24. CHEMICAL VARIATION IN GLASS-WHOLE ROCK PAIRS FROM INDIVIDUAL COOLING UNITS IN HOLES 417D AND 418A¹

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INTRODUCTION

The excellent core recovery at Sites 417 and 418 has made it possible to define many discrete cooling units, of which many are preserved as a complete interconnected core. A "cooling unit" is any physically distinct rock unit bounded by identifiable chilled margins, and may be of extrusive or intrusive igneous origin. The dimensions of a unit may vary accordingly, from half a meter or less in the case of a pillow cross-section, to tens of meters in the case of a massive flow or sill. A cooling unit may or may not coincide with a lithologic unit or chemical unit. A pillowed lava flow may be made up of hundreds of cooling units which are indistinguishable on chemical and petrographic criteria, whereas a massive flow may be chemically and petrographically distinct from cooling units above and below; in the latter case the massive flow might represent a single cooling unit which also is a distinct chemical and lithologic unit.

Many of the cooling units recognized in Holes 417D and 418A show significant textural and mineralogical variation. There is always a general coarsening of grain size from the glassy rim toward a central zone which may have a doleritic, holocrystalline texture. Phenocrysts also vary considerably in abundance and in the relative proportions of plagioclase, olivine, and pyroxene comprising the phenocryst assemblage, though in these cores plagioclase is always the dominant phenocryst phase.

For this preliminary study we have selected crystalline rock samples which are closely associated with glass selected for microprobe analysis at the Smithsonian Institution and included in the glass data set reported by Byerly and Sinton (this volume). In this preliminary investigation we have not attempted to define the total extent of chemical variation throughout a complete cooling unit, but have limited the investigation to a comparison of these closely associated glass-whole rock pairs.

ANALYTICAL TECHNIQUES

Rock chips were carefully hand picked to remove palagonite, carbonate, altered zones, and smectite veins to minimize alteration effects in the geochemical data. Major elements were determined by X-ray fluorescence analyses (XRF) on fused glass discs following the technique of Norrish and Hutton (1969). Precision and accuracy of the technique is indicated in Table 1A from the analyses of the USGS reference rock W-1.

The trace elements Ni, Co, Cr, Cu, Zn, V, Y, Zr, Sr, and Rb were determined by XRF on powdered samples following the technique of Brown et al. (1973). The accuracy of the technique is indicated from analyses of reference rocks in Table 1B. Precision is generally better than ± 5 per cent. In some cases (indicated in Tables 2 and 3) Co, Cr, Hf, and Sc were determined by instrumental neutron activation analysis (INAA), and Sr and Rb by isotope dilution mass spectrometry (IDMS). Indication of the precision and accuracy of these measurements can be found in Frey et al. (1974) and Hart and Brooks (1974). Other indications of the precision and accuracy can be found from analyses of interlaboratory standards (Staudigel, this volume). B, Li, and Ba were determined by direct-reading optical emission spectrometry. Details of the technique and precision and accuracy $(\pm 10\%)$ can be found in Thompson and Bankston (1969).

Concurrent with this study, a selection of these same samples was analyzed for rare earth elements and for strontium and oxygen isotopes. These data are presented and discussed in detail in separate presentations (Staudigel, Hart, and Frey, this volume; Muehlenbachs, this volume).

Minerals were analyzed by the computer-automated electron microprobe at the Massachusetts Institute of Technology. Standards and correction procedures are the same as in our previous studies of DSDP material (Frey et al., 1974). Interlaboratory comparisons performed by Jarosewich et al. (1978) and Staudigel (this volume) show that the agreement for all major elements is generally good; Na shows considerable scatter. No systematic difference

TABLE 1A X-Ray Fluorescence Major Element Analyses of Reference Rock W-1 Run With Site 417 and 418 Samples

	Mean Composition ^a	Standard Deviation	Recommended
SiOn	53.36	± 0.318	52.97
TiO	1.09	± 0.007	1.08
AloÕa	15.20	± 0.099	15.12
FeOc	10.23	± 0.043	10.04
MgO	6.78	± 0.182	6.66
CaO	10.94	± 0.779	11.03
Na ₂ O	2.42	± 0.267	2.16
K20	0.65	± 0.001	0.64
PoOs	0.15	± 0.003	0.14
MnO	0.17	± 0.001	0.17

^aMean and standard deviation of 10 analyses.

^bFrom Flanagan, 1973, corrected for ignition loss.

^cTotal Fe reported as FeO.

¹Woods Hole Oceanographic Institution Contribution 4176.

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TABLE 1B X-Ray Fluorescence Trace Element Analyses of Reference Rocks Run with Site 417 and 418 Samples

	_1	BCR-1	-	W-1	MRG-1		
	Found	Recomm. ^a	Found	Recomm. ^a	Found	Recomm.b	
Zn	123	120	83	86	184	185	
Cu	21	18	112	110	129	135	
Ni	16	16	78	76	190	200	
Cr	15	17	117	114	419	420	
V	398	399	262	264	541	520	
Co	35	37	47	47	86	87	
Zr	187	190	103	105	107	100	
Y	37	37	25	25	17	20	
Sr	329	330	191	190	269	260	
Rb	47	47	22	21	7	8	

^aFlanagan, 1973.

