34. COMPARISON OF EXPERIMENTALLY CRYSTALLIZED AND NATURAL SPINELS FROM LEG 135¹

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ABSTRACT

Spinel synthesis experiments performed on samples from Ocean Drilling Program Leg 135 provide constraints for the formation of naturally occurring spinels in these rocks. We evaluated the effect of temperature, fO2, and magma composition on the Cr# and Mg# of spinel synthesized at a pressure of 1 atm. The experimental evidence suggests that the spinels from Hole 839B must have crystallized above 1200°C to produce Mg#s of 0.70 to 0.75 (cores) and Cr#s of 0.74 to 0.76. Core-to-rim decreases in the Mg# but not in the Cr# of the natural spinels were not reproduced in equilibrium experiments and reflect disequilibrium reactions in the rocks. This zoning implies that the spinel cores grew from a parent magma that had lower Al₂O₃ but similar Mg# to the host rock and that mixing of the parent and an evolved magma occurred shortly before eruption. We calculated a reaction constant (K1) involving Al and Cr exchange between Mg-rich spinel and liquid that is dependent on temperature and fO2, which enables us to predict the Cr#s of the liquid in equilibrium with a given spinel composition.

INTRODUCTION

Oxide minerals may indicate the temperature and pressure of their formation in a magma, the chemical composition and oxidation state of their host magma, and the processes affecting these magmas (Hill and Roeder, 1974; Fisk and Bence, 1980; Dick and Bullen, 1984; Allan et al., 1988; Anderson et al., 1991; Roeder and Reynolds, 1991; Allan, 1992). In basaltic magmas, the oxide minerals rich in Cr and Al (spinels) are particularly useful indicators because they crystallize at high temperatures and usually are present in trace amounts; thus, they have little impact on the major elements in the host magma (Irvine, 1965, 1967; Thy, 1983; Barnes, 1986; Barsdell, 1988). The effect of magma chemistry, temperature, and pressure on spinel chemistry is calibrated by experimentally synthesizing spinels at a variety of conditions from a variety of basalts.

Most experimental data for spinels in basalts are for tholeiites from mid-ocean ridges (Hill and Roeder, 1974; Fisk and Bence, 1980; Roeder and Reynolds, 1991), alkalic rocks, or continental arc basalts (Sack, 1982); few studies have been done on rocks from ocean arcs or backarc basins. Primitive, spinel-bearing, arc-like basalts with high Mg, Cr, and Ni from Hole 839B and more normal backarc basin basalts with some spinel from Hole 834B on Leg 135 (Parson, Hawkins, Allan, et al., 1992) provide an opportunity to explore spinels as petrogenetic indicators in this arc/backarc environment.

This study is an attempt to understand the relationship between spinel composition and oxygen fugacity, temperature, and composition of the basalts from two sites in the Lau Basin. We synthesized spinels in these basalts at temperatures of 1150° to 1350°C and at oxidizing and reducing conditions. To determine the effect of magma composition on spinel composition, we have also synthesized spinel from one of the basalts (839) to which was added either Mg or Al.

TERMS AND SAMPLE DESCRIPTIONS

The oxide minerals that are found in Sites 834 and 839 have Mg greater than Fe and high Al and high Cr abundances (Allan, this volume). Those from Site 834 have more Al than Cr and low Fe3+ abundances and would be termed "magnesiochromites" (Sigurdsson and Schilling, 1976), and those from Site 839 have more Cr than Al and low Fe3+ and would be termed "chromian spinels" (Sigurdsson and Schilling, 1976). For simplicity, however, we refer to oxide minerals from both of these sites as spinels throughout this paper.

Site 834 is 330 km from the Tofua Arc, and Site 839 is 220 km from the arc (Parson, Hawkins, Allan, et al., 1992). Table 1 summarizes the chemistry and petrography of the two units from which our samples were selected for experiments. The chemical analyses for Hole 834B Unit 7 and Hole 839B Unit 3 are shipboard X-ray fluorescence (XRF) analyses. The modal abundance data are for thin sections from intervals close to the samples analyzed on board (Parson, Hawkins, Allan, et al., 1992). Because we have studied a single sample from each site, throughout the text we have abbreviated the designation of Sample 135-834B-30R-3, 101-105 cm, to Sample 834 and that of Sample 135-839B-23R-1, 24-27 cm, to Sample 839.

These two starting compositions (Table 1) were selected to be representative of the more Mg-rich compositions from each site. Sample 834 is from about 20 m above the base of Unit 7, which is about 74 m thick. A thin section taken from Piece 1G (105-107 cm) is a highly phyric plagioclase basalt. It contains 16% plagioclase and 1% olivine phenocrysts. Plagioclase grains are up to 3 mm long. Olivine grains are up to 1.8 mm in diameter. Spinel is a trace component but is found in plagioclase, olivine, and groundmass. Alteration consists of minor and local replacement of mesostasis with clays (Parson, Hawkins, Allan, et al., 1992).

Chemically, Sample 834 is more similar to Lau Basin backarc basin tholeiites than to the Tonga Arc in that its trace element abundance ratios are intermediate between arc and MORB (Ewart, this volume; Hawkins and Allan, this volume; Parson, Hawkins, Allan, et al., 1992). Spinels from Unit 7 have Mg numbers [Mg#; Mg²⁺/(Mg²⁺ + Fe^{2+})] that range from 0.56 to 0.72; however, in Section 135-834B-30R-3 (from which our sample is derived), the range is 0.66 to 0.68. The chrome number $[Cr#; Cr^{3+}/(Cr^{3+} + Al^{3+})]$ for Unit 7 spinels ranges from 0.41 to 0.48, but those from Section 135-834B-30R-3 are uniform at 0.45 (Allan, this volume).

Sample 839 is from about 19.5 m above the base of the 58-m-thick Unit 3. The closest thin section to our sample (135-839B-23R-1, 24-26 cm) is a highly phyric clinopyroxene olivine basalt. Phenocryst content is 11%-17% and consists primarily of olivine. Olivine phenocrysts are from 0.5 to 3 mm in diameter. They are euhedral to subhedral and can contain small spinel inclusions up to 0.02 mm. Isolated subhedral spinel crystals also occur up to 0.4 mm in the groundmass and are darker than those in olivine. Clinopyroxene

¹ Hawkins, J., Parson, L., Allan, J., et al., 1994. Proc. ODP, Sci. Results, 135: College Station, TX (Ocean Drilling Program).

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Table 1. Starting compositions for experiments.

