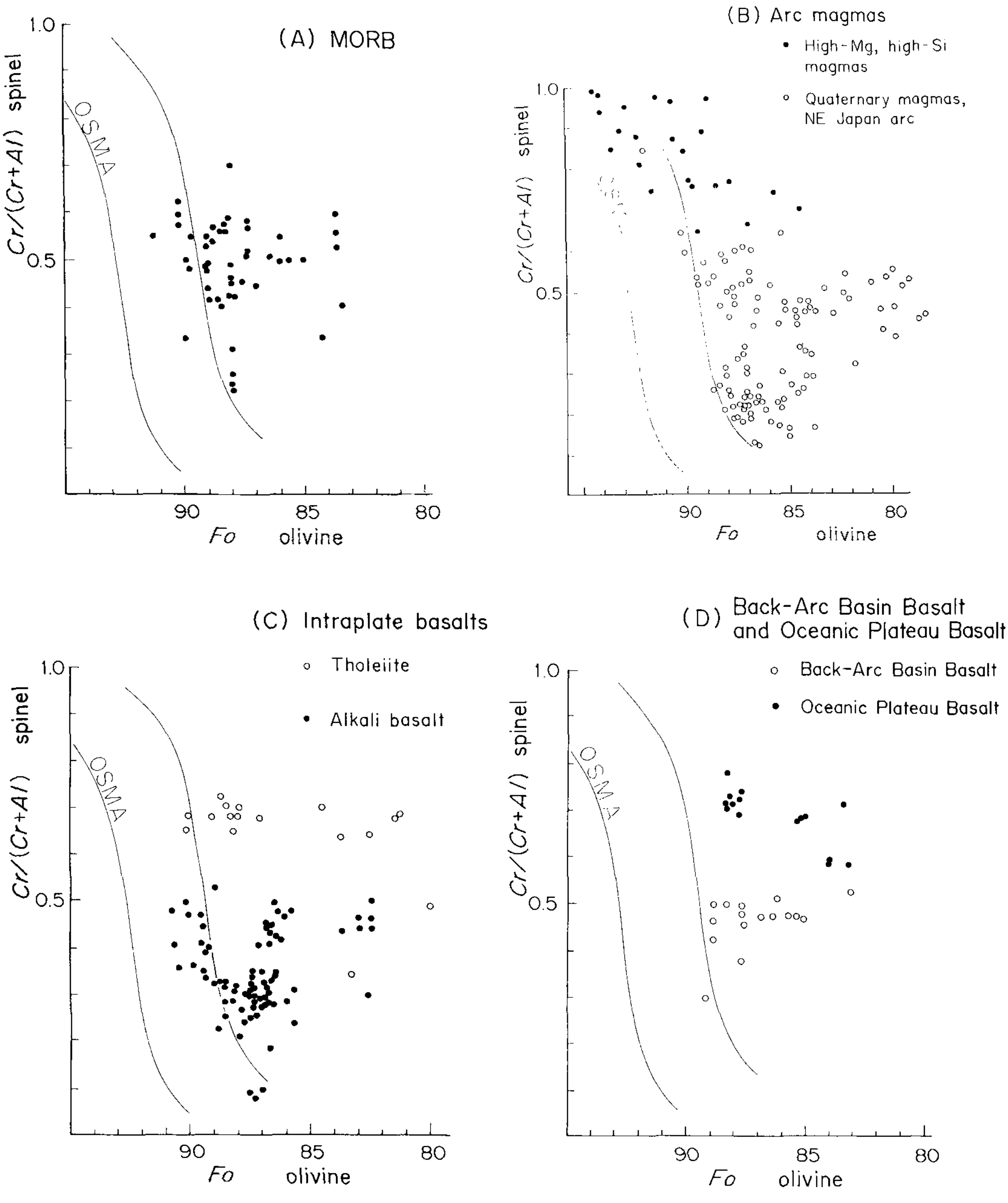

FIG. 3. Fo–Cr# relationships of Mg-rich magmas. OSMA, olivine–spinel mantle array (Arai, 1987, 1990*a*). (A) MORB. (B) Arc magmas. (C) Intraplate basalts. (D) Back-arc basin basalts and oceanic plateau basalts (see Tokuyama and Batiza, 1981). Data source: (A), Arai (1981), Donaldson and Brown (1977), Frey *et al.*, (1974), Sigurdsson and Schilling (1976); (B) Arai (unpublished), Arai and Takahashi (1987), Bloomer and Hawkins (1987), Crawford (1980), Graham and Hackett (1987), Johnson *et al.* (1985), Kuroda *et al.* (1978), Ramsay *et al.* (1984), Shiraki and Kuroda (1977), Tatsumi and Ishizaka (1981), Umino (1986), Walker and Cameron (1983), Yamamoto (1983); (C) Arai (1990*b*), Basaltic Volcanism Study Project (1981), Clague *et al.* (1980), Evans and Wright (1972), Gunn *et al.* (1970), Hawkins and Melchior (1983), Krishnamurthy and Cox (1977), Upton *et al.* (1984), Wilkinson and Hensel (1988); (D) Ishizuki *et al.* (1990), Mattey *et al.* (1981), Ridley *et al.* (1974), Saunders and Tarney (1979), Shcheka (1981), Stoeser (1975), Tokuyama and Batiza (1981).

