53. CHROMIAN SPINELS IN COSTA RICA BASALTS, DEEP SEA DRILLING PROJECT SITE 505—A PRELIMINARY INTERPRETATION OF ELECTRON MICROPROBE ANALYSES

Toshio Furuta and Hidekazu Tokuyama, Ocean Research Institute, University of Tokyo, Nakano, Tokyo 164 Japan

ABSTRACT

The compositions of chrome spinels of Costa Rica Rift basalts from Deep Sea Drilling Project Site 505 vary depending on their occurrences as (1) inclusions in olivine crystals, (2) inclusions in plagioclase crystals, and (3) isolated crystals in variolitic or glassy samples. The variations are a consequence of (1) changes of melt compositions as crystallization proceeds, and (2) contrasting behavior of olivine and plagioclase in competition with spinels for Al and Mg. Some spinels have skeletal rims compositionally less magnesian than mineral cores; however, the cores do not appear to be xenocrysts, unlike some texturally similar spinels in Mid-Atlantic Ridge basalts.

INTRODUCTION

Chromian spinels are characteristic accessory minerals in the Costa Rica Rift basalts, occurring as tiny euhedral and subhedral crystals included in or attached to olivine phenocrysts or plagioclase phenocrysts. They also occur in variolitic glass at pillow margins. Their paragenesis indicates that they probably are products of the earliest phase of crystallization of basaltic magma. It has been suggested that some of these spinels coexisted and were equilibrated with primitive basaltic liquid (e.g., Irvine, 1965, 1967; Sigurdsson and Schilling, 1976). Therefore, it is interesting to clarify the genesis of the chromian spinel and the early stage of crystallization of the basaltic magma. We will report here on chemical compositions of chromian spinels in submarine basalts from DSDP Site 505 (01°54.8'N; 83°47.4’W), on the Costa Rica Rift.

SAMPLES

Samples for this study were drilled at DSDP Site 505 from the Costa Rica Rift during Leg 69. The crustal age of Site 505 is estimated to be about 3.9 m.y. on the basis of magnetic anomalies (Langseth et al., this volume). The total recovery of basalt was 0.5 meters from Hole 505A and 6.85 meters from Hole 505B. All recovered rocks are sparsely to moderately plagioclase-olivine-phryic basalts with a few chromian-spinel crystals; the rocks are petrographically and chemically almost identical (Etoubleau et al., this volume). The average composition of 10 whole-rock samples from 505A and 505B is given in Table 1. Chromian spinel occurs in olivine and plagioclase phenocrysts and variolitic glasses (Fig. 1). Spinels included in olivine or plagioclase are subhedral or anhedral, but most of them occur as isolated grains and are euhedral. Some of these grains show a distinct outer rim which has a skeletal texture. Table 2 shows the modes of occurrence of spinels as inclusions in phenocrysts and isolated grains. The Fo component of coexisting olivine phenocrysts, obtained by electron microprobe, is also shown.

RESULTS

More than 50 chromian spinels were analyzed for this study, using a JXA-5 (JEOL) electron microprobe. Most samples were analyzed for nine elements (Si, Al, Ti, Fe, Mn, Mg, Cr, Ni, V). Twenty-four representative analyses of spinels and structural formulas are shown in Table 3, where the data are recalculated as structural formulas on the basis of 4-oxygens stoichiometry. Chemical compositions of the spinels have relatively small variation (Table 3; Fig. 2), like the coexisting olivine phenocrysts (Fo86.89). Chromian spinels in these samples are relatively high in the ratio Cr/(Cr + Al)—0.38 to 0.55—and moderate in the ratio Mg/(Mg + Fe2+)—0.55 to 0.70. In this respect, they closely resemble spinels termed “magnesiochromite” in Mid-Atlantic Ridge basalts (Sigurdsson and Schilling, 1976; Fig. 2A). Distinctions among the present spinels with different modes of occurrence are revealed when their chemical compositions are plotted on the plane of the spinel compositional prism, Cr/(Cr + Al) versus Mg/(Mg + Fe2+). Spinels included in olivine phenocrysts have relatively low values of the ratio Cr/(Cr + Al) (dashed line in Fig. 2B). Spinels in-

Table 1. Average chemical composition of 10 fresh basalts from Holes 505A and 505B (based on shipboard XRF analyses obtained by J. Etoubleau).

