# 3. VOLATILE COMPONENTS IN BASALTS AND BASALTIC GLASSES FROM THE EPR AT 9°30'N1

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#### ABSTRACT

Major and minor volatile concentrations and ferric/ferrous ratios of basaltic glasses, microcrystalline basalts, and finegrained basalts from Hole 864A at the East Pacific Rise, 9°30'N, are presented. The average concentrations of volatile components in the basaltic glasses are 0.27 wt% H<sub>2</sub>O, 0.04 wt% CO<sub>2</sub>, 0.085 wt% S, 0.3 ppm N<sub>2</sub>, and  $1.2 \times 10^{-5}$  cm<sup>3</sup> STP/g He. These are typical volatile concentrations of N-MORBs. CO and CH<sub>4</sub> are subordinate gas species, of which the total is <10<sup>-4</sup> cm<sup>3</sup>/g. Fe<sup>3+</sup>/ $\Sigma$ Fe ratios are about 0.11 in the glasses, which corresponds to oxygen fugacities of more than one log unit below the fayalite-magnetite-quartz buffer. Fe<sup>3+</sup>/ $\Sigma$ Fe ratios are slightly higher in the basalts, indicating that the inner parts of the volcanic flows are more oxidized than the glassy rinds. Concentrations of sulfur appear to be slightly higher in the basalts than in the glass, which is the opposite of what one would expect.

Vacuum-crushing of the glasses yielded virtually pure  $CO_2$  in the vesicles, followed by  $N_2$ ,  $H_2$ ,  $H_2$ O, He, Ar, and  $CH_4$ . The glasses are supersaturated with respect to  $CO_2$  (290 ppm dissolved  $CO_2$ ) as a result of incomplete degassing upon rapid ascent of the basaltic liquids. About 100 ppm  $CO_2$  are trapped in vesicles, which corresponds to a vesicularity of 0.2%.

# INTRODUCTION

The volatile contents of oceanic basalts have been studied in a number of investigations during the past two decades (e.g., Anderson, 1974; Moore et al., 1977; Delaney et al., 1978; Byers et al., 1984; Jambon and Zimmermann, 1987). The primary goal of these studies was to understand volatile fluxes from the mantle source regions to the surface and degassing processes upon melt ascent and eruption. Highly vesiculated "popping rocks" that have been sampled on the Mid-Atlantic Ridge (e.g., Hekinian et al., 1973) possibly represent undegassed melts from the upper mantle (Sarda and Graham, 1990; Javoy and Pineau, 1991), whereas many other magmas were degassed and had been reequilibrated when they resided in axial magma chambers. Recent studies have shown that mid-ocean ridge basalts (MORB) are degassed to variable extents (e.g., Fine and Stolper, 1986). Degassing appears to be dominated by the extent of CO<sub>2</sub> supersaturation and ascent velocities of magmas (Sparks, 1978; Bottinga and Javoy, 1990).

In this study, we investigated the volatile contents of partly crystalline basalts and glassy rinds from volcanic flows recovered from Hole 864A during Ocean Drilling Program (ODP) Leg 142 on the East Pacific Rise (EPR) at 9°30'N. The site is located at a depth of 2581 m on the axis of the EPR, in the central floor of a so-called "axial summit caldera" (Haymon et al., 1991). The area was flooded by a 3-m-thick and 60-m-wide massive basalt flow that is underlain by lobate and sheeted flows (Storms, Batiza, et al., 1993).

We present major volatile ( $H_2O$ ,  $CO_2$ , S), minor gas (e.g.,  $N_2$ , He, CH<sub>4</sub>), and ferric/ferrous data for basaltic glasses and basalts. Our studies include determinations of total volatile concentrations and analyses of gases trapped in vesicles. The results contribute to understanding of degassing processes in this ridge area and the distribution mechanisms of volatiles within volcanic flows.

# SAMPLE PREPARATION AND ANALYTICAL PROCEDURES

The studied samples range from fine-grained aphyric basalts to completely fresh MORB glasses drilled during Leg 142 on the East Pacific Rise at 9°30'N. Detailed petrographic descriptions were reported in Shipboard Scientific Party (1993). Table 1 lists the average major element compositions of the two lithological units drilled during Leg 142.

The basalt and glass fragments were cleaned ultrasonically in distilled water. All samples were carefully handpicked under a binocular microscope. Only fragments free of alteration products and phenocrysts were used. We distinguished between completely fresh glass fragments (GL), microcrystalline basalts (MC), and fine-grained basalts (FG), which appear to represent the inner part of a volcanic flow.

We selected fragments ranging from 1 to 2 mm in size to determine both minor gas concentrations and  $CO_2$ . For each sample, an aliquot was ground in an agate vial for ferrous iron and major volatile determinations. Large, uncrushed glass fragments (several mm in size, 170 to 370 mg) were used in the vacuum-crushing experiments.