	5	
Hole:	834B	839B
Core, section:	30R-3	23R-1
Interval (cm):	101-105	24-27
Unit:	7	3
Sample label:	834	839
SiO ₂	49.96	50.43
TiO ₂	1.25	0.59
Al ₂ O ₃	17.67	12.66
Fe ₂ O ₃	8.99	10.36
MnO	0.13	0.17
MgO	7.84	14.86
CaO	12.15	10.92
Na ₂ O	2.59	1.21
K ₂ Õ	0.05	0.26
P205	0.12	0.07
Total	100.75	101.53
LOI	0.79	0.37
Cr (ppm)	285	1740
	Modal abun	dances (%
Interval (cm)	105-107	24-26
Plagioclase:		
Phenocryst	15.7	-
Groundmass	45.0	5-7
Clinopyroxene:		10 BI
Phenocryst	_	1-2
Groundmass	30.0	10-15
Olivine:		100 100
Phenocryst	0.9	10-15
Groundmass	2.3	3-5
Opaques:		
Phenocryst	-	
Groundmass	3.2	Tr
Mesostasis	2.7	60
Vesicles	0.2	20-25

Notes: Chemistry is from shipboard analyses by X-ray fluorescence. Chemistry and modal abundances are from Parson, Hawkins, Allan, et al. (1992). LOI = loss on ignition, and Tr = trace.

occurs as groundmass crystals less than 0.3 mm long and rarely as subhedral to euhedral, tabular to equant, isolated crystals in glomerocrysts up to 1.2 mm in length. Some crystals are sector zoned. The unit shows little evidence of alteration.

Sample 839 is chemically similar to primitive island-arc tholeiites by virtue of its MgO content of almost 15 wt% and by its trace element signature (Parson, Hawkins, Allan, et al., 1992). The unusually high compatible trace element abundances of Cr (1740 ppm) and Ni (320 ppm) in Sample 839 suggest accumulation of spinel and olivine. In fact, glass analyses from Unit 3 have nonprimitive compositions (MgO = 7.07, SiO₂ = 52.14) (Allan, this volume). The high Cr and MgO of this sample relative to the glass does not affect our results other than to increase the range of temperatures over which spinel and olivine crystallize (Hill and Roeder, 1974). Spinels from Sample 839 have a wider range of Mg# (0.50–0.75) than those from Sample 834 and higher Cr# (around 0.75). Spinels from both Samples 834 and 839 have similar Fe³⁺# of 0.06 to 0.10 (Allan, this volume).

TECHNIQUES

Sample Preparation

Whole-rock powders of the two starting compositions were ground to about 80 mesh (180 μ m). Splits of Sample 839 were mixed with either 3 wt% Al₂O₃ (839Al) or 3 wt% MgCO₃ (839Mg). (Using MgCO₃ rather than MgO as a source of Mg does not affect our results because MgCO₃ decomposes at about 750°C and the CO₂ escapes from the sample.) For each experiment, about 0.05 g of each of the two natural samples (834 and 839) and of the two mixtures (839Al and 839Mg) was mixed with polyvinyl alcohol and attached to loops of 0.127-mm Pt wire.

Run Procedure

Each of the four samples was suspended from a quenchable basket inside a Deltech vertical quench furnace. The temperature of the furnace was raised above 1400°C for at least 2 hr to ensure that no crystals remained. Runs at 1400°C appeared crystal-free, but the Cr content of these runs indicate that about 0.5 wt% spinel could have remained unmelted. The furnace temperature was then lowered to the run temperature for at least 2 days. The temperature was controlled by an external Pt-Pt10Rh thermocouple to within 2°C, and the interior furnace temperature was monitored by a second Pt-Pt10Rh thermocouple suspended inside the furnace with the samples. This thermocouple was calibrated to the melting point of gold at 1064.5°C. Oxygen fugacity was controlled with a mixture of CO2 and H2 gases. The oxygen fugacity was periodically checked during each run with a Y-stabilized zirconia cell calibrated at the iron-wustite transition at 1300°C. Oxygen fugacity remained constant during each run within ±0.1 log unit.

Diffusion of Fe from the sample to the platinum loop (Fisk and Bence, 1980; Grove, 1981; Roeder and Reynolds, 1991) was minimized by using the same Pt loop for each composition throughout the experiment. New loops, when needed, were made by melting the starting compositions for 2 hr on the loop. The loop was then quenched and the sample discarded.

At the end of each run, the charges were quenched in distilled water. Part of each sample was examined in transmitted light to determine crystallinity and phases present. Some of each sample was mounted in epoxy, and ground and polished for analysis by microprobe.

Microprobe Procedure

All analyses were performed on a Cameca SX-50 four-spectrometer microprobe at Oregon State University Electron Microprobe Laboratory. Standards consisted of natural minerals and basalt glass from the Smithsonian reference collection (Jarosewich et al., 1980) and a commercially prepared standard block (Astimex Scientific LTD, 16 Edgewood Crescent, Toronto, Canada, as well as some pure element standards. Measured concentrations were corrected for atomic number, absorption, and fluorescence effects with software provided with the microprobe.

Spinels

The standards for spinel analyses included Tiebaghi chromite for Mg and Cr, rutile for Ti, pure V, pyroxmangite for Mn, Minas Gerais magnetite for Fe, synthetic nickel silicate for Ni, and Brazil gahnite for Zn and Al. Si and Na were measured to evaluate beam overlap with glass. Samples were analyzed with an accelerating voltage of 15 kV, a beam current of 50 nA, a tightly focused beam, and 10-s counting times for each element. Mn was reduced empirically because of interference of the Cr K α and the Mn K α peaks, assuming a linear relationship between the Cr content of the spinel and the magnitude of the Mn interference. Fe³⁺ was calculated by normalizing all cations to 3.0, assuming Fe was the only multivalent cation, and by partitioning Fe between Fe³⁺ and Fe²⁺ to result in 4.0 oxygens. The precision and accuracy for these elements, based on multiple analyses of Tiebaghi chromite, are reported in Table 2.

Glasses

Glasses coexisting with chromites were analyzed using the following standards: Makaopuhi basalt glass for Si, Ti, Al, Fe, and Ca; Kakanui anorthoclase for Na; Kakanui augite for Mg; Durango fluorapatite for P; Hohenfels sanidine for K; pyroxmangite for Mn; and Tiebaghi chromite for Cr. Analytical conditions were 15-kV accelerating voltage, 50-nA beam current, defocused beam (approximately 30 µm), and 10-s counting times for all elements except Cr, which was

Table 2. Analytical precision for multiple analyses of standards.

	Average	SD	Reported
Tiebaghi chromite:			
SiO ₂	0.07	0.01	NR
TiO ₂	0.12	0.02	NR
Al ₂ Ô ₂	9.96	0.16	9.92
Cr ₂ O ₃	59.92	0.34	60.50
Fe ₂ O ₂	3.66	0.46	NR
FeO	9.56	0.45	13.04
MnO	0.17	0.02	0.11
MgO	15.52	0.29	15.20
ZnO	0.06	0.03	NR
NiO	0.17	0.02	NR
V205	0.10	0.02	NR
Na ₂ O	0.01	0.01	NR
Total	99.31		98.77
	N = 62		
Makaopuhi glass:			
SiO ₂	50.60	0.15	50.94
TiO ₂	4.05	0.02	4.06
Al ₂ Õ ₃	12.39	0.05	12.49
FeO	13.28	0.17	13.30
MnO	0.20	0.01	0.15
MgO	5.03	0.05	5.08
CaO	8.89	0.05	9.30
Na ₂ O	2.61	0.16	2.66
K ₂ Ô	0.85	0.01	0.82
P ₂ O ₅	0.46	0.04	0.38
Total	98.36		99.18
Cr (ppm)	$^{45}_{N=7}$	11	NR

Notes: SD = one standard deviation, NR = not reported, and N = number of analyses. Where Fe₂O₃ is not reported, FeO is total iron. Reported values are from Jarosewich et al. (1980) for Tiebaghi chromite, USNM 117075, and Makaopuhi glass, USNM 113498/1 VG-A99.

counted for 500 s. Na was always analyzed first and was not significantly different from analyses made with 30-nA beam current. Precision for these elements is reported in Table 2, based on multiple analyses of the Makaopuhi basalt glass.