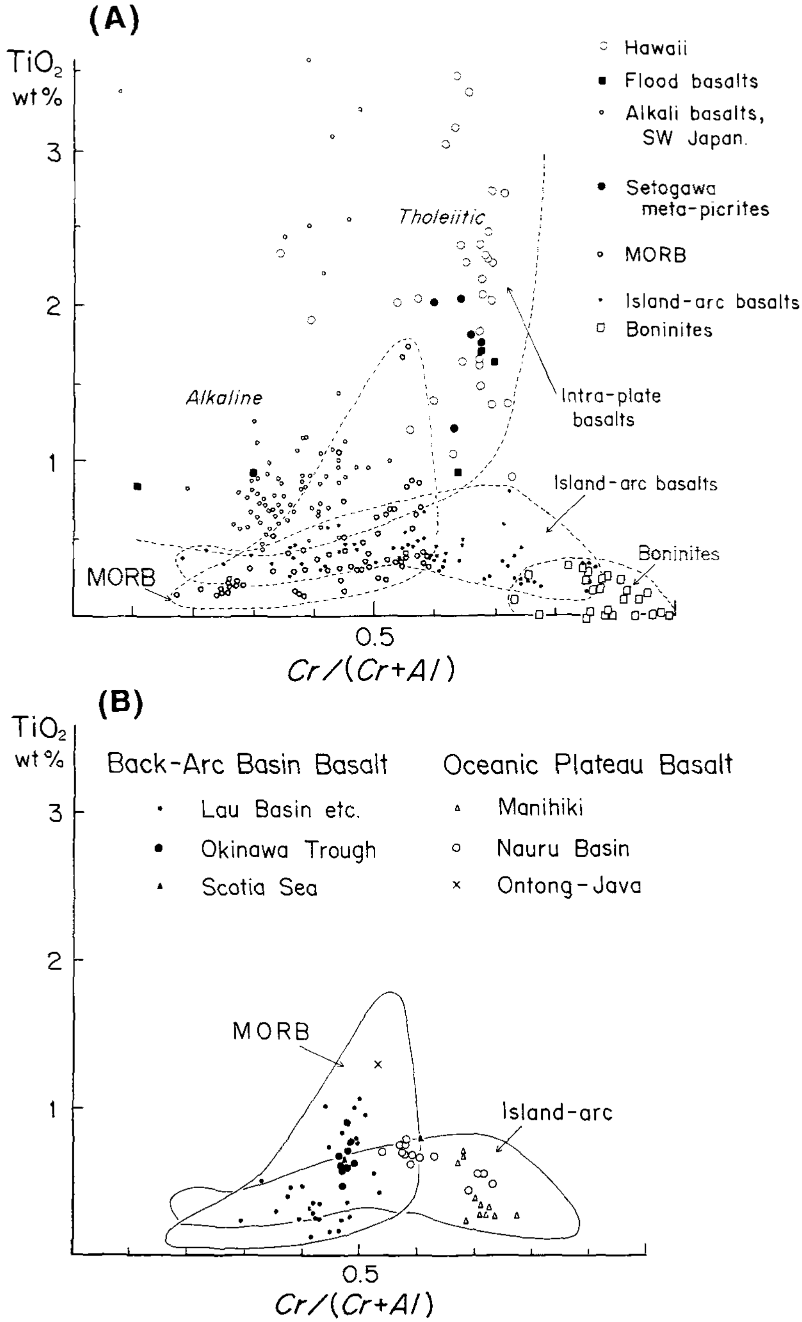

FIG. 4. Cr#–TiO_2 relationships of chromian spinels from Mg-rich magmas. Spinels with $Fe^{3+}\# < 0.2$ are chosen for convenience. (A) Three main magma groups (MORB, island-arc magmas and intraplate basalts). Boninites include high-Mg andesites. Note that the main part of MORB spinels is indistinguishable from island-arc basalt spinels. Setogawa meta-picrite spinels (Ishida *et al.*, 1990) are plotted for comparison. (B) Back-arc basin and oceanic plateau basalts. Data soruces are the same as that for Fig. 3.