Table 1. Major element composition of Hole 864A samples.<sup>a</sup>

	Uni	t 1	Unit 2		
	Average	lσ	Average	1σ	
SiO,	49.91	0.12	49.71	0.10	
TiO <sub>2</sub>	1.64	0.01	1.78	0.04	
Al <sub>2</sub> Õ <sub>1</sub>	14.30	0.08	14.03	0.09	
Fe <sub>2</sub> O <sub>1</sub>	11.61	0.05	12.09	0.18	
MnO	0.20	0.01	0.21	0.00	
MgO	7.30	0.11	7.15	0.18	
CaO	11.72	0.05	11.45	0.06	
Na <sub>2</sub> O	2.55	0.03	2.63	0.02	
K <sub>2</sub> Ô	0.14	0.02	0.14	0.00	
P205	0.11	0.01	0.12	0.01	
Total	99.49		99.30		

<sup>a</sup> From Shipboard Scientific Party (1993). All samples studied in this paper belong to Unit 1, except Sample 142-864A-5Z-1, 20-24 cm, which belongs to Unit 2.

<sup>&</sup>lt;sup>1</sup> Batiza, R., Storms, M.A., and Allan, J.F. (Eds.), 1995. Proc. ODP, Sci. Results, 142: College Station, TX (Ocean Drilling Program).

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Sulfur,  $H_2O^+$ , and  $CO_2$  were analyzed using LECO<sup>TM</sup> SC 132 and RC 412 instruments, respectively. The sample powders were dried at 110°C for 12 hr before analysis. Sulfur was detected as SO<sub>2</sub> that had been produced by heating a mixture of sample powder and  $V_2O_5$  to 1500°C. This method was calibrated using a LECO<sup>TM</sup> coal standard containing 3600 ppm S. Analytical precision is better than 5% as checked by measuring replicates of a MORB (laboratory standard).

 $H_2O^+$  and  $CO_2$  were determined as they were released during heating in a temperature range from 500° to 1050°C.  $H_2O^+$  concentrations were calculated by integrating the peak areas over the whole temperature range. The concentration of  $CO_2$  that was dissolved in the glass as  $CO_3^{2-}$  ( $CO_2^{(s)}$ ) was calculated by employing the peaks at the highest temperatures (>900°C) only. This procedure was calibrated using a calcium oxalate (LECO<sup>™</sup> standard) and checked against USGS reference rocks. The analytical precision is better than 10%.

Additionally, total CO<sub>2</sub> (CO<sub>2</sub><sup>(t)</sup>) was obtained using a Stroehlein<sup>TM</sup> Coulomat 701 after heating sample fragments at 1200°C in an oxygen flow. Nine replicates of a MORB (laboratory standard) yielded 218 ± 23 (2 $\sigma$ ) ppm CO<sub>2</sub>. We refer the reader to Des Marais (1986) for a compilation and evaluation of different techniques for CO<sub>2</sub> determinations and their problems.

Ferrous iron was determined by a standard manganometric titration technique, following HF/H<sub>2</sub>SO<sub>4</sub> decomposition (Potts, 1992). Analytical accuracy and precision were checked by repeatedly measuring the USGS reference rock MRG-1, yielding  $8.65 \pm 0.03$  wt% FeO. Fe<sub>2</sub>O<sub>3</sub><sup>total</sup> data were taken from Shipboard Scientific Party (1993) as reported in Table 1.

## Mass Spectrometry

We determined minor gas contents of the Leg 142 samples using a quadrupole mass spectrometer (QMS) Balzers<sup>TM</sup> QMG 112, combined with gas separation and calibration line.

A schematic diagram is shown in Figure 1. Gases were released either by vacuum-heating or by vacuum-crushing the rock fragments with a squeezer (Fig. 2).

Total gas contents were determined by heating about 200 mg of sample material in a molybdenum crucible, which was placed in an alumina tube. Prior to analysis, this tube and the crucible were heated to 1400°C to decrease the blank values to an acceptable level. The sample was baked at 120°C in vacuum overnight to remove adsorbed gases and moisture from the fragment surfaces. The furnace then was heated to 1400°C, with a heating rate of 30°C/min. During the heating, a cold trap at liquid nitrogen temperature separated H2O, CO2, H2S, and other condensable gases from the noncondensable gases (N2, He, Ar, H2, CH4, CO). The noncondensable fraction was led into the mass spectrometer via an orifice after the maximum temperature was maintained for 30 min. After the furnace had cooled down, the same procedure was repeated to obtain the blank values, which were subtracted from the sample intensities before the concentrations were calculated. Four replicates of Sample 142-864A-1M-6, 0-75 cm yielded the following analytical precision (2 $\sigma$ ): N<sub>2</sub>, 0.05ppm; He, 2 × 10-8 cm3STP/g; CH4, 7 × 10-7 cm3STP/g; CO, 2 × 10-5 cm3STP/g; and  $H_2$ , 13 × 10<sup>-4</sup> cm<sup>3</sup>STP/g.

