2. Mg-Fe PARTITIONING BETWEEN PLAGIOCLASE AND LIQUID IN BASALTS OF HOLE 504B, ODP LEG 111: A STUDY OF MELTING AT 1 ATM¹

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ABSTRACT

The effect of oxygen fugacity (f_{O2}) on the partition relationship of Mg and Fe between plagioclase and sillicate liquid was investigated at 1 atm for basaltic samples recovered during ODP Leg 111 from Hole 504B. Samples 111-504B-143R-2 (Piece 8) and 111-504B-169R-1 (Piece 1) have plagioclase as the liquidus phase. The distribution coefficient of Mg between plagioclase and melt is constant at about 0.04 against the variation of f_{O2} , whereas that of Fe (total Fe) varies from 0.3 at $f_{O2} = 0.2$ atm to 0.03 at $f_{O2} = 10^{-11.5}$ at 1200°C. The distribution coefficient of Mg is slightly higher than that calculated from the phenocryst and bulk-rock compositions, suggesting a kinetic disequilibrium effect on the distribution of Mg in plagioclase. Because Mg, Fe, and Fe³⁺ have similar diffusion coefficients in silicate melt, the disequilibrium effect is greatly reduced for the exchange reaction of Mg and total Fe between plagioclase and liquid. The exchange partition coefficient is highly dependent on f_{O2} , with log f_{O2} ranging from -0.7 to -11.5 at approximately 1200°C. Using this relationship, the f_{O2} of crystallization of the magmas is estimated to be near the one defined by the fayalite-quartz-magnetite assemblage.

INTRODUCTION

Mg and Fe are important minor constituents of plagioclase in oceanic ridge basalts. Bryan (1974) described the sector-zoned distribution of Mg and Fe in some ocean-floor basalts, with Mg and Fe occupying the tetrahedral site of plagioclase. In examining Fe and Mg accommodation in plagioclase, Longhi et al. (1976) observed variable distribution coefficients of Fe between plagioclase and liquid among lunar and terrestrial basalts, which they ascribed to the effect of oxygen fugacity (fo2). Drake and Weill (1975) reported that fo2 affects the distribution coefficient of europium between plagioclase and liquid; divalent and trivalent europium have different distribution coefficients, and hence the distribution coefficient of total Eu could depend on the for of the crystallizing magmas. Similarly, ferric and ferrous iron may have different partition coefficients, and the partition coefficient of total Fe can be used as an indicator of the redox states of magmas.

In this study, the author conducted melting experiments at 1 atm on two basalt samples recovered from Hole 504B during Ocean Drilling Program (ODP) Leg 111 to determine if the Mg-Fe partitioning between plagioclase and silicate liquids can be used to estimate the f_{02} of the magmas. Problems concerning the formulation of the exchange partition coefficient of Mg and Fe between plagioclase and magma are also discussed in this paper.

Hole 504B Basalt Samples

Two samples of relatively fresh basalts were analyzed in this study. Bulk-rock chemical and modal compositions of the samples are listed in Table 1.

Sample 111-504B-143R-2 (Piece 8) is a sparsely phyric olivine-plagioclase basalt with #Mg (= 100 × Mg/[Mg + Fe]) of 65. Olivine phenocrysts are completely altered to clay minerals and can be identified only by their pseudomorphic forms. The pseudomorphs are euhedral, ranging from 0.1 to 1 mm in diameter. Rare chromian spinel octahedra are included in the pseudomorphs. Plagioclase phenocrysts are also euhedral and tabular and are 0.1–1.5 mm across. Plagioclase phenocrysts commonly show steplike normal zoning at the rim. The compositions of the cores of plagioclase phenocrysts are An_{80-88} , whereas compositions of the margin and groundmass plagioclase are An_{45-80} . MgO contents of the cores of the plagioclase phenocrysts are uniformly about 0.2–0.3 wt%, whereas Mg contents of the rim and groundmass plagioclase attain maximum values of 0.3–0.4 wt% at An_{70-75} , from which they decrease as the An content decreases (Fig. 1).

FeO (total Fe) concentrations of the cores of the plagioclase phenocrysts in Sample 111-504B-143R-2 (Piece 8) are about 0.4 wt%. The FeO concentration of plagioclase increases monotonously vs. decreases in the An component to about 1.0 wt% at An₅₀₋₆₀ (Fig. 1). The groundmass constituents are plagioclase, augite, titanomagnetite, and interstitial clay minerals, which may be the alteration product of mesostasis. The groundmass has a subophitic texture and is almost holocrystalline.