^bAbbey, 1976.

between the Smithsonian and M.I.T. probes could be detected.

PETROGRAPHY AND MINERALOGY

The major phenocryst phases are plagioclase, olivine, and clinopyroxene. Magnetite occurs both as microphenocrysts and groundmass microlites. Spinel was found as a minor phenocryst phase in Hole 418A basalts. Where plagioclase occurs in varying proportions (5-25 vol. %) throughout both Holes 417D and 418A, olivine and clinopyroxene roughly increase in abundance towards the base of Hole 418A. Their abundance varies from 0 to 5 vol. per cent (olivine) and from 0 to 7 vol. per cent (clinopyroxene). Major changes in liquid (glass) composition, as given by Byerly and Sinton (this volume), are usually accompanied by major changes in mafic phenocryst abundances (see also Robinson et al., this volume). All phenocryst phases show significant variability in abundance even within single cooling units.

Plagioclase occurs both as individual, mostly euhedral phenocrysts up to several millimeters in size, and as glomerocrysts with clinopyroxene and minor olivine. Glomerocrysts form "bow-ties" or subophitic, often gabbroic, glomerocrysts. In Hole 418A, plagioclase composition ranges from Ab54 in a phenocryst rim to Ab9.3 in the center of a phenocryst in the most maficmelts in unit C as defined by Byerly and Sinton (this volume). Most phenocryst interiors, however, vary from roughly Ab14 to Ab24 (averages given in Table 4). Even though single crystals can vary by 25 mol. per cent Ab, there is a rough correlation of plagioclase composition with liquid composition (high in Ab in high-TiO2liquids) and cooling rate (higher Ab in massive units). The amount of minor elements increases towards the rim of the phenocrysts, FeO and Mg being incorporated roughly in equal molar amounts (wt. % FeO is approximately 2×wt. % MgO).

Olivine usually occurs as individual, euhedral phenocrysts < 1 mm in size. Fresh olivine occurs throughout Hole

TABLE 2 Whole Rock Major Element and Trace Element Analyses, Hole 417D

	26-3, 40	27-7, 14	33-4, 20	35-5,9	35-5, 126	38-3, 123	42-5, 115	49-2, 23	53-2, 61	60-6, 50	68-4, 20	69-1, 122
Glass ^a												
Equivalent	(2901)	(2848)		(2859)			(2866)	(2873)	(2873)			
SiO ₂	49.65	49.62	49.03	48.60	49.34	48.30.	48.73	49.03	49.10	46.23	48.23	49.15
TiO ₂	1.62	1.45	1.38	1.41	1.42	1.40	1.53	1.66	1.58	1.27	1.52	1.31
Al2Õ3	16.62	16.51	16.07	17.33	16.77	16.50	15.50	16.61	14.89	16.65	16.06	16.52
Fe2O3	4.41	4.79	3.41	5.29	4.63	4.89	4.58	4.87	5.07	4.01	5.74	7.19
FeÕ	5.24	5.04	6.92	4.35	5.24	5.53	5.53	5.14	6.52	4.74	5.33	3.45
MnO	0.13	0.13	0.15	0.12	0.14	0.14	0.16	0.15	0.15	0.22	0.13	0.17
MgO	6.18	6.19	6.82	5.53	6.28	6.30	6.96	6.43	6.62	6.45	7.12	7.43
CaO	11.23	11.52	12.10	12.07	11.81	11.94	12.67	11.03	11.93	14.88	10.44	11.98
Na ₂ O	2.34	2.11	1.95	1.89	2.12	1.72	2.13	2.37	1.97	2.22	2.30	2.04
K20	0.42 ^b	0.64	0.07	0.85	0.56	0.50	0.05	0.34 ^b	0.41	0.08 ^b	0.08	0.05 ^b
P205	0.15	0.13	0.11	0.14	0.15	0.14	0.16	0.16	0.14	0.13	0.12	0.14
HOC	1.29	1.23	0.86	1.61	1.28	1.72	1.01	1.39	1.13	1.08	1.77	0.86
cõ ₂	0.72	.69	0.50	.50	.67	1.28	1.18	1.00	.56	2.86	.85	0.32
Sum	100.00	100.05	99.37	100.54	100.37	100.36	100.14	100.68	100.07	100.81	99.69	100.61
Rb	4.16 ^b	9	<1	12	9	8	<1	5.69 ^b	10	0.32 ^b	<1	0.37
Sr	115.90	108	90	112	109	108	111	117.9 ^b	97	114.6 ^b	108	97.9
Ba	8.2 ^b	9	6	10	9	39	5	8.9 ^b	3	5.5 ^b	14	9.6 ^b
Li	6	6	4	7	7	7	5	6	4	5	4	4
В	13	18	<2	23	14	18	6	7	24	2	2	5
Y	41	36	28	35	38	37	37	36	41	32	40	34
Zr	103	94	73	92	116	92	96	104	96	77	97	85
Hf	2.51 ^c							2.74 ^C	~ ~			2.15 ^c
Sc	49.27 ^c							51.26 ^c				41.44 ^c
V	400	366	341	356	350	335	367	420	403	313	368	315
Ċr	224.9°	236	183	245	246	226	222	230.2C	221	199.2°	274	176
Co	57.1°	56	40	48	51	45	51	45.9C	47	38.6 ^C	45	42
Ni	138	103	62	75	94	88	104	89	88	87	93	96
Cu	102	91	54	112	82	95	102	102	99	88	99	83
Zn	100	93	61	109	98	89	87	90	94	74	80	69

^aUSNM number of corresponding glass (Byerly and Sinton, this volume).

