# 33. Cr-SPINEL IN DEPLETED BASALTS FROM THE LAU BASIN BACKARC: PETROGENETIC HISTORY FROM Mg-Fe CRYSTAL-LIQUID EXCHANGE<sup>1</sup>

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## ABSTRACT

Cr-spinels in cores drilled during Ocean Drilling Program Leg 135 exhibit wide variations in composition and morphology that reflect complex petrogenetic histories. These Cr-spinels are found within basaltic lava flows that erupted in north-trending sub-basins within the Lau Basin backarc. Cr-spinels from Sites 834 and 836 occur as euhedral groundmass grains and inclusions in plagioclase, and range up to 300 µm in size. These Cr-spinels are similar in composition, morphology, and mode of occurrence to Cr-spinels found within depleted, N-type mid-ocean-ridge basalts (N-MORB), reflecting similar crystallization conditions and host lava composition to N-MORB. Their compositional range is relatively narrow, with Cr/(Cr + Al + Fe<sup>3+</sup>) (Cr#) and Mg/(Mg + Fe<sup>2+</sup>) (Mg#) varying from 0.38 to 0.48 and 0.56 to 0.72, respectively; like Cr-spinels from N-MORB, they contain low amounts of TiO<sub>2</sub> (0.37%–1.05%) and Fe<sup>3+</sup>/(Cr + Al + Fe<sup>3+</sup>) (Fe<sup>3+</sup>#; <0.11). In contrast, Cr-spinels from Site 839 have much higher Cr# at a given Mg#, with Cr# varying from 0.52 to 0.76 and Mg# varying from 0.27 to 0.75. These Cr-spinels are similar in composition to those from primitive, boninitic or low-Al<sub>2</sub>O<sub>3</sub> arc basalts, sharing their low TiO<sub>2</sub> and Fe<sup>3+</sup># (typically below 0.35% and 0.1, respectively for spinel grain interiors). Site 839 Cr-spinels occur as small (to 50 µm) euhedra within strongly zoned olivine or as unusually large (to 3 mm), euhedral to subhedral megacrysts. These megacrysts are strongly zoned in Mg#, but they display little zoning in Cr#, providing evidence of strong compositional disequilibria with the host melt. The magnesian cores of the megacrysts crystallized from primitive, near-primary melts derived from harzburgitic or highly depleted lherzolitic sources, and they provide evidence that the Site 839 spinel-bearing lavas were derived by the mixing of melt with a Mg# of 0.75 – 0.80 and evolved, Cr-spinel barren melt with a Mg# < 0.6 shortly before eruption.

## INTRODUCTION

Cr-spinel is a common, if trace, constituent of primitive basaltic magmas worldwide. In view of its widespread occurrence, it is underused for exploring petrological phenomena. As an illustration, only a few studies of backarc basin Cr-spinel have been made (e.g., Dick and Bullen, 1984; Hawkins and Melchior, 1985; Allan, 1992; Forsythe and Fisk, this volume), even though the complex crystal chemistry of Cr-spinel provides a wealth of opportunities for its use as a petrogenetic indicator of both intensive and extensive variables (Irvine, 1965, 1967; Fisk and Bence, 1980; Sack, 1982; Roeder and Reynolds, 1991; Sack and Ghiorso, 1991a, 1991b). In particular, Cr-spinel is a highly sensitive indicator of mineral-melt equilibria and disequilibria, with recent studies using several approaches to determine pathways of magma evolution (Fisk and Bence, 1980; Natland, 1989; Roeder and Reynolds, 1991; Scowen et al., 1991; Allan, 1992).

In this chapter, I report the results of a study of Cr-spinel from Leg 135 basalts collected by coring in the Lau Basin, a backarc basin to the Tofua Arc (Fig. 1; Parson, Hawkins, Allan, et al., 1992). The tectonic evolution of this backarc basin is complex, with basin formation caused initially by brittle extension followed by subsequent seafloor spreading (see Parson and Hawkins, this volume, for an extensive discussion). The spinel-bearing lavas, which consist of tholeiites from Sites 834 and 836 and Al-poor basalts from Site 839, occur in north-south fault sub-basins that formed at various tectonic stages within the Lau Basin. The approximate minimum ages of eruption for these samples are 3.8–5.6 Ma for Site 834, 0.6 Ma for Site 836, and 1.9 Ma for Site 839 (Parson, Hawkins, Allan, et al., 1992; Styzen, this volume); lavas from Sites 834 and 839 likely represent basalts erupted during brittle extension of previously existing arc crust, whereas Site 836 was probably cored in faulted oceanic crust formed by seafloor spreading during

southward progression of the Eastern Lau Spreading Center (ELSC) ridge propagator (Parson, Hawkins, Allan, et al., 1992; Ewart et al., this volume; Parson and Hawkins, this volume). As such, these samples record earlier phases of volcanism in this backarc basin, and Crspinel composition in these early and proto-backarc basin lavas may be used to deduce magmatic and mantle source variation during the Lau Basin formation. The principle foci of this work are (1) to determine the original silicate liquid melt compositions in lava samples lacking glass, and (2) to determine the petrogenetic history of the host magmas, including the inference of mantle source character. Olivine was also analyzed to examine spinel-olivine exchange equilibria and to check the magmatic predictions made by the spinel. Readers should refer to Parson, Hawkins, Allan, et al. (1992) and Hawkins and Allan (this volume) for additional petrographic and mineralogical descriptions of rock samples from Leg 135, and to Forsythe and Fisk (this volume) for a complementary experimental study of Cr-spinel from Site 834 and 839 samples. Due to the difficulty of modeling trivalent cation exchange between spinel and silicate liquid when direct knowledge of Fe3+/Fe2+ and Cr3+/Cr2+ in the melt and spinel is poorly known (Allan, 1992), this work will focus on a study of melt  $Mg/(Mg + Fe^{2+})$ . For discussion of trivalent cation behavior, readers should refer to Forsythe and Fisk (this volume), who consider Al and Cr exchange between spinel and host melt.

#### ANALYTICAL METHODS

Cr-spinel-bearing rock samples were analyzed to provide a compositional framework for the mineralogical studies. Due to the rarity of glassy material in the core and restrictions on glass sampling, only whole-rock powders were available for major and trace element analysis. Whole-rock analyses shown in Table 1 represent both shipboard X-ray fluorescence (XRF) (Parson, Hawkins, Allan, et al., 1992) and instrumental neutron activation analyses (INAA) of powder from adjacent locations in the core. The INNA analyses were obtained at Texas A&M University using an on-campus TRIGA reactor for irradiation and counting facilities in the Center for Chemical Characterization. Samples were run in duplicate (both irradiation and counting),

<sup>&</sup>lt;sup>1</sup> Hawkins, J., Parson, L., Allan, J., et al., 1994. Proc. ODP, Sci. Results, 135: College Station, TX (Ocean Drilling Program).

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Figure 1. Location map of Lau Basin backarc sites drilled during Leg 135 (from Parson, Hawkins, Allan, et al., 1992). CLSC, ELSC, VF, and MTJ refer to the Central Lau Spreading Center, the Eastern Lau Spreading Center, the Valu Fa Spreading Center, and the Mangatolu Triple Junction, respectively.

Table 1. Whole-rock analyses of Cr-spinel-bearing lavas.

Hole:	834A	834B	834B	834B	834B	834B	836A	839A	839B	839B	839B	839B	839B	839B	839B
Core, section:	12X-CC	22R-2	26R-1	28R-1	30R-3	33R-2	5X-1	24X-1	12R-2	15R-1	16R-1	19R-1	20R-1	23R-1	26R-1
XRF Interval (cm):	13-15	29-33		44-50	101-105	111-115	3-9	0-6	25-32	34-39	106-111	50-56	74-80	24-27	23-29
INAA Interval (cm):			53	35	94	105	0	19	20	27	60	59	81	7	18
Unit or subunit:	1A	7	7	7	7	7	3	1	1	1	1	3	3	3	4
Major elements (wt%):															
SiO	49.78	49.95		49.87	49.96	49.53	49 34	53.03	52.36	53.28	52.28	50.63	50.20	50.43	51.64
TiO	1.40	1.28		1.20	1.25	1.12	0.75	0.65	0.60	0.65	0.66	0.58	0.57	0.59	0.57
Al <sub>2</sub> Ő2	17.51	17.12		17.92	17.67	18.01	16.62	15.06	15.15	14.98	14.94	12.75	12.48	12.66	14.33
Fe <sub>2</sub> O <sub>2</sub>	9.41	9.01		8.44	8.99	8.58	8.8	10.04	9.94	10.16	10.14	9.93	10.18	10.36	9.42
MnO	0.15	0.12		0.12	0.13	0.12	0.17	0.17	0.16	0.19	0.18	0.16	0.17	0.17	0.17
MgO	5.06	8.27		7.46	7.84	7.58	8.66	9.00	9.35	9.40	9.18	14.15	15.20	14.86	9.72
CaO	12.71	11.84		12.44	12.15	12.33	14.1	11.66	11.88	11.52	11.61	10.98	10.88	10.92	13.64
Na <sub>2</sub> O	3.08	2.60		2.52	2.59	2.67	1.72	1.35	1.66	1.37	1.36	1.28	1.23	1.21	1.15
K <sub>2</sub> Ô	0.26	0.03		0.02	0.05	0.04	0.12	0.23	0.24	0.30	0.29	0.32	0.29	0.26	0.22
P <sub>2</sub> O <sub>6</sub>	0.15	0.11		0.11	0.12	0.11	0.06	0.07	0.08	0.07	0.08	0.07	0.07	0.07	0.04
Total	99.48	100.32		100.07	100.74	100.13	100.4	101.26	101.40	101.90	100.69	100.85	101.27	101.54	100.92
LOI	1.01	1.46		0.67	0.79	1.53	0.32	0.22	0.33	-0.06	-0.08	0.61	0.27	0.37	0.00
Mg#	0.56	0.68		0.67	0.67	0.673	0.696	0.68	0.69	0.68	0.68	0.77	0.78	0.77	0.71
Trace elements (ppm):															
Cr*	267	254		304	285	293	344	618	637	503	686	1229	1398	1740	445
Ni*	53	96		100	96	89	117	126	143	139	136	283	320	320	92
$\mathbf{V}^*$				193	200	191	244	294	279	295	290	242	243	245	256
Cu*	99	67		65	67	72	100	102	95	131	104	72	72	83	105
Zn*	47	49		45	46	47	44	55	63	58	58	56	55	57	51
Rb*	5	<1		1	<1	<1	3	5	11	14	7	4	5	4	3
Sr*	245	150		162	168	164	155	148	143	145	146	137	163	137	117
Y*	28	27		25	25	25	18	16	14	15	15	14	14	15	15
Zr*	120	94		93	99	98	43	32	29	30	32	33	33	33	27
Nb*	2	1		1	1	1	1	1	1	<1	1	1	1	1	1
Ba*	41	9		16	15	14	20	78	45	63	77	62	55	54	44
Ce*	22	7		11	8	16	11	5	8	9	5	12	9	10	6
Na			1.99	2.10	1.92	1.97			1.07	1.17	1.14	1.14		1.08	1.03
Fe			5.64	5.69	5.93	5.9	7.2	7.26	6.63	6.47	6.93	6.98	6.51	7.06	6.47
Sc			31.1	31.4	32.9	34	43	42.9	40.6	40.1	43.1	49.7	35.2	38.2	44.2
Cr			294	310	320	321	348	715	535	1113	1048	992	1163	1502	503
Co			35.4	36.3	36.8	37	40	40.4	38.0	39.0	42.3	49.4	49.4	56.4	41.7
Zn			77	74	80	83	85	102	86	90	92	81	81	90	89
Sr			167	168	<119	167	ND	161	113	<93	<160	<136	85	133	<133
La			2.82	2.63	3.31	2.8	1.5	1.68	1.82	1.43	1.64	2.44	2.16	1.98	1.29
Ce			9.5	8.7	9.4	9.6	4.5	5.2	4.7	5.8	8.6	10.7	7.6	10.3	2.6
Sm			2.83	2.83	3.12	2.9	1.6	1.64	1.70	1.47	1.59	1.81	1.57	1.68	1.46
Eu			1.10	1.03	1.10	1.1	0.7	0.67	0.61	0.56	0.62	0.66	0.56	0.55	0.52
Tb			0.57	0.61	0.59	0.6	0.3	0.37	0.30	0.40	0.34	0.37	0.36	0.24	0.28
Yb			2.30	2.25	2.37	2.1	1.8	1.85	1.48	1.52	1.56	1.34	1.30	1.28	1.35
Lu			0.41	0.36	0.47	0.4	0.3	0.40	0.27	0.29	0.24	0.29	0.18	0.26	0.40
Hf			2.22	2.12	2.27	2.2	1.1	0.95	0.73	0.80	0.78	0.92	0.90	0.84	0.73
Та			0.08	0.08	0.10	0.2	< 0.07	< 0.07	0.07	< 0.06	< 0.08	< 0.07	< 0.07	< 0.07	< 0.07
Th			ND	ND	ND	ND	ND	ND	0.21	<.19	ND	ND	ND	ND	ND
(La/Sm)N			0.61	0.57	0.65	0.6	0.6	0.62	0.65	0.59	0.63	0.82	0.84	0.72	0.54