One of the goals of this study was to obtain precise Cr values for the experimental glasses, which have usually not been reported in previous studies of undoped natural compositions. Homogeneous natural glasses with Cr abundances determined by XRF were provided to us by S. Delong. The Cr contents (by XRF) of these glasses ranged from 39 to 296 ppm, which has been compared to our microprobe analyses in Figure 1. Linear regression of this data produces a line with a slope of 1.03 ± 0.02 (1 σ) and a y-axis intercept of -15 ± 10 ppm (1 σ).

The similarity of the XRF and microprobe data indicates that no secondary correction is needed for probe analyses between 40 and 300 ppm Cr. The extension of the regression line passes through our Cr-augite standard at 5800 ppm Cr, which indicates that our probe analyses of 300 to 1260 ppm Cr also do not need to be corrected. Below 200 ppm Cr, the percent standard deviation of the microprobe analyses is greater than $\pm 10\%$. From 200 to 300 ppm Cr, however, our precision is better than 10%. All but two of our experimental glasses have more than 200 ppm Cr, so we expect Cr precision to be better than 10%.

Sources of Error

Spinels synthesized in basalts are often less than 2 μ m which makes them difficult to analyze by microprobe (Roeder and Reynolds, 1991). This was also a problem in our experiments. In addition, some spinels in our runs contained glass inclusions, making analyses even more difficult. For this reason, almost all of the spinel grains were located under the beam while observing the rate meter for Si K α . The beam was assumed to be centered on the grain when X-ray intensities for Si K α were similar to the Si background values. Analyses containing more than 1 wt% SiO₂ or totaling less than 98 wt% were discarded.



Figure 1. Reported values for glass Cr standards by XRF (S. Delong, pers. comm., 1991) and the values obtained by our microprobe. The line is a linear regression fit to all the data. Standard deviations are discussed in the Methods section.

Other potential problems in experimental work of this type are the loss of volatile elements from the sample to the furnace chamber and loss of Fe from the sample to the Pt loop. Although our glasses have 1 wt% or less (absolute) variation in Na for all glasses, we do not consider this to be significant in this study because of the low concentration of Na in the starting compositions and its incompatibility in the liquidus mineral phases.

The expected iron loss to the Pt wire loop can be estimated from the temperature and fO_2 of the experiment as well as the sample mass and the volume of interaction of the sample and the Pt loop (Grove, 1981). Our sample size and Pt wire were chosen to minimize Fe loss (minimum sample size of about 0.01 g and Pt wire diameter of 0.12 mm); however, some runs suffered more iron loss than expected, possibly because of a smaller than planned sample size. This does not present a serious problem for our study. The effect of iron loss from an experiment is to increase the Mg# of the melt, resulting in higher Mg# of the equilibrium spinel than would be expected for the starting composition. Therefore, a comparison of Mg#s of natural and synthetic spinels must be done with caution; however, because the equilibrium constant we determine is applicable to spinels and melts independent of their Fe contents, the iron loss from our charges does not affect our conclusions.

RESULTS

Spinel Occurrence

The experimental conditions and run products are presented in Table 3. Phase boundaries for 839Al experiments (experiments for which we had the greatest percentage of success) are summarized in Figure 2. Differences between this phase diagram and those for 839 and 839Mg are minor and consistent with the differences in the major element chemistry of the starting compositions. Although spinel was not observed in our 1400°C experiments run at quartz-fayalitemagnetite (QFM) fO2 buffer, we have inferred the spinel liquidus above 1400°C by the low Cr abundance of the glass (about 500 ppm), compared with the Cr abundance in the starting composition (about 1700 ppm). The Cr level in the glass can be explained by the presence of <0.5 wt% spinel, an amount that could have escaped detection. Olivine joins spinel on the liquidus above 1300°C, and these two phases crystallize together down to below 1200°C. Plagioclase was expected in the lower temperature runs, but it was not observed, probably because of delayed nucleation caused by the initial fusion at 1450°C (Lofgren and Donaldson, 1975).

No spinels were found in runs at any temperature at 2 log units below QFM except in the 839Al composition at 1200°C. Other

Ta	able 3	. Ex	perimental	conditions	and	run	products.

	Run	Temperature	Run	Duration						
Sample	no.	(°C)	fO ₂	(hr)	Glass	Spinel	Olivine	Clinopyroxene	Orthopyroxene	Plagioclase
834	R17	1153	OFM+2	57	A	А	Р	А		
834	R10	1201	QFM-2	48	P					
834	R15	1260	OFM	62	P					
834	R 8	1300	QFM-2	63						
834	R11	1300	OFM	66	P	P?	P?			
834	R6	1300	OFM+2	56	P	P?	P			
834	R13	1400	QFM	62	Р					
839	R17	1153	QFM+2	57	A	А	A	A		P ?
839	R16	1164	QFM	51	P	P	A	A		
839	R10	1201	QFM-2	48	P		P			
839	R 7	1201	QFM+2	48	A	A	P?			
839	R15	1260	QFM	62	P	P	A			
839	R5	1298	QFM	15	P	P	P			
839	R 8	1300	QFM-2	63	P		P			
839	R11	1300	QFM	66	Р	P?	P			
839	R6	1300	QFM+2	56	P	P?	P			
839	R13	1400	QFM	62	Р					
839A1	R17	1153	QFM+2	57	Р	Р	Р	А	А	P?
839A1	R16	1164	QFM	51	P	P	A	A		
839AI	R10	1201	QFM-2	48	A	A	Р			
839A1	R 7	1201	QFM+2	48	A	A	P			
839A1	R15	1260	QFM	62	P	P	Α			
839A1	R5	1298	QFM	15	A	A	P ?			
839A1	R8	1300	QFM-2	63	P					
839A1	R11	1300	QFM	66	A	A	P?			
839A1	R6	1300	QFM+2	56	P	Р	P			
839AI	R13	1400	QFM	62	P	1				
839AI	R9	1400	QFM-2	60	Р					
839Mg	R17	1153	QFM+2	57	Р	Р	Α			P ?
839Mg	R16	1164	QFM	51	A	A	A	A		
839Mg	R10	1201	QFM-2	48	P		Р			
839Mg	R7	1201	QFM+2	48	A	Р	P			
839Mg	R15	1260	QFM	62	A	A	A			
839Mg	R5	1298	QFM	15	A	A	Р			
839Mg	R 8	1300	QFM-2	63	P		Р			
839Mg	R11	1300	QFM	66	Р	P	Р			
839Mg	R6	1300	QFM+2	56	A	Р	Р			
839Mg	R14	1400	QFM+2	58	P	I				

Notes: QFM = quartz-fayalite-magnetite buffer. QFM+2 and QFM-2 indicate experiments 2 log units above and below QFM, respectively. A = phase analyzed, I = inferred from chemistry, and P = phase present. Olivine, clinopyroxene, and orthopyroxene were analyzed in some runs, but those results are not reported here.