^bDetermined by IDMS.

^cDetermined by INAA.

1:	5-2, 0	17-3, 40	18-4, 40	22-1, 46	24-1, 59	30-3, 4	41-3, 100	42-3, 68	45-2, 131	52-5, 75	55-6, 15	57-2, 113
Glass ^a												
Equivalent (3	3040)					(2939)		(3041)		(3021)	(3020)	(3025)
SiO ₂ 4	49.81	48.62	49.55	48.15	49.73	48.37	47.88	47.36	48.41	49.41	49.83	48.37
TiO ₂	1.20	1.22	1.13	1.13	1.22	1.23	1.13	.99	1.05	1.12	1.30	1.40
$Al_2 \tilde{O}_3$ 1	17.48	17.23	16.57	15.98	17.45	16.24	16.49	17.29	17.28	16.77	15.34	16.90
Fe203	3.88	3.51	3.82	3.87	4.68	4.29	4.91	3.82	3.51	4.22	4.17	3.71
FeÕ	4.84	4.64	5.63	5.14	4.15	5.24	4.25	4.54	4.94	5.33	6.32	6.22
MnO	0.11	0.14	0.16	0.16	0.09	0.18	0.18	0.11	0.15	0.15	0.18	0.13
MgO	6.76	7.09	7.55	7.27	5:69	7.24	5.93	6.57	7.17	6.78	7.69	5.45
CaO 1	11.57	12.74	12.41	12.64	11.66	12.62	13.16	12.15	13.04	12.68	12.28	12.89
Na ₂ O	2.53	2.58	1.80	2.47	2.86	1.89	2.15	2.39	2.03	1.80	2.22	2.08
K20	0.34 ^D	0.14 ^b	0.05 ^b	0.03	0.29	0.15	1.33 ^b	0.21 ^b	0.15	0.13	0.07	0.12
P205	0.14	0.14	0.13	0.14	0.13	0.14	0.13	0.09	0.11	0.12	0.14	0.09
H ₂ O ^c	1.18	1.13	0.76	1.02	1.39	0.89	1.54	1.30	1.26	1.09	0.72	1.08
cõ ₂	0.54	1.21	0.45	0.97	0.64	0.81	1.59	0.55	1.36	0.58	0.41	0.61
Sum 10	00.38	100.06	100.35	100.38	99.98	99.26	100.74	100.16	100.46	100.18	100.75	99.05
Rb	3.02b	1.33b	0.41b	1	4	3.5	9.48b	2.31b	2	3	<1	2.96b
Sr 11	14.0b	120.9b	110.7b	113	117	106	376.2b	116.5b	106	103	105	105.7b
Ba 1	10.9b	13.9b	7.1b	5	7	4	5.6b	4	6	4	5	7.5b
Li	5	7	4	8	4	3	7	5	5	4	5	6
B	19	31	14	46	19	49	79	3	38	8	2	8
Y 3	30	28	29	28	30	32	33	25	29	31	34	36
Zr	78	75	73	73	78	78	67	64	70	73	83	87
Hf	1.830			1.88 ^c				1.60 ^c				2.170
Sc 4	46.01 ^c	21 23		46.20 ^c				47.00 ^c	222	67273	10010/	44.49 ^c
V 32	21	319	295	302	326	325	303	268	293	299	336	353
Cr 21	12.20	223	212	249.3°	248	264	294	346.3 ^c	319	292	280	216.4 ^c
Co 4	43.70	58	41	41.6 ^c	69	49	50	42.7 ^c	52	50	48	42.30
Ni S	94	97	76	83	95	107	115	125	136	131	110	89
Cu S	99	104	102	97	106	99	98	93	98	102	107	93
Zn 8	81	73	60	68	68	81	73	63	68	72	80	80

 TABLE 3

 Whole Rock Major Element and Trace Element Analyses, Hole 418A, Except as Indicated

^aUSNM number of corresponding glass (Byerly and Sinton, this volume).

^bDetermined by IDMS.

^cDetermined by INAA.

418A, mostly in glassy selvages. In crystalline interiors of individual cooling units olivine is usually replaced by smectite and/or carbonate. Olivine shows a limited compositional range from Fos₂ to Fos₇. The olivine composition is clearly related to the corresponding composition (Fo-content decreases with TiO₂ of glass). Single olivine crystals are very homogeneous. An average analysis is given in Table 4.