Notes: Placement of samples in core denoted by hole, section, core, and interval (cm) designations, as measured from top of section. X-ray fluorescence (XRF) analyses are from Parson, Hawkins, Allan, et al. (1992), with XRF trace elements denoted by an asterisk (\*); discussion of errors is given in Parson, Hawkins, Allan, et al. (1992). Other element analyses are by instrumental neutron activation analysis; true analytical uncertainty from multiple analysis of each sample is Na = 0.02%, Fe = 0.12%, Sc = 0.7 ppm, Cr = 11 ppm, Co = 0.6 ppm, Zn = 3 ppm, Sr = 29 ppm, La = 0.08 ppm, Ce = 0.3 ppm, Sm = 0.04 ppm, Eu = 0.02 ppm, Tb = 0.06 ppm, Yb = 0.05 ppm, Lu = 0.03 ppm, Hf = 0.06 ppm, Ta = 0.02 ppm, and Th = 0.06 ppm. La/Sm normalized to chondritic ratios (Masuda et al., 1973). Mg/(Mg + Fe<sup>2+</sup>) (Mg#) calculated assuming Fe<sup>3+</sup>/Fe<sup>Total</sup> of 0.15 and 0.10; (La/Sm)<sub>N</sub> ratios are chondrite normalized (Masuda et al., 1973). ND = not determined.

with 2-hr counts obtained at 7–12 days, 28–33 days, and 4 months using lead-shielded Ortec coaxial intrinsic germanium detectors. These high-resolution detectors have efficiencies of 22%–24% relative to a 3 × 3 in. NaI detector crystal at a distance of 25 cm, and have resolutions of 1.64–1.68 KeV at FWHM of the 1332 KeV line of <sup>60</sup>Co. Dead-time was kept below 5% during counting. The NBS standard flyash SRM1633a was used as the multiple element standard (Korotev, 1987), with its Tb content corrected to 2.53 ppm (L. Korotev, pers. comm., 1991). Spectral analyses and peak-height evaluations were made using a software package from Nuclear Data, with U- and Thseries overlap and interference corrections performed by hand (Glascock et al., 1986; Landsberger, 1986; Landsberger and Simsons, 1987). Material was not available from Site 834 Unit 1 for analysis by INAA.

Major and minor element glass analyses were obtained by the author only for Site 839 Unit 3 (Table 2). These analyses were performed on the Texas A&M Cameca SX50 microprobe using a combination of glass and mineral standards, with Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, and P counted for 30 s with a 20-µm wide beam. Na and K were counted first to avoid alkali loss. The analyses were then slightly normalized, using corrections derived from repeated analysis of the Smithsonian standard VG-2 (Jarosowich et al., 1980). Cr and Cl were counted for 450 s, and F was counted for 600 s, using chromite, scapolite and F-phlogopite standards. Additional VG-2normalized glass analyses of spinel-bearing units are reported from Hawkins and Allan (this volume) in Table 3; these analyses were made by J. Hawkins on the Scripps Institution of Oceanography Cameca Camebax microprobe and represent eruptive unit averages.

All microprobe mineral analyses were obtained on the Cameca SX50 microprobe using international oxide standards, 20- to 30-s count times, and a 1-µm focused beam. For the Cr-spinel analyses, Si and Ca were counted for 10 s and are used primarily as a check for beam overlap on surrounding silicate minerals or glass. Corrections for Ti overlap on V were made by noting V counting rates on Ti metal and V-free rutile.

All probe traverses shown in the figures were derived from full 10 or 11 element analyses. The position of every stored point to be analyzed on a given traverse was checked before analysis to ensure that it fell on a smoothly polished surface. Traverse point analyses with corrected totals not between 98.5% and 101.5% were removed from the published traverses.

Table 2. Glass analysis of Site 839 Unit 3.

		VG-2
		normalized
Major eleme	ents (wt%):	
SiO <sub>2</sub>	52.14	52.6
TiO <sub>2</sub>	0.7	0.68
Al <sub>2</sub> Õ <sub>3</sub>	15.6	15.64
FeO	8.57	8.69
MnO	0.15	0.15
MgO	7.07	6.8
CaO	12.72	12.49
Na <sub>2</sub> O	1.8	1.75
K <sub>2</sub> Ô	0.3	0.28
P205	0.08	0.07
Total	99.13	99.15
Mg#	0.634	0.621
Trace eleme	nts (ppm):	
Cr	0.013	
F	0.027	
Cl	0.104	

Notes: Seven discrete analyses represented. The standard deviation of the analysis is  $SiO^2 = 0.31\%$ ,  $TiO_2 = 0.02\%$ ,  $Al_2O_3\% = 0.09\%$ , FeO = 0.17%, MnO = 0.02%, MgO = 0.06%, CaO = 0.13%,  $Na_2O = 0.05\%$ ,  $K_2O = 0.01\%$ ,  $P_2O_5 = 0.03\%$ , Cr = 0.005%, F = 0.008%, and Cl = 0.003%. VG-2 normalized analysis represents Unit 3 glass normalized to repeated (15) analyses of Juan de Fuca glass standard VG-2 (Jarosowich et al., 1980).

Table 3. Glass analyses of Cr-spinel-bearing units.

Site:	83	34	8	34	8	36	8	39
Unit or subunit:	1	A		7		3		3
Determinations:	4	2	1	6		3		6
		SD		SD		SD		SD
SiO <sub>2</sub>	50.40	0.32	50.03	0.49	49.53	0.29	52.60	0.35
TiO <sub>2</sub>	1.48	0.01	1.36	0.03	0.88	0.02	0.70	0.01
AI <sub>2</sub> O <sup>3</sup>	16.37	0.25	16.34	0.22	15.74	0.09	15.82	0.28
FeO	8.71	0.03	8.78	0.16	9.11	0.21	8.57	0.09
MnO	0.20	0.01	0.17	0.03	0.18	0.03	0.18	0.02
MgO	6.87	0.13	7.80	0.24	7.89	0.05	6.47	0.14
CaO	11.87	0.07	11.90	0.19	13.76	0.16	12.19	0.18
Na <sub>2</sub> O	3.39	0.02	3.10	0.15	2.05	0.01	1.77	0.04
K <sub>2</sub> Ô	0.13	0.01	0.09	0.01	0.06	0.00	0.31	0.01
P <sub>2</sub> O <sub>5</sub>	0.17	0.04	0.12	0.02	0.07	0.03	0.10	0.01
Total	99.59		99.69		99.27		98.71	
Mg#	0.623		0.651		0.645		0.613	

Notes: Data from Hawkins and Allan (this volume). Determinations represent number of distinct, VG-2 normalized analyses of individual samples averaged over the individual unit.

## CHEMISTRY OF HOST LAVAS

Analyses of Cr-spinel-bearing units are given in Tables 1-3, and the data are plotted in Figure 2. All are classified as representing individual or composite lava flows emanating from single eruptive episodes (Parson, Hawkins, Allan, et al., 1992). The Cr-spinel-bearing units are compositionally all basalts, most containing high Mg/(Mg + Fe2+) (Mg#), Cr, and Ni. Host lavas from Site 834 are tholeiites similar in major element composition to depleted mid-ocean-ridge basalts (N-MORBs; Sun and McDonough, 1989) and are characterized by slightly concave-downward, chondrite-normalized, rare-earth patterns (Fig. 2); Unit 1 is significantly more evolved than Unit 7 (Table 1; Hawkins and Allan, this volume). These Site 834 basalts differ from N-MORB in exhibiting notable relative depletions in the high-fieldstrength elements (HFSEs) Ta and Nb, and in having general enrichments in the large-ion-lithophile elements (LILEs) (Fig. 2). They are more enriched in incompatible elements than lavas from the actively spreading East Lau Spreading Center (ELSC, as shown in Fig. 1), but fall within the compositional range shown by the more enriched lavas of the actively spreading Central Lau Spreading Center (CLSC, as shown in Fig. 1; Hawkins and Allan, this volume).



Figure 2. Chondrite-normalized (Masuda et al., 1973; Leedy values/1.2246) and N-MORB-normalized (Sun and McDonough, 1989) analyses of Cr-spinel bearing lavas from Leg 135. Analyses from Table 1.

Unit 3 from Site 836 (Table 1) shares the LILE enrichment of the Site 834 lavas, but differs from them and from N-MORB in being markedly lower in Na<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, and other incompatible elements (Fig. 2). It is quite similar in composition to the more primitive of lavas from the ELSC (Hawkins and Allan, this volume). Lavas from Site 839 are even more depleted in these elements than those from Site 836; in addition, they are characterized by having very low Al<sub>2</sub>O<sub>3</sub> and variable Ce concentrations (Table 1 and Fig. 2), the latter likely representing seawater alteration or variable sediment incorporation during eruption (Hawkins and Allan, this volume). Depletion in the HFSEs Ta, Nb, Zr, Hf, and Ti are especially pronounced compared to N-MORB (Fig. 2). Ewart et al. (this volume) emphasized the arc-like compositional affinities of these units, noting the similarity of their N-MORB-normalized enrichment patterns to the more primitive low-Al basalts from the Holocene Tofua/Tonga-Kermadec Arc. These similarities led them to speculate that Site 839 samples may represent early Tofua Arc volcanism that has been split from the current arc by eastern Lau Basin seafloor spreading.

## DESCRIPTION OF Cr-SPINEL

Cr-spinel analyses were obtained from Units 1 and 7 from Site 834, Unit 3 from Site 836, and Units 1, 3, and 4 from Site 839 (Fig. 3 and Tables 4–6). Cr-spinel was identified by the Leg 135 Shipboard Scientific party in Units 1, 3, 5, 7, and 13 at Site 834; in Units 3 and 4 at Site 836; and in Units 1, 3, 4, 6, and 8 at Site 839 (Parson, Hawkins, Allan, et al., 1992). No Cr-spinel was found in thin sections cut on shore from Site 834 Unit 13; shipboard thin sections were not available from this unit for analysis. The lack of material precluded analysis from Site 834 Unit 3. Rare Cr-spinel jacketed with magnetite was described from Site 836 Unit 4 (Parson, Hawkins, Allan, et al.,



Figure 3. Analyses of Leg 135 Cr-spinel. Fields show analytical range of spinel within N-MORB from the East Pacific Rise and adjacent seamounts (Allan et al., 1988, 1989), and in tholeites from the Lau Basin (LBB; Hawkins and Melchior, 1985). Cr-spinel from Sites 834 and 836 are distinctly MORB-like in composition, whereas those from Site 839 are distinctly richer in Cr/(Cr +  $Al + Fe^{3+}$ ) at a given Mg/(Mg + Fe<sup>2+</sup>).

1992); spinel was not identified in this unit on shore in the same thin sections where the original identification was made. Cr-spinels were not analyzed from Site 839 Units 6 and 8, as these units likely represent cored borehole lag deposits from upsection units that were displaced by pipe reaming (Parson, Hawkins, Allan, et al., 1992). Petrographic notes in this section draw heavily from the observations of Parson, Hawkins, Allan, et al. (1992).