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*Total iron as FeO.
Figure 1. A. Reflected-light photomicrograph of a spinel with skeletal texture in Sample 505B-5-1, 31-33 cm. Spinel grain is approximately 160 µm across and sits in variolitic glass. Chemical analyses of this grain are shown in Table 3; analysis No. 21 is on the core and No. 22 on rim of this grain. Small bright minerals are titanomagnetites. B. Reflected-light photomicrograph of a spinel in Sample 505B-3-2, 86-88 cm. Spinel grain is approximately 25 µm across and is included in plagioclase. C. Transmitted-light photomicrograph of a spinel in Sample 505B-4-1, 10-12 cm. Spinel grain is about 35 µm across and is included in olivine. D. Reflected-light photomicrograph of a spinel in Sample 505B-6-1, 109-111 cm. Spinel grain is about 60 µm across and is attached to olivine (lower left) and plagioclase (right and above) in variolitic glass. Microprobe analysis across this showing compositional zoning spinel is shown in Figure 3. E. Reflected-light photomicrograph of a spinel in Sample 505B-4-1, 10-12 cm. Spinel grain is about 25 µm in diameter and is included in plagioclase. The upper part of this grain (brighter part) is titanomagnetite. F. Reflected-light photomicrograph of a spinel in Sample 505B-5-1, 31-33 cm. Spinel grain is about 30 µm in diameter and is included in altered olivine.
basalts are not highly variable and are slightly poorer in 
0.4 to 0.5, (2) titaniferous magnesiochromite, and (3) 
pared with the spinels from Mid-Atlantic Ridge basalts 
three types: (1) magnesiochromite with Cr/(Cr + Al) = 
basalts into three types; (1) spinels enriched in A1 
correlate with the following occurrences: (1) spinels in-
ity, we can distinguish compositional differences, which 
2+ 
Mg/(Mg + Fe 
crime spinel with Cr/(Cr + Al) = 0.23 to 0.27. Com-
and with reaction coronas, (2) spinels enriched in Cr 
2+ 
3 
trates in Plagioclase phenocrysts have high-
Cr/(Cr + Al) ratios (broken line in Fig. 2B). The 
Cr/(Cr + Al) ratios of spinels in variolitic basaltic glass are 
scattered; nevertheless, the range of Cr/(Cr + Al) of these 
three types of spinels in the present samples is very lim-
ited compared with the range in spinels from Mid-
Atlantic Ridge basalts indicated on Figure 2A (Sigurds-
son and Schilling, 1976). As shown in Table 2, most 
samples have the three types of spinels in the same thin-
section.

The chemical zoning of several grains of spinel is 
shown in Table 3 (21-22, 23-24) and in Figure 2B (shown 
by arrows). The result of a microprobe analysis on a eu-
chedral spinel crystal in Sample 505B-6-1, 109-111 cm is 
shown in Figure 3. This spinel is attached to olivine and 
plagioclase phenocrysts in variolitic glass. Al2O3 and 
MgO contents decrease from core to rim. On the con-
trary, FeO* and TiO2 contents increase from core to rim. 
Cr2O3 content is constant. The chemical zoning of most 
of the analyzed spinels is typified by the trend in Sample 
505B-6-1, 109-111 cm (with one exception); however, 
zoning of spinels having skeletal rims in variolitic glass is 
different; Cr/(Cr + Al) increases from core to margin 
and Mg/(Mg + Fe2+) decreases.