Clinopyroxene occurs mostly as subhedral individual phenocrysts up to roughly 1 mm in size in subophitic glomerocrysts. Euhedral, often nearly spherical xenocrysts are common and are up to several millimeters in size. Clinopyroxene phenocrysts are usually zoned, e.g., En41 Fs25 Wo34 (rim) — En47 F\$17 Wo36 (center). An analyzed xenocryst is comparatively homogeneous (En51 Fs8 Wo41 — En54 Fs59 Wo38). Average analyses are given in Table 4.

CHEMICAL VARIATION IN HOLES 417D AND 418A

Our major and trace element data for whole rock basalt samples are presented in Tables 2 and 3. Similar to the plots presented by Bryan and Flower (this volume) and Flower and Bryan (this volume) for the shipboard chemical analyses, we have plotted some critical major element parameters in Figures 1 and 2. Comparison with the shipboard analyses indicate that our data cover most of the known range of variation at Holes 417D and 418A and no exceptional analyses have been found. There is considerable overlap of major and trace element abundances, and no distinct grouping is encountered.

Plots of Y versus Zr (Figure 3) or Zr versus TiO₂ (Figure 4) show strong correlation and similarity between the two sites. These are elements insensitive to weathering (Thompson, 1973) and, being incompatible elements, i.e., preferably partitioned into the liquid phase, their ratios are not significantly affected by crystal accumulation or fractional crystallization. The Y/Zr ratio is relatively constant and the data plot on a straight line passing through the origin (Figure 3). Other incompatible elements like Ti, V and REE (Staudigel et al., this volume) also show relatively constant ratios. This suggests a similar homogeneous source region for the baslats from both sites.

Figure 5 shows a plot of Ni versus TiO₂ for the two sites. The variability of the glass data (Byerly and Sinton, this volume) suggests fractional crystallization up to 34 per cent, always including olivine (up to 5.4%). Because Ni is preferentially partitioned into olivine, increasing fractionation (indicated by increasing TiO₂ content) should be accompanied by decreasing Ni. This trend shows considerable scatter, as seen in Figure 5, which may reflect crystal accumulation or redistribution.

The trace elements B, Li, Rb, and occasionally Sr and Ba, show variability reflecting low temperature alteration

60-5, 133	62-4, 104	64-4, 82	69-3, 63	73-1, 127	76-1, 4	76-2, 99	77-2, 47	79-4, 88 (Dike)	79-4, 88	80-2, 123	86-5, 29	418B- 35-5, 78
	1046121212		V647815-937									
10.02	(3047)	(3049)	(3051)	(3029)	(3027)	11.11	40.21	(3052)	10.01	40.05	(3032)	(3035)
48.03	49.50	48.46	48.70	49.55	49.39	46.66	48.31	49.22	48.84	49.85	48.76	50.67
1.48	1.56	1.29	1.20	1.20	1.29	1.00	1.29	1.21	1.23	1.24	1.17	17.24
15.74	15.91	16.14	10.47	15.94	16.30	14.92	14.99	15.08	15.96	16.10	17.15	17.30
4.72	3.93	3.87	3.84	5.99	4.17	4.40	4.18	n.d.	3.46	5.72	4.21	3.88
5.83	0.02	5.63	0.22	0.03	5.45	5.50	5.55	9.57	5.05	0.32	5.14	4.25
0.15	0.17	0.16	0.17	0.17	0.10	0.13	0.18	0.16	0.17	0.17	0.14	0.09
6.05	6.84	6.18	1.25	12.40	1.59	0.92	0.92	12.09	0.50	7.18	5.78	0.01
1203	12.04	13.86	12.60	12.40	2.26	15.29	14.04	12.98	13.33	12.83	13.54	11.29
2.31	1.92 0.00b	2.35	1.80	2.05	2.30 0.22b	2.25 0.10b	1.76	1.70	2.17	1.73	2.08 0.07b	2.44
0.03	0.220	0.07	0.12	0.06	0.23	0.10	0.01	0.24	0.03	0.01	0.07	0.88
0.09	0.16	0.15	0.12	0.14	0.14	0.13	0.16	0.15	0.14	0.12	0.13	0.12
0.94	1.03	0.95	0.92	0.79	1.20	0.95	0.64	1.08	0.02	0.76	1.10	1.27
0.97	0.68	1.25	0.49	0.42	0.54	3.09	2.41	1.20	1.24	0.40	0.80	0.00
98.95	100.55	100.33	99.92	100.56	100.68	99.38	100.42	100.05	99.59	100.49	100.13	100.16
<1	3.84b	1.45b	1.56 ^b	<1	1.45b	2.55b	<1	<1	1	<1	1.07b	7
126	116.5b	112.5 ^b	109.1b	105	122.1b	127.4b	129	117	109	99	107.8b	115
6	11.5b	7.9b	16.9 ^b	6	8	5	8	11	6	2	5.8b	11
4	5	5	1	2	2	4	2	1	3	1	1	7
46	8	29	2	<2	<2	4	<2	9	<2	<2	<2	14
38	40	33	33	33	33	28	33	31	32	31	30	29
97	102	85	84	81	84	67	86	80	78	78	77	80
	2.51 ^c			2.16 ^c		1.40 ^c				1.98 ^c	1.69 ^c	
	45.95 ^c			46.04 ^c		43.16 ^c				44.87 ^c	43.62 ^c	
364	385	340	327	338	337	281	334	319	315	320	316	331
192	209.7 ^c	183	222	230.6 ^c	198	259.7 ^c	154	259	181	270.2 ^c	304.5 ^c	244
45	44.9 ^c	48	47	43.6 ^c	46	41.2 ^c	44	47	41	48.3 ^c	43.7 ^c	59
86	93	79	90	85	78	123	81	101	65	91	118	98
92	94	104	84	90	89	99	100	94	84	95	96	99
79	93	82	76	78	83	57	70	71	64	70	73	82