# Petrography

#### Site 834

Unit 1 is a sparsely phyric plagioclase olivine basalt recovered only as rubble from 106 to 113 m below seafloor (mbsf) in Hole 834A. It represents the youngest basalt recovered at the site and overlies sediment of about 3.8 Ma in age (Parson, Hawkins, Allan, et al., 1992). Euhedral plagioclase as large as 2 mm in size is the principle phenocryst phase (as much as 2 vol%), forming glomeroporphyritic clusters. Vesicularity is high (10%–45%). Olivine phenocrysts occur in trace quantities. The dominant groundmass phase is microlitic plagioclase, joined by minor amounts of euhedral olivine, fanlike bundles of clinopyroxene, tiny (<4  $\mu$ m) skeletal magnetite, and variably altered mesostasis. Dark brown Cr-spinel occurs as small (<40  $\mu$ m), rare euhedral grains enclosed within or adjacent to plagioclase phenocrysts. Unit 7 is the thickest of the Site 834 igneous units, with a defined thickness of 74 m in core (from 214 to 288 mbsf in Hole 834B; Parson, Hawkins, Allan, et al., 1992). The upper portion of the unit consists of pillowed flows, whereas the lower 20–40 m is more massive. Overall, the unit is composed of highly phyric plagioclase basalt, notable both for abundant, euhedral plagioclase phenocrysts (as large as 5 mm and over 15 vol%) and for the large (as large as 0.3 mm), abundant dark brown to opaque Cr-spinel most commonly found as euhedral crystals within or embedded within the sides of plagioclase phenocrysts. Olivine also occurs as a phenocryst (as large as 2 mm and 1 vol%), but it is not found in contact with Cr-spinel. The ground-mass is dominated by elongate plagioclase microlites and elongate to acicular clinopyroxene. Alteration in this unit is low. Plates 1A and 1B illustrate several occurrences of Cr-spinel from this unit, particularly the association with plagioclase.

#### Chemistry

Cr-spinels from Unit 1 are compositionally similar to those from MORB (Sigurdsson and Schilling, 1976; Basaltic Volcanism Study Project, 1981; Dick and Bullen, 1984; Allan et al., 1988; Fig. 3). They contain low amounts of TiO<sub>2</sub> (<1.05%) and minor amounts of V<sub>2</sub>O<sub>3</sub>, MnO, NiO, and ZnO (Tables 4–6). Groundmass spinel rims exhibit consistently lower Mg# and higher Cr/(Cr + Al + Fe<sup>3+</sup>) (Cr#) and TiO<sub>2</sub> than do cores of groundmass grains or spinel inclusions (Analyses 3 and 6–7 in Table 4). These variations are consistent with spinel crystal chemical energetics that reflect strong coupling between Fe<sup>2+</sup> and Cr<sup>3+</sup> and Mg<sup>2+</sup> and Al<sup>3+</sup> in the spinel solid solution (Sack, 1982; Sack and Ghiorso, 1991a, 1991b), and likely represent crystallization from a rapidly evolving and fractionating melt.

The Cr-spinels of Unit 7 contain lower TiO<sub>2</sub> and Fe<sup>3+</sup>/(Cr + Al + Fe<sup>3+</sup>) (Fe<sup>3+</sup>#) than do those of Unit 1 (Fig. 3 and Tables 4-6), but otherwise they are similar in composition. Although spinel inclusions are relatively unzoned (Analyses 10-11 and 14-15 in Table 4), groundmass crystals typically show minor zoning (Fig. 4; Analyses 12-13 and 16-17 in Table 4). In samples where zoning is minor in free spinel crystals, olivine also only shows minor zoning (Fig. 4). Spinel zoning is more pronounced in Sample 135-834B-22R-2, Piece 2C, which has a relatively coarse groundmass (Analyses 8-9 in Table Unlike the zoning shown by other spinels of Units 1 and 7, TiO<sub>2</sub> and Cr# do not increase with decreasing Mg# from core to rim. Similar decoupling of divalent and trivalent cations has been observed in Cr-spinels that have changed composition as a result of metamorphic processes (Allan, 1992; Sack, 1980). Under such conditions, the divalent cations are mobile and the trivalent cations are often not. Spinel crystal chemical energetics make it unlikely that such a decoupling could occur during crystal growth (Sack, 1980; Forsythe and Fisk, this volume), and instead imply that such changes are a result of reequilibration of the Cr-spinel with Fe-rich, interstitial, residual melt during extended cooling associated with lava crystallization.

## Site 836

## Petrography

The spinel-bearing Unit 3 consists of fragments of sparsely phyric, vesicular (15–20 vol%) olivine-plagioclase basalt intercalated with sediments. This unit occurs in core from about 20 to 26 mbsf in Hole 836A and from about 18 to 23 mbsf in Hole 836B. Plagioclase (as large as 1 mm in size; 1–2 vol%) is blocky and sometimes forms glomeroporphyritic clumps; sparse crystals of olivine are found in the groundmass or associated with the plagioclase crystal clumps. Groundmass textures in the analyzed samples range from spherulitic to microlitic, with abundant disseminated plagioclase microlites the dominant groundmass phase. Trace crystals (0.02–0.1 mm across) of blocky, euhedral dark brown Cr-spinel are found as inclusions in plagioclase or as crystals in the groundmass, sometimes attached to olivine (Plate 1C).

#### Table 4. Representative Cr-spinel analyses.

					0011	0011	0244	0240	0240	024D	024D	924D	924D	934B	924B	834B
Hole:	834A	834A	834A	834A	834A	834A	834A	834D	0.04D	26P 1	26P-1	28R-1	28R-1	30R-3	30R-3	30R-3
Core section:	12X-CC	12X-CC	12X-CC	13A-1	132-1	13A-1	13A-1	228-2	228-2	52 65	52 65	25 42	35 42	04_104	94_104	94-104
Interval (cm):	0-3	0-3	0-3	0-10	0-10	0-10	0-10	28-29	28-29	10	11	12	13	14	15	16
Analysis no.:	1	2	3	4	2	D	IDICD	0	MD	IDC	IDD	GM	GP	IPC	IPP	GC
Description:	IPC	IPR	GR	IPC	IPR	IP/GC	IP/GR	MC	MIK	IPC	7	7	7	7	7	7
Unit:	1	1	1	1	1	1	- E	/	/	/	1	1	/	'	'	. /
SiO	0.05	0.05	0.08	0.06	0.06	0.04	0.05	0.05	0.11	0.07	0.05	0.05	0.06	0.02	0.02	0.04
TiO	0.96	0.94	1.10	0.91	0.91	0.94	1.05	0.71	0.71	0.46	0.42	0.54	0.58	0.65	0.62	0.65
AlaÓa	26.57	25.55	23.26	26.60	26.59	26.66	25.44	27.07	26.49	31.71	31.62	29.96	31.00	28.68	28.42	28.98
V <sub>2</sub> O <sub>2</sub>	0.18	0.23	0.26	0.24	0.17	0.20	0.22	0.20	0.23	0.15	0.16	0.14	0.12	0.17	0.16	0.22
Cr <sub>2</sub> O <sub>2</sub>	35.06	34.58	35.50	34.22	34.62	35.09	35.40	37.56	37.04	33.38	33.23	35.05	33.64	35.89	35.58	35.90
FeO	21.83	21.65	24.54	21.55	21.42	22.50	23.50	19.13	23.16	17.76	17.42	17.62	19.44	18.19	18.70	18.74
MnO	0.19	0.09	0.18	0.13	0.15	0.15	0.61	0.08	0.17	0.13	0.08	0.11	0.13	0.12	0.09	0.09
NiO	0.12	0.12	0.11	0.12	0.10	0.11	0.11	0.16	0.08	0.18	0.21	0.16	0.12	0.21	0.17	0.16
ZnO	0.00	0.00	0.00	0.04	0.09	0.14	0.19	0.00	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MgO	14.44	14.47	12.90	14.37	14.42	14.14	13.31	15.47	12.55	16.47	16.55	15.84	15.28	15.75	15.47	15.49
CaO	0.08	0.20	0.17	0.16	0.19	0.07	0.16	0.00	0.07	0.09	0.17	0.01	0.05	0.05	0.18	0.01
Total	99.48	97.88	98.10	98.40	98.72	100.04	100.04	100.43	100.69	100.40	99.91	99.48	100.42	99.73	99.41	100.28
RFe <sub>2</sub> O <sub>3</sub>	7.96	8.61	9.31	8.02	7.94	8.08	8.55	6.38	6.01	6.18	6.27	5.40	5.92	6.05	6.42	5.81
RFeO	14.67	13.90	16.16	14.33	14.27	15.23	15.81	13.39	17.76	12.20	11.77	12.76	14.12	12.74	12.92	13.52
R <sub>Total</sub>	100.28	98.74	99.03	99.20	99.52	100.85	100.90	101.07	101.29	101.02	100.54	100.02	101.01	100.34	100.05	100.86
Cr/(Cr + Al)	0.469	0.476	0.506	0.463	0.466	0.469	0.483	0.482	0.484	0.414	0.413	0.440	0.421	0.456	0.456	0.454
Mg/(Mg + Fe)	0.637	0.650	0.587	0.641	0.643	0.623	0.600	0.673	0.557	0.706	0.715	0.689	0.659	0.688	0.681	0.6/1
$Fe^{3+}/(Cr + Al + Fe^{3+})$	0.092	0.101	0.112	0.094	0.092	0.093	0.100	0.072	0.069	0.068	0.069	0.061	0.066	0.068	0.073	0.065
$Cr/(Cr + Al + Fe^{3+})$	0.426	0.428	0.449	0.420	0.423	0.425	0.434	0.447	0.450	0.386	0.385	0.413	0.393	0.425	0.423	0.424
$Al/(Cr + Al + Fe^{3+})$	0.482	0.471	0.439	0.487	0.485	0.482	0.466	0.481	0.480	0.546	0.546	0.526	0.541	0.507	0.504	0.511
Predicted melt Mg#	0.616	0.634	0.583	0.619	0.621	0.602	0.585	0.652	0.534	0.664	0.673	0.651	0.615	0.658	0.652	0.639
Hole:	839B	839B	839B	839B	839B	839B	839B 8	39B 83	9B 839	B 839	B 839B	839B	839F	8 839B	839B	

839B	839B	839B	839B	839B	839B	839B	839B	839B	839B	839B	839B	839B	839B	839B	839B
12R-2	12R-2	15R-1	15R-1	15R-1	15R-1	15R-1	19R-1	19R-1	19R-1	19R-1	19R-1	20R-1	20R-1	20R-1	23R-1
20-24	20-24	27-31	27-31	27-31	27-31	27-31	59-63	59-63	59-63	59-63	59-63	81-85	81-85	81-85	28-31
32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47
PM	PR	MC	GR	IO	PC	PR	PC	PM	PR	IO	IO	IO	PC	PR	IO
1	1	1	1	1	1	1	3	3	3	3	3	3	3	3	3
0.03	0.00	0.09	0.03	0.10	0.00	0.04	0.04	0.04	0.10	0.03	0.06	0.07	0.11	0.02	0.02
0.24	0.23	0.25	0.63	1.15	0.23	0.29	0.36	0.29	0.39	0.43	0.37	0.38	0.21	0.26	0.36
11.80	11.05	11.21	12.83	12.54	12.76	10.76	15.67	14.20	12.11	12.98	12.52	12.69	9.84	11.47	12.37
0.07	0.10	0.05	0.22	0.25	0.06	0.14	0.10	0.11	0.12	0.13	0.09	0.11	0.07	0.08	0.13
55.40	53.23	57.88	45.43	41.05	52.69	50.09	50.54	51.92	50.66	48.02	48.66	50.88	59.94	52.97	53.54
18.21	23.01	14.74	29.57	35.18	23.30	32.04	15.98	18.60	24.08	24.22	24.26	21.14	15.08	22.58	19.00
0.12	0.17	0.08	0.20	0.23	0.17	0.23	0.10	0.08	0.16	0.15	0.19	0.07	0.05	0.13	0.13
0.17	0.14	0.19	0.08	0.09	0.17	0.03	0.20	0.18	0.11	0.09	0.08	0.19	0.23	0.11	0.12
0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
13.16	9.82	15.48	9.44	7.29	9.91	5.19	16.25	13.87	10.89	11.86	11.33	12.77	15.03	11.53	13.70
0.02	0.06	0.00	0.17	0.06	0.00	0.11	0.02	0.03	0.17	0.00	0.01	0.00	0.00	0.06	0.01
99.23	97.82	100.04	98.58	97.93	99.29	98.92	99.28	99.32	98.79	97.91	97.57	98.31	100.56	99.22	99.37
5.14	5.54	4.97	11.14	13.26	5.16	7.22	7.05	6.21	7.78	9.52	8.94	7.59	4.58	7.25	6.59
13.58	18.03	10.27	19.54	23.25	18.66	25.54	9.64	13.01	17.08	15.65	16.21	14.31	10.95	16.06	13.06
99.74	98.38	100.54	99.69	99.26	99.81	99.64	99.98	99.94	99.57	98.87	98.47	99.07	101.02	99.95	100.03
0.759	0.764	0.776	0.704	0.687	0.735	0.757	0.684	0.710	0.737	0.713	0.723	0.729	0.803	0.756	0.744
0.633	0.493	0.729	0.462	0.358	0.486	0.266	0.750	0.655	0.532	0.575	0.555	0.614	0.710	0.561	0.651
0.063	0.070	0.060	0.141	0.174	0.064	0.094	0.083	0.075	0.097	0.119	0.112	0.094	0.055	0.090	0.080
0.711	0.710	0.730	0.604	0.567	0.688	0.686	0.627	0.657	0.666	0.628	0.642	0.661	0.759	0.688	0.684
0.226	0.220	0.211	0.255	0.258	0.248	0.220	0.290	0.268	0.237	0.253	0.246	0.246	0.186	0.222	0.236
0.705	0.577	0.792	0.539	0.429	0.559	0.339	0.791	0.712	0.610	0.647	0.631	0.683	0.782	0.644	0.719
	8.39B 12R-2 20-24 32 PM 1 0.03 0.24 11.80 0.07 55.40 18.21 0.17 0.00 13.16 0.02 99.23 5.14 13.58 99.74 0.759 0.633 0.711 0.226 0.705	839B         839B           12R-2         12R-2           20-24         20-24           32         33           PM         PR           1         1           0.03         0.00           0.24         0.23           11.80         11.05           0.07         0.10           55.40         53.23           18.21         23.01           0.12         0.17           0.17         0.14           0.00         0.06           99.23         97.82           5.14         5.54           13.58         18.03           99.74         98.38           0.759         0.764           0.633         0.493           0.063         0.070           0.711         0.710           0.226         0.220           0.705         0.577	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$										