Vesicle gas compositions were determined using a gas-tight ion source (ionization chamber <2 cm<sup>3</sup>) directly connected to the separation line. This modification significantly lowered the detection limits for all gas species. Vesicle gases were partly liberated by crushing the glass fragments in a squeezer (Fig. 2) connected to the mass-spectrometer. An attached PYREX<sup>TM</sup> sample carrier enabled us to load up to six samples into the squeezer. The samples were baked at 80°C overnight during which time the system was evacuated at 2 × 10<sup>-8</sup> mbar. Single glass fragments several millimeters in size were crushed in the squeezer for each run. The condensable gases also were removed from the gas mixture with a liquid nitrogen trap, and the noncondensable gases were allowed to enter the ionization chamber via a bypass system. After measuring  $N_2$ , Ar, He,  $H_2$ , CH<sub>4</sub>, and CO concentrations, the system was evacuated for 15 min. The cold trap was then removed so that  $H_2O$  and  $CO_2$  became vaporized. In a second step these gases were measured via an orifice.

Blank values were checked by crushing gas-free quartz fragments. The mass-spectrometer is calibrated periodically with both pure gases and certified gas mixtures. Mass interferences are corrected using the intensities of subsidiary masses (i.e., m/e = 15 for CH<sub>4</sub>, m/e = 12 for CO, and m/e = 14 for N<sub>2</sub>).



Figure 1. Schematic sketch of the equipment employed for gas analysis. G = ionization gauges; V1 through V5 = bellow valves; TMP = turbo-molecular pump; RP = rotary pump.



Figure 2. Sketch of a sample squeezer used in the vacuum-crushing experiments (after Funkhouser et al., 1971).

Table 2. Major volatile compositions, ferric/ferrous ratios, and calculated fO2 and fS2 values of Hole 864A samples.

Core, section, interval (cm)	Туре	CO <sub>2</sub> (ppm)	H <sub>2</sub> O (wt%)	S (ppm)	FeO (wt%)	Fe <sup>3+</sup> /ΣFe	log fO <sub>2</sub>	$\log fS_2$	log S
142-864A-									
1M-3, 0-35	GL	360	0.27	840	9.10	0.123	-8.75	-0.587	-1.076
1M-5, 0-100	GL	445	0.27	860	9.29	0.115	-9.13	-1.329	-1.066
1M-6, 0-75	GL	375	0.27	830	9.38	0.104	-9.33	-0.740	-1.081
1M-3, 55-85	MC	410	0.25	890	9.17	0.125	-8.89	-1.030	-1.051
1M-5, 0-100	MC	420	0.28	980	9.06	0.137	-8.68	-0.606	-1.009
1M-6, 0-75	MC	335	0.27	1030	9.11	0.130	-8.77	-0.375	-0.987
3Z-1, 0-6	MC	440	0.20	1190	n.d.	n.d.	n.d.	n.d.	n.d.
5Z-1, 20-24	FG	200	0.25	950	9.49	0.137	-8.79	-0.515	-1.022
1M-3, 100-150	FG	300	0.32	1150	8.74	0.168	-8.14	0.396	-0.939
1M-5, 100-135	FG	355	0.32	1060	8.78	0.163	-8.20	-0.052	-0.975
1M-6, 75-135	FG	260	0.29	1100	8.87	0.152	-8.35	-0.199	-0.959

Notes: GL = glass, MC = microcrystalline basalt, FG = fine-grained basalt, n.d. = not determined, H<sub>2</sub>O and S were determined by IR-spectroscopy (LECO), CO<sub>2</sub> by a coulometrical method (Coulomat 701), and FeO by manganometric titration. Fe<sub>2</sub>O<sub>3</sub><sup>total</sup> concentrations were taken from Shipboard Scientific Party (1993) mean values (see Table 1).

#### Limitations of the Method

Possible reaction of  $H_2S$  and  $SO_2$  with the stainless steel tubing is one of the problems associated with our gas-inlet system. Hydrogen may be produced through vacuum-heating and by dissociation of water and hydrocarbons.  $H_2$  also may diffuse through the alumina tube to some extent. CO and CH<sub>4</sub> concentrations (measured after heating the sample) can be influenced by high-temperature reactions (e.g., cracking of carbonaceous or organic compounds).