TABLE 3 - Continued

TABLE 4 Average Mineral Compositions in Site 418 Basalts

	Olivine ^a	Clinopy	roxene	Plagioclase		
		Phenocryst	Xenocryst	Ab 14 ^a	Ab 24	
	12 ^b	18 ^b	10 ^b	18 ^b	12 ^b	
SiO ₂	38.54	51.50	52.80	46.94	49.03	
TiO ₂	0.07	0.55	0.32	0.02	0.02	
Al2Õ3	0.09	3.38	2.66	33.30	31.61	
FeO	15.06	7.23	5.40	0.43	0.44	
MgO	45.74	17.09	18.56	0.21	0.28	
MnO	0.27	0.19	0.18	0.01	0.05	
CaO	0.38	19.28	19.48	17.20	15.35	
Na ₂ O	0.01	0.22	0.24	1.59	2.63	
K2O	0.00	0.00	0.00	0.01	0.02	
Cr203	0.07	0.37	0.68	0.02	0.01	
Sum	100.23	99.81	100.32	99.73	99.44	

^aCompositions used for least-squares calculations.

^bNumber of averaged analyses.

processes. They are generally positively correlated with increasing K_2O , H_2O , and Fe_2O_3/FeO as would be expected with increasing alteration.

In Tables 5A and 5B, we show average compositions for some trace elements based on TiO₂ contents. In general, particularly in Hole 418A, the role of fractional crystallization in explaining the ranges is clearly documented. Incompatible elements such as Sr, Y, Zr, V, and Zn show increasing concentration with increasing TiO₂ in both sites. Compatible elements such as Cr, Ni, and Cu apparently



Figure 1. Al₂O₃ vs. TiO₂ in Holes 417D and 418A whole rocks.

show decreasing concentrations with increasing TiO_2 in Hole 418A. This correlation is reversed as seen in Hole 417D where the compatible elements show relatively high concentrations at higher TiO_2 contents, this effect possibly being due to crystal accumulation as discussed in a later section.

Although no obvious chemical groupings or differences are readily detectable between the two sites or within a given site, there are no simple systematic trends from top to





Figure 2. FeO vs. TiO₂ in Holes 417D and 418A whole rocks.



Figure 3. Y vs. Zr in Holes 417D and 418A whole rocks.



Figure 4. Zr vs. TiO₂ in Holes 417D and 418A whole rocks.



Figure 5. Ni vs. TiO₂ in Holes 417D and 418A whole rocks.

TABLE 5A Average Trace Element Compositions of Hole 417D Basalts Grouped by TiO₂ Contents

		2. T	
	1.2-1.4% TiO ₂ (N = 3)	1.4-1.6% TiO ₂ (N = 7)	1.6-1.8% TiO ₂ (N = 2)
Sr	101	108	117
Y	31	38	39
Zr	78	97	104
v	323	364	410
Zn	68	93	95
Cr	186	239	228
Ni	82	92	114
Cu	75	97	102

TABLE 5B Average Trace Element Compositions of Hole 418A Basalts Grouped by TiO₂ Contents

	<1.2% TiO ₂ (N = 8)	1.2-1.4% TiO ₂ (N = 13)	>1.4% TiO ₂ (N = 3)
Sr	112	113	116
Y	29	32	38
Zr	71	81	95
V	295	327	367
Zn	67	75	84
Cr	285	225	206
Ni	113	90	89
Cu	98	96	93
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bottom in either hole. Chemical groupings are recognized only according to stratigraphic entities or cooling units. In Table 5C we show averages for the trace element contents of various such units recognized by Byerly and Sinton (this volume) and Robinson et al. (this volume) and based on glass chemistry and lithology in Hole 418A basalts. In the upper part of Hole 418A (glass groups A-F) the incompatible elements of our whole rock analyses show typical low pressure fractionation characteristics, e.g., high Sr, Y, Zr, V, and Zn at high Ti, FeO/MgO. The compatible elements show a less systematic behavior which might re-

TABLE 5C Average Trace Element Composition of Site 418A Basalts Grouped Stratigraphically and by Previously Recognized Chemical Units

Glass group ^a	A, B	C-E	н	1	J			
Chemical group	1	11	111	IV	v	VI	VII	VIII
Number of samples	(N=7)	(N=3)	(N=3)	(N=1)	(N=2)	(N=5)	(N=1)	(N=1)
Sr	114	108	116	113	107	121	99	108
Y	30	28	38	33	33	31	31	30
Zr	75	69	95	85	82	79	78	77
v	313	287	367	340	332	317	320	316
Zn	71	68	84	82	77	69	70	73
Cr	243	319	206	183	222	210	270	305
Ni	95	131	89	79	87	90	91	118
Cu	101	98	93	104	87	93	95	96