Notes: Analyses are recalculated by stoichiometry according to the methods of Carmichael (1967). P = phenocrysts, M = microphenocrysts, and G = groundmass-sized crystals (although can represent crystals in glass). C = core, R = rim, and I = inclusion, with "P" denoting inclusion in plagioclase and "O" denoting inclusion in olivine. Predicted melt Mg# represents calculated equilibrium melt Mg/(Mg + Fe<sup>2+</sup>) based upon methods of Allan (1992) as discussed in text. Hole, core, section, and interval (cm) designations follow standard ODP conventions and represent area in core from which analyses were made.

## Chemistry

Site 836 Cr-spinels are compositionally similar to MORB Crspinels, and overlap in most major and minor elements with Cr-spinels from Site 834 (Fig. 3 and Tables 4–6). They differ from Site 834 Cr-spinels in having generally lower  $TiO_2$ , which likely reflects the lower  $TiO_2$  of the host lava (Table 1). Zoning in most Site 836 spinels is minor (Analyses 18–19 and 23–24; Table 4); groundmass Cr-spinel from the more coarsely crystalline Sample 135-836A-5X-1, 37–40 cm, has slightly lower Mg# than do groundmass Cr-spinels from Sample 135-836B-2R-1, 14–16 cm (e.g., Analyses 18–19 in Table 4). The core of one slightly zoned groundmass spinel shown in Plate 1C has moderately higher Mg# than do the other spinel analyses (see Analyses 21–22 in Table 4); the adjacent olivine crystal shows similar zoning in Mg# (see Analyses 8–9 in Table 7).

# Site 839

# Petrography

Unit 1 is a holocrystalline, highly vesicular (10%-40% vesicles), aphyric to moderately phyric clinopyroxene-olivine basalt lacking

Table 4	(continu	eu).												
834B	836A	836A	836A	836B	836B	836B	836B	839A	839A	839A	839A	839A	839B	839B
30R-3	5X-1	5X-1	5X-1	2R-1	2R-1	2R-1	2R-1	24X-1	24X-1	24X-1	24X-1	24X-1	12R-2	12R-2
94-104	37-40	37-40	37-40	14-16	14-16	14-16	14-16	19-22	19-22	19-22	19-22	19-22	20-24	20-24
17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
GR	GC	GR	IPC	GC	GR	GC	GR	IO	GC	GR	PC	PR	ю	PC
7	3	3	3	3	3	3	3	1	1	1	1	1	1	1
0.12	0.05	0.07	0.02	0.03	0.04	0.05	0.07	0.01	0.14	0.15	0.02	0.01	0.30	0.05
0.70	0.37	0.50	0.40	0.39	0.41	0.43	0.45	0.24	0.26	0.31	0.25	0.26	0.52	0.23
28.64	28.77	25.02	29.19	28.64	28.88	28.04	27.80	10.97	12.62	13.07	12.40	12.34	14.99	11.50
0.15	0.15	0.24	0.14	0.16	0.18	0.18	0.18	0.17	0.13	0.11	0.09	0.08	0.28	0.10
35.55	35.50	38.29	34.92	36.36	35.31	36.04	35.75	52.12	53.28	51.70	55.99	53.10	41.26	56.63
19.64	19.90	21.48	19.25	18.73	19.24	20.28	20.23	23.76	22.76	24.03	16.58	23.56	28.80	16.07
0.15	0.07	0.12	0.10	0.10	0.16	0.14	0.14	0.17	0.15	0.23	0.09	0.11	0.13	0.05
0.11	0.10	0.05	0.10	0.15	0.17	0.16	0.11	0.11	0.07	0.11	0.17	0.20	0.11	0.16
0.00	0.12	0.06	0.12	0.02	0.09	0.15	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00
15.07	14.97	14.13	15.16	15.86	15.29	15.18	15.06	10.66	10.97	9.17	14.74	10.21	12.32	14.40
0.08	0.03	0.12	0.12	0.05	0.06	0.04	0.00	0.03	0.03	0.10	0.03	0.06	0.03	0.02
100.21	100.03	100.08	99.52	100.49	99.83	100.69	99.84	98.25	100.40	98.97	100.34	99.93	98.73	99.19
6.11	6.65	7.50	6.53	6.74	6.67	7.43	7.26	7.53	5.65	4.62	5.47	5.79	14.19	4.83
14.14	13.92	14.73	13.38	12.66	13.24	13.59	13.69	16.98	17.68	19.87	11.65	18.35	16.03	11.73
100.82	100.70	100.83	100.17	101.17	100.50	101.43	100.57	99.00	100.96	99.44	100.89	100.51	100.15	99.67
0.454	0.453	0.506	0.445	0.460	0.451	0.463	0.463	0.761	0.739	0.726	0.752	0.743	0.649	0.768
0.655	0.657	0.631	0.669	0.691	0.673	0.666	0.662	0.528	0.525	0.451	0.693	0.498	0.578	0.686
0.069	0.075	0.086	0.073	0.075	0.075	0.083	0.082	0.095	0.069	0.058	0.065	0.072	0.175	0.059
0.423	0.419	0.463	0.412	0.425	0.417	0.424	0.425	0.689	0.688	0.684	0.703	0.689	0.535	0.723
0.508	0.506	0.451	0.514	0.500	0.508	0.492	0.493	0.216	0.243	0.258	0.232	0.239	0.290	0.219
0.623	0.628	0.623	0.637	0.665	0.644	0.643	0.639	0.616	0.598	0.517	0.756	0.575	0.640	0.754

Table 4 (anti-mad)

839B	839B	839B	839B	839B	839B	839B	839B	839B	839B	839B	839B	839B	839B	839B	839B	839B
23R-1	23R-1	23R-1	23R-1	23R-1	23R-1	23R-	25R-1	25R-1	25R-1	25R-1	25R-1	25R-1	25R-1	25R-1	25R-1	25R-1
28-31	28-31	7-11	28-31	28-31	7-11	7-111	35-38	35-38	35-38	35-38	35-38	35-38	35-38	43-45	43-45	43-45
48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64
GC	GR	IO	PC	PR	PC	PR	GC	GR	MM	MR	IOR	IOC	IOR	IO	IO	IO
3	3	3	3	3	3	3	3	3	3	3	3	3	3	4	4	4
0.05	0.08	0.09	0.03	0.08	0.03	0.10	0.09	0.18	0.10	0.07	0.08	0.06	0.08	0.02	0.10	0.08
0.34	0.34	0.36	0.26	0.34	0.25	0.30	1.62	0.65	0.27	0.30	0.35	0.38	0.32	0.37	0.36	0.38
11.83	12.02	12.16	13.16	12.32	11.82	11.51	16.47	12.91	11.96	11.49	11.74	12.46	12.54	14.45	14.02	13.92
0.10	0.09	0.15	0.11	0.09	0.08	0.10	0.29	0.14	0.10	0.10	0.12	0.09	0.11	0.19	0.18	0.13
53.77	52.75	52.92	54.95	50.69	55.99	53.44	41.00	46.66	56.13	53.51	53.08	54.41	53.30	48.65	48.64	49.07
19.83	21.48	20.13	15.80	23.24	15.29	22.24	26.31	28.66	16.40	21.61	19.72	18.00	17.68	21.71	21.93	21.31
0.08	0.11	0.09	0.05	0.14	0.00	0.18	0.13	0.21	0.00	0.11	0.11	0.13	0.11	0.10	0.11	0.14
0.17	0.14	0.12	0.23	0.04	0.13	0.13	0.23	0.04	0.19	0.08	0.14	0.16	0.15	0.09	0.08	0.07
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.07	0.02	0.17	0.00	0.04	0.03	0.00	0.00	0.00
13.21	11.54	14.03	15.23	11.61	15.52	11.45	13.26	8.06	14.73	11.85	13.47	14.66	14.54	12.90	13.05	13.02
0.06	0.12	0.01	0.04	0.17	0.01	0.15	0.11	0.27	0.00	0.17	0.03	0.00	0.00	0.02	0.05	0.00
99.41	98.68	100.06	99.86	98.71	99.12	99.59	99.54	97.85	99.90	99.46	98.84	100.39	98.86	98.51	98.52	98.12
6.79	6.08	8.03	5.51	8.03	5.71	6.63	12.01	8.05	5.27	6.77	7.24	6.72	6.68	8.09	8.58	7.99
13.72	16.01	12.91	10.84	16.02	10.15	16.27	15.51	21.42	11.65	15.52	13.21	11.95	11.66	14.43	14.21	14.12
00.09	99.29	100.86	100.42	99.52	99.69	100.26	100.74	98.66	100.43	100.14	99.57	101.06	99.53	99.32	99.38	98.92
0.753	0.746	0.745	0.737	0.734	0.761	0.757	0.625	0.708	0.759	0.757	0.752	0.745	0.740	0.693	0.699	0.703
0.632	0.562	0.660	0.715	0.564	0.732	0.556	0.604	0.401	0.693	0.576	0.645	0.686	0.690	0.614	0.621	0.622
0.083	0.076	0.097	0.066	0.100	0.069	0.082	0.148	0.104	0.064	0.084	0.089	0.081	0.081	0.099	0.105	0.098
0.691	0.690	0.672	0.688	0.661	0.708	0.695	0.533	0.634	0.711	0.694	0.685	0.685	0.680	0.625	0.626	0.634
0.226	0.234	0.230	0.246	0.239	0.223	0.223	0.319	0.262	0.226	0.222	0.226	0.234	0.239	0.277	0.269	0.268
0.705	0.637	0.729	0.771	0.640	0.792	0.637	0.645	0.468	0.757	0.657	0.717	0.750	0.752	0.674	0.682	0.683

sampled glassy or spherulitic quench facies (Parson, Hawkins, Allan, et al., 1992). It was recovered in Hole 839A from 206 to 218 mbsf (total depth) and in Hole 839B from 214 to 257 mbsf. The unit interior has diabasic texture, whereas the unit margins are more phyric, with rounded and resorbed olivine phenocrysts (as large as 2 mm) dominating (as much as several volume percent) over anhedral to subhedral clinopyroxene phenocrysts (<1 vol% and as large as 1 mm). The unit is overlain by upper Pliocene sediment, and represents a massive (about 40–50 m thick) eruptive unit consisting of thick (>5 m) flows (Parson, Hawkins, Allan, et al., 1992). This rather coarse-grained unit is notable for the very large (as large as several millimeters across), deep red, irregular, rounded, and embayed Cr-spinel megacrysts and glomerocrysts that it contains (Plates 2A–2C). Cr-spinel also occurs as small (5 to 50  $\mu$ m in size), euhedral inclusions within olivine phenocrysts.

mass oxide phase is Ti-rich magnetite, forming euhedral to skeletal grains as large as 0.3 mm (see Hawkins and Allan, this volume).