DISCUSSION

Spinel compositions vary widely in oceanic basalts. 
Fisk and Bence (1980) classified spinels from FAMOUS 
basalts into three types; (1) spinels enriched in Al2O3 
and with reaction coronas, (2) spinels enriched in Cr2O3 
and without reaction coronas, and (3) spinels intermedi-
ate in Al2O3 and Cr2O3. Sigurdsson and Schilling (1976) 
divided spinels from Mid-Atlantic Ridge basalts into 
three types: (1) magnesiochromite with Cr/(Cr + Al) = 
0.4 to 0.5, (2) titaniferous magnesiochromite, and (3) 
chrome spinel with Cr/(Cr + Al) = 0.23 to 0.27. Com-
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and FAMOUS basalts, spinels from the Costa Rica Rift 
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Mg/(Mg + Fe2+) (Fig. 2A). Despite this small variabil-
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ity, we can distinguish compositional differences, which 
correlate with the following occurrences: (1) spinels in-
cluded in olivine, (2) spinels included in plagioclase, and 
(3) isolated spinels in variolitic glass.

The Cr/(Cr + Al) ratio of spinels included in olivine 
phenocrysts is lower when plotted on a plane of the spi-
nel compositional prism, Cr/(Cr + Al) versus Mg/(Mg + 
Fe2+). The Cr/(Cr + Al) ratio of the spinel increases 
with decreasing Mg/(Mg + Fe) (Fig. 2B). From results 
of experimental crystallization of chrome spinels (Fisk 
and Bence, 1980), the Cr/(Cr + Al) of spinel coexisting 
with olivine decreases with decreasing temperature be-
tween 1250 and 1200°C at fO2-10^-9.5. However, at 
fO2-10^-8.5 the Cr/(Cr + Al) of the spinel coexisting with 
olivine increased from 0.413 to 0.464 as temperature 
was decreased from 1250 to 1230°C. At still higher oxy-
genous fugacities (fO2 of 10^-7.5), the Cr/(Cr + Al) increased 
from 0.413 to 0.454 as temperature was decreased from 
1250 to 1232°C. Consequently, for Cr/(Cr + Al) to 
decrease with decreasing temperature, low fO2 seems 
required, causing reduction of Cr3+ to Cr2+ in the melt. 
The Mg/(Mg + Fe2+) of spinel decreases with decreasing 
temperature at all oxygen fugacities between 10^-7.5 
and 10^-9.5 (Fisk and Bence, 1980). This probably re-

ducing Mg/(Mg + Fe2+) of the melt caused by 
oblivine crystallization (Fisk and Bence, 1980). This 

crystalization of spinels included in olivine to decrease 
gradually in Mg/(Mg + Fe2+) and increase in Cr/(Cr + Al) 
as a consequence of decreasing temperature rather than 
changes in fO2. Based on comparisons with experimental 
data, fO2 was probably 10^-8.5 or greater.

Spinels included in plagioclase phenocrysts have high-
er Cr/(Cr + Al) than those included in olivine (Fig. 2B). 
The Cr/(Cr + Al) of spinel increases markedly, once 
plagioclase starts to form, probably because plagioclase 
takes up to much Al (Fisk and Bence, 1980). The Cr/(Cr + 
Al) of the spinel decreases slightly as Mg/(Mg + Fe2+) 
decreases. This is caused by the increasing volume of 
spinel, and consequent decrease of Cr in the melt, with 
decreasing temperature (Fisk and Bence, 1980).

Thus we consider that crystallization of spinels from 
Costa Rica Rift basalts depends on the following.

1) Spinel crystallized during the first stage increases 
Cr/(Cr + Al) and decreases in Mg/(Mg + Fe2+) with 
decreasing temperature, rather than changes in fO2 (Fig. 
2B, arrow I).

2) When temperature decreases to the temperature at 
which plagioclase begins to crystallize, the Cr/(Cr + Al) 
of spinel increases markedly (Fig. 2B, arrow II).

3) Spinel crystallized during the third stage decreases 
slightly in Cr/(Cr + Al) as Mg/(Mg + Fe2+) decreases 
with decreasing temperature (Fig. 2B, arrow III).

The chemical composition of isolated spinel in vari-
olitic glass is scattered on a plane of the compositional 
prism, Cr/(Cr + Al) versus Mg/(Mg + Fe2+) (Fig. 2B). 
This probably reflects growth of spinels at each of the 
three above-mentioned stages.