^aByerly and Sinton (this volume). ^bRobinson et al. (this volume).

flect the influence of crystal accumulation. The complex interdigitation of these various compositions must reflect a complex tapping of a single magma at various stages of fractionation and/or refilling of the magma chamber, or tapping of two separate magmas at different stages of fractionation. If two magmas are invoked, our chemical data would suggest they are derived from the same or very similar man-

tle sources. The relatively low Rb, Ba, Sr, Y, and Zr contents confirm the rare earth evidence presented by Staudigel et al. (this volume), indicating that these basalts are typical large ion lithophile (LIL) element depleted mid-ocean ridge basalts. The present ridge axis at 22°N is similarly LIL element depleted (Melson et al., 1968; Bryan and Sargent, 1979). Thus it appears that the influence of the Azores "plume" or "blob" (Schilling, 1975) presently seen on the Mid-Atlantic Ridge axis from 37° to 30°N latitude did not extend to the ridge at 22°N during Cretaceous time. Indeed, data from DSDP Site 335, Leg 37 (Bryan and Thompson, 1977) suggest that the Azores plume activity was not present 15 million years ago even at 36°N latitude.

COMPARISON OF GLASS-WHOLE ROCK COMPOSITIONS

Our analyzed whole rock samples have been selected so that in most cases they are physically within a few centimeters of the analyzed glasses. Thus, there is no doubt that these samples represent identical magmas. Subtle variations which might be produced, for example, by successive injections of different magmas through a lava tube or into a sill, are therefore most likely excluded in this data set. Assuming that all samples are perfectly fresh and unmodified by interaction with sea water, and that no systematic instrumental differences exist between the microprobe and X-ray fluorescence analytical methods, the only compositional differences which should exist are those reflecting the phenocryst assemblage included in the whole rock analysis, or those small changes that might result from fine-scale inhomogeneity in the rock. Unfortunately, the selective sampling close to glass margins results in the inclusion of palagonitized glass in many samples, and many of the crystalline rock samples are affected to some extent by submarine low temperature alteration and the precipitation of secondary CaCO₃ (Donnelly et al., this volume). This is clearly seen in the covariance of elements such as K, B, Li, and Rb with H2O content and Fe2O3/FeO ratio. The contents of K, H₂O, and Fe₂O₃/FeO tend to be systematically higher in the whole rock analyses compared to glasses.

Following a practice adopted on shipboard as outlined in the site reports, we originally attempted to correct our analyses by subtracting an amount of CaO equal to that required to convert all CO2 to CaCO3 and, because all Fe is determined as FeO in the microprobe glass analyses, we converted all Fe₂O₃ to FeO. However, we abandoned the carbonate correction because it appeared to over-correct for the addition of CaO as carbonate. We believe this occurs because CaO also is leached from the rock matrix during interaction with sea water. Thus, in more altered samples, the addition of CaO as carbonate veins partly or completely compensates for the loss of CaO in the rock matrix. Thus, we have recalculated the whole rock analyses to 100 per cent volatile-free, with all Fe as FeO, but have made no adjustment in CaO other than that required by the normalization procedure. The microprobe analyses were normalized to 100 per cent only if they initially totaled 99 per cent or less or 101 per cent or more; otherwise the original summation was retained. These normalized whole rock and probe analyses have been used in the graphical plots (Figures 6 and 7) and calculations (Table 6).

Composition relations between glasses and their corresponding whole rock equivalents can be visualized in an MgO variation diagram (Figure 6) in which the corresponding glass-whole rock pairs are indicated by tie lines. Vectors drawn from two arbitrarily chosen points at either end of the data distribution show the trends to be expected from addition of plagioclase, pyroxene, or olivine. The tie lines fall into two categories - one in which all tie lines are approximately parallel to the plagioclase vector, leading to MgO depletion in whole rock relative to glass, and another group that appears to require a mixture of plagioclase and mafic phases and which leads to MgO enrichment in the whole rock relative to the glass. Both trends obviously lead the whole rock compositions away from the liquidus trends, as defined by the chemical variation of the glasses, indicating that the phenocryst distribution has been modified since the melt was extracted from the magma chamber. It is also shown in Figure 6 that phenocryst accumulation can modify the whole rock composition considerably. The difference between glass-whole rock can amount to more than the total range observed in glass compositions for Si, Mg, Al, and Ca, and to more than one-third for parameters like Ti or Fe (e.g., Sample 418A-79-4, 88 cm).

Further insight into these relations is given by a plot of glass-whole rock pairs in the normative ternary plagioclase-pyroxene-olivine (Figure 7), in which the glasses lie along an apparent cotectic similar to that displayed by glasses from FAMOUS and most other DSDP sites (Bryan et al., 1976). The tie lines again fall into two general groups, one set projecting distinctly away from the cotectic into the plagioclase field, and the second set also projecting into the plagioclase field, but trending at a low angle to the cotectic. These trends suggest that whole rock compositions are the result of mixtures of liquid plus one of two populations of cumulate phenocryst assemblages, one consisting almost entirely of plagioclase and the second also dominated by plagioclase but with significant amounts of olivine or pyroxene.