Sample 111-504B-169R-1 (Piece 1) is a sparsely phyric olivine-augite-plagioclase basalt. Olivine is completely altered to clay minerals, comprising about 1% of the rock volume. The euhedral olivine pseudomorphs are 0.1–1 mm in diameter. The fresh augite phenocrysts show idiomorphic short-prismatic forms, are 0.2-2 mm in length, and comprise about 2% of the modal content. Augite compositions are subcalcic augite, with Cr_2O_3 contents of 0.5 wt% in the magnesian cores. Plagioclase phenocrysts, which form 1.4% of the rock volume, are euhedral, tabular, and 0.2-1 mm long. The An contents of the cores of the plagioclase phenocrysts range from 80 to 90. MgO contents are 0.2-0.3 wt% for the cores of plagioclase phenocrysts, whereas FeO (total Fe as FeO) contents increase from 0.4 to 1 wt% as the An contents of the plagioclase decrease.

EXPERIMENTAL METHODS

The wire-loop method (Presnall and Brenner, 1974; Donaldson et al., 1975) was used for the phase equilibrium and element partitioning experiments in this study. All runs were made at 1-atm pressure in a vertical quench furnace of Siliconit with SiC heating elements at the Faculty of Integrated Arts and Sciences Building, Hiroshima University. The f_{O_2} was controlled by mixing CO₂ and H₂ gases, with the mixing ratio determined by the thermodynamic calculation performed by Dr. A. Tsuchiyama after the method of Nafziger et al. (1971). The f_{O_2} of the furnace was calibrated against the reaction Ni + 0.5O₂ = NiO at the

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Table 1. ODP	Leg 111	basalt samples	from	Hole 504B.	ē
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Sample		143R-2 (Piece	8)		169R-1 (Piece 1)						
Phase Volume	^a Bulk	Plagioclase phenocryst 4.7	Olivine phenocryst 0.7	^b Bulk	Plagioclase phenocryst 1.4	Clinopyroxene phenocryst 1.8	Olivine phenocryst 1.1				
Averaged analyses	l 6	18	Altered	4	7	1	Altered				
SiO ₂	49.21 (25)	46.98 (50)		49.88 (28)	46.77 (58)	53.06					
TiO ₂	0.84 (21)	0.02 (01)		1.10 (05)	0.01 (01)	0.25					
Al2O2	15.91 (12)	33.19 (38)		14.88 (15)	33.58 (51)	2.69					
FeÕ	8.50 (10)	0.38 (05)		9.40 (39)	0.43 (04)	4.89					
MnO	0.11 (02)	0.05 (02)		0.15 (05)	0.01 (02)	0.14					
MgO	8.96 (06)	0.23 (03)		8.42 (14)	0.23 (02)	18.53					
CaO	12.90 (19)	17.59 (39)		13.14 (15)	17.68 (26)	20.38					
Na ₂ O	1.88 (03)	1.80 (19)		1.95 (04)	1.63 (24)	0.18					
K ₂ Õ Cr ₂ O ₃	0.01 (01)	0.00 (00)		0.01 (01)	0.01 (01)	0.01 0.60					
	98.32	100.24		98.93	100.35	100.73					

Note: Numbers in parentheses denote one standard deviation in terms of least units cited.

^a Electronprobe microanalyses of glass (run 43A, Table 2).

^b Electronprobe microanalyses of glass (run 44B, Table 2).

sample sites. Across the temperature range of $1150^{\circ}-1260^{\circ}$ C, f_{O2} was accurate to within 0.5 log units. The temperature was measured with Pt-Pt/13Rh thermocouples calibrated against the melting point of gold and diopside at the sample sites. The temperature measurements are accurate to within 5°C.

Two types of melting schedules were used (Fig. 2). The equilibrium liquidus temperature of plagioclase was determined with the fusion (or heating) experiment (Gibb, 1974), in which the temperature is raised to a fixed value without overshooting and then maintained for a certain period before quenching the charges in distilled water. Because of the lack of fresh olivine crystals in the starting materials, the temperature of olivine appearance could not be determined.

The growth (or cooling) experiment was used to nucleate and grow crystals from completely molten liquids. Initially, the charge temperature is raised to 1300° C for 1 hr, and then dropped to a fixed temperature within 10 min without undershooting. The temperature is maintained for a certain period, after which the charges are dropped into distilled water by electrically cutting the platinum wire hanging the wire loop.

Because supercooling effects are inevitable in the growth of crystals in basaltic melts (Gibb, 1974; Donaldson, 1979; Baker and Grove, 1985), seeded runs were made with fusion time schedules to grow plagioclase at a small degree of undercooling ($\Delta T = 15^{\circ}-25^{\circ}C$) for 43-46 hr. The initial pellets consisted of fused glass powder and plagioclase seed crystals; however, the plagioclase growth rate was too low to produce overgrowth on the seeded plagioclase for electronprobe microanalyses. Reversed experiments would be difficult to achieve in runs of reasonable duration because of the slow diffusion rates of ferric and ferrous irons and magnesium in plagioclase, as noted in the seeded experiments. Only the growth experiments were used to determine element partition coefficients.