Figure 2. Experimentally determined phase boundaries for Sample 839Al. Run numbers given next to data points. Lines separate fields of various assemblages as marked. Dashed line is the inferred olivine—in line above QFM.

workers have observed this phenomena and attribute it to lower abundances of Cr^{3+} at lower fO₂ (Hill and Roeder, 1974; Fisk and Bence, 1980; Roeder and Reynolds, 1991).

The spinels occur as equant, euhedral to anhedral, brownish yellow grains up to $50 \,\mu\text{m}$ in diameter, although most fall below $10 \,\mu\text{m}$. These grains often include substantial areas of glass and are primarily sur-

rounded by groundmass or are in contact with olivine grains. Because of the small size of the spinels and their often skeletal nature, only a few core-rim analyses of individual grains could be performed. These data show little or no variation within the grain (Table 4).

Experiments on the natural 834 composition (Table 4) unfortunately produced only one run with spinels large enough to analyze.

Table 4.	Spine	composi	itions	from	experimental	runs.
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	Run																
Sample	no.	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	ZnO	NiO	V_2O_5	Na ₂ O	Total	Cr#	Fe ³⁺ #	Mg#
834	R17	0.17	0.55	41.50	13.08	15.01	12.45	0.10	17.17	0.00	0.22	0.06	0.01	100.31	0.17	0.16	0.71
839	R7	0.27	0.53	19.18	35.27	15.67	14.09	0.22	13.40	0.00	0.07	0.14	0.00	98.85	0.55	0.19	0.63
839	R7	0.24	0.62	19.24	34.06	16.55	14.44	0.18	13.24	0.03	0.13	0.10	0.00	98.82	0.54	0.20	0.62
839	R17	0.34	0.58	35.71	4.02	27.65	15.64	0.15	13.89	0.00	0.27	0.05	0.01	98.31	0.07	0.31	0.61
839A1	R5	0.22	0.29	28.53	39.16	4.80	4.46	0.15	20.58	0.05	0.03	0.18	0.06	98.49	0.48	0.05	0.89
839A1	R7	0.58	0.43	29.38	29.01	11.87	10.22	0.27	16.85	0.00	0.08	0.08	0.01	98.78	0.40	0.13	0.75
839A1	R7	0.94	0.41	29.28	28.80	11.93	10.26	0.19	16.78	0.00	0.05	0.07	0.00	98.72	0.40	0.14	0.74
839A1	R10	0.42	0.21	44.09	24.42	2.06	5.13	0.11	21.69	0.07	0.00	0.47	0.00	98.67	0.27	0.02	0.88
839A1	R10	0.13	0.20	43.49	25.53	1.06	6.40	0.14	20.77	0.02	0.02	0.46	0.01	98.21	0.28	0.01	0.85
839A1	R10(r)	0.17	0.25	37.65	31.50	1.63	6.96	0.14	19.92	0.01	0.02	0.63	0.01	98.87	0.36	0.02	0.84
839A1	R10(c)	0.17	0.27	36.55	32.62	1.35	7.46	0.17	19.43	0.00	0.00	0.70	0.02	98.74	0.38	0.01	0.82
839A1	R11(r)	0.11	0.21	25.74	44.41	2.53	7.88	0.16	18.29	0.00	0.00	0.23	0.00	99.56	0.54	0.03	0.81
839A1	R11(c)	0.13	0.25	25.68	44.46	2.38	8.02	0.14	18.22	0.02	0.00	0.20	0.01	99.51	0.54	0.03	0.80
839Mg	R5	0.27	0.21	15.72	53.85	3.48	6.23	0.22	17.98	0.04	0.04	0.18	0.00	98.21	0.70	0.04	0.84
839Mg	R6	0.17	0.26	22.56	46.06	4.21	4.96	0.14	19.60	0.05	0.03	0.15	0.02	98.22	0.58	0.05	0.88
839Mg	R 7	0.34	0.58	19.68	34.37	15.93	14.02	0.21	13.51	0.04	0.08	0.09	0.00	98.84	0.54	0.19	0.63
839Mg	R15	0.17	0.33	17.55	50,85	3.92	7.10	0.18	17.66	0.06	0.07	0.18	0.00	98.06	0.66	0.05	0.82
839Mg	R15	0.12	0.33	18.52	49.66	4.27	7.02	0.21	17.85	0.00	0.06	0.22	0.01	98.27	0.64	0.05	0.82
839Mg	R15	0.19	0.30	18.03	50.39	4.13	6.83	0.19	17.89	0.00	0.00	0.20	0.00	98.16	0.65	0.05	0.82
839Mg	R16	0.18	0.48	20.24	43.13	6.25	14.21	0.29	13.36	0.00	0.00	0.41	0.00	98.54	0.59	0.08	0.63
839Mg	R16	0.76	0.46	22.26	40.39	6.96	13.67	0.22	13.94	0.00	0.04	0.32	0.01	99.03	0.55	0.08	0.65

Notes: Fe_2O_3 calculated according to spinel stoichiometry of three cations and four oxygen atoms. Cr# = Cr/(Cr + Al); $Fe^{3+}# = Fe^{3+}/(Cr + Al + Fe^{3+})$; $Mg# = Mg/(Mg + Fe^{2+})$; all calculated using cation fractions. (r) = rim analysis, and (c) = core analysis.

This spinel composition is reported along with its coexisting glass and is plotted on some figures for comparison. However, because its composition is more aluminous than the natural spinel found in the 834 sample, we think that our experimental spinel either crystallized at a much lower temperature than the natural spinel, or that it reflects the effect of suppression of plagioclase crystallization in a rock that has accumulated plagioclase (see discussion below).

GENERAL SPINEL CHEMISTRY

Spinel compositions are often characterized by the variables Cr/(Cr + Al) (abbreviated as Cr#) and Mg/(Mg + Fe²⁺) (Mg#) because these parameters describe most of the chemical variation in low-TiO₂, low-Fe³⁺ spinels. Fe³⁺ can substitute for Al or Cr in spinels, and some of our diagrams and tables use Fe³⁺/(Cr + Al + Fe³⁺), hereafter referred to as Fe³⁺# to indicate the magnitude of this Fe³⁺ substitution. Over the temperature and fO₂ range of our experiments, Cr# varies dramatically from less than 0.07 to 0.70 (Table 4). Mg# variation is more restricted and ranges from about 0.61 to about 0.89 and Fe³⁺# ranges from 0.01 to 0.31.