Figure 6. MgO variation diagram for glass-whole rock pairs from Holes 417D and 418A. • = glass analyses (Byerly and Sinton, this volume), and \Box = whole rock analyses. Corresponding glass-whole rock compositions are connected by tielines. Vectors indicate the effect of crystal accumulation of 3 vol. % olivine (.... line), 2 vol. % clinopyroxene (----- line), and 10 vol. % plagioclase (----- line). In the CaO, Al₂O₃ and SiO₂ diagrams, the plagioclase vectors are shown for two compositions – Ab₁₄ and Ab₂₄. Mineral compositions are taken from Table 2.



Figure 7. (a, b). Ternary normative pyroxene-olivine-plagioclase plot for glasses (●) and corresponding whole-rock samples (△) from Holes 417D and 418A. Corresponding pairs are joined by tielines. (Pyroxene is total normative diopside, eustatite, and ferro-silite plus hypersthene.)

The phenocryst assemblage for each glass-whole rock pair was determined by modal analyses, and also theoretically calculated by least-squares mass balance calculations. Modal analyses were carried out using an automatic pointcounting stage. Usually 1500 counts gave representative analyses of an individual thin section, however, the phenocryst distribution can vary considerably even on thin section scale. The modal analyses for olivine and clinopyroxene are particularly biased by alteration effects and grain size, i.e., olivine is often weathered and replaced, and both olivine and clinopyroxene are generally smaller crystals than plagioclase and thus distinction from groundmass crystals is difficult. Modal data are given in column B of Table 6 in volume fractions while other data are in weight per cent. Considering those difficulties and biases, agreement between calculated and empirical "modes" are generally good. The most important point brought out in Table 6 is that both calculated and observed mineral assemblages are impoverished in pyroxene and olivine in the MgO-depleted data sets, whereas significant amounts of these minerals occur in the phenocryst assemblages of the MgO-enriched data sets.

 TiO_2 in whole rock analyses of plagioclase dominated-MgO depleted trends is often slightly higher than plagioclase accumulation would suggest (Figure 6). This is often accompanied by an anomalously high Fe and Cr in the whole rock. Both effects probably indicate titanomagnetite accumulation, and this was observed in thin section in all such cases.

Because of the lack of trace element data for glasses, we are unable to demonstrate any convincing relationship between the nature and degree of phenocryst accumulation in these basalts, and the pattern of trace element enrichments

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or depletions in our whole rock analyses, although generally olivine-rich samples clearly have higher Ni and Cr contents. Lack of other significant trace element correlations probably reflects the dominance of plagioclase in all cumulate assemblages, but also must arise because these assemblages are added in varying proportions to liquids which themselves range over a considerable spectrum of compositions. A more rigorous evaluation of the effect of mineral cumulates on trace elements will thus require trace element analyses on specific glass samples. Also, in spite of the importance of plagioclase as a cumulate phenocryst phase, we have not detected a positive europium anomaly in any of our rare earth patterns for these samples (Staudigel, Hart, and Frey, this volume). This suggests that the plagioclase composition is anorthite-rich and hence does not take up much europium. This is consistent with the relatively calcic plagioclase composition (Table 4) which has worked well in our least-squares calculations (Table 6).

SUMMARY

Graphical constructions, least-squares calculations, and petrographic observations all indicate that secular crystal accumulation has played an important role in modifying initial liquid compositions. The variation within glasswhole rock pairs can amount to more than the total range observed for the glass compositions.

The cumulate phenocryst assemblages tend to fall into two categories, those in which plagioclase is the only important mineral, and those in which plagioclase is accompanied by olivine and/or pyroxene. The exact nature and extent of the chemical changes depend on the amount and proportions of phenocrysts, but generally involve significant increases in CaO and Al₂O₃ and decreases in FeO and TiO₂ in the

TABLE 6 Unweighted Least-Squares Approximation to Selected Whole Rock Compositions Calculated as a Linear Combination of the Equivalent Glass Composition and the Average Phenocryst Mineral Compositions in Table 1