RESULTS

The experimental results are presented in Table 2 and Figure 3. The plagioclase liquidus temperatures were determined by the heating experiment. Sample 111-504B-143R-2 (Piece 8) yielded a liquidus temperature of $1253^{\circ} \pm 3^{\circ}$ C, whereas Sample 111-504B-169R-1 (Piece 1) yielded $1235^{\circ} \pm 5^{\circ}$ C. The cooling experiments showed the marked delay of plagioclase nucleation demonstrated by Gibb (1974) and Tsuchiyama (1983). Undercooling by about 30°C yielded nucleation and growth of plagioclase (Fig. 3).

Electron microprobe analyses of the phases in the experimental charge are shown in Table 3. Glasses are chemically homogeneous, but plagioclase crystals may be slightly zoned (Fig. 4). Therefore, only the rim compositions of the plagioclases were used in this work. Although Longhi et al. (1976) suggested considerable effects of secondary fluorescence in analyzing iron in plagioclase rims, the iron contents of the plagioclase cores and rims within a charge are within the analytical errors (Fig. 4). Some of the runs conducted at reduced conditions show iron loss from the glass (e.g., run 41A) as a result of the use of undoped 0.1-mm-diameter platinum wire. The errors induced by this effect are mostly within the analytical errors of the partition coefficients.

The An contents of the plagioclases are well correlated to the CaO/Na₂O ratio and/or the normative An/(An + Ab) ratio of the coexisting glass. The most calcic plagioclase obtained in these experiments has an An content of about 84 (run 15A; Table 3). As one of the most calcic compositions reported in experimental products of ocean-floor basalts (Fukuyama and Hamuro, 1978; Walker et al., 1979; Grove and Bryan, 1983; Tormey et al., 1987), these data reflect the highly depleted chemical characteristics of the Hole 504B basalts (Autio and Rhodes, 1982; Natland et al., 1982). The calcic plagioclase coexisted with glass that has a CaO/Na₂O ratio of about 7. Therefore, the highly calcic plagioclase phenocrysts (An₈₅₋₉₀) common in ocean-floor basalts possibly crystallized from a calcic melt (CaO/Na₂O = 7-9), as suggested by Elthon and Casey (1985).

As Bryan (1974) noted, Mg and Fe occupy the tetrahedral sites of plagioclase. In this study, for values of \log_{102} between -0.7 and -11.5, the cationic contents of Ca + Na + K (oxygen = 8.0) of plagioclases are approximately unity, suggesting that magnesium and ferrous and ferric iron are accommodated in the tetrahedral sites of plagioclase. They probably form the components NaFeSi₃O₈, CaFe2Si₂O₈, and Ca(MgFe)Si₃O₈ in plagioclase. These provisional components may play an important role in the formulation of the partition coefficients of Mg and Fe between plagioclase and liquid as a function of f_{02} .

The MgO and FeO (total Fe as FeO) contents of plagioclase of the experimental charges are plotted in Figure 1. The MgO contents of plagioclase are about 0.4 wt% and are not correlated with the f_{O2} values of the run conditions. On the other hand, the FeO (total Fe as FeO) contents of plagioclase vary with the f_{O2} conditions. The FeO contents of plagioclase are less than 0.3 wt% for reduced conditions, 0.4–0.7 wt% for fayalitemagnetite-quartz assemblage redox conditions, and up to 3 wt% for more oxidizing conditions (Fig. 1). This marked dependence was first noted by Longhi et al. (1976), based on the distribution coefficients of Fe between plagioclase and liquid in lunar and terrestrial basalts. In this work, the author conducted partitioning experiments in a much wider span of f_{O2} conditions to



Figure 1. MgO and FeO contents of plagioclase in natural rocks and experimental charges. The variation of MgO and FeO contents of natural plagioclase are controlled by temperature, solution properties of plagioclase, and liquid composition. The plotted values from experimental plagioclase demonstrate the strong effect of f_{O2} on the distribution of FeO in plagioclase. The discrepancy between the MgO abundances of natural and experimental plagioclases indicates the kinetic disequilibrium effect on element partitioning.

formulate the partitioning of Mg and Fe between plagioclase and liquid as a function of f_{O2} .