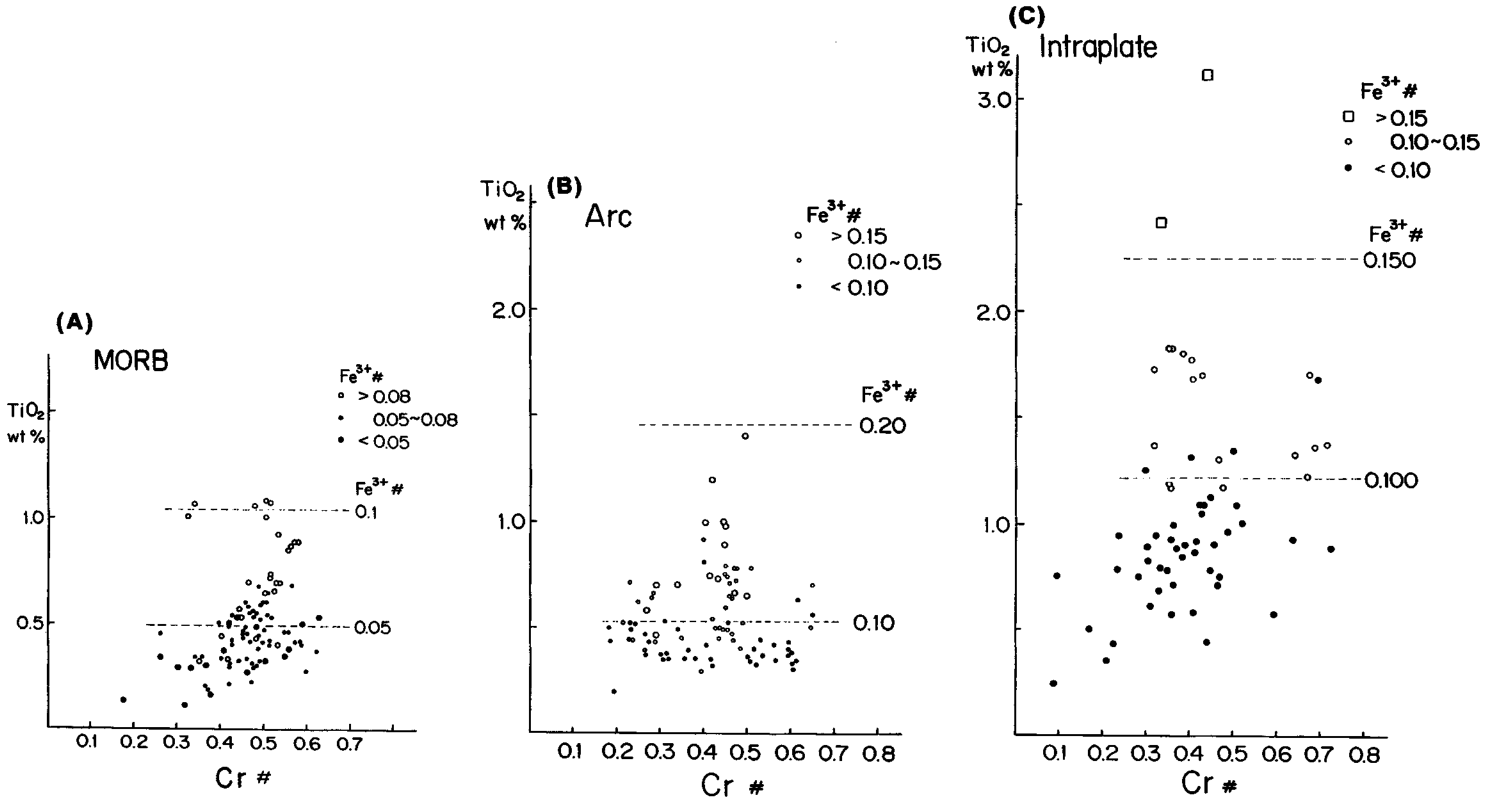

FIG. 5. Relationships between Cr# and TiO_2 content of chromian spinel contoured by Fe^{3+}# for three magma groups. Note that the TiO_2 content of spinel at comparable Fe^{3+}# is different for the three magma groups. Data sources are the same as in Fig. 3.

