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ANALYTICAL TECHNIQUES FOR DETERMINING A MICRO QUANTITY OF CO_2 IN VOLCANIC GLASS BY LASER PROBE MASS SPECTROMETRY

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ABSTRACT

An analytical system has been developed for determining a micro quantity (0.1–1ng) of CO_2 in volcanic glass. It consists of a Nd-YAG laser for the selective heating of small areas of volcanic glass and a gas chromatogragh-mass spectrometer for measuirng the absolute amount of the CO_2 extracted from the glass. The carbon dioxide concentrations of the glass samples were calculated from the mass of the melted glass and the measured amount of CO_2. The glass sample ground to a thickness of less than 100 μm was pierced by a laser beam. The volume of the melted glass was controlled by changing the duration of the laser beam. The mass of the melted gl*d*ss was calculated from its volume and density.

Analysis of homogenized basaltic glass with a bulk CO_2 concentration of 326 ppm gave a CO_2 concentration of 270 ± 70 ppm when the extracted CO_2 was more than 0.6 ng. Glass inclusions larger than 100 μm in diameter can be analyzed by the present method with an accuracy of ± 70 ppm when the CO_2 concentration is 300 ppm.

INTRODUCTION

Volatile materials play an important role in the evolution of magmas and volcanic eruption. During its ascent, mgma may become saturated with volatiles because of a general decrease in their solutilities in silicate melts with a decrease in pressure. Formation of a gas phase would lead to a decrease in the bulh density of the magma, thereby accelerating its acent. In a cooling magma chamber, crystallization of volatile-free minerals also would cause a concentration of volatiles that might result in saturation. Expansion of the resulting gsa pahse might then induce a volcanic eruption.

The major volatile components in magma are H_2O, CO_2 S and C1. Of these, CO_2 has a low solubility in silicate melts at low pressures (30–800 ppm at 0.1–2 kbar, Stolper and Holloway, 1987; Fogel and Rutherford, 1990; Pan et al., 1991); therefore, a CO_2-rich gas phase may form in an ascending magma. For this reason, CO_2 is now believed to be the essential component that drives a deep-seated magma to a shallow depth in the earth's crust, thereby inducing an eruption.

A large amount of CO_2-rich gas was emitted during the 1980 eruption of Mount St. Helens (Casadevall and Greenland, 1981; Barnes, 1984). The phase equilibrium relations of the dacitic pumices that erupted from the volcano indicated that CO_2 constituted 30–50% of the gas phase present in the preeruptive magma (Rutherford et al., 1985). In ihe 1986 disaster at Lake Nyos, Cameroon, the almost pure CO_2 gas that was suddenly released from the crater lake killed more than 1700 people (Kusakabe et al., 1989). The CO_2 was most likely derived from the basaltic

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magma responsible for the formation of Lake Nyos maar (Kusakabe and Sano, 1992). Because the CO_2 in magma can have a direct or indirect effect on volcanic processes, measurements of the CO_2 content of magmas are essential if we are to understand the behavior of CO_2 during the ascent of magma and volcanic eruptions and to obtain basic information about the mitigation of natural volcanic disasters.

The CO_2 contents of the magmas in mid-oceanic ridge basalts (MORB) have been measured in quenched MORB glasses which are believed to retain their original gas concentrations because of the enormous hydrostatic pressure exerted at the sites of submarine eruptions (Moore and Schilling, 1973). The groundmass glass in volcanic rocks effused onto the surface of the earth, however, are not suitable for estimating the CO_2 concentrations of pre-eruptive magmsa because these rocks have most likely been degassed before or at the time of eruption, or both. In a magma chamber crystals may trap the surrounding silicate melt during their growth. The melt is quenched at the time of eruption as glass inclusions in a phenocryst. Protected by the thick harness of the host crystal, the degassing of the glass inclusions and contamination by extraneous volatiles after trapping are negligible (Anderson, 1973). For this reason glass inclusions in phenocrysts are the most suitable samples for measuring volatile concentrations of pre-eruptive magmas. Until recently, however, it has been difficult to measure the CO_2 concentrations of glass inclusions because the size of such inclusions is very small (50–200 μm) and the sensitivity of available analytical methods was not sufficient (Saito and Kusakabe, 1989).