The simple weight ratio distribution coefficients of Mg and Fe between plagioclase and liquid are shown in Figure 5, along with the partition coefficients observed in the natural samples (phenocryst and bulk rock). The distribution coefficients of Mg in the natural systems are distinctly lower than those in the experimental systems. This discrepancy implies that kinetic disequilibrium plays a role in the distribution of Mg between plagioclase and liquid. Because the experimental plagioclase crystallized at temperatures 30° - 70° C less than that of the liquidus, the degree of supersaturation is much larger than in the natural systems. The larger degree of supercooling of the experimental systems might have induced more rapid growth of plagioclase, which, in turn, promoted the incorporation of impurities (MgO, FeO, etc.). The distribution coefficients determined by the experiments, therefore, may not represent the true equilibrium value, although the pseudoequilibrium conditions of the partitioning would be attained in terms of the exchange reaction of Mg and Fe between plagioclase and liquid, as discussed in the next section.

FORMULATION OF THE PARTITION COEFFICIENTS OF MG AND FE BETWEEN PLAGIOCLASE AND LIQUID

Kinetic disequilibrium of the partitioning of elements between crystals and liquids is caused both by the buildup of concentration gradients near growing crystals (Burton et al., 1953; Albarede and Bottinga, 1972) and by the boundary effects of crystal/liquid interfaces. The latter are commonly observed as



Figure 2. Experimental procedures used in this study.

sector zonings in igneous minerals (e.g., Nakamura, 1973; Hollister and Gancarz, 1970). Bryan (1974) described sector zonings of plagioclase in some ocean-floor basalts in which both Mg and Fe are concentrated in the (001) sectors in comparison with the (010) sectors. The cooperative behaviors of Mg and Fe in sector-zoned plagioclase suggest that the interface effects are nearly equal for magnesium and iron.

The first cause of disequilibrium partitioning, the buildup of concentration gradients near growing crystals, is determined mainly by the diffusion coefficients and distribution coefficients of the elements involved. Burton et al. (1953) gave an equation of the effective distribution coefficient as

$$D' = D/(D + [1-D]\exp[-Vd/R]),$$

where D is the equilibrium distribution coefficient and V, d, and R are growth rate, thickness of diffusion layer, and diffusion coefficient of the element, respectively. Diffusion coefficients of Mg, Fe^{2+} , and Fe^{3+} are estimated to be $10^{-6.6}$, $10^{-6.7}$, and $10^{-7.0}$ cm²/s, according to the empirical correlation between R and Z^2r (Hofmann, 1980), where Z is the valence and r is the ionic radius of elements. Equilibrium distribution coefficients of Mg, Fe²⁺, and Fe³⁺ are provisionally calculated to be 0.042, 0.012, and 0.66, based on the model formulation discussed in the following paragraph. V, the growth rate, is on the order of 3×10^{-5} cm²/s (Dowty, 1980), whereas d, the thickness of the diffusion layer, is supposed to be 10^{-3} cm. From these values, the departure of the effective distribution coefficients from the equilibrium distribution coefficients are calculated as D'/D to be 1.12, 1.16, and 1.09 for Mg, Fe²⁺, and Fe3+, respectively. Although the variables such as the growth rate may differ from one experiment to another, the sense and magnitude of the departure from equilibrium would be similar for the distribution coefficients of Mg, Fe²⁺, and Fe³⁺ in a crystallizing system. Therefore, in considering the exchange partition coefficient of Mg and Fe between plagioclase and liquid, $K = (Mg/Fe)_{plagioclase}/(Mg/Fe)_{liquid}$, the disequilibrium effects are much less than in the case of simple ratio distribution coefficients.

As noted previously, Mg and ferrous iron are incorporated in plagioclase as a $Ca(Mg,Fe)Si_3O_8$ component, whereas ferric iron may go into plagioclase as NaFeSi₃O₈ or CaFe₂Si₂O₈ compo-

nents. Therefore, the equilibrium exchange reactions are formulated as follows:

1

$$CaMgSi_{3}O_{8} + FeO = CaFeSi_{3}O_{8} + MgO$$
(1)

$$NaFeSi_{3}O_{8} + 0.5Al_{2}O_{3} = NaAlSi_{3}O_{8} + 0.5Fe_{2}O_{3}$$
 (2)

Assuming that the activity coefficients of the components in plagioclase and melt are constant, an exchange partition coefficient of Mg and Fe between plagioclase and magma can be formulated by a linear combination of the preceding reactions using the equation of redox states of iron in liquid of Kilinc et al. (1983). From the compositional data of runs 42A ($f_{O2} = 10^{-7}$) and 79A ($f_{O2} = 10^{-11.5}$), the apparent reaction constants of equations (1) and (2) are 4.09 and 3.49, respectively. The distribution coefficients of Mg, Fe²⁺, and Fe³⁺ are 0.042, 0.012, and 0.66, respectively. However, this model does not fit all of the experimental data, in part because of the nonideal behavior of the Mg and Fe components in plagioclase solid solution, and in part because of the probable decomposition reaction of ferric-rich plagioclase under oxidized conditions. Therefore, an empirical approach was taken in this study in estimating the redox state of magmas.