			1	MgO-Enric	hed Trends			
	417D-	42-5	418A-	79-4	418A-	73-1	418A-	76-1
	A	В	A	В	A	В	А	В
SiO ₂	50.18	49.96	50.46	50.37	49.97	50.08	49.56	50.13
TiO	1.39	1.57	1.18	1.24	1.20	1.29	1.21	1.31
AlaŐa	15.93	15.89	15.33	15.43	16.02	16.11	16.41	16.54
FeO	9.97	9.99	9.47	9.79	9.53	9.72	9.34	9.32
MgO	7.10	7.14	7.53	7.57	7.76	7.84	7.51	7.70
CaO	12.98	12.99	13.10	13.29	12.34	12.53	11.97	12.09
Na ₂ O	2.11	2.18	2.02	1.74	2.10	2.05	2.21	2.40
Glass/ Ground-								
mass	0.7944	0.732	0.7346	0.799	0.7948	0.770	0.8373	0.856
Plag.	0.1328	0.201	0.1461	0.151	0.1395	0.180	0.1330	0.116
Cpx	0.0659	0.022	0.1021	0.033	0.0315	0.040	0.0314	0.027
Olivine	0.0105	0.045	0.011	0.017	0.0361	0.010	-0.0072	-
			М	gO-Enrich	ed Trends			
				417D-42-	5, 115			
ago ag				A	В			
SiO ₂				50.18	49.96			
1102				1.39	1.57			
AI203				15.93	15.89			
FeO				9.97	9.99			
MgO				7.10	7.14			
CaO				12.98	12.99			
Na ₂ O				2.11	2.18			
Glass/Gro	oundmass			0.7944	0.732			
Plag.				0.1328	0.201			
Cpx.				0.0659	0.022			
Olivine				0.0105	0.045			
	1		141-271-071	MgO-Dej	pleted	14041212		
	418A-	57-2	418A	-42-3	418A-5	52-5	417D-	35-5
0:0	<u>A</u>	<u>B</u>	<u>A</u>	B	A	B	A	<u>B</u>
SIO2	50.02	49.88	49.68	49.92	50.54	50.37	50.37	50.08
1102	1.36	1.44	1.01	1.04	1.10	1.14	1.38	1.45
Al ₂ O ₃	17.31	17.43	18.27	18.22	17.13	17.10	18.04	17.86
FeO	9.56	9.85	8.53	8.15	9.30	9.31	9.73	9.39
MgO	5.43	5.62	6.93	6.93	6.98	6.91	5.89	5.70
CaO	12.62	13.29	13.09	12.81	13.01	12.93	12.81	12.44
Na ₂ O	2.29	2.14	2.27	2.52	2.24	1.88	2.17	1.95
Glass/ Ground-	2.242454							
mass	0.8680	0.770	0.9111	0.793	0.8879	0.791	0.8285	0.740
Plag.	0.1496	0.223	0.1217	0.207	0.1156	0.204	0.1885	0.250
Cpx.	-0.0046	0.000	-0.0174	-	0.0098		-0.0041	0.010
Olivine	-0.0191	0.006	-0.0078	-	-0.0072	0.005	-0.0010	0.005

Note: The oxides MnO, K_2O , and P_2O_5 were not included in the calculations due to deficiencies in the data base or to uncertainties introduced by weathering effects. In each pair, composition A is calculated, B is observed. See text for discussion of data normalization. Glass and mineral proportions given as weight fractions of mixture.

whole rock data compared to glasses. As is made especially clear by vectors and glass-whole rock pairs plotted in Figure 6, these cumulate phenocryst effects produce considerable scatter in the whole rock data and may significantly change the slope or even the sign of major element covariances in the whole rock compared to the glass data. We conclude from whole rock trace element and major element data, and from microprobe glass analyses, that the magmas at Holes 417 and 418A were formed from a very homogeneous source (by high degree of partial melting) and were subsequently modified by two magmatic processes: shallow level crystal fractionation which yielded the variation in liquid (glass) composition; and by phenocryst redistribution by crystal settling or floating in thick flows and/or dynamic sorting in lava tubes or dikes which yielded the variation in whole rock compositions. This latter process seems to be particularly important in subaqueous lava systems where laminar flow in thin dikes and in lava tubes is more common than turbulent flow, which is less efficient in redistributing phenocrysts. We have shown by calculations (Table 6) and graphic representation (Figure 6) that rather small amounts (2-3%) of a mineral of rather extreme composition, such as olivine or titanomagnetite can significantly modify "characteristic" chemical parameters like FeO, MgO, and TiO₂ while plagioclase produces significant variations in Al₂O₃ and CaO. These locally produced compositional changes contribute to the scatter of whole rock data and tend to mask or even to reverse subtle variation trends in the basalt liquids, represented by the glass data. We suggest that these liquid (glass) compositions are much more likely to reflect fundamental magmatic processes; at least they should be easier to interpret as they should have little or no compositional "overprint" due to alteration and crystal accumulation.

The nature of phenocryst assemblages may still provide important clues to physical processes operating on magmas. It is not clear, for example, why phenocryst assemblages should tend to fall into two distinct populations, but such relations have been observed before, for example in the FAMOUS area (Bryan and Moore, 1977). Such contrasted populations might arise from mixing of two distinct magmas, or could depend on whether segregation is accomplished primarily by gravity or by a dynamic process such as flow differentiation. It is evident that basalts from Holes 417D and 418A provide many opportunities for more detailed investigation of such processes.

ACKNOWLEDGMENTS

We thank Brian Schroeder, Don Bankston, and Margaret Sulanowska for help in the laboratory, and G. Byerly and J. Sinton for providing additional glass analyses. The manuscript was critically reviewed by F.A. Frey. H. Staudigel was supported by ONR Grant N-00014-75-C0291 to S.R. Hart, and at an early stage by the Deutsche Forschungsgemeinschaft, a travel grant was provided by the Fulbright Foundation. Bryan and Thompson were supported by NSF Grant OCE-15858. All support is gratefully acknowledged.

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