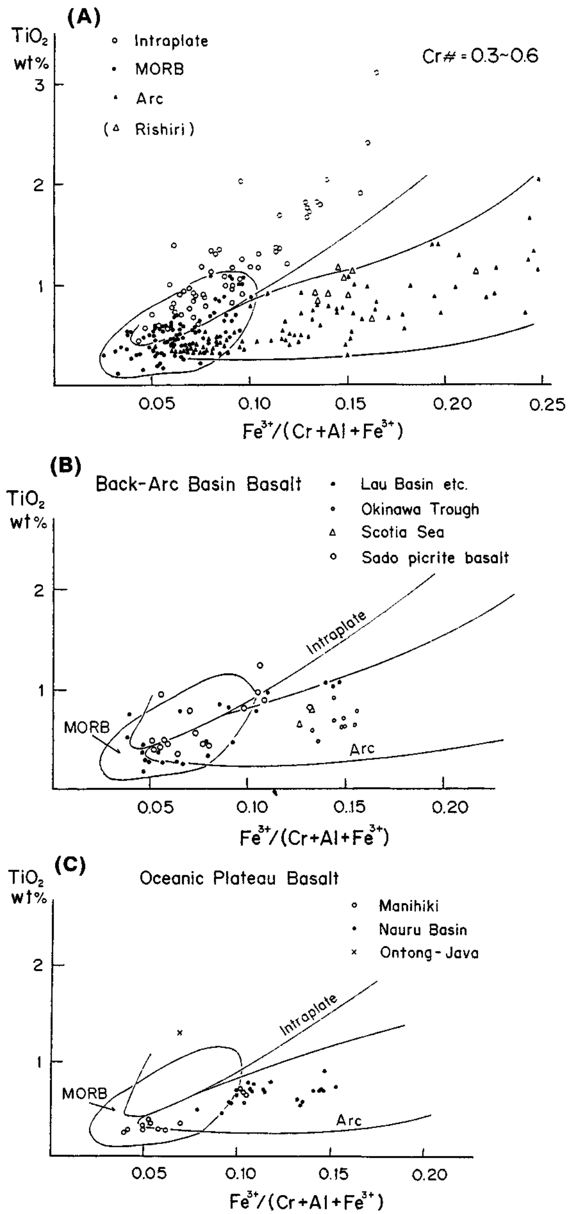

FIG. 6. Relationships between Fe^{3+}# and TiO_2 content of chromian spinel in Mg-rich magmas. (A) Three main magma groups (intraplate basalts, MORB and arc magmas). Spinels with Cr# from 0.3 to 0.6 are considered. Note that intraplate basalt spinels are perfectly distinguished from arc magma spinels. See text for details. (B) Back-arc basin basalts. Spinels from Sado picrite basalt in the Sea of Japan off Niigata are plotted for comparison (see text). Data soruce: Lau Basin and other west Mariana region, Mattey *et al.* (1981), Ridley *et al.* (1974); Okinawa Trough, Ishizuka *et al.* (1990); Scotia Sea, Saunders and Tarney (1979). (C) Oceanic plateau basalts. Data sources: Manihiki Plateau, Clague (1976); Nauru Basin, Shcheka (1981), Tokuyama and Batiza (1981); Ontong-Java Plateau, Stoeser (1975).