Another problem is the adsorption of gases on the stainless steel tubing or fresh surfaces produced when the samples are crushed. Gas adsorption on steel is largely minimized by baking the whole system at 80°C continuously. Gas adsorption on basalt glass surfaces increases in the order N<sub>2</sub>-CH<sub>4</sub>-CO-CO<sub>2</sub>-H<sub>2</sub>O (Barker and Torkelson, 1975). Though we cannot rule out the possibility that adsorption had changed the ratios of the liberated gases to some extent, we feel that it probably is not a substantial problem here. As compared to ball-milling techniques or crushing in a stainless steel tube, the volume of the employed sample squeezer is small, and the released gas can enter the gas analyzer immediately after crushing.

### RESULTS

#### **Oxidation States and Major Volatiles**

The results of the ferric/ferrous, H2O, CO2, and S determinations and the calculated values for fO2 and fS2 are listed in Table 2. Oxygen fugacities were calculated using the equation of Sack et al. (1980) with the coefficients of Kress and Carmichael (1991), as recommended by Wallace and Carmichael (1992). Oxygen fugacities calculated for the basalt glasses, microcrystalline basalts, and fine-grained basalts are depicted in Figure 3. The glass data display oxygen fugacities well below the fayalite-magnetite-quartz (FMQ) buffer. The relative oxygen fugacity,  $\Delta NNO (\log_{10} fO_2[sample] - \log_{10} fO_2[Ni-$ NiO, NNO]), was calculated as in Christie et al. (1986). The ΔNNO values vary from -1.15 to -1.74 for the basalt glasses (FMQ = -0.78), placing them at the upper end of the range defined for fresh MORB glasses by Christie et al. (1986). The fine-grained basalts have markedly higher fO<sub>2</sub> ( $\Delta$ NNO from -0.54 to -1.2), and the microcrystalline basalts are intermediate in their  $\Delta$ NNO values (-1.08 to -1.29). The basalt data therefore tend toward the MORB average of NNO ≈-0.3 of Christie et al. (1986) and verify their finding that the cores of pillows and volcanic flow are significantly oxidized relative to their glassy rinds, though the differences between glasses and more crystalline basalts are less pronounced in our study.

Determinations of the water contents yielded 0.27 wt%  $H_2O$  for all basalt glasses. The microcrystalline basalts have about the same water concentrations (0.25–0.28 wt%  $H_2O$ ), indicating that neither a



Figure 3. Oxygen fugacity plotted vs. the inverse absolute temperature. Solid circles = glasses; open circles = microcrystalline basalts; open squares = fine-grained basalts. NNO and FMQ buffers are from Sack et al. (1980). (See text for details.)

gain of water from alteration nor a loss of water as a result of degassing upon crystallization occurred. In contrast, the microcrystalline basalts are more variable in their water contents, which range from 0.25 to 0.32 wt% H<sub>2</sub>O.

The CO<sub>2</sub> data reported in Table 2 are total CO<sub>2</sub> concentrations, including dissolved CO<sub>2</sub>, vesicle CO<sub>2</sub>, and graphite that may have precipitated upon cooling (Coulomat 701 data on glass fragments). A significant contribution of adsorbed CO<sub>2</sub> to the total concentrations can be ruled out, because the grain size was large (1-2 mm) and the samples were not precleaned with acids. The basalt glasses and microcrystalline basalts have, on average, higher CO<sub>2</sub> concentrations (390 ppm) than the fine-grained basalts (280 ppm).

The CO<sub>2</sub> dissolved in the glass as CO<sub>3</sub><sup>2-</sup> (Fine and Stolper, 1986) was released only at high temperatures, when all vesicles were decrepitated. We calculated the concentrations of CO<sub>2</sub> dissolved in the glass CO<sub>2</sub><sup>(6)</sup> by employing only the CO<sub>2</sub> peaks for temperatures > 900°C (LECO<sup>TM</sup> RC 412 data). Fourteen measurements of glass fragments and powdered glasses yielded 270 to 320 ppm CO<sub>2</sub><sup>(5)</sup> with an average of 290 ± 14 (2 $\sigma$ ) ppm.

The fact that both powdered and unpowdered samples have the same  $CO_2$  concentrations argues against the possibility that any significant contribution of vesicle  $CO_2$  or adsorbed  $CO_2$  existed in this case.

The basalt glasses have sulfur contents of about 850 ppm (Table 2). Calculation of the sulfur fugacities, using the method of Wallace and Carmichael (1992), showed that all glasses are undersaturated with respect to sulfur (Fig. 4). Surprisingly, the crystalline basalts exhibit somewhat higher S concentrations than the glasses. All data were checked two or three times by running replicates, and the differences exceed the analytical uncertainties. This finding contrasts with previous observations which show that the flow interiors always have



Figure 4. Sulfur concentrations plotted vs. sulfur fugacity. Symbols as in Figure 3. Solid line = saturation curve for sulfur in basaltic liquids from Wallace and Carmichael (1992). Note that all samples are undersaturated with respect to sulfur.

lower S concentrations than the glassy rinds (e.g., Moore and Fabbi, 1971). A loss of S from the basalts can be explained by oxidation and subsequent removal of S during oxidative alteration or by degassing of SO<sub>2</sub> (e.g., Erzinger, 1989). The latter process is common in subaerial and shallow-water eruptions (e.g., Gerlach, 1980), but is probably not at work at higher pressures (>100 bar).