Equilibrium conditions for the experiments are supported by the similar compositions of spinel grains within single samples (Figs. 3-5). Also, where core and rim compositions were obtained, compositions were uniform with only slight decreases in Mg# and Fe³⁺# and increases in Cr# from core to rim (Table 4). Spinel grains analyzed from Run 10 do show a greater than expected range in Cr#, but these do not affect the arguments presented below.

Sample 839, Run 17, has higher Fe^{3+} (Fe^{3+} #=0.31) than is common for spinels; it also has a much higher Al content relative to Cr. It is probable that this is a result of the combination of low temperature, high fO₂, and higher crystallinity of the charge. The spinels in this charge are commonly enclosed in other phases and may represent compositions controlled by local diffusion (Roeder et al., 1979).

Spinel Cr#

The Cr# in spinel is determined by several independent factors, as illustrated in Figure 3. We see that Cr# decreases as temperature decreases for the series of 839Mg runs at QFM and 1298°, 1260°, and 1164°C. Cr# also decreases as Al increases in the melt (i.e., Samples 839Mg and 839Al, Run 7, 1200°C, QFM+2). (Al in the melt also increases as temperature decreases in the 839Mg series first mentioned.)



Figure 3. Spinel Cr# vs. 10,000/T for selected runs of Samples 839Mg (open diamonds) and 839Al (filled diamonds). Run numbers are indicated next to points, and dashed lines separate data for same sample at different fO₂ values.

In addition, Cr# may increase or decrease with increasing fO_2 as a result of a competing reaction with Fe³⁺, as discussed in the next section.

These variations in Cr# as a function of magma composition, temperature, and oxygen fugacity may be understood in the light of previous experimental studies. Hill and Roeder (1974), Fisk and Bence (1980), and Roeder and Reynolds (1991) observed that the solubility of Cr in experimental melts depends on temperature and fO₂. For a fixed starting composition and fO₂, increasing temperature results in increasing Cr in the melt (e.g., Sample 839Mg, Runs 16 to 15 to 5; Table 5). Following the analogy suggested by Roeder and Reynolds (1991), we attribute this to an increase in the octahedral sites available for Cr in the melt at higher temperatures. As fO₂ decreases for the same composition and temperature (e.g., Sample 839Al, Runs 10 to 7), dissolved Cr increases in the melt. This is probably because of the reduction of Cr^{3+} to Cr^{2+} , which has a higher solubility in silicate melts (Hill and Roeder, 1974, Fisk and Bence,

Table 5.	Average	compositions,	standard	deviations,	and	numbers o	f measureme	ents of	glasses	coexisting	with
spinels.											

Sample	Run no.	SiO ₂	TiO ₂	Al ₂ O ₃	FeOt	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total	Cr (ppm)	FeO	Fe ₂ O ₃
834	R17 SD, N = 11 (5)	49.80	1.27 0.48	18.15 0.03	8.74 0.11	0.13 0.10	6.82 0.02	12.15 0.07	2.00 0.25	0.09 0.05	0.03 0.01	99.18 0.02	48	7.83 23	1.01
839	R7 SD, <i>N</i> =11(5)	52.80	0.67 1.08	15.25 0.02	8.68 0.23	0.16 0.79	8.49 0.03	12.33 0.11	1.81 0.46	0.26 0.07	0.03 0.02	100.50 0.02	298	7.67 20	1.12
839	R17 SD, N=11(5)	48.62	0.77 0.20	16.27 0.04	11.78 0.59	0.15 0.50	7.77 0.03	12.20 0.39	0.96 0.20	0.16 0.05	0.03 0.02	98.69 0.02	193	10.7 105	1.24
839A1	R5 SD, <i>N</i> =10	50.64	0.60 0.52	15.60 0.01	6.34 0.41	0.18 1.12	13.03 0.03	10.59 0.11	1.67 0.07	0.25 0.16	0.05 0.05	99.10 0.03	1000	6.11 178	0.26
839A1	R7 SD, <i>N</i> =15	53.69	0.86 0.24	15.51 0.03	6.90 0.10	0.19 0.12	8.86 0.03	$\begin{array}{c} 12.34\\ 0.13\end{array}$	1.83 0.23	0.32 0.03	0.03 0.01	100.54 0.03	326	6.09 21	0.90
839AI	R10 SD, <i>N</i> =7(4)	51.7	0.69 0.23	18.87 0.02	4.59 0.08	0.16 0.18	10.33 0.02	13.15 0.09	0.73 0.35	0.16 0.02	0.02 0.02	$\begin{array}{c} 100.48\\ 0.02 \end{array}$	535	4.53 23	0.06
839A1	R11 SD, <i>N</i> =7	52.0	$\begin{array}{c} 0.58\\ 0.14\end{array}$	15.61 0.01	6.27 0.09	0.17 0.13	$\substack{14.84\\0.03}$	10.83 0.22	0.63 0.20	0.09 0.02	0.05 0.01	101.19 0.03	981	6.07 26	0.22
839Mg	R5 SD, <i>N</i> =8	53.1	0.63 0.61	14.24 0.02	4.35 0.18	0.17 0.21	12.90 0.04	11.45 0.21	1.78 0.15	0.27 0.08	0.05 0.01	99.14 0.03	1260	4.16 133	0.21
839Mg	R6 SD, <i>N</i> =5	50.4	0.57 0.19	15.27 0.01	7.38 0.08	0.18 0.13	12.86 0.01	$\begin{array}{c} 10.28\\ 0.10\end{array}$	1.56 0.06	0.20 0.03	0.03 0.01	98.85 0.02	597	6.70 33	0.76
839Mg	R7 SD, <i>N</i> =7	52.5	0.70 0.33	15.26 0.03	8.74 0.08	0.15 0.12	8.12 0.03	13.13 0.05	1.79 0.07	0.26 0.04	0.03 0.01	100.70 0.03	NA	7.70	1.16
839Mg	R15 SD, N=10(4)	54.2	0.69 0.83	14.74 0.03	4.86 0.16	0.17 0.18	11.45 0.03	12.49 0.10	1.07 0.19	0.23 0.03	0.05 0.02	100.03 0.02	766	4.65 14	0.22
839Mg	R16 SD, <i>N</i> =11(5)	53.4	0.75 0.19	17.08 0.02	7.27 0.38	$\begin{array}{c} 0.15\\ 0.14\end{array}$	7.23 0.02	12.34 0.09	1.46 0.30	0.28 0.03	0.07 0.01	100.09 0.03	256	6.96 14	0.34

Notes: FeO and Fe₂O₃ are calculated according to Sacket al. (1980). The first number under each column is an average of Nanalysesin wt%, with numbers in parentheses indicating where N for the Cr analyses is different. The second number under each column is the 1σ standard deviation. NA = not analyzed.

1980). For instance, Roeder and Reynolds (1991) suggest that Cr^{2+} should be about half of all Cr at 1300°C at QFM while falling to 0.1 of all Cr at 1300°C at QFM+2.

Roeder and Reynolds (1991) also suggest Cr solubility is related to melt Fe concentration. Although Fe loss created variable Fe concentrations in some of our runs, this effect on melt Cr concentration was not specifically evaluated.