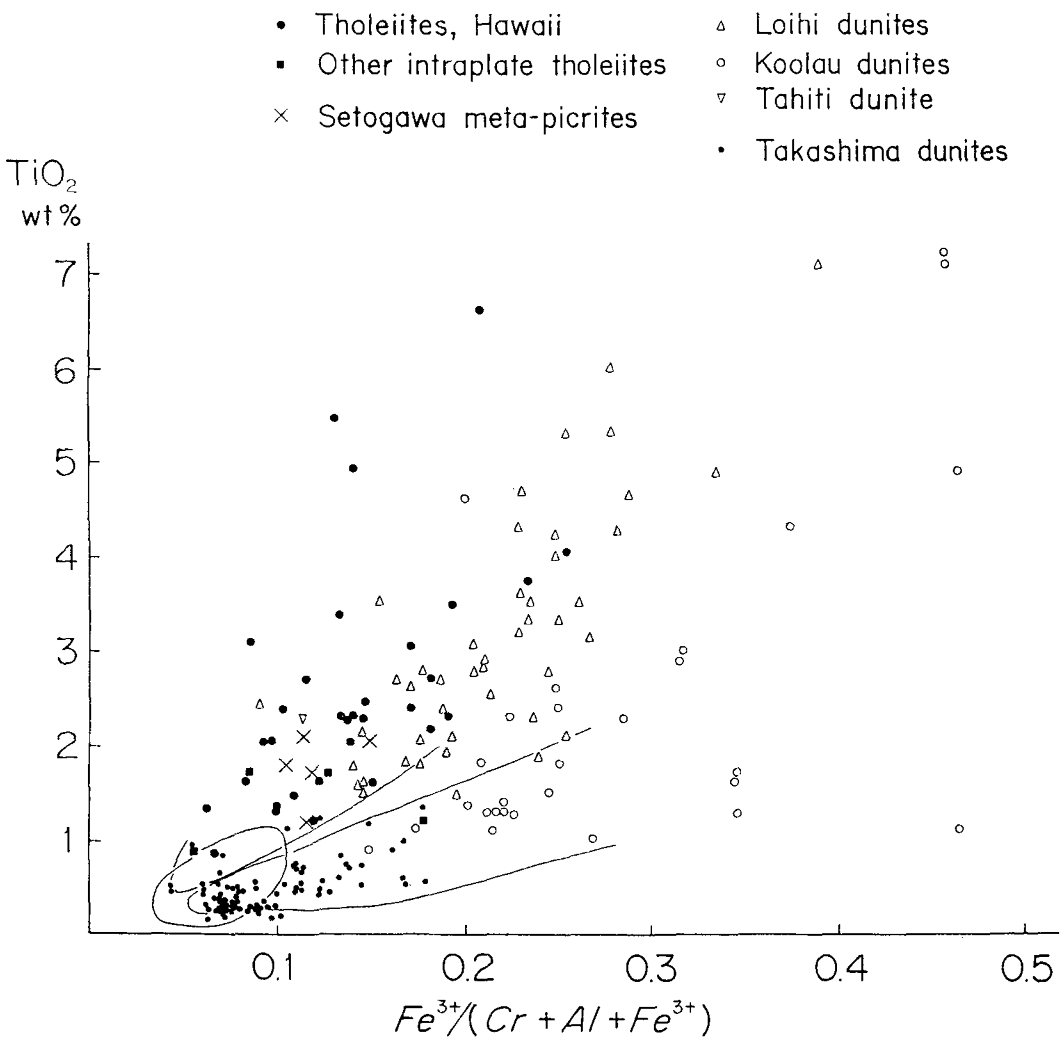

FIG. 7. Relationships between Fe^{3+}# and TiO_2 content of chromian spinel for intraplate tholeiites and dunites and Takashima arc dunites. Discrimination lines are the same as those in Fig. 6. Data sources: Tholeiites from Hawaii and related places, Basaltic Volcanism Study Project (1981), Clague *et al.* (1980), Evans and Wright (1972), Hawkins and Melchior (1983), Wilkinson and Hensel (1988); Other intraplate tholeiites, Gunn *et al.* (1970), Krishnamurthy and Cox (1977), Upton *et al.* (1984); Setogawa meta-picrite, Ishida *et al.* (1990); Loihi dunites, Clague (1988); Koolau dunites, Sen and Presnall (1986); Tahiti dunite, Tracy (1980); Takashima dunites, Arai and Kobayashi (unpublished).

igneous rocks. It is also useful to estimate the provenance of detrital spinel particles which are of igneous origin. They should be carefully applied because the TiO_2 content and Fe^{3+}# of igneous spinels can be altered during above-solidus cooling (e.g. Scowen *et al.*, 1991).

(*1*) *Parental magma for dunites*. Dunites are essentially bimineralic, composed of olivine + chromian spinel. Estimation of the kind of magma from which dunites were precipitated is, therefore, possibly based on the chemistry of spinel alone.

Large numbers of dunite xenoliths are included in a Cenozoic alkali basalt exposed at Takashima, northern Kyushu, southwest Japan arc (Ishibashi, 1971; Kobayashi and Arai, 1978) (Fig. 7). They are weakly tectonised but mineralogical characteristics of igneous stage are possibly preserved. They are closely associated with various kinds of pyroxenite xenoliths of both Group I and Group