The Costa Rica Rift spinels show two types of com-
positional zoning. One is characterized by increasing 
Cr/(Cr + Al) with decreasing Mg/(Mg + Fe2+) from 
core to margin (Table 3, 23 and 24). Similar zoning has 
been reported by Ridley (1977). The other is character-
under conditions different than those of the Mid-Atlantic Ridge spinels with skeletal rims formed in elongated plagioclase, diam. 50 µm. 2. 505A-2-1, 45-47 cm, brown subhedral spinel included in olivine in variolitic glass, diam. 15 µm. 3. 505B-1-1, 115-117 cm, small spinel partially replaced by chromite in plagioclase in variolitic glass, diam. 12 µm. 4. 505B-1-1, 115-117 cm, brown subhedral spinel attached to plagioclase in variolitic glass, diam. 20 µm. 5. 505B-2-1, 115-117 cm, brown subhedral spinel included in olivine in variolitic glass, diam. 20 µm. 6. 505B-2-2, 81-83 cm, small brown spinel in plagioclase in variolitic glass, diam. 15 µm. 7. 505B-2-2, 81-83 cm, brown subhedral spinel included in plagioclase in variolitic glass, diam. 18 µm. 8. 505B-3-1, 114-116 cm, rim of brown rectangular spinel attached to plagioclase in variolitic glass, diam. 25 µm. 9. Core of crystal in No. 10. 505B-3-1, 114-116 cm, rim of brown subhedral spinel attached to plagioclase in variolitic glass, diam. 40 µm. 10. Core of crystal in No. 10. 505B-3-1, 114-116 cm, small spinel in plagioclase in variolitic glass, diam. 13 µm. 11. 505B-3-1, 114-116 cm, brown euhedral spinel in altered olivine, diam. 60 µm. 12. 505B-3-2, 86-88 cm, subhedral spinel included in plagioclase, diam. 15 µm. 13. 505B-3-2, 86-88 cm, subhedral spinel included in plagioclase, diam. 20 µm. 14. 505B-4-1, 10-12 cm, brown subhedral spinel included in olivine, diam. 25 µm. 15. 505B-4-1, 10-12 cm, brown subhedral spinel included in plagioclase, diam. 50 µm. 16. 505B-5-1, 110-111 cm, brown subhedral spinel included in olivine, diam. 25 µm. 17. 505B-5-1, 110-111 cm, brown subhedral spinel included in plagioclase, diam. 30 µm. 18. 505B-5-1, 110-111 cm, brown subhedral spinel included in plagioclase, diam. 30 µm. 19. 505B-5-1, 110-111 cm, brown subhedral spinel included in olivine, diam. 30 µm. 20. 505B-5-1, 110-111 cm, brown subhedral spinel included in olivine, diam. 30 µm. 21. 505B-5-1, 110-111 cm, brown subhedral spinel included in olivine, diam. 30 µm. 22. 505B-5-1, 110-111 cm, brown subhedral spinel included in olivine, diam. 30 µm. 23. 505B-5-1, 110-111 cm, brown subhedral spinel included in olivine, diam. 30 µm. 24. 505B-5-1, 110-111 cm, brown subhedral spinel included in olivine, diam. 30 µm. 25. 505B-5-1, 110-111 cm, brown subhedral spinel included in olivine, diam. 30 µm. 26. 505B-5-1, 110-111 cm, brown subhedral spinel included in olivine, diam. 30 µm. 27. 505B-5-1, 110-111 cm, brown subhedral spinel included in olivine, diam. 30 µm. 28. 505B-5-2, 6-8 cm, brown subhedral spinel included in olivine, diam. 30 µm.

**REFERENCES**


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Figure 2. A. Cr/(Cr + Al) versus Mg/(Mg + Fe²⁺) spinels for Mid-Atlantic Ridge and Costa Rica Rift basalts: (i) Sigurdsson and Schilling (1976); (ii) Dick and Bryan (1979); (iii) this study. B. Plots of composition of spinels from the Costa Rica Rift basalts: circles = spinels in variolitic glass; crosses = spinels in olivine; squares = spinels in plagioclase. See text for discussion of arrows.
Figure 3. Compositional variation across a euhedral spinel in Sample 505B-6-1, 109-111 cm. The numbers refer to analyses listed in Table 3 and Figure 2. A photomicrograph of this grain is shown in Figure 1D.