Unit 3 is a glassy to holocrystalline, vesicular (10–20 vol% vesicles), crystal-rich, moderately to highly phyric clinopyroxeneolivine basalt. It was mapped in core for over 58 m (276–334 mbsf in Hole 839B), and consists of a number of very thin flows or pillows that probably represent a single eruptive event (Parson, Hawkins, Allan, et al., 1992). The phenocryst and crystal abundances increase steadily downcore, with large (to 5 mm in size), euhedral to subhedral olivine being the dominant phenocryst phase (as much as 15 vol%). Although greatly subordinate in abundance to olivine, euhedral to subhedral clinopyroxene also occurs as phenocrysts, occurring up to 1.5 mm in size and comprising up to several percent of the rock. Olivine and clinopyroxene both form seriate textures, with well-formed crystals often making up another 15–20 vol% (most of it

Table 5. Cr-spinel compositional range.

Site	Unit	Spinel analyses	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	$V_2O_3$	Cr <sub>2</sub> O <sub>3</sub>	Total FeO	MnO	NiO	ZnO	MgO
834	1	24	0.90-1.05	23.3-26.7	0.17-0.28	34.6-35.9	21.7-24.5	0.13-0.17	0.08-0.15	0.02-0.20	12.8-14.9
834	7	68	0.42 - 0.75	25.3-32.4	0.12-0.26	32.7-39.6	17.4-23.2	0.06-0.17	0.06-0.22	0.00-0.13	12.6-16.6
836	3	21	0.37-0.56	23.6-29.2	0.14-0.23	34.2-39.6	18.7-21.6	0.07-0.16	0.05-0.17	0.00-0.15	1
839	1	111	0.17-1.15	9.9-14.0	0.04-0.30	39.3-57.9	14.7-34.4	0.04-0.24	0.03-0.27	0.00-0.07	5.2-15.8
839	3	237	0.20-1.62	9.7-16.5	0.02-0.29	41.0-59.9	15.1-26.0	0.00-0.24	0.00-0.27	0.00-0.17	8.1-16.3
839	4	4	0.36-0.39	13.9-14.5	0.13-0.19	47.6-49.1	21.3-22.1	0.10-0.14	0.07-0.09	NA	12.8-13.1

Notes: Range in oxide analyses shown by Leg 135 Cr-spinel, arranged by unit. ZnO not analyzed (NA) in Site 839 Unit 4 spinels.

Table 6. Mineralogical summary.

Site	Unit	Spinel analyses	Spinel Mg#	Spinel Cr#	Spinel Fe#	Olivine analyses	Olivine Mg#	Spinel melt Mg#	Olivine melt Mg#
834	1	24	0.59-0.65	0.43-0.45	0.09-0.11	14	85-86	0.58-0.63	0.60-0.63
834	7	68	0.56-0.72	0.38-0.48	0.06-0.08	36	83-87	0.53-0.67	0.57-0.65
836	3	21	0.63-0.69	0.41 - 0.48	0.07-0.10	15	82-88	0.62-0.67	0.56-0.66
839	1	111	0.27-0.73	0.52-0.73	0.05-0.18	34	81-91	0.34-0.79	0.53-0.74
839	3	237	0.46-0.75	0.53-0.76	0.05-0.15	201	76-92	0.47-0.80	0.46-0.77
839	4	4	0.61-0.62	0.62-0.63	0.10-0.11	22	81-89	0.67-0.68	0.54-0.69

Notes: Range in calculated composition and equilibrium liquid composition from Leg 135 Cr-spinel and olivine, arranged by unit.  $Mg# = Mg/(Mg + Fe^{2*})$ ,  $Cr# = Cr/(Cr + Al + Fe^{3*})$ , and  $Fe# = Fe^{3*}/(Cr + Al + Fe^{3*})$ ; Cr-spinel melt Mg# and olivine melt Mg# represent calculated melt Mg# based upon methods of Allan (1992) and Roeder and Emslie (1970), as discussed in text.

olivine) of the rock in the groundmass. The abundance of olivine, the very high MgO concentrations of the whole-rock samples (Table 1), and the low MgO content of the interstitial glass (Table 2) suggests that substantial olivine accumulation in the magma took place, and that the unit represents a picrite. Elongate microlites of plagioclase are another groundmass constituent, increasing in size and abundance as the groundmass coarsens, as do small (as little as  $60 \ \mu$ m), skeletal grains of Ti-rich magnetite. Glassy margins of flows lack plagioclase and Ti-rich magnetite.

Cr-spinel occurs in a variety of sizes in Unit 3, with representative examples shown in Plates 2D–2F. Sharply euhedral crystals of spinel are found in quenched glass or in the groundmass in sizes ranging from 30  $\mu$ m to over 2 mm across. The size of the larger spinel euhedra are extraordinary, with no comparably sized euhedral spinel from glassy basalts reported in the literature. Where the groundmass is holocrystalline, small (<100  $\mu$ m) spinel crystals are absent and larger ones are slightly rounded. Euhedra of Cr-spinel (10–50  $\mu$ m in size) are abundantly found as inclusions within euhedral olivine (Plates 2D and 2F).

Unit 4 is a highly vesicular ( $\approx$ 30 vol% vesicles), crystal-rich, olivine-clinopyroxene basalt. It was mapped in core for about 19 m (334–353 mbsf) and represents a flow unit comprised of pillows or a series of thin flows (Parson, Hawkins, Allan, et al., 1992). Although the number of larger crystals that can be classified as phenocrysts (greater than about 0.5 mm) is small (1–2 vol% euhedral olivine and euhedral-subhedral clinopyroxene), the groundmass is dominated by seriate clinopyroxene and olivine crystals that comprise at least 20 vol% of the rock. Clinopyroxene dominates over olivine in about an 8-1 ratio, with the rest of the groundmass comprised of cryptocrystalline quench mesostasis, elongate plagioclase microlites, and tiny (several  $\mu$ m) grains of rare magnetite. Cr-spinel is found solely as occasional small (10–25  $\mu$ m across), brown, euhedral inclusions in olivine crystals of all sizes.

#### Chemistry

The total range in Cr-spinel composition from Unit 1 is shown in Figure 3 and in Tables 5 and 6, with representative spinel analyses shown in Table 4. Figure 3 shows that the Cr-spinels have substantially higher Cr# at a given Mg# than spinels from MORBs or the more MORB-like lavas from Sites 834 and 836. NiO, ZnO, and MnO are minor constituents of the Unit 1 spinels (Table 4), with MnO

typically increasing and NiO decreasing from megacryst core to rim (see Analyses 31–33 and 37–38 in Table 4).

Analytical traverses across the large Cr-spinel megacrysts show a striking range in composition. Large spinels from the unit margins have highly magnesian cores with Mg# approaching 0.7; in contrast, their rims have much lower Mg#, with values approaching as low as 0.3 (Spinel Traverses 839A-24X1, 839B-12R2, and 839B-16R1; Fig. 5). Cores of large Cr-spinel grains from the unit interior have much lower Mg# (Spinel Traverses 839B-15R1-T1 and 839B-15R1-T3; Fig. 5), with some grains showing little variability in composition (Spinel Traverse 839B-15R1-T3; Fig. 5). Curiously, all traverses of large Cr-spinel grains show little variation or only slight increases in Cr#, despite the large declines in Mg# between Cr-spinel cores and rims.

Cr-spinel inclusions in olivine share the high Cr# of the Cr-spinel megacrysts, but typically have lower Mg# (Analysis 25 in Table 4). Several Cr-spinel inclusions in the outer portions of olivine phenocrysts and a groundmass Cr-spinel crystal rim exhibit substantially higher amounts of TiO<sub>2</sub> (see Analyses 30 and 35–36 in Table 4) than the megacrysts and other inclusions, which typically have below 0.4% TiO<sub>2</sub>.

In the finest grained upper portion of Unit 1, large, round olivine phenocrysts show core-to-rim variations in Mg# similar to those exhibited by the spinels (Olivine Traverse 839A-24X1; Fig. 5). Within the interior of Unit 1, both the core Mg# and the core-to-rim variations in phenocrystic olivine Mg# are lower (Analyses 12–13 in Table 7), again mirroring the Cr-spinel variations.

Unit 3 Cr-spinel show similarly high Cr# at a given Mg#, but the overall range in composition and zoning of the megacrysts is less (Tables 4-6 and Fig. 3). The cores of the large, discrete Cr-spinel megacrysts exhibit even higher amounts of Mg# (as much as 0.75; see Spinel Traverses 839B-20R1, 839B-23R1-T2, 839B-23R1-T4, and 839B-25R1 in Fig. 6 and Analyses 39, 51, and 53 in Table 4). In contrast, nearly all Cr-spinel rims in contact with fine-grained quench mesostasis or glass exhibit Mg# ratios in the narrow range of 0.53-0.57 (Table 4 and Fig. 6). Although the zoning in Mg# in these large crystals is substantial, Cr# again shows little variation from core to rim. Back-scattered electron images of these Cr-spinels (Plate 3) image these compositional variations poorly, but they do show that Cr-spinel megacrysts in the coarser groundmasses can be rimmed by thin ( $\approx 2 \,\mu m$ ) bands of Ti-rich magnetite. Ridley (1977) found similar magnetite rims on Cr-spinels from Rhum and Muck in Scotland. TiO2 is very low in nearly all Unit 3 Cr-spinels (<0.4%, with rims and



Figure 4. Core-to-rim microprobe traverses across olivine and Cr-spinel from Site 834 Unit 7 (Sample 135-834B-30R-3, 94–104 cm). Mg# = Mg/(Mg + Fe<sup>2+</sup>) and Cr# = Cr/(Cr + Al + Fe<sup>3+</sup>). Melt Mg# refers to equilibrium melt Mg# calculated either from olivine (Roeder and Emslie, 1970) or Cr-spinel (Allan, 1992) compositions (see text for algorithm explanations). Note that both phases are only slightly zoned, and that their calculated equilibrium melt Mg# closely match.

inclusions showing slightly higher values; Table 4), the sole exception being a small ( $35 \times 30 \ \mu m$ ) groundmass grain (Analyses 55–56 in Table 4). MnO, NiO, and ZnO are again minor constituents (Tables 4–5), with MnO increasing and NiO decreasing from core to rim.

The abundant Unit 3 Cr-spinel inclusions in olivine show a similar range in composition to the Cr-spinel megacrysts. The larger host olivine crystals are typically zoned in composition, with Figure 6 showing two examples occurring in quench glass. Cr-spinel inclusions in the higher Mg# cores of these zoned olivines contain higher Mg# than do Cr-spinels found in the outer, lower Mg# olivine margins. Examples shown in Table 4 include Analyses 47, 50, and 60–61, found within olivine phenocryst cores, and Analysis 43, which is included within an olivine phenocryst rim. Individual spinel inclusions are typically unzoned (Analyses 60–61 in Table 4).

Unit 4 Cr-spinel inclusions show only a narrow range in composition (Tables 4–6), sharing the high Cr# and Mg# and low  $TiO_2$  nature of the other Site 839 spinels. The host olivines (as well as other, non-spinel-bearing olivine) are sharply zoned, with Fo<sub>89</sub> cores and Fo<sub>81.5–82.5</sub> rims (see Analyses 25–27 in Table 7).

# INTERPRETATIVE ANALYTICAL METHODS: INFERRING MELT Mg/(Mg + Fe<sup>2+</sup>)

In this paper, I use an algorithm that directly determines coexisting melt Mg# from a given spinel composition, similar to the approach using olivine composition (e.g., Roeder and Emslie, 1970; Ulmer, 1989). This algorithm was used by Allan (1992) to determine melt composition from relict Cr-spinels of highly altered lavas and sills from the Japan Sea, with the derivation produced in full here to show where analytical assumptions were made. The algorithm is based upon the spinel model adopted by Allan et al. (1988) to examine directly spinel-melt, Mg-Fe exchange equilibria in natural basaltic magmas.