II in the sense of Frey and Prinz (1978) (Ishibashi, 1971; Kobayashi and Arai, 1978). Chromian spinels from the dunitic xenoliths are plotted in the TiO_2–Fe^{3+}# diagram (Fig. 7). A majority lie within the field of arc magma, which may indicate that the Takashima dunites are cumulates from arc magmas. According to Arai (1989), dunite xenoliths in the Cenozoic alkali basalts erupted on the southwest Japan arc could be of cumulus origin from arc magmas.

Dunite xenoliths from Hawaii contain relatively Ti-rich spinel (Sen and Presnall, 1986; Clague, 1988). Spinels from the dunite and wehrlite xenoliths from Loihi (Clague, 1988) are almost included in the region of intraplate basalts (Fig. 7). Thus, they could be cumulates from intraplate basalt (alkali basalt), as concluded by Clague (1988). The origin of the dunite xenoliths from Koolau Volcano, Oahu, is, however, not simple. Ti content and Cr# of the Koolau dunite spinels are almost identical to those in the Hawaiian shield-building tholeiites as described by Sen and Presnall (1986). However, the Fe^{3+}# is higher at comparable Ti contents in the former spinels than in the latter ones, seemingly implying an arc origin (Fig. 7). As this is clearly incorrect, the Koolau dunite xenoliths could be cumulates from the Hawaiian shield building in slowly cooled magma chambers where cationic diffusion was effective. Fe^{3+} ions can move more easily through olivine than Ti^{4+} from surrounding (residual) melts (Scowen *et al.*, 1991).