The exchange partition coefficient of Mg and total Fe between plagioclase and liquid as a function of f_{O2} is plotted in Figure 6. The figure demonstrates a good correlation between the exchange partition coefficient and f_{O2} . However, any additional dependence of the partition coefficient on temperature and composition of the phases has not been resolved. Accordingly, Figure 6 applies only to estimating the approximate redox conditions of ocean floor basalt.

REDOX CONDITIONS OF LEG 111 BASALT SAMPLES

The natural logarithms of the exchange partition coefficients of Mg and total Fe between plagioclase and bulk-rock samples (Table 1) are from -0.50 to -0.55. Applying the relation in Figure 6 results in an f_{02} for the Hole 504B basalt samples that coincides with those defined by fayalite-quartz-magnetite buffer assemblage. Longhi et al. (1976) reported the natural logarithm of the average exchange partition coefficient for mid-ocean ridge basalts as -0.34, which corresponds to slightly more reducing conditions than that of fayalite-magnetite-quartz buffer assemblage in application to the experimental data (Fig. 5).

Christie et al. (1986) discussed the redox states of oceanridge basalts based on the ferric/ferrous ratios of freshly chilled margin glasses. Their results indicate that most of these for values are 0-2 orders of magnitude lower than those of the fayalitemagnetite-quartz assemblage. The overall results of this study harmonize with Christie et al.'s (1986) results. Whereas the method of Mg-Fe exchange partitioning between phenocryst plagioclase and bulk-rock composition may give information about the intratelluric phenocryst crystallization stage of magma evolution, the method of Christie et al. (1986; after Kilinc et al., 1983) records the conditions of erupted magmas. In addition, the estimation of the redox states of magmas by Mg-Fe exchange partitioning between plagioclase and liquid is widely applicable because of the widespread occurrences of plagioclase phenocrysts in volcanic rocks and the apparently low susceptibility of the Mg and Fe contents in basalt and plagioclase to alteration.

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				Phases ^a (%)						
Run	Temperature (°C)	Log f _{O2}	Duration (hr)	Glass	Calcium-rich plagioclase	Olivine	Clinopyroxene	Magnetite		
Samp	le 111-504B-1431	R-2 (Piece	: 8)							
Fusio	n experiment									
04A	1200	-8.0	9.0	60	· 20	_	20	—		
05A	1250	-8.0	1.0	>99	<1		—	—		
06A	1240	-8.0	2.1	99	1	_				
08A	1180	-8.0	13.0	30	40		30	—		
10A	1220	-8.0	1.4	90	20		<1	=		
12A	1150	-8.0	9.2	10	50	_	40	_		
13A	1210	- 8.0	12.3	60	30	?	10	_		
14A	1190	-8.0	10.6	40	40	_	20	—		
22A	1255	-8.0	3.5	100	-	—	—			
43A	1300	-0.7	0.6	100	_		_	_		
Growt	th experiment									
15A	1220	-8.0	47.4	98	2	-		—		
16A	1200	-8.0	73.0	77	20	3	—			
104	1240	- 8.0	33.1	100						
24A	1210	-8.0	25.0	99	1					
25A	1240	- 6.0	13.0	100	<u> </u>		_			
26A	1220	-6.0	19.5	95	5		—	—		
34A	1180	-8.8	24.7	73	20	5	2			
35A	1200	-10.0	32.1	88	10	2	—	_		
41A	1220	-9.7	26.4	100	1			_		
45A	1220	-9.0	39.5	>99	<1	_	_	_		
46A	1220	-8.0 39		>99	<1	_	_	_		
48A	1230	-8.0	24.4	100	-	—	—	—		
50A	1200	-0.7	42.9	83	15	_	_	2		
51A	1200	-3.9	42.1	84	15	_		1		
52A 79A	1200	- 11.5	42.9	85	15	2	_	<1		
Samp	le 111-504B-1691	R-1 (Piece	: 1)			-				
Fusio	n experiment									
03B	1240	-75	3.4	100		2000	2-2			
04B	1200	-8.0	9.0	82	15	=	3	_		
08B	1180	-8.0	13.0	60	30	_	10	—		
09B	1230	-8.0	1.4	99	1	_	—	—		
10B	1220	-8.0	1.0	95	5	_	_			
118	1210	-8.0	2.8	93	7			—		
12B	1210	-8.0	12.3	95	50	2	40	_		
14B	1190	-8.0	10.6	60	30	÷	10	_		
44B	1300	-0.7	0.4	100	—		·			
Growt	th experiment									
05B	1220	-8.0	47.4	100	-	-	—	—		
16B	1200	-8.0	73.0	95	5	_	_	—		
18B	1240	-8.0	31.5	100	_	_		-		
19B	1230	-8.0	23.0	100	—	—	-	—		
26B	1220	-6.0	19.5	100	_					
34B	1180	- 8.8	24.7	95	5	-				
35B	1200	-10.0	32.1	99	1	977	_	-		
39B	1250	-8.0	25.1	100	-			—		
41B	1220	-9.7	26.4	100		\rightarrow	—			
42B	1220	- 7.0	34.5	100						
46B	1220	-8.0	39.5	100		Ξ		=		
47B	1200	-8.0	23.0	>99	<1	_	_	—		
48B	1230	-8.0	24.4	100	_	-	—	-		
50B	1200	-0.7	42.9	93	5	-	-	2		
51B	1200	-3.9	42.1	97	3		—	<1		
79B	1200	-11.5	97.5	98	2	_		-		
	.200		21.2	20	-					