The relatively high S concentrations in the crystalline basalts of this study indicate that these basalts have been preserved from oxidative alteration. The fact that the sulfur concentrations in the basalts exceed those of the glasses might indicate a cumulation of sulfide globules in the flow interior that may have occurred upon crystallization, though there is no direct petrographic evidence for this.

#### **Minor Gases**

The determinations of  $N_2$ , He, CH<sub>4</sub>, CO, and H<sub>2</sub> concentrations released upon heating the samples are listed in Table 3 and depicted in Figure 5. The data include gases dissolved in the glass or minerals and vesicle gases. Nitrogen concentrations range from 0.2 to 0.9 ppm, which is at the lower end of the variations in N<sub>2</sub> concentrations in MORB observed so far (0.2–2.8 ppm; Sakai et al., 1984; Exley et al., 1987; Heinschild, 1990; Bach, 1991; Marty and Lenoble, 1992). The glass data vary in a small range from 0.2 to 0.3 ppm, whereas the basalt data tend to display somewhat higher N<sub>2</sub> concentrations and larger scatter. The elevated N<sub>2</sub> concentrations of three basalts may be the result of some contamination with organic N. The presence of organic N in basalts was proposed by Marty and Lenoble (1992) who found that N<sub>2</sub> was partly released at low temperatures. The presence of NH<sup>+</sup><sub>4</sub>, gained during oxidative alteration, is another possible explanation for higher N contents in the basalts (Heinschild, 1990).

He concentrations are 1.1 to  $1.3 \times 10^{-5}$  cm<sup>3</sup> STP/g in the basalt glasses, but 50 to 100 times lower in the crystalline basalts. The glass data are similar to He concentrations of other MORB glasses from the



Figure 5. Plots of He,  $CH_4$ ,  $CO_2$ , and CO vs.  $N_2$ . Symbols as in Figure 3. Note that there is no obvious correlation between the concentrations of different gas species.

EPR (0.5–2.6  $\times$  10<sup>-5</sup> cm<sup>3</sup>/g; Fisher, 1986). The fine-grained and the microcrystalline basalts have lost their He through diffusion subsequent to crystallization.

He concentrations of the basalts range from 14 to  $45 \times 10^{-8}$  cm<sup>3</sup> STP/g and are somewhat higher than the average value for fresh basalts ( $8 \pm 11 \times 10^{-8}$  cm<sup>3</sup> STP/g; Fisher, 1986). Altered basalts and diabases have even lower He concentrations, below  $10 \times 10^{-8}$  cm<sup>3</sup> STP/g (Fisher, 1986; Erzinger, 1989).

The CH<sub>4</sub>, CO, and H<sub>2</sub> data have to be interpreted with great caution, because CO-producing as well as CH<sub>4</sub>-consuming reactions can take place when heating the samples.

$$CO_2 + H_2 \leftrightarrow CO + H_2O,$$
 (1)

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2.$$
 (2)

Notable amounts of hydrogen probably were produced by cracking carbonaceous compounds and water.

Therefore, we argue that our  $H_2$  and CO data may reflect maximum concentrations, and our  $CH_4$  data may reflect minimum concentrations of the samples. However, the same reactions take place in the opposite direction (i.e., CO- and  $H_2$ -consuming and  $CH_4$ -producing) upon cooling of the quenched lava. The initial concentrations of these gases in the MORB melt thus cannot be determined by the method employed.

Table 3. Minor gas composition of Hole 864A samples released by vacuum-heating and determined by quadrupole mass spectrometry.

Core, section, interval (cm)	Туре	H <sub>2</sub> (10 <sup>-7</sup> cm <sup>3</sup> /g)	N <sub>2</sub> (ppm)	He (10 <sup>-7</sup> cm <sup>3</sup> /g)	CH <sub>4</sub> (10 <sup>-6</sup> cm <sup>3</sup> /g)	CO (10 <sup>-5</sup> cm <sup>3</sup> /g)
142-864A-					0.00	222.04
1M-3, 0-35	GL	22	0.31	110	2.8	8.7
1M-5, 0-100	GL	17	0.22	130	2.2	4.0
1M-6, 0-75	GL	21	0.28	130	1.8	2.7
1M-3, 55-85	MC	6	0.87	3.1	3.7	3.2
1M-5, 0-100	MC	13	0.32	4.5	3.3	4.9
1M-6, 0-75	MC	1	0.26	1.7	2.0	1.2
3Z-1, 0-6	MC	14	0.54	2.5	3.8	2.8
5Z-1, 20-24	FG	16	0.29	2.8	3.4	3.6
1M-3, 100-150	FG	17	0.93	3.9	2.2	3.3
1M-5, 100-135	FG	6	0.16	1.4	1.4	1.1
1M-6, 75-150	FG	n.d.	0.36	n.d.	2.3	0.6

Notes: GL = glass, MC = microcrystalline basalt, FG = fine-grained basalt, n.d. = not determined.