(*2*) *Magma type estimation of some basalts and metabasalts*. Weakly to intermediately metamorphosed mafic rocks (schistose green rocks) are exposed at the northern part of the Setogawa region, central Japan (Ishida *et al.*, 1990). The region is the southernmost part of the Shimanto belt, which is a Cretaceous-Tertiary accretionary prism (e.g. Taira *et al.*, 1989). The schistose green rocks are sometimes enriched in oblate chlorite clots which include relic chromian spinel grains (Fig. 8A). The chlorite clots are interpreted to be deformed pseudomorphs of olivine and the rocks are, therefore, meta-picrite basalts (Ishida *et al.*, 1990) (Fig. 8A). The relic chromian spinels may preserve their trivalent cation ratios and TiO_2 contents (Ishida *et al.*, 1990), and are plotted both in Cr#–TiO_2 and in Fe^{3+}#–TiO_2 diagrams (Figs. 4A and 7). They all lie in the field of intraplate tholeiite and are strikingly similar to those in the Hawaiian tholeiites (Figs. 4A and 9). The original rocks of the Setogawa meta-picrite basalts are expected to be Hawaiian-type intraplate tholeiites enriched with olivine (Wilkinson and Hensel, 1988; Ishida *et al.*, 1990). In the adjacent areas (e.g. the Circum-Izu Massif ser-

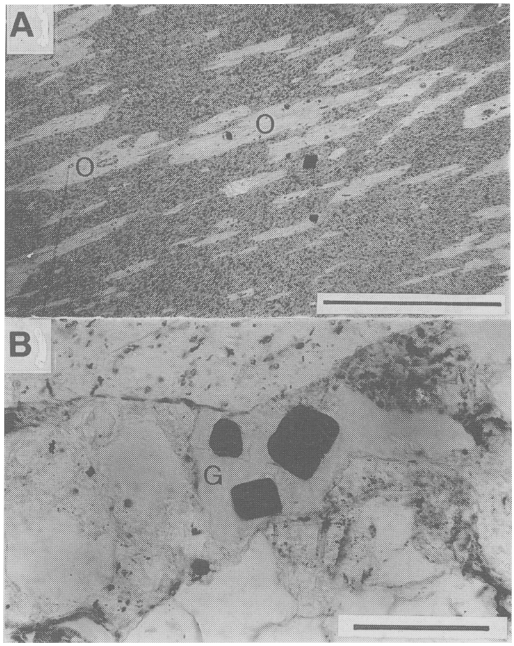

FIG. 8. Photomicrographs. Plane-polarized light. (A) Shistose meta-picrite basalt fromn the Setogawa belt, central Japan. White lenses (O) are chlorite aggregates after olivine. Black dots in the centre are chromian spinel microphenocryst and inclusion in olivine, which often survive metamorphism. Scale, 5 mm. (B) Euhedral chromian spinel grains in altered volcanic glass (G) from Sanchu Cretaceous sandstone, Kanto Mountains, central Japan. Scale 0.1 mm.

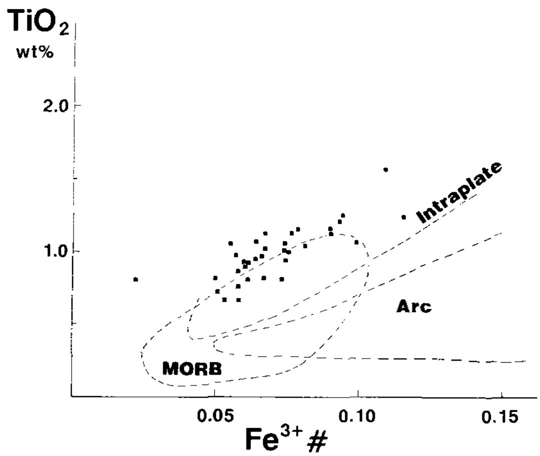

FIG. 9. Relationships between Fe^{3+}# and TiO_2 content of detrital chromium spinels in the Sanchu Cretaceous sandstone, central Japan.

pentine belt of Arai, 1991, and Arai and Okada, 1991) fresh Miocene picritic basalts are exposed both as pillow basalts and as dykes (e.g. Sameshima, 1960; Kanehira, 1976). Their bulk chemistry is remarkably similar to some Hawaiian olivine-rich tholeiites (Ishida *et al.*, 1988, 1990).