Spinel Fe³⁺#

The amount of Fe³⁺ in spinel should reflect fO_2 conditions at equilibrium. However, Ballhaus et al. (1991) point out that redox equilibrium in spinels can be difficult to achieve in reversal experiments. All of our experiments involve synthesis of spinel from liquid that has been above the liquidus, so our spinel redox should reflect equilibrium at run conditions. For one starting composition at QFM, Fe³⁺# in spinel increases only slightly with decreasing temperature (Runs 5 to 15 to 16, Fig. 4). For runs at QFM+2, however, Fe³⁺# rises dramatically as temperature drops (Runs 6 to 7 to 17). This is probably a result of increased Fe³⁺ in the melt, combined with increasing Fe in spinel with decreasing temperature. Spinel Fe³⁺#, therefore, increases because of the ability of Fe³⁺ to replace Cr³⁺ in the spinel structure. Consistent with this logic, spinels in runs at QFM-2 have much lower Fe³⁺# than those at higher fO₂.

Spinel Mg#

The Mg# of a spinel should correlate well with the Mg# of the melt because of the rapid exchange of Mg and Fe²⁺ (Hill and Roeder, 1974; Fisk and Bence, 1980; Roeder and Reynolds, 1991; Allan, 1992, also in this volume). Furthermore, Fe²⁺ is the dominant iron species in the melt in the fO₂ range of our experiments, so Mg# in the melt is not strongly influenced by changes in fO₂. Spinel Mg#, therefore, can be



Figure 4. Spinel Fe^{3+#} vs. 10,000/T for all the experiments. Symbols refer to different compositions according to the legend and the numbers are runs. Lines connect experiments of Sample 839Mg at similar fO₂ buffers. (The QFM+2 line was extended to lower temperatures using the undoped composition because these two compositions produced similar spinel compositions.)

used to determine the existence of equilibrium between natural spinels and host glasses. For our experiments, the Mg# of the spinel decreases by about the same amount as the Mg# of the melt for similar compositions and at constant fO_2 (Fig. 5), in agreement with previous workers.

DISCUSSION

The primary aim of this study is to relate spinel composition to temperature, fO_2 , and the natural melt compositions. An in-depth treatment by Allan of the spinels found in the rocks from Holes 834 and 839 can be found elsewhere in this volume. In general, the spinels



Figure 5. Mg# of spinels from Sample 839Mg vs. Mg# of coexisting melts. Numbers, light lines, and symbols are as in previous figures. Heavy line identified as 839 spinel cores is the approximate range of natural spinel cores analyzed by Allan (this volume) plotted vs. a mid-range Mg# value that he calculated for the equilibrium melt.



Figure 6. Cr# vs. Mg# for spinels from our experiments (filled circles = Samples 839, 839Mg, and 839Al; open circle = Sample 834 composition) and Allan's (this volume) analyses (filled squares = Sample 839; open squares = Sample 834).

are euhedral and can be very large (see sample description). Chemically, they exhibit zoning in Mg# but little change in Cr# from core to rim (Fig. 6). The Mg# ranges from 0.73 in the cores to 0.55 on the rims; the Cr#, however, varies little from 0.75 with perhaps a slight increase at the rim. The Fe³⁺# in all spinels is below 0.15.

Spinel compositions from Samples 839Mg and 839 are similar when synthesized under identical experimental conditions. The experimental melt and spinel Mg#s for 839Mg are compared with natural spinels in Figure 5. Based on the correlation of Mg#s of spinel and melt from the experiments, the Mg# of the cores in natural spinels suggests a melt Mg# of between 0.72 and 0.79. For the rims, the melt should have a Mg# of 0.60. In agreement with this, Allan (this volume) predicts a Mg# of melt in equilibrium with the cores to be 0.79 and for rims of about 0.63. The only glass analysis available from the same unit as our Sample 839 (Allan, this volume) indicates that it is close to equilibrium with the rims (Mg# around 0.63). Therefore, based on Mg#s for the Mg-doped sample runs, experimental data support the argument that cores formed between 1250° and 1220°C (midway between 839Mg Runs 15 and 16). Keeping in mind that correcting for Fe-loss from the runs at higher temperatures (Runs 5 and 15) would shift their compositions down the line toward Run 16, the true crystallization temperature is more likely to be near 1250°C.

In terms of trivalent cations, the absence of experimental spinels with Cr#s as high as the cores of the natural spinels (Fig. 6) has two important implications. First, we infer that our starting composition has higher Al than the liquid in equilibrium with the spinel cores because, even in our 1300°C runs, the highest Cr# is only 0.70. The high Al content of the spinel from the one run on a Site 834 sample is probably related to the high plagioclase content of this rock and the suppression of plagioclase crystallization in our experiment. Plagioclase crystallization can be suppressed in experiments when nuclei are destroyed at superliquidus temperatures (Lofgren and Donaldson, 1975). The initial fusion temperature at >1400°C destroyed all plagioclase nuclei in Sample 834. This would result in a dramatically higher Al content in the glass and a lower relative Cr, which should favor a more aluminous spinel. The glass analyses (Table 4) support this idea.

We also infer that the Mg# and Cr# characteristic of the spinel rims from Hole 839 Unit 3 are not consistent with equilibrium crystallization. Our data suggest that spinel Mg#s must covary with Cr#s and that a spinel with 0.55 Mg# should also have a Cr# between 0.5 and 0.6 (inferred from Fig. 3 by interpolating between Runs 15 and 16). It is difficult, therefore, to envision how natural spinels with decreasing Mg#s and constant-to-rising Cr#s arise from equilibrium magma chamber process.

We next chose to examine the data for temperature influence on spinel composition by the mineral-melt exchange reaction:

$$MgCr_2O_4(sp) + Al_2O_3(liq) = MgAl_2O_4(sp) + Cr_2O_3(liq),$$
 (1)

for which the equilibrium constant may be written:

$$K_1 = a(sp) / a(Mg - chr) \cdot a(Cr_2O_3(liq)) / a(Al_2O_3(liq)),$$

where a(X) indicates the activity of component X. This reaction was chosen as being appropriate because the spinels in this study have more Mg than Fe, and because Cr and Al dominate the trivalent cation composition.

Taking into account the nonideal solid solution behavior between the spinel components, we used the activity model derived by Sack and Ghiorso (1991) to calculate the activity of the end-member spinel components (Table 6). As expected, spinel sensu stricto (MgAl₂O₄) and Mg-chromite (MgCr₂O₄) components have the highest activities, indicating the significance of the reaction. These components have activities similar to but larger than the FeAl₂O₄ and FeCr₂O₄ endmembers. The Ti and Fe³⁺ end-member spinels have activities almost an order of magnitude lower than the Mg-Fe-Al-Cr components.

The activities of Cr [a(Cr)] and Al [a(Al)] in the glass were calculated using the two-lattice melt model of Nielsen and Drake (1979) (Table 7). In this model, the activity of aluminum available for spinel formation is Al in excess of that combined with Na and K in NaAl and KAl in the network-former lattice. Cr activity is equivalent to the cation mole fraction of Cr relative to the sum of the network modifiers only.