Figure 6. Mass pyrogram for Section 142-864A-1M-6, 0-75 cm, showing typical gas release pattern of CO<sub>2</sub>, SO<sub>2</sub>, N<sub>2</sub>, He, and Ar. Note the bimodal release behavior of most gases.

We note that the basalts appear to have somewhat lower  $H_2$  and CO concentrations, which may indicate a loss of  $H_2$  and CO upon cooling and crystallizing. This is consistent with the higher fO<sub>2</sub> values in the basalts. No obvious correlation between the concentrations of different gas species was observed (Fig. 5).

## **Mass Pyrograms**

Figure 6 depicts a typical mass pyrogram obtained by heating a basaltic glass sample while simultaneously monitoring the intensities of 10 masses with the QMS. Only small amounts of gases were released below 750°C. Above these temperatures, CO<sub>2</sub>, He, Ar, and H<sub>2</sub>O (not shown) exhibit a bimodal release behavior. At the softening point of basalt glass (750°–800°C), CO<sub>2</sub>, He, H<sub>2</sub>O, and Ar are liberated. A second release of CO<sub>2</sub>, He, and Ar, accompanied by N<sub>2</sub>, was observed from 900° to 950°C. Above 900°C, CO<sub>2</sub> is continuously degassing up to 1100°C, when small amounts of SO<sub>2</sub> also were detected. Water shows a second, larger peak at 950°–1000°C being larger than the first one. Neither H<sub>2</sub>S nor CH<sub>4</sub> were detected during heating. We could not prove whether CO was released because of mass inferences with CO<sub>2</sub>. The mass pyrogram is similar to those that Byers et al. (1986) obtained from EPR 21°N basalt glasses, but they found notable amounts of reduced carbon species (CO and CH<sub>4</sub>).

### Vesicle Gas Compositions

Vesicle gas compositions were determined in single glass fragments of Interval 142-864A-1M-6, 0-75cm, and the results of five replicates are listed in Table 4. CO<sub>2</sub> is the by far most abundant gas species in the vesicles, followed by N2, H2, H2O, He, Ar, and CH4. CO, H2S, and SO2 could not be detected. Table 5 shows a comparison of the vesicle gas composition with the results of a previous study on a mid-ocean ridge "popping rock" (Javoy and Pineau, 1991). Whereas these authors also found considerable amounts of H<sub>2</sub>O in the vesicles, our H2O concentrations are extremely low and the vesicle gas is virtually pure CO2. The H2O/CO2 ratios of Javoy and Pineau (1991) and Jambon and Zimmermann (1987) are 0.05 to 0.07, which is close to the equilibrium with the dissolved CO2 and H2O in the glass. The much lower H<sub>2</sub>O/CO<sub>2</sub> values of this work (<0.01) mean either that vesicle gases are heterogenous in composition and only the CO2-rich vesicles were opened upon crushing or that they display a disequilibrium. However, our results support the finding that H2O is much more soluble in basaltic melts as compared to CO2. The He/Ar ratios vary

Table 4. Vesicle gas composition of interval 142-864A-1M-6, 0-75 cm.

1	2	3	4	5
99.53	99.26	99.24	99.63	98.37
0.08	0.09	0.12	0.08	0.68
0.09	0.24	0.24	0.08	0.74
0.27	0.38	0.37	0.20	0.16
tr.	tr.	tr.	tr.	tr.
n.d.	n.d.	n.d.	n.d.	n.d.
145	285	291	96	503
31	29	28	23	53
0.0144	0.0026	0.0020	0.0199	0.0006
256	211	165	276	97
4.6	10.0	10.3	4.2	9.5
	1 99.53 0.08 0.09 0.27 tr. n.d. 145 31 0.0144 256 4.6	1 2   99.53 99.26   0.08 0.09   0.09 0.24   0.27 0.38   tr. tr.   n.d. n.d.   145 285   31 29   0.0144 0.0026   256 211   4.6 10.0	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

Notes: n.d. = not determined, tr. = trace.

Table 5. Comparison of vesicle gas compositions of different basalt glasses.