Cr-spinel is a complex mineral solution best described by reciprocal solution theory (Wood and Nicholls, 1978; Sack, 1982; Sack and Ghiorso, 1991a, 1991b). Spinel solution energetics must be accounted for if spinel compositions are to be used to infer coexisting melt composition. Here I use a simplified version of the crystal chemical model of spinel derived by Sack (1982), assuming that spinel behaves as an ideal reciprocal solution model (Allan et al., 1988). This model assumes ideal mixing between Mg and Fe2+ in the host melt and follows the experimental results of Roeder and Reynolds (1991) in regarding the pressure effect on spinel-melt equilibrium as negligible over the pressures of interest (< 10 kbar). Although more complex spinel models have become recently available (Sack and Ghiorso, 1991a, 1991b), the simpler model used here has proved quite robust in predicting the composition of quenched glasses enclosing Cr-spinels (Allan, 1992; published data on N-MORBs from Allan et al., 1987, 1988, 1989, as well as unpublished data from N-, T-, and E-MORBS from the northern Juan de Fuca Ridge). From Allan (1992), a distribution coefficient may be defined for spinel-melt Mg-Fe<sup>2+</sup> equilibrium:

$$K_D^{Sp-Liq} = \begin{pmatrix} X & \underset{M_S^{2^*}}{\operatorname{M}_{Fe^{2^*}}} \\ X & \underset{Fe^{2^*}}{\operatorname{Ind}} \end{pmatrix} \begin{pmatrix} X & \underset{Fe^{2^*}}{\operatorname{Fe^{2^*}}} \\ X & \underset{M_S^{2^*}}{\operatorname{Spinel}} \end{pmatrix}.$$
(1)

Because of the reciprocal solution behavior within spinel, this  $K_D$  will change with spinel composition. Following Sack (1982), Allan et al. (1988), and Allan (1992), the Mg-Fe<sup>2+</sup> exchange between spinel and melt may be written as

$$\ln K_{D}^{SP-LIQ} = -\frac{\Delta \overline{G}_{EX}^{\circ}}{RT} + \frac{\Delta \mu_{23}^{\circ}}{RT} (X_{3}) + \frac{\Delta \mu_{24}^{\circ}}{RT} (X_{4}) + \frac{\Delta \mu_{25}^{\circ}}{RT} (X_{5}) , \quad (2)$$

$$\Delta \overline{G}_{EX}^{\circ} = (\overline{G}_{MgO}^{\circ LQ} - \overline{G}_{FeO}^{\circ LQ}) + (\overline{G}_{FeAl_{2}O_{4}}^{\circ SP} - \overline{G}_{MgAl_{2}O_{4}}^{\circ SP}) ,$$

$$\Delta \mu_{23}^{\circ} = (\overline{G}_{MgCr_{2}O_{4}}^{\circ SP} + \overline{G}_{FeAl_{2}O_{4}}^{\circ SP}) - (\overline{G}_{FeCr_{2}O_{4}}^{\circ SP} + \overline{G}_{MgAl_{2}O_{4}}^{\circ SP}) ,$$

$$\Delta \mu_{24}^{\circ} = \left(\frac{1}{2} \overline{G}_{Mg2TO_{4}}^{\circ SP} + \overline{G}_{FeAl_{2}O_{4}}\right) - \left(\overline{G}_{FeCr_{2}O_{4}}^{\circ SP} + \overline{G}_{MgAl_{2}O_{4}}^{\circ SP}\right) ,$$

$$\Delta \mu_{25}^{\circ} = (\overline{G}_{Mg2TO_{4}}^{\circ SP} + \overline{G}_{FeAl_{2}O_{4}}^{\circ SP}) - (\overline{G}_{FeO_{4}}^{\circ SP} + \overline{G}_{MgAl_{2}O_{4}}^{\circ SP}) ,$$

$$\Delta \mu_{25}^{\circ} = (\overline{G}_{MgEFeO_{4}}^{\circ SP} + \overline{G}_{FeAl_{2}O_{4}}^{\circ SP}) - (\overline{G}_{FeO_{4}}^{\circ SP} + \overline{G}_{MgAl_{2}O_{4}}^{\circ SP}) ,$$

where

$$X_3 = \frac{1}{2} \eta_{Cr^{3+}}, X_4 = \eta_{Tr^{4+}}^{SP}, X_5 = \frac{1}{2} \eta_{Fe^{3+}}^{SP}$$

and the  $\eta_i$  terms are the number of i cations in a formula unit based on three cations (Sack, 1982; Hill and Sack, 1987). Given the spinel composition, a reasonable temperature of crystallization, and the values for  $\Delta \overline{G}\,^\circ_{EX}$ ,  $\Delta \mu^\circ_{23}$ ,  $\Delta \mu^\circ_{24}$ , and  $\Delta \mu^\circ_{25}$ , the (Mg/Fe<sup>2+</sup>) ratio of the melt that crystallized the spinels may be explicitly solved as

$$\left(\frac{Mg^{2+}}{Fe^{2+}}\right)^{\text{liquid}} = \left(\frac{Mg^{2+}}{Fe^{2+}}\right)^{\text{spinel}} \times e^{\left(\left(-\Delta \overline{G}_{ex}^{*} + \Delta \mu_{2s}^{*}(X_{3}) + \Delta \mu_{2s}^{*}(X_{4}) + \Delta \mu_{2s}^{*}(X_{3})\right)/RT\right)}.$$
(3)

573

#### Table 7. Representative olivine analyses.

Hole:	834A	834A	834B	834B	834B	836A	836A	836B	836B	836B	839A	839B	839B
Core, section:	12X-CC	13X-1	22R-2	26R-1	28R-1	5X-1	5X-1	2R-1	2R-1	2R-1	24X-1	15R-1	15R-1
Interval (cm):	0-3	0-10	28-29	53-65	35-42	37-40	37-40	14-16	14-16	14-16	19-22	27-31	27-31
Analysis no.:	1	2	3	4	5	6	7	8	9	10	11	12	13
Description:	G	G	GR	G	G	GC	GR	GC	GR	GR	PR	PC	PR
Unit:	1	1	7	7	7	3	3	3	3	3	1	1	1
Major elements (wt%):													
SiO <sub>2</sub>	39.45	38.96	39.89	39.08	40.07	39.56	38.80	40.48	40.26	40.36	39.33	39.23	38.91
FeO	13.66	14.34	13.27	14.49	12.49	12.11	16.74	12.02	12.74	12.49	14.09	15.99	18.16
MnO	0.23	0.24	0.23	0.25	0.17	0.20	0.25	0.21	0.21	0.23	0.23	0.22	0.30
NiO	0.14	0.09	0.18	0.17	0.21	0.21	0.12	0.17	0.13	0.15	0.19	0.13	0.19
MgO	46.19	45.77	47.00	45.90	47.39	47.60	44.00	48.08	47.60	47.56	46.09	44.33	42.42
CaO	0.34	0.37	0.34	0.31	0.35	0.35	0.36	0.33	0.33	0.35	0.20	0.20	0.23
Total	100.00	99.78	100.90	100.19	100.68	100.04	100.28	101.28	101.27	101.13	100.13	100.10	100.21
Fo	0.858	0.851	0.863	0.850		0.875	0.824	0.877	0.869	0.872	0.854	0.832	0.806
Predicted melt Mg# Coexisting spinel analysis no. Predicted melt Mg# Ol–Sp T (°C)	0.619	0.606	0.630	0.604	0.646	0.654	0.558	0,658	0.643 21 0.644	0.647 24 0.639	0.611 25 0.616	0.572	0.529

Notes: P = phenocrysts, M = microphenocrysts, G = groundmass-sized crystals (although can represent crystals in glass). C = core, and R = rim. Fo = olivine forsterite content. Predicted melt Mg# represents calculated equilibrium melt Mg# based upon methods of Roeder and Emslie (1970) using olivine-silicate liquid K<sub>D</sub> of 0.27, as discussed in text. Where analyzed, coexisting Cr-spinel sample number and corresponding calculated equilibrium melt Mg# are given. Olivine-spinel geothermometry calculated from a program provided by R. Sack, based upon the spinel solution model of Sack and Ghiorso (1991a, 1991b). Hole, core, section, and interval (cm) designations follow standard ODP conventions and represent area in core from which analyses were made.

Values of  $\Delta \mu^{\circ}_{23}$ ,  $\Delta \mu^{\circ}_{24}$ , and  $\Delta \mu^{\circ}_{25}$ , determined experimentally by Hill and Sack (1987), are 4.80,  $3.5561 + (0.0015698 \cdot T^{\circ}_{K})$ , and 6.39 kcal/gfmw, respectively.  $\Delta \overline{G}^{\circ}_{EX}$  may be derived algebraically (Allan, 1992), borrowing an equation for spinel-melt Mg-Fe<sup>2+</sup> exchange equilibria from Hill and Sack (1987):

$$\ln K_{D}^{Ol-Sp} = -\frac{\Delta \overline{G}_{EX}^{0}}{RT} + \frac{\Delta \mu_{23}^{0}}{RT} (X_{3}) + \frac{\Delta \mu_{24}^{0}}{RT} (X_{4}) + \frac{\Delta \mu_{25}^{0}}{RT} (X_{5}) + \frac{o\iota \Delta \overline{G}_{X}^{0}}{2RT} \left\{ 1 - 2X_{Fa}^{Ol} \right\}$$
(4)

where the last term represents a correction for the non-ideal solution behavior of olivine. The experimentally determined values for the olivine-liquid  $\Delta \overline{G}^{\circ}_{EX}$  and for  ${}^{Ol}\Delta \overline{G}^{O}_{X}$  are 1.33795 – (0.0009539  $\cdot T_{K}$ ) and 1.68 kcal/gfw, respectively (Hill and Sack, 1987). In addition, one must assume a K<sub>D</sub> for olivine-liquid Mg-Fe<sup>2+</sup> exchange and an average composition of olivine, with this last assumption having only a very minor effect. Although the commonly accepted value of this K<sub>D</sub> for olivine-melt exchange is about 0.3 (Roeder and Emslie, 1970; Ulmer, 1989), most MORB-like tholeiitic basalts where quench glass has been analyzed yield values that average about 0.27 (Bender et al., 1978; Perfit and Fornari, 1983; Allan et al., 1989). Analyses of glass-olivine pairs in these Lau Basin backarc sites are more consistent with the 0.27 K<sub>D</sub> value (Hawkins and Allan, this volume); the practical effect of this assumption is a lowering of the predicted  $Mg/(Mg + Fe^{2+})$  by about 0.02 from that predicted using a K<sub>D</sub> of 0.3. Assuming an average magmatic temperature of about 1200°C (consistent with crystallization temperatures of Forsythe and Fisk, this volume), the derived  $\Delta \overline{G}^{\circ}_{EX}$ from these values and equations using the olivine-spinel exchange data of Hill and Sack (1987) is 3.14 kcal/gmfw.

The validity of this approach is shown by the success of the spinel model in matching the actual quenched-glass compositions and in predicting melt Mg# similar to those predicted from the coexisting olivine. Glass was available to the author for analysis from Site 839 Unit 23 (the results are given in Table 2). Figure 6 illustrates the transects of three spinel phenocrysts in the quenched glass analyzed (Spinel Transect 839B-23R1-T2) and fine-grained quench mesostasis (Spinel Transects 839B-20R1, 839B-23R1-T4, and 839B-25R1) from this unit. Other examples of Cr-spinel phenocryst rim compositions in contact with glass are given in Table 4 (Analyses 49 and 52). The predicted Mg# for coexisting melt from these Cr-spinel phenocryst rim analyses closely matches that of the analyzed glass (assuming that

Fe<sup>3+</sup>/total Fe is 0.15) and with those predicted from the rims of olivine phenocrysts occurring within the glass (Olivine Transects 839B-23R1-T2 and 839B-23R1-T3 in Fig. 6, assuming a  $K_D$  of 0.27 for olivine-melt Mg-Fe<sup>2+</sup> exchange).