Table 2. Experimental results of Leg 111 basalt samples.

^a Estimated by microscopic observation.

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F	HASE REL	ATIONS ($\log fO_2 = -$	8)	
	• : pre	esent	 : absent 	t	
<u>م</u>	: olivine,	p: plagioc	ase, c: cli	nopyroxen	e
	(143-	2-8)	(169-	-1-1)	
1260-	opc	opc	opc	opc	-
	• • •				
T°C -	• • •				1
1240 -	• • •	•••	•••	•••	-
-	• • •	•••	• • •		-
1220 -	• • •	• • •	• • •	•••	-
	• • •	• • •	• • •	•••	-
1200 -	•	• •	• • •	• • •	-
-	• • •		• • •		-
1180 -	• • •	 0 0 0 	• • •	• • •	-
	FUSION	GROWTH	FUSION	GROWTH	

Figure 3. Phase relations of Leg 111 ocean-floor basalts from two Hole 504B samples. The discrepancy between the results of the fusion and growth experiments is due largely to the delay of nucleation and growth in the latter method.

Fable 3. Electron microprobe analyses	of run products from experiments of	on ODP Leg 111 basalts.	See Table 2 for run conditions
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Run Phase	Averaged analyses	SiO ₂	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Others	Total
Sample 1	11-504B-143	R-2 (Piece 8)											
15A gl	12	49.35 (26)	0.84 (04)	15.71 (25)	8.22 (28)	0.22 (03)	9.42 (19)	13.39 (12)	1.49 (04)	0.01 (01)			98.65
pl	9	47.93 (26)	0.03 (01)	32.34 (22)	0.42 (05)	0.04 (02)	0.35 (02)	17.12 (18)	1.86 (06)	0.00 (00)			100.09
16A gl	11	50.11 (32)	1.18 (04)	14.17 (18)	9.37 (25)	0.20 (03)	8.85 (19)	13.26 (23)	1.58 (03)	0.02 (02)			98.74
pl	10	48.01 (61)	0.04 (02)	32.21 (26)	0.65 (13)	0.01 (01)	0.34 (04)	16.76 (26)	2.03 (21)	0.01 (01)			100.06
ol	16	39.48 (19)	0.00 (00)	0.05 (01)	13.21 (34)	0.18 (02)	46.50 (46)	0.33 (02)	0.03 (01)			NiO 0.15 (02)	99.93
26A gl	23	48.74 (27)	0.86 (05)	14.94 (31)	8.96 (20)	0.22 (03)	9.57 (17)	13.19 (17)	1.60 (05)	0.01 (01)			98.09
pl	14	47.81 (36)	0.05 (01)	30.89 (25)	1.88 (06)	0.05 (01)	0.38 (03)	16.80 (25)	1.92 (10)	0.00 (00)			99.78
34A gl	7	50.60 (38)	1.38 (06)	13.29 (17)	10.63 (19)	0.21 (02)	7.81 (19)	13.30 (14)	1.81 (08)	0.02 (01)			99.05
pl	7	49.30 (39)	0.02 (02)	31.72 (28)	0.75 (11)	0.02 (01)	0.41 (06)	16.24 (30)	2.40 (07)	0.01 (01)			100.87
ol	7	39.18 (40)	0.01 (02)	0.07 (02)	16.09 (52)	0.28 (04)	44.34 (65)	0.42 (03)	0.02 (01)	$Cr_2O_3 0.04 (02)$		NiO 0.10 (02)	100.55
ср	2	52.78 (09)	0.48 (02)	3.28 (44)	6.78 (05)	0.22 (02)	18.68 (49)	18.78 (86)	0.14 (02)			Cr ₂ O ₃ 0.22 (07)	101.36
35A gl	5	50.38 (57)	1.14 (06)	14.79 (31)	8.82 (19)	0.17 (04)	8.73 (47)	13.37 (09)	1.64 (04)	0.02 (00)			99.06
pl	8	48.31 (50)	0.00 (01)	32.42 (19)	0.32 (06)	0.02 (01)	0.35 (02)	16.57 (21)	2.19 (07)	0.01 (01)			100.19
ol	13	39.49 (58)	0.00 (00)	0.06 (01)	13.65 (33)	0.17 (03)	46.28 (46)	0.37 (02)	0.03 (01)	Cr ₂ O ₃ 0.05 (02)		NiO 0.07 (02)	100.17
41A gl	5	49.90 (13)	0.86 (03)	16.23 (12)	7.40 (08)	0.11 (01)	9.31 (12)	13.35 (14)	1.49 (02)	0.01 (01)			98.66
pl	5	47.90 (30)	0.01 (01)	32.40 (16)	0.30 (05)	0.00 (00)	0.37 (01)	16.68 (07)	1.99 (05)	0.01 (00)			99.66
45A gl	6	49.74 (14)	0.83 (01)	16.17 (23)	7.77 (13)	0.12 (02)	9.18 (09)	13.22 (13)	1.60 (03)	0.01 (00)			98.64
pl	5	48.22 (25)	0.02 (01)	32.48 (14)	0.36 (03)	0.00 (00)	0.35 (01)	16.60 (08)	2.12 (09)	0.00 (00)			100.15
46A gl	8	49.48 (31)	0.89 (06)	15.85 (31)	8.12 (11)	0.12 (03)	9.31 (11)	13.20 (12)	1.70 (06)	0.02 (01)			98.69
pl	8	48.04 (28)	0.03 (02)	32.43 (11)	0.41 (03)	0.00 (00)	0.37 (01)	16.70 (20)	2.07 (05)	0.01 (00)	100000000000000000000000000000000000000		100.06