	2πD43 <sup>a</sup>		864A-1M-6, 0-75 cm		
	(mean)	(range)	(mean)	(range)	
CO <sub>2</sub> (vol%)	94.95	73-97	99.21	98.4-99.6	
H <sub>2</sub> O (vol%)	4.93	3.2-26.5	0.21	0.08-0.68	
$N_2$ (vol%)	0.12	0.10-0.12	0.27	0.16-0.38	
H <sub>2</sub> (vol%)	0.003	0-0.027	0.28	0.08-0.74	
CO (vol ppm)	7	0-46	-	-	
CH <sub>4</sub> (vol ppm)	2	0.4-5.0	tr	tr	
He (vol ppm)	32.6	29-42	264	96-503	
Ar (vol ppm)	23.9	20-24	32.8	23-53	
He/Ar	1.36	1.20 - 1.92	7.7	4.2 - 10.3	
V (%)	17			≈0.2	

Note: tr = trace.

<sup>a</sup> Javoy and Pineau (1991) "popping rock."

b This study.

from 4.2 to 10.3, which is similar to the He/Ar ratios in vesicle gas of a Mid-Atlantic MORB reported by Jambon et al. (1985).

A large proportion of the total He and N<sub>2</sub> contents appears to reside in the vesicles. The concentration of N<sub>2</sub> trapped in the vesicles is 0.06 to 0.19 ppm corresponding to 20% to 60% of the total N<sub>2</sub> of about 0.3 ppm. Also, 3 to  $8 \times 10^{-6}$  cm<sup>3</sup>/g He in the vesicles correspond to 20% to 60% of the total He ( $13 \times 10^{-6}$  cm<sup>3</sup>/g; Tables 3 and 4). The amount of CO<sub>2</sub> trapped in the vesicles is 30 to 140 ppm.

#### DISCUSSION

The Leg 142 basalt glasses are supersaturated with respect to CO<sub>2</sub>, as is indicated by their high concentrations of dissolved CO<sub>2</sub> (290  $\pm$ 14 ppm). The solubility of CO<sub>2</sub> in basaltic melts has been experimentally determined several times in recent years and was reported as being 0.55 ppm CO<sub>2</sub>/bar (Trull et al., 1991), 0.49 ppm CO<sub>2</sub>/bar (Pawley et al., 1992), and 0.44 ppm CO<sub>2</sub>/bar (Stolper and Holloway, 1988). Based on these data, the concentration of CO<sub>2</sub> in a saturated MORB melt erupting at a depth of 2580 m (258 bars) is between 114 and 142 ppm. The concentration of dissolved CO<sub>2</sub> in the Leg 142 basalt glasses is about 290 ppm and indicates supersaturation.

When Harris (1981) and Des Marais and Moore (1984) found a linear relationship between  $CO_2$  content and depth of submarine basalt glasses, they interpreted this correlation as the solubility of  $CO_2$ in basaltic melts as a function of the pressure (eruption depth). Fine and Stolper (1986), however, could not confirm a linear relationship between the depth of eruption and concentrations of dissolved  $CO_2$  in a larger sample set. This nonrelationship was interpreted subsequently as indicating variable degrees of supersaturation resulting from incomplete degassing upon rapid ascent of the basaltic liquids (Stolper and Holloway, 1988; Dixon et al., 1988; Bottinga and Javoy, 1989). The mechanism of  $CO_2$  bubble nucleation and growth were described by Bottinga and Javoy (1990) and earlier by Sparks (1978). The rate of bubble nucleation depends on the degree of supersaturation. Supersaturation of a few hundred bars CO2 results in low nucleation rates. The ascent velocities of basaltic melts in dikes are around 1 m/s (Delaney and Pollard, 1982) or even higher (Spence et al., 1987). The melt ascent from a magma chamber at a depth of 1.7 km therefore would take less than 0.5 hr. Low nucleation rates and low growth rates of CO2-rich bubbles, which result from slow diffusion of CO2 in basaltic melts (Watson et al., 1982), act together with high ascent velocities as limiting factors for CO2 degassing. Stolper and Holloway (1988) argued that the maximum concentration of dissolved CO<sub>2</sub> in basaltic glasses from an area can be used to estimate the minimum depth of an axial magma chamber. The concentrations of CO<sub>2</sub> dissolved in the Leg 142 basalt glasses (290  $\pm$  14 ppm) are lower than the maximum CO<sub>2</sub> content of EPR 21°N basalt glasses of 360 ppm observed by Stolper and Holloway (1988). Using their solubility data, 290 ppm CO<sub>2</sub> is soluble at a CO<sub>2</sub> pressure of 660 bar. Assuming the average density of the basaltic crust is 2.8 g/cm3, the data imply a magma chamber depth of 1.4 km. This is above the depth of seismic reflectors at 1.7 km, which Detrick et al. (1987) interpreted as the top of an axial magma chamber. We therefore suggest that the basaltic liquid has lost a small amount of CO2 through vesiculation and degassing during ascent in the volcanic conduit. Assuming that vesiculation took place, but that the vesicles were not separated from the basaltic liquid, the total concentrations of CO2 can be used to calculate the pressure at which this amount of CO2 was soluble in the melt. The average total CO2 concentration of the Leg 142 basalt glasses (390 ppm) corresponds to equilibration pressures of 710 to 890 bars or a magma chamber depth of 1.6 to 2.3 km, depending on which solubility data are used.