Table 7 lists other predicted melt Mg# ratios from analyzed coexisting spinel-olivine pairs. These pairs represent either crystals touching in the groundmass or Cr-spinel inclusions in olivine, with analyses spaced as closely together as possible. Agreement in the predicted ratios is quite close, with differences in Mg# typically much less than 0.01. Although no analyzed spinel-olivine pairs are present at Site 834, the ranges in Mg# predicted from Cr-spinel and olivine are reasonably close (Table 6), and traverses of olivine and spinel in the fine-grained samples yield remarkably similar estimates of melt Mg# (Fig. 4), which in general closely match those calculated from glass analyses (Table 3) reported elsewhere in this volume (Nilsson, this volume).

## DISCUSSION

The data clearly show two compositional and morphological groups of Cr-spinel from Leg 135 lavas. As discussed earlier, the Cr-spinels from Sites 834 and 836 are similar to MORB Cr-spinel in composition and nature of occurrence, reflecting similarities in magmatic compositions, host mantle source compositions (likely spinel lherzolite), and crystallization conditions to that of MORB (Dick and Bullen, 1984; Allan et al., 1988). In contrast, the Site 839 Cr-spinels are much higher in Cr# at a given Mg# than MORB spinels, instead closely resembling Cr-spinel from high-Mg, low-Al, arc-related boninites and basalts (Dick and Bullen, 1984), consistent with the arclike chemistry of the host lavas. The Mg-rich cores of these spinels have substantially lower Al2O3 than spinels from abyssal dunites; instead, they are quite similar in composition to some Cr-rich spinels associated with extremely depleted alpine peridotites and ophiolitic ultramafics thought to originate in association with volcanic arcs, such as those found within the Troodos and Josephine ophiolites (Dick and Bullen, 1984). In addition, the Site 839 Cr-spinel megacrysts are an order of magnitude larger in size than those from MORB or Sites 834 and 836, indicating very different conditions of crystallization.

### Cr-spinel from Sites 834 and 836

Cr-spinels in the finer grained portions of lavas from Sites 834 and 836 exhibit only minor compositional variations, indicating that they represent near-equilibrium liquidus compositions. Exceptions are found where the groundmass is coarser grained, where spinel has

#### Table 7 (continued).

Hole:	839B	839B	839B	839B	839B	839B	839B	839B	839B	839B	839B	839B	839B	839B
Core, section:	19R-1	19R-1	19R-1	20R-1	23R-1	23R-1	23R-1	23R-1	25R-1	25R-1	25R-1	25R-1	25R-1	25R-1
Interval (cm):	59-63	59-63	50-53	81-85	28-31	28-31	7 to 11	28-31	35-38	35-38	35-38	43-45	43-45	43-45
Analysis no.:	14	15	16	17	18	19	20	21	22	23	24	25	26	27
Description:	MM	MR	GR	PC	PC	PR	PM	PM	GR	PM	PC	PR	PC	PC
Unit:	3	3	3	3	3	3	3	3	3	3	3	4	4	4
Major elements (wt%):														
SiO <sub>2</sub>	40.06	40.75	37.46	39.24	40.17	39.28	39.89	40.07	39.63	40.67	40.41	39.63	40.51	40.60
FeO	12.37	12.66	22.44	10.78	8.97	13.32	9.18	9.00	12.20	9.62	8.32	16.53	10.67	10.75
MnO	0.16	0.23	0.28	0.20	0.16	0.18	0.16	0.16	0.22	0.16	0.13	0.28	0.17	0.20
NiO	0.19	0.13	0.07	0.34	0.31	0.15	0.28	0.25	0.16	0.32	0.34	0.09	0.18	0.18
MgO	47.47	47.31	39.40	48.93	50.25	46.73	49.97	49.98	47.60	50.02	50.93	43.62	48.63	48.41
CaO	0.23	0.21	0.24	0.17	0.18	0.26	0.20	0.19	0.25	0.20	0.20	0.25	0.22	0.23
Total	100.48	101.28	99.89	99.65	100.05	99.92	99.68	99.64	100.06	100.98	100.33	100.40	100.39	100.37
Fo	0.872	0.869	0.76	0.890	0.909	0.862	0.907	0.906	0.874	0.903	0.916	0.825	0.890	0.889
Predicted melt Mg#	0.649	0.643	0.46	0.686	0.729	0.628	0.724	0.723	0.652	0.715	0.747	0.559	0.687	0.684
Coexisting spinel analysis no.	42	43		44			50	47	58	59	61		64	63
Predicted melt Mg#	0.647	0.631		0.683			0.729	0.719	0.657	0.717	0.752		0.683	0.682
Ol-Sp T (°C)	1246	1218		1219			1230	1158	1251	1221	1211		1213	1224

reequilibrated with Fe-rich interstitial melt during extended cooling. Nevertheless, the core of a moderately zoned spinel groundmass grain from Site 836 shown in Plate 1C (Analysis 21 in Table 4) may retain evidence of derivation from a more primitive parental melt. This spinel core analysis predicts a melt Mg# somewhat higher (0.665) than that predicted by its associated spinel rim (Analysis 22 in Table 4) and other Site 836 spinel inclusions and groundmass grains (about 0.64 in the finer grained Sample 135-836B-2R-1, 14-16 cm; see Analyses 22 and 24 in Table 4). An attached olivine crystal (Analyses 8-9 in Table 7) is also zoned, with its more magnesian core predicting similarly higher melt Mg#. Analyzed glass compositions (Table 3; Hawkins and Allan, this volume) show that the melt Mg# was indeed about 0.64 upon eruption, indicating that minor amounts of olivine fractionation occurred since initial spinel crystallization. A similar example of evidence for more primitive parental melt is shown by Analyses 10-11 of a Cr-spinel inclusion within plagioclase from Site 834 Unit 7 (Table 4). These Cr-spinels grew from a melt of about Mg# 0.67, higher than that analyzed for the quenched glass (Table 3).

A significant result from the Site 834 Unit 1 spinel analyses is that the whole-rock composition reported for Unit 1 (Table 1) cannot represent the parental melt of the analyzed Unit 1 spinels. The spinel and olivine analyses predict melt Mg# of 0.58–0.63, the higher Mg# ratios quite similar to the glass Mg# (Table 3). These Mg# ratios are substantially higher than the whole-rock Mg# of 0.56 (Table 1), indicating that Unit 1, recovered as pieces of rubble in two cores (with mineral and glass analyses performed on different pieces of rubble than the whole-rock analysis), actually represents multiple eruptive units that had variable chemistry.

## **Cr-spinel from Site 839**

The zoned, high Mg# Cr-spinel megacrysts of Units 1 and 3 from Site 839 have very similar compositional characteristics, and therefore likely share a similar origin. The principle differences between spinels from the two units are that (1) small, groundmass Cr-spinels are lacking in Unit 1, but they are present in Unit 3; and (2) the megacrysts of the coarser grained Unit 1 are resorbed and exhibit much greater zonation in terms of Mg#. These similarities and differences are crucial for understanding the origin of these large Crspinels, particularly in determining whether they grew from a melt or instead represent Cr-spinel xenocrysts originating from partially digested peridotitic wallrock. Unit 3 will be discussed first, because the finer grained nature of the host rock and availability of quenched glass affords more confident petrogenetic interpretation.

## Unit 3

A key feature of the Unit 3 Cr-spinels residing in glass or finely quenched mesostasis is that their rim compositions match the Mg# of the host glass (Tables 2-3 and Fig. 6) and therefore indicate equilibrium with the melt in terms of Mg#. The strong zoning in Cr-spinel megacryst Mg# accompanied by only minor change in Cr# indicates that equilibrium crystal growth from an evolving parental liquid did not produce the zoning. As discussed in relation to Site 834 spinels, there is strong energetic coupling between Fe<sup>2+</sup> and Cr<sup>3+</sup> and Mg<sup>2+</sup> and A13+ in the spinel solid solution (Sack, 1982; Sack and Ghiorso, 1991a, 1991b). This is reflected by the size of the chemical potential of the appropriate exchange reaction ( $\mu^{\circ}_{23}$ ) associated with Equation 2 above. The chemical potential of this reaction (4.8 kcal/gfmw) is greater than that derived here for Mg-Fe2+ exchange between melt and Cr-spinel (3.14 kcal/gfmw), indicating that growth of Cr-spinel from an evolving liquid should produce spinel with declining Mg# and increasing Cr# (shown experimentally for a Site 839 Unit 3 sample by Forsythe and Fisk, this volume). This decoupling of the divalent cations from the trivalent cations is well documented in spinels that have undergone compositional reequilibration as a result of metamorphic or hydrothermal alteration processes (Roeder et al., 1979; Engi and Evans, 1980; Sack, 1980; Franzson et al., 1986; Allan, 1992). Therefore, the zoning in these Cr-spinel megacrysts is almost certainly due to reequilibration of a previously crystallized spinel megacryst with an already evolved silicate liquid (Forsythe et al., this volume). In this light, smaller crystals of Cr-spinel would be more likely to have reequilibrated in Mg#, leading to the lower predicted melt Mg# of the smaller Cr-spinel crystal cores (Analyses 48 and 55 in Table 4).

Several lines of evidence are consistent with this interpretation, and also indicate that the spinel megacrysts grew from a primitive melt rather than represent wallrock xenocrysts. First, Cr-spinel inclusions in the more magnesian olivine phenocryst cores also predict high melt Mg# (Table 4); these certainly grew from silicate liquids. Second, olivine phenocrysts show similar zoning in  $Mg/(Mg + Fe^{2+})$ , with their cores also having crystallized from melts of very high Mg# (Fig. 6). The spinel inclusions in the outer margins of the olivine phenocrysts have reequilibrated along with the olivine margins, as shown by the similarity in predicted melt Mg# in joint analysis pairs (Table 7). Similar reequilibration of spinel inclusions in olivine has been reported within cooling Kileauea Iki lava lake samples by Scowen et al. (1991). Third, experimental evidence (Forsythe and Fisk, this volume) clearly shows that the most magnesian spinel megacryst interiors are in equilibrium with low Al<sub>2</sub>O<sub>3</sub>, high Mg# melt, whereas the low Mg#, high Cr# megacryst margins do not represent equilibrium phase compositions under magmatic conditions. This evidence is supported by olivinespinel geothermometry calculations shown in Table 7 and based upon the spinel crystal-chemical model of Sack and Ghiorso (1991a, 1991b, 1991c). This spinel crystal-chemical model more fully accounts for the non-ideal solution behavior of the chromite component in the spinel structure than the simpler model used here; as a result, the nonequili-



Figure 5. Core-to-rim microprobe traverses across zoned olivine and Cr-spinel from Site 839 Unit 1 (Samples 135-839A-24X-1, 19–22 cm; 135-839B-12R-2, 20-24 cm; 135-839B-15R-1, 27–31 cm; and 135-839B-16R-1, 60–63 cm). Mg# = Mg/(Mg + Fe<sup>2+</sup>) and Cr# = Cr/(Cr + Al + Fe<sup>3+</sup>). Melt Mg# refers to equilibrium melt Mg# calculated from either olivine (Roeder and Emslie, 1970) or Cr-spinel (Allan, 1992) compositions (see text for algorithm explanations). Interiors of Cr-spinel and olivine from the upper and lower portions of the unit show evidence of crystallization from a melt of very high Mg# (0.74–0.77), with their margins showing substantial reequilibration in Mg# (but not Cr#) with residual liquid during extended unit cooling. Cr-spinel from Samples 135-839A-24X-1, 19–22 cm, and 135-839B-12R-2, 20–24 cm (representing the finer grained upper portion of the unit), show the least reequilibration. In contrast, Cr-spinel from the unit interior (Cr-spinel Traverses 839B-15R1-T1 and -T3) show spinel interiors that have equilibrated with melts of much lower Mg# (0.55–0.56); Traverse 839B-15R1-T3 abuts against a clinopyroxene grain that apparently armored the Cr-spinel grain margin from continued reequilibration during cooling.