50A gl	6	50.28 (21)	1.14 (02)	13.31 (13)	8.58 (22)	0.17 (02)	10.42 (15)	12.90 (07)	1.65 (07)	0.01 (00)	0.09 (02)		98.55
pl	7	48.62 (10)	0.03 (02)	29.90 (23)	2.77 (15)	0.00 (00)	0.45 (02)	16.07 (25)	2.40 (09)	0.00 (00)	0.05 (04)	194000 00049-0050	100.29
mt	9	0.14 (02)	0.57 (03)	9.86 (66)	61.40 (93)	0.36 (03)	17.63 (54)	0.08 (03)	0.02 (01)	Cr ₂ O ₃ 2.59 (37)	0.27	NiO 0.43 (05)	93.08
51A gl	5	49.60 (20)	1.05 (02)	13.84 (10)	9.44 (12)	0.15 (02)	10.23 (05)	12.82 (17)	1.57 (10)	0.01 (00)	0.08 (03)		98.79
pl	4	48.53 (20)	0.01 (01)	30.72 (25)	2.01 (04)	0.00 (00)	0.41 (03)	16.43 (17)	2.26 (10)	0.00 (00)	0.04 (03)	0.02.000	100.41
mt	2	0.15	0.67	10.76	57.07	0.24	14.55	0.18	0.01	Cr ₂ O ₃ 10.10		NiO 0.41	94.14
52A gl	7	49.61 (24)	1.07 (03)	13.92 (16)	9.53 (26)	0.15 (03)	10.24 (10)	12.67 (06)	1.69 (03)	0.01 (00)	0.12 (02)		99.01
pl	6	43.43 (54)	0.01 (02)	31.48 (28)	1.30 (09)	0.00 (00)	0.37 (01)	16.48 (33)	2.30 (20)	0.00 (00)	0.04 (02)		100.41
mt	1	0.15	0.70	11.69	55.12	0.23	13.96	0.23	0.01	Cr ₂ O ₃ 12.15	0.24	NiO 0.39	94.87
79A gl	7	51.96 (58)	1.29 (04)	13.97 (15)	7.90 (34)	0.16 (02)	8.56 (12)	13.77 (12)	0.84 (02)	0.01 (00)	0.07 (04)		98.53
pl	6	48.49 (61)	0.01 (01)	32.45 (22)	0.24 (04)	0.00 (00)	0.42 (02)	17.07 (34)	1.87 (23)	0.00 (00)			100.55
ol	4	39.56 (16)	0.00 (01)	0.11 (01)	13.62 (14)	0.21 (01)	45.77 (25)	0.37 (02)	0.01 (00)	Cr ₂ O ₃ 0.05 (00)		NiO 0.03 (02)	99.73
Sample 1	11-504B-169H	R-1 (Piece 1)											
16B gl	3	51.06 (27)	1.08 (03)	14.73 (07)	8.93 (15)	0.18 (04)	8.83 (04)	13.27 (18)	1.75 (05)	0.01 (01)			99.84
pl	8	48.10 (27)	0.02 (01)	31.84 (31)	0.64 (09)	0.01 (02)	0.37 (04)	16.53 (22)	2.18 (05)	0.02 (01)			99.71
34B gl	4	50.43 (35)	1.18 (04)	13.92 (36)	9.38 (18)	0.18 (03)	9.33 (28)	13.28 (22)	1.75 (04)	0.02 (01)			99.47
pl	3	49.27 (05)	0.01 (01)	31.37 (26)	0.58 (01)	0.03 (00)	0.41 (01)	15.86 (08)	2.58 (06)	0.02 (01)			100.13
35B gl	3	50.50 (16)	1.07 (04)	15.16 (10)	8.30 (23)	0.15 (02)	8.62 (06)	13.43 (08)	1.62 (07)	0.02 (01)			98.87
pl	3	48.62 (30)	0.04 (01)	32.15 (29)	0.39 (04)	0.02 (00)	0.38 (04)	16.41 (09)	2.28 (07)	0.02 (01)			100.31
47B gl	8	50.01 (27)	1.01 (07)	14.78 (40)	8.66 (27)	0.12 (03)	8.58 (21)	13.31 (06)	1.81 (07)	0.01 (01)			98.29
pl	6	48.42 (22)	0.02 (01)	31.57 (26)	0.54 (06)	0.00 (00)	0.39 (03)	16.23 (17)	2.37 (10)	0.00 (00)			99.54
50B gl	5	50.56 (11)	1.19 (03)	13.21 (07)	9.35 (18)	0.13 (01)	9.25 (12)	13.08 (16)	1.72 (03)	0.01 (01)	0.09 (04)		98.59
pl	7	49.04 (57)	0.02 (01)	29.64 (40)	2.86 (11)	0.00 (00)	0.45 (02)	15.90 (30)	2.50 (10)	0.00 (00)	0.02 (02)		100.43
mt	4	0.20 (07)	0.53 (03)	8.10 (11)	64.75 (43)	0.36 (02)	16.82 (17)	0.07 (03)	0.00 (01)	Cr2O3 2.56 (16)		NiO 0.41 (02)	93.80
51B gl	5	50.76 (15)	1.13 (03)	13.70 (16)	9.52 (13)	0.13 (02)	9.15 (09)	13.13 (05)	1.75 (06)	0.00 (00)	0.10 (01)		99.37
pl	6	49.38 (43)	0.02 (01)	30.23 (28)	2.09 (08)	0.00 (00)	0.41 (02)	16.00 (17)	2.50 (10)	0.00 (00)	0.04 (00)		100.67
52B gl	5	50.95 (43)	1.04 (07)	14.10 (29)	9.27 (07)	0.11 (02)	9.08 (22)	13.05 (10)	1.78 (07)	0.00 (00)	0.12 (06)		99.50
pl	6	49.51 (38)	0.01 (01)	30.80 (85)	1.41 (28)	0.00 (00)	0.40 (04)	15.96 (33)	2.51 (13)	0.00 (00)	0.03 (02)		100.63
79B gl	5	52.44 (29)	1.13 (03)	14.44 (20)	7.35 (21)	0.14 (01)	9.41 (22)	13.38 (20)	0.91 (02)	0.01 (00)	0.06 (03)		99.27
pl	6	48.33 (39)	0.01 (01)	32.32 (26)	0.21 (04)	0.00 (00)	0.46 (03)	17.01 (31)	1.85 (15)	0.00 (00)	0.0000000000		100.19