A sheet of picrite basalt exposed at the Sado island in the Sea of Japan off Niigata (Yamakawa and Chihara, 1968) is a member of Ogi Basalts (Yamakawa and Chihara, 1968) of Miocene (11 to 15 Ma) (Shinmura, 1990). The TiO_2–Fe^{3+}# relationships of spinels in the sheet indicate a character intermediate between intraplate and arc magmas for the picrite (Fig. 6B). The spinels are more enriched in Fe^{3+} than MORB spinels and are almost included in the region of the back-arc basin basalt spinels (Fig. 6B). The Sado picrite basalt could be an olivine-cumulate back-arc basin basalt. This suggestion is supported by the fact that the climax of the Sea of Japan opening, *ca.* 15 Ma (Otofuji *et al.*, 1985), is synchronous with the beginning of the Ogi Basalt eruption (Shinmura, 1990).

(3) Source rock of detrital chromian spinel grains. Conglomerates and sandstones from the Sanchu belt, Kanto Mountains, central Japan, frequently contain detrital chromian spinel particles (Arai and Hisada, 1991). The Sanchu sediments are of Cretaceous age and filled a fore-arc basin (Hisada *et al.*, 1991). The detrital spinels can be divided into two groups, low- and high-Ti ones (Arai and Hisada, 1991). The low-Ti spinels may have been derived from spatially associated serpentinites because the spinel chemistry is almost identical for the both (Arai and Hisada, 1991). The high-Ti detrital spinels often occur as small euhedra in chlorite aggregates, which may be after volcanic glass or more frequently after olivine (or other magnesian minerals) (Fig. 8). The high $Mg/(Mg + Fe^{2+})$ ratio of the high-Ti detrital spinels relative to the low-Ti ones points to high-temperature crystallization of the high-Ti spinels (Arai and Hisada, 1991), and Fig. 9 suggests that the magmas were intraplate basalts. Volcanic rocks containing analogous high-Ti spinels are absent in neighbouring areas; the source volcanics to the Sanchu high-Ti detrital spinels have been entirely eroded.

Conclusions

The chemistry of chromian spinels in volcanic rocks is mainly dependent on the chemistry of magma from which they are precipitated. The Ti content of spinel potentially discriminates the magma type because the Ti content of basalts is different for the three main primary magma clans (MORB, arc basalts and andesites, and intraplate basalts) at a given MgO/FeO* ratio. The TiO_2 content of spinels normalized by the $Fe^{3+}/(Cr + Al + Fe^{3+})$ ratio successfully discriminates the three primary magma clans (especially arc magmas from intraplate magmas). Spinels from the oceanic plateau basalts and from the back-arc basin basalts have distinctive TiO_2–Fe^{3+}# relationships. The intraplate basalt (except for oceanic plateau basalt) spinels have the highest TiO_2 contents and the arc magma spinels have the highest TiO_2 contents and the arc magma spinels the lowest. The results were successfully applied to estimate parental magmas for dunite cumulates, original magma chemistry of altered or metamorphosed volcanics, and provenance of detrital chromian spinel particles.

Acknowledgements

The author wishes to acknowledge Dr. C. Donaldson for his constructive comments, which helped to improve the manuscript. He also thanks Dr. K. Hisada for his discussion on the Sanchu detrital spinels. He is grateful to Mr. K. Nakamura for drafting some figures used in this paper.

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[*Manuscript received 29 July 1991: revised 6 October 1991*]