Figure 6. Core-to-rim microprobe traverses across zoned olivine and Cr-spinel from Site 839 Unit 3 (Samples 135-839B-20R-1, 81–85 cm; -23R-1, 7–11 cm; -23R-1, 28–31 cm; and -25R-1, 35–38 cm). Mg# =  $Mg/(Mg + Fe^{2+})$  and  $Cr# = Cr/(Cr + Al + Fe^{3+})$ . Melt Mg# refers to equilibrium melt Mg# calculated either from olivine (Roeder and Emslie, 1970) or Cr-spinel (Allan, 1992) compositions (see text for algorithm explanations). All traverses represent analyses of mineral grains in quench glass or fine-grained mesostasis. Note that the Cr-spinel zoning is pronounced only in the divalent cations (Mg#) and not in the trivalent cations (Cr#). Rim compositions of both the Cr-spinel and the olivine consistently predict equilibration with a melt having Mg# of 0.63–0.64, similar to the Mg# of the analyzed glass (Table 2). In contrast, Cr-spinel and olivine cores both crystallized from melts of much higher Mg#, indicating profound disequilibria with the host glass (quenched host melt) and strong evidence for magma mixing.

brium trivalent cation compositions of the megacrysts cause geologically unreasonable variations in predicted geothermometry to be produced (lower Mg/[Mg +  $Fe^{2+}$ ] olivine-spinel pairs should not produce higher magmatic temperature estimates, in accordance with the results of Forsythe and Fisk, this volume). Finally, the low Cr of the Unit 3 glass composition (about 130 ppm; Table 2) suggests that Cr-spinel may not be stable within the melt (Allan et al., 1988), a deduction supported by the thin Ti-rich magnetite rims found on spinel megacryst grains within mesostases (Plate 3).

Overall, the evidence suggests that a highly primitive magma with a Mg# above 0.75 and perhaps approaching 0.80 rapidly mixed with a much more evolved magma shortly before eruption, perhaps within a shallow magma chamber. The presence of a single small (30 by 35  $\mu$ m), Ti-rich, Cr-spinel crystal in the groundmass (Analyses 55–56 in Table 4) is perplexing, but may reflect growth from an evolved melt. Andesitic Units 2 and 9 at Site 839 represent candidate evolved magmas for mixing; they have Mg/(Mg + Fe<sup>2+</sup>) of 0.43–0.50 (Parson, Hawkins, Allan, et al., 1992) and lack Cr-spinel. The mixing event must have occurred relatively soon before eruption to have preserved the sharp zoning seen in the Unit 3 olivine, as the work of Helz (1980, 1987) shows that olivine reequilibration within melt is rapid.

## Unit 1

In the light of the above evidence for the similar Unit 3 spinels, the high Mg# cores of the zoned Unit 1 Cr-spinel megacrysts (Fig. 5) can be deduced to have crystallized from primitive melts with low Al<sub>2</sub>O<sub>3</sub> and Mg# ratios of 0.75 or above. These estimates are far higher than the Mg# of the analyzed whole-rock samples (Table 1). The zoned olivine phenocryst cores at the top of the unit also contain evidence for this primitive parental liquid, with similar estimates of magmatic Mg# (Fig. 5). The relatively Ti-rich Cr-spinel inclusions and groundmass grain rim (Table 4) may have crystallized from a more evolved melt. In contrast, the low Mg# ratios of the other Ti-poor Cr-spinel megacryst rims represent reequilibration of these Cr-spinels with Fe-rich, interstitial, residual silicate liquid during extended cooling, as reflected by the relatively coarse groundmass grain size. These residual liquids were highly corrosive to the megacrysts, resulting in both Cr-spinel dissolution and reequilibration.

As in the Unit 3 samples, Unit 1 appears to represent a hybrid unit resulting from magma mixing between primitive and more evolved melts shortly before eruption. In the absence of other evidence, the relatively unzoned interiors of Cr-spinel megacrysts from the middle of Unit 1 (Cr-spinel Traverses 839B-15R1-T1 and 839B-15R1-T3; Fig. 5) may provide an estimate for the hybrid melt Mg# after mixing. The Cr-spinels in this portion of the unit appear to have completely reequilibrated with melt having an Mg# of about 0.54-0.57, with the megacryst rim of Cr-spinel Traverse 839B-15R1-T3 having been shielded from the interstitial residual silicate liquids where it abuts against a clinopyroxene grain. An estimate of 0.60 for the melt Mg# in the finer grained top of the unit is given by the phenocryst rim composition of Olivine Traverse 839A-24X1 (Fig. 5); other olivine phenocryst rims give estimates of 0.59-0.61, whereas groundmass olivine grains from the unit top give lower estimates of 0.54-0.57, consistent with the Cr-spinel estimates.

## Petrogenesis of Units 1 and 3

Any successful model for the petrogenesis of these host lavas must explain the large size of the Cr-spinel megacrysts and the relative abundance of Cr-spinel in Unit 3, both represented in the extraordinarily high Cr contents of the whole-rock analyses reported in Table 1. The primitive liquids required to produce such magnesian Crspinels could represent direct melts of a highly depleted mantle (such as harzburgite or low-Al, clinopyroxene-poor lherzolite), the depleted character required by the low Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> nature of the megacrysts (Basaltic Volcanism Study Project, 1981; Dick and Bullen, 1984).

578

Stokes Law calculations, assuming a melt density of 2.7 gm/cm3 (Carmichael et al., 1974), a Cr-spinel density of 4.6 g/cm3 (Klein and Hurlbut, 1985), and a viscosity of about 100 poise (Carmichael et al., 1974), show that grain settling velocities for the larger Cr-spinel crystals range from 0.04 cm/s for crystals of 2-mm diameter to 0.002 cm/s for crystals of 0.5-mm diameter. These velocities indicate that magmatic conditions cannot have been quiescent for the larger Crspinels to crystallize without settling out of the magma. The euhedral shapes of the Cr-spinels found in glass or fine grained groundmasses indicate growth while suspended within a liquid and not within a crystal mush on the floor of a magma chamber. Rapid spinel growth resulting from crustal assimilation or magma mixing with evolved magmas within crustal magma chambers has been invoked to explain the formation of spinel-rich layers in basic layered intrusions (Henderson and Suddaby, 1971; Irvine, 1975, 1977; Ridley, 1977; Dick and Bullen, 1984), but it is difficult to see how such an event could have crystallized such highly magnesian Cr-spinels. However, the relatively picritic nature of the Unit 3 lavas requires a means of crystal concentration, perhaps a cumulate zone near the base of a shortlived convecting magma chamber fed by primitive magma. The most straightforward explanation of Units 1 and 3 petrogenesis is that they represent infusion of new, evolved magma from a separate magma batch into the lower crystal-rich, cumulate portion of such a magma chamber, with subsequent rapid eruption. A second, less likely explanation is that the magma-mixing events represent self-mixing within a strongly zoned magma chamber, although this would require keeping near-primary melt and highly evolved melt in separate parts of a magma chamber where active upwelling must occur.

## Unit 4

Unit 4 Cr-spinels, together with the high Mg# host olivine cores they are found within, record evidence of a parental melt having an Mg# of about 0.68 and a temperature of about 1210°-1220°C (Tables 4, 6, and 7). Although this Mg# ratio approaches that of the wholerock analysis given in Table 1, the crystal-rich nature of the unit, the sharply zoned olivine, and the consistently low Mg# of the olivine rims (which predict eruptive melt Mg# of 0.54-0.56) indicates that the unit did not evolve by simple crystal retention during crystal fractionation before and during eruption. Instead, magma mixing involving a crystal-laden, more primitive melt with Mg# of 0.68 and a more evolved melt with Mg# of less than 0.54-0.56 probably occurred shortly before eruption, thereby producing and retaining the sharply zoned nature of the olivine. This magma-mixing event could represent either infusion of new magma into the lower crystal-rich portion of a preexisting magma chamber, or could represent selfmixing within a similarly well-zoned magma chamber. Unit 4, like other Site 839 basalts, represents a composite unit, and so its petrogenesis cannot be modeled with confidence using either whole-rock or glass data.

#### CONCLUSIONS

Cr-spinel from Sites 834 and 836 are similar to those analyzed from depleted N-type MORB in both composition and crystal morphology, sharing their low ferric iron and TiO<sub>2</sub>. Cr-spinels from Site 834 Unit 1 show that the recovered Unit 1 in core represents fragments of more than one eruptive unit, because the analyzed Cr-spinels in one Unit 1 sample crystallized from a melt substantially higher in Mg# than that indicated by a whole-rock analysis of another Unit 1 sample (Parson, Hawkins, Allan, et al., 1992).

Extraordinarily large (as much as several millimeters) Cr-spinel megacrysts within Site 839 lavas grew from primitive melts that have the characteristics of parental low- $Al_2O_3$  arc basalts. These melts had Mg#s from 0.75 to 0.8, representing near-primary mantle melts derived from highly depleted harzburgite or lherzolite.

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Plate 1. Photomicrographs in combined transmitted and reflected light. **A.** Photomicrograph of Sample 135-834B-22R-2, 28–29 cm, from Site 834 Unit 7 (3.5 mm across) that shows crystals of Cr-spinel (arrow points to Cr-spinel of Analyses 8–9 in Table 4) attached to phenocrysts of plagioclase. **B.** Photomicrograph of Sample 135-834B-30R-3, 94–104 cm, from Site 834 Unit 7 (1.75 mm across) that shows Cr-spinel inclusions in plagioclase (open arrow points to Cr-spinel of Analyses 14–15 in Table 4) or attached to plagioclase (closed arrow points to Cr-spinel of traverse in Fig. 4 and Analyses 16–17 in Table 4). Note the coarser groundmass of Sample 135-834B-22R-2, 28–29 cm; groundmass Cr-spinel rims from this sample have low Mg# because of substantial reequilibration with interstitial liquid during cooling. **C.** Photomicrograph of Sample 135-836B-2R-1, 14–16 cm, from Site 836 Unit 3 (3.5 mm across), with bar pointing to attached groundmass Cr-spinel (Analyses 21–22 in Table 4) and olivine (Analyses 8–9 in Table 7). The Cr-spinel and olivine cores and rims predict similar melt Mg# of 0.665, 0.658, 0.644, and 0.643, respectively. The melt compositions predicted from these rim analyses are very close to that analyzed in glasses from this unit (0.642–0.649, with an average of 0.645; Hawkins and Allan, this volume, and Table 3, this chapter). The more Mg-rich Cr-spinel and olivine cores retain evidence of a higher Mg# parental melt.



Plate 2. Photomicrographs (in combined transmitted and reflected light) of Site 839 Cr-spinels. A. 1.75 mm across. **B.** 3.5 mm across. **D-F.** All 3.5 mm across. Plates 2A–2C show rounded, resorbed Cr-spinel megacrysts from Unit 1 (Samples 135-839B-12R-2, 20–24 cm, -15R-1, 27–31 cm, and -16R-1, 60–63 cm). These samples are from the top, middle, and bottom of the unit, respectively; note that the groundmass is significantly finer grained at the top and bottom, with the coarse unit interior exhibiting an intergranular character. Microprobe traverses of these Cr-spinel grains are given in Figure 5 (Cr-spinel Traverses 839B-12R2, 839B-15R1-T1, and 839B-16R1-T1, respectively); corresponding point analyses are given in Table 4 (Analyses 28–29 for Traverse 839A-24X1; Analyses 31–33 for Traverse 839B-12R2; Analyses 37–38 for Traverse 839B-15R1-T1). Plates 2D–2F show euhedral to subhedral Cr-spinel crystals and inclusions in olivine phenocrysts from Unit 3; note the olivine phyric nature of the lavas. Plate 2D shows Cr-spinel crystals in quench glass from Sample 135-839B-23R-1, 28–31 cm; the large arrow points to the Cr-spinel of Cr-spinel Traverse 839B-23R1-T2 (Fig. 6) and Analyses 51–52 (Table 4), whereas the small arrow points to the Cr-spinel of Cr-spinel of Cr-spinel of Cr-spinel Traverse 839B-23R1-T4 (from Sample 135-839B-23R-1, 7–11 cm; Fig. 6) and Analyses 53–54 (Table 4). Plate 2F shows the Cr-spinel of Cr-spinel Traverse 839B-25R1 (from Sample 135-839B-25R-1, 35–38 cm; Fig. 6); note the small (<50 µm) spinel inclusions in the adjacent olivine.





Plate 3. Digitally enhanced back-scattered electron images of spinel. A. Profoundly zoned Cr-spinel phenocryst of Sample 135-839B-25R-1, 35–38 cm (Cr-spinel of Plate 2F); note that the zoning in Mg# is only poorly shown. B. 2- $\mu$ m-wide, Ti-rich magnetite rim of Cr-spinel phenocryst in the relatively coarse intergranular groundmass of Sample 135-839B-19R-1, 50–53 cm.