Roeder and Reynolds (1991) point out that the Cr^{2+}/Cr^{3+} ratio in the liquid can be as high as 1 in natural silicate liquids at magmatic conditions. We use their empirical relationship to calculate Cr^{2+}/Cr^{3+} and the activity of Cr^{3+} from the total activity of Cr. We then introduce the ratio, $Cr^{3+}\# = a(Cr^{3+})/[a(Al)+a(Cr^{3+})]$, or, in other words, the activity of trivalent Cr in the melt (not the total activity of Cr) and the activity of the network modifying Al (not the total Al).

With these activities, we calculated the linear regression for Equation 1 (Fig. 7) from our data. One glass composition in which Cr was

Table 6. Activities of spinel components calculated using the model of Sack and Ghiorso (1991).

	Run	_			_				
Sample	no.	a(hc)	a(sp)	a(usp)	a(mt)	a(Mg-Ti)	a(Mg-Fe)	a(chr)	a(Mg-chr)
834	R17	0.3126	0.3959	0.0215	0.1285	0.0177	0.0710	0.0367	0.0303
839	R7	0.1803	0.2406	0.0111	0.0677	0.0156	0.0326	0.1377	0.1398
839	R7	0.1839	0.2422	0.0128	0.0752	0.0170	0.0361	0.1313	0.1305
839	R17	0.3391	0.3833	0.0189	0.3095	0.0124	0.1647	0.0040	0.0028
839A1	R5	0.0866	0.3154	0.0014	0.0039	0.0191	0.0062	0.0722	0.2310
839A1	R7	0.2006	0.3251	0.0087	0.0480	0.0157	0.0313	0.0975	0.1184
839A1	R7	0.2008	0.3250	0.0083	0.0492	0.0149	0.0320	0.0969	0.1174
839A1	R10	0.1626	0.4434	0.0031	0.0018	0.0149	0.0022	0.0652	0.1314
839A1	R10	0.2006	0.4324	0.0045	0.0005	0.0135	0.0005	0.0863	0.1377
839A1	R10	0.1844	0.3903	0.0048	0.0011	0.0157	0.0009	0.1090	0.1770
839A1	R10	0.1936	0.3808	0.0058	0.0007	0.0166	0.0006	0.1212	0.1838
839A1	R11	0.1358	0.2756	0.0025	0.0015	0.0124	0.0013	0.1416	0.2552
839A1	R11	0.1377	0.2749	0.0031	0.0014	0.0147	0.0011	0.1441	0.2553
839Mg	R5	0.0652	0.1793	0.0013	0.0018	0.0200	0.0019	0.1414	0.3733
839Mg	R6	0.0762	0.2594	0.0013	0.0027	0.0204	0.0038	0.0940	0.2942
839Mg	R7	0.1836	0.2461	0.0119	0.0703	0.0165	0.0344	0.1322	0.1342
839Mg	R15	0.0863	0.2085	0.0028	0.0029	0.0268	0.0026	0.1506	0.3326
839Mg	R15	0.0902	0.2197	0.0029	0.0035	0.0260	0.0031	0.1441	0.3180
839Mg	R15	0.0854	0.2145	0.0024	0.0031	0.0244	0.0029	0.1433	0.3283
839Mg	R16	0.2075	0.2475	0.0141	0.0139	0.0194	0.0052	0.2258	0.2059
839Mg	R16	0.2163	0.2670	0.0136	0.0181	0.0180	0.0073	0.2017	0.1885

Notes: a(X) = activity of spinel component X in spinel calculated from Table 4 according to the model of Sack and Ghiorso (1991). hc = hercynite, sp = spinel, usp = ulvo-spinel, mt = magnetite, Mg-Ti = magnesium-titanium spinels, and Mg-Fe = magnesium-iron spinels.

Table 7. Activities of glass components based on the Nielsen and Dr	rake (1979) modification of Bottinga and Weill's (1972)
two-lattice melt model.	

		Ne	Network formers		Network modifiers									
Sample	Run no.	a(NaAl)	a(KAl)	a(Si)	a(Mg)	a(Al)	a(P)	a(Ca)	a(Ti)	a(Cr)	a(Mn)	a(Fe)		
834	R17	0.0721	0.0022	0.9258	0.2074	0.3552	0.0005	0.2658	0.0195	0.00008	0.0023	0.1491		
839 839	R7 R17	0.0621 0.0366	0.0059 0.0040	0.9320 0.9595	0.2640 0.2211	0.2945 0.3270	0.0005 0.0005	0.2755 0.2497	0.0106 0.0110	$\begin{array}{c} 0.00071 \\ 0.00041 \end{array}$	0.0028 0.0024	0.1513 0.1880		
839Al 839Al 839Al 839Al 839Al	R5 R7 R10 R11	0.0597 0.0616 0.0266 0.0229	0.0058 0.0070 0.0037 0.0022	0.9345 0.9313 0.9696 0.9750	0.3758 0.2786 0.2816 0.3897	0.2872 0.3021 0.3772 0.3005	0.0008 0.0006 0.0003 0.0008	0.2196 0.2790 0.2577 0.2045	0.0088 0.0136 0.0094 0.0077	0.00227 0.00080 0.00113 0.00203	0.0030 0.0033 0.0025 0.0025	0.1026 0.1219 0.0701 0.0923		
839Mg 839Mg 839Mg 839Mg 839Mg 839Mg	R5 R6 R7 R15 R16	0.0605 0.0565 0.0616 0.0366 0.0500	0.0061 0.0048 0.0059 0.0052 0.0064	0.9334 0.9387 0.9325 0.9582 0.9436	0.3931 0.3706 0.2505 0.3393 0.2254	0.2654 0.2842 0.2934 0.2982 0.3544	0.0009 0.0005 0.0006 0.0008 0.0013	0.2507 0.2128 0.2909 0.2660 0.2767	0.0097 0.0083 0.0109 0.0102 0.0117	0.00303 0.00133 NA 0.00178 0.00060	0.0029 0.0030 0.0025 0.0029 0.0026	0.0743 0.1193 0.1512 0.0807 0.1272		

Notes: a(X) = activity of melt component X calculated from Table 5 according to the two-lattice model of Nielsen and Drake (1979), which assumes no mixing between lattices and ideal mixing within lattices. NA = not analyzed.

not analyzed and one composition at 1153°C (Run 17, Sample 839) were excluded from the calculations. (This last point was excluded from the regression because of the above-mentioned kinetic effect on plagioclase, the additional complication of higher Fe³⁺ in the spinel, and the poor precision of the Cr analysis of the glass.)