The restriction of the interpretation of  $CO_2$  data in basalt glasses lies within the analytical errors. For instance, Fine and Stolper (1986) found that Fourier transform infrared (FTIR) spectroscopy yields notably lower concentrations of dissolved  $CO_2$ , as compared to other analytical techniques. We therefore note that our data may display maximum  $CO_2$  concentrations, and the dissolved  $CO_2$  contents should be verified by FTIR studies, which will be a topic of our ongoing investigations.

The differences between total and dissolved CO<sub>2</sub> concentrations are about 100 ppm (0.05 cm<sup>3</sup> STP/g). This is in accord with the 30 to 140 ppm CO<sub>2</sub> in the vesicles yielded by the vacuum crushing experiments (Table 4). A value of 100 ppm CO<sub>2</sub> in vesicles corresponds to a vesicularity of about 0.2%, assuming the glass transition temperature is 1000°C, p = 258 bar, and  $\rho = 2.7$  g/cm<sup>3</sup>. A surprising result of the vesicle gas analysis was the virtual absence of CH<sub>4</sub> and CO. The CO/CO<sub>2</sub> ratio is expected to be about 0.2 in a basaltic liquid at 1300°C, 250 bar, and oxygen fugacities one log unit below the QMF (Holloway, 1987). The markedly lower CO/CO<sub>2</sub> ratios displayed by the total gas concentrations of the Leg 142 basalt glasses and the absence of CO in vesicles (Table 4) can be explained by reequilibration at lower temperatures. Upon cooling, CO is consumed by carbon-precipitating reactions (Javoy and Pineau, 1991), as follows:

$$2CO \leftrightarrow CO_2 + C,$$
 (3)

$$CO+H_2 \leftrightarrow C + H_2O.$$
 (4)

The low methane concentrations in the vesicles indicate that  $CH_4$  production by the reaction

$$CO_2 + H_2 \leftrightarrow CH_4 + 2H_2$$
 (5)

did not occur, though it is favored by temperature decrease (Javoy and Pineau, 1991).

The  $H_2/H_2O$  ratios of the vesicle gas (>1) are markedly higher than they could have been in the basaltic liquid (<0.05; Holloway, 1987). This indicates that, again, reequilibration reactions must have

changed the gas composition upon quenching and cooling. Hydrogen may have been produced by the water-consuming reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2,$$
 (6)

which is favored by temperature decrease.

The high degree of  $CO_2$  supersaturation discussed earlier is a typical feature of melts that did not degas significantly during ascent and eruption. In the course of degassing, He/Ar should increase in the melt and decrease in the gas phase as a result of the higher solubility of He in basaltic melt (e.g., Jambon et al., 1985). The average He/Ar in MORB is 11± 7 (Fisher, 1986). Vesicle gases in basalts that suffered notable degassing should therefore reveal significantly lower He/Ar. Such low He/Ar (mostly <5) in vesicles was observed by Jambon et al. (1985), Sarda and Graham (1990), and Javoy and Pineau (1991). Our samples, however, show He/Ar ratios in the range of the average He/Ar in MORBs consistent with the assumption that no significant degassing occurred.

We interpret the observed vesicle gas composition as evidence for incomplete and kinetically limited degassing as a result of rapid melt ascent.

#### CONCLUSIONS

1. Concentrations of major volatile components in the Leg 142 basaltic glasses are typical for N-MORB (0.27 wt%  $H_2O$ , 0.04 wt%  $CO_2$ , 0.085 wt% S).

2. Concentrations of other minor gases are at the lower end of the N-MORB range reported in the literature (0.3 ppm N<sub>2</sub>,  $1.2 \times 10^{-5}$  cm<sup>3</sup>STP/g He, CO + CH<sub>4</sub> <  $10^{-4}$  cm<sup>3</sup>STP/g).

3. The fO<sub>2</sub> of the basaltic glasses (calculated based on ferric/ferrous ratios) are well below the FMQ buffer. Crystalline basalts yield higher fO<sub>2</sub>, indicating slight oxidation.

4. Vesicle gases released by vacuum-crushing of the glasses are virtually pure  $CO_2$ , followed by  $H_2$ ,  $N_2$ ,  $H_2O$ , He, Ar, and  $CH_4$ .

5. About 25% of the total  $CO_2$  concentration is trapped in vesicles. The concentration of  $CO_2$  dissolved in the glass (290 ± 14 ppm) displays supersaturation as a result of incomplete degassing during rapid ascent of the melts.

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