Note: cp = clinopyroxene; gl = glass; mt = magnetite; ol = olivine; pl = plagioclase. Numbers in parenthesis denote one standard deviation in terms of least units cited.

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Figure 4. Compositional profiles of plagioclase in the product of run 26A (conditions given in Table 2). Some crystals show reverse zoning in terms of the Ca/(Ca + Na) ratio. Only the rim composition was used to calculate the partition coefficients.



Figure 5. Variations in the Fe³⁺/(total Fe) ratio of the liquid from Sample 111-504B-143R-2 (Piece 8). The composition was calculated with the equation of Kilinc et al. (1983). The lower portion of the figure shows the natural logarithm of distribution coefficients of FeO^{*} and MgO between plagioclase and liquid against the variation of the natural logarithm of f_{O_2} . D(Mg) is independent on f_{O_2} while D(Fe) illustrates marked dependence upon the variation of log f_{O_2} . FMQ = fayalite-magnetite-quartz assemblage.



Figure 6. Natural logarithm of the exchange partition coefficient of Mg and Fe between plagioclase and magmas vs. the logarithm of f_{02} obtained in this work. The partition coefficients calculated from the phenocryst core and bulk-rock composition (shown on the right side of the figure) indicate the redox state of iron in the Leg 111 basalt samples is near that defined by fayalite-magnetite-quartz (FMQ) assemblage.