The variation of the equilibrium constant (\bar{K}_1) with temperature (Fig. 7) suggests that it is possible to estimate liquid Cr^{3+} # if spinel composition, temperature, and fO₂ are known by means of the following equation:

$$K_1 \cdot a(Mg-chr)/a(sp) = a(Cr_2O_3)/a(Al_2O_3).$$
 (2)

Note that K_1 is primarily dependent on temperature, but the $Cr_2O_3(liq)$, and therefore $a(Cr_2O_3)$, is dependent on fO_2 (Roeder and Reynolds, 1991). Hence, Equation 2 is constrained by temperature, fO_2 , and spinel composition. Details of the calculation are given in the Appendix. (Eq. 2 should be equally useful in predicting spinel compositions from a given liquid composition.) To test the usefulness of this expression for calculating the Cr^{3+} #s of the melt, we applied it to the experimental data of Roeder and Reynolds (1991). Figure 8 shows the Cr^{3+} # calculated from their spinel compositions on the *x*-axis and the Cr^{3+} #s of the coexisting glass compositions on the *y*-axis. The Cr^{3+} #s derived from their analyzed glasses and our calculated values are in good agreement, even for their wider fO₂, temperature, and compositional range. Thus, the expression predicts Cr# in melt from Cr# in spinel when temperature and fO₂ are known.

CONCLUSIONS

Even though our Sample 839 has clearly accumulated olivine and spinel, the initial parent composition must have had the same or higher Mg# based on both the spinel and olivine cores. Its hybrid character is shown by the Fe-rich rims on spinels and the single glass analysis (Allan, this volume), which shows a host liquid with higher Al and Si and lower Mg than the equilibrium composition predicted from the phenocryst compositions. Such higher Al liquids may be expected to



Figure 7. Values of $-lnK_1$ calculated for each of the experimental spinel-average glass pairs. Symbols are the same as in Figure 4. The line is a linear regression calculated for the points shown. Values of K_1 were used to produce Figure 8 from the temperature and spinel compositions reported by Roeder and Reynolds (1991).



Figure 8. Cr^{3+} # on the *y*-axis is for the glass from microprobe data of Roeder and Reynolds (1991) and calculated as described in discussion section. Cr^{3+} # on the *x*-axis calculated from Roeder and Reynolds (1991) spinels and our reaction constant, K₁.

be in equilibrium with lower Cr# spinels than the natural spinel phenocrysts, which is what we observed. Therefore, based on our experiments and the equations derived by us and Allan (this volume), the following conclusions may be reached:

 Comparison of the Cr#s and Mg#s of the natural spinels and our synthesized spinels indicates that crystallization must have taken place at high temperatures (1200°–1250°C, most likely closer to 1250°C).

2. Oxygen fugacity must have been near the QFM buffer because Cr-spinel probably would not have formed at lower fO_2 and the Cr content of spinel at higher fO_2 would have been lower than observed in the phenocrysts. Furthermore, Al must have some effect on the stabilization of Cr-spinel because the only run containing spinel at the lower fO_2 was the one doped with Al₂O₃.

3. Zoning of the Mg#s (0.50–0.75) of the natural spinel probably results from changes in the melt Mg#s. However, the Cr# in these spinels does not vary and, because Mg# and Cr# should both decrease

as equilibrium crystallization occurs, it must reflect the effect of disequilibrium (Scowen et al., 1991). Based on our experiments and previous studies, decoupling these elements even under open-system processes is difficult to envision.

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^{*} Abbreviations for names of organizations and publication titles in ODP reference lists follow the style given in *Chemical Abstracts Service Source Index* (published by American Chemical Society).

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APPENDIX

Procedure for Calculating -In K1

1. Mole fractions of elements in spinel with minor components (Mn, Ni, Zn, V) ignored.

2. Sack and Ghiorso (1991) parameters for spinel composition.

3. Sack and Ghiorso (1991) spinel activity calculation.

4. Cation mole fractions for coexisting glass.

5. Activities of elements in the glass by the Nielsen and Drake (1979) two-lattice melt model.

6. Activity of Cr³⁺ from f(O₂) and two-lattice activity of Cr (Roeder and Reynolds, 1991).

7. -In K1 for that mineral-melt pair from Equation 1 using the calculated activities.

An example using data from the tables for Sample 834, Run 17:

1.	Mg 0.239 (Calculat	Al 0.457 ted from v	Ti 0.004 values in T	Cr 0.097 able 4.)	Fe ²⁺ 0.099	Fe ³⁺ 0.1041	Total 1				
2.	X2 0.718	X3 0.145	X4 0.012	X5 0.158	Temperatu 1426	ure (K)					
	where	X2 = Mg $X3 = Cr$ $X4 = Ti$ $X5 = (2/2)$	g • 3, • 1.5, • 3, and 3 - Al - Ci	r – 2 • Ti)	• 1.5.						
3.	a(hc) 0.313	a(sp) 0.396	a(usp) 0.021	a(mt) 0.128	a(Mg-Ti) 0.018	a(Mg-Fe) 0.071	a(chr) 0.037	a(Mg-0 0.030	chr)		
4.	Na 0.036	Mg 0.095	A1 0.2	Si 0.466	P 0.0002	K 0.0011	Ca 0.122	Ti 0.009	Cr 0.00005	Mn 0.001	Fe 0.068
5.	a(NaAl) 0.072	a(KAl) 0.002	a(Si) 0.926	a(Mg) 0.207	a(Al) 0.355	a(P) 0.0005	a(Ca) 0.266	a(Ti) 0.02	a(Cr) 0.00008	a(Mn) 0.002	a(Fe) 0.149
	where	a(NaAl) a(KAl) = a(Si) = S a(Mg) = a(Al) = (a(P) = P a(Ca) = a(Ti) = T a(Cr) = 0 a(Mn) = a(Fet) =	= Na/(Na = K/(Na + Si/(Na = K (Al - Na - /[Mg + (A Ca/[Mg + fi/[Mg + (Cr/[Mg + Mn/[Mg + Fet/[Mg +	+ K + Si), K + Si), + Si), + (Al – Na K)/[Mg + l – Na – K (Al – Na – (Al – Na – (Al – Na – + (Al – Na	(A - K) + P + (AI - Na - K) + P + Ca - K) +	Ca + Ti + C $K) + P + Ca$ $+ Ti + Cr + 1$ $Ca + Ti + Cr + 1$ $a + Ti + Cr + 1$ $a + Ti + Cr + 1$ $Ca + Ti + Cr$ $Ca + Ti + C$	Cr + Mn + Ti + Mn + Fe + Mn + Fe + Mn + F + Mn + F Cr + Mn + Tr	+ Fe], Cr + Mn], Fe], Fe], Fe], + Fe], an - Fe].	+ Fe], nd		
6.	log f(-7.05	(O ₂) (QFM+2)		Cr ²⁺ /Cr ³ 0.36	+liq 6		a(Cr ³⁺) 0.0000) 6			
	where	Cr^{2+}/Cr^{2} a(Cr ³⁺) :	$a^{3+} = 10^{[(-0)]}$ = a(Cr)/[(0	.28 • log f O ₂ Cr ²⁺ /Cr ³⁺)	(-2.41) = -2.41 and $(+1)$.						
7.	-ln K ₁ 6.099										
	where	$K_1 = -ln$	(a(sp) • X	(Cr ³⁺]/[a(1	Mg-chr) • a(Al)].					