Determination of the CO_2 concentrations of glass inclusions has been made possible by (1) vacuum fusion extraction followed by manometric measurements (Harris and Anderson, 1983, 1984; Sommer and Schramn, 1983); (2) the vacuum fusion technique combined with quadrupole mass spetrrometry (Delaney et al., 1978; Garcia et al., 1979; Muenow et al., 1979); (3) Fourier transform infrared spectroscopy (FTIR, Anderson et al., 1989; Metrich et al., 1990); and (4) laser decrepitation mass spectrometry (Yonover et al., 1989). Because in analysis by the vacuum fusion thchnique the host crystals and other materials that surround the glass inclusions also are heated, the CO_2 present in materials other than the glass inclusions also may be extracted and produce a positive error in the CO_2 concentration of the glass inclusions. Consequently, a microprobe analysis has to be developed for the selective analysis of glass inclusions. The FTIR technique is a rapid, nondestructive and highly sensitive method that is characterized by a high spatial resolution (Fine and Stolper, 1986); but the molar absorption coefficeints of individual IR spectra are greatly dependent on the chemical composition of the inclusion glass. For this reason, the FTIR technique has been applied only to glasses that have a limited chemical compositions (Stolper et al., 1987; Dixon et al., 1988; Fogel and Rutherford, 1990). In contrast, the laser probe technique can selectively heat an glass inclusion as small as 10 μm in diameter independent of the glass composition. Subsequent mass spectrometry has also a high sensitivity. Yonover et al. (1989) applied the laser probe technique to MORB glasses, but reported only the CO_2/H_2O ratios. We have developed a "quantitative" laser microporbe technique for determining a minute amount of CO_2 dissolved in glass inclusions. We here describe the analytical details of this laser probe technique and preliminary results of the CO_2 analysis of quenched glasses from Mariana Trough basalts.

ANALYTICAL SYSTEM

The glass inclusions in magmas are of various sizes, from less than 10 μm to rarley greater than 200 μm. A single glass inclusion with a diameter of 100 μm may contain 0.1–1 ng CO_2 depending on the concentration. In order to analyze such small amounts of CO_2, we used as the analytical method selective heating with a laser probe to extract the CO_2 and followed it by gas chromatography-mass spectrometry (GC-MS) (Fig. 1). The volatile materials extracted under vacuum were transferred quickly to a GC column by He carrier gas keeping their adsorption to

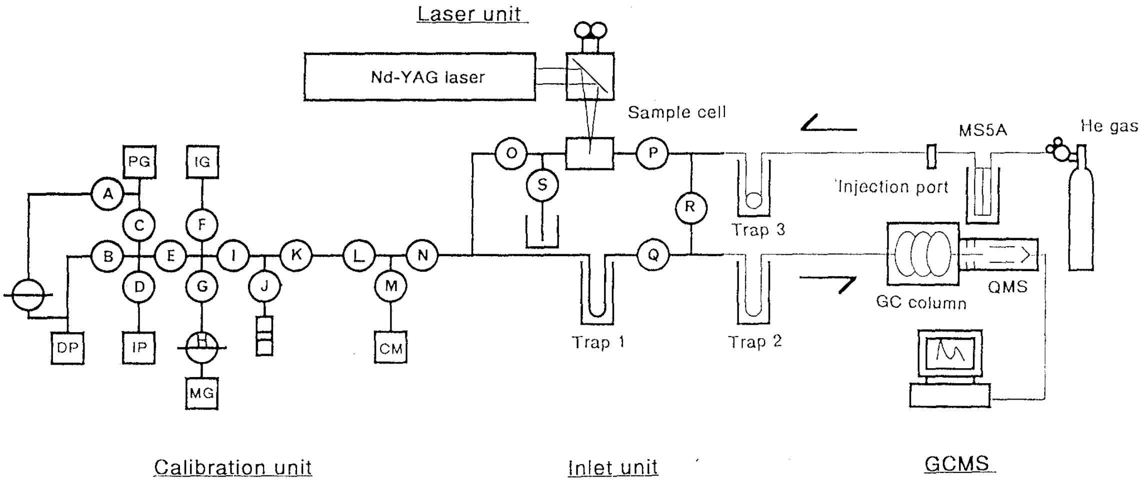

Fig. 1 Schematic diagram of the laserprobe-GCMS system for the analysis of micro quantities of CO_2 in volcanic glass.

the wall of the analytical line which was heated to 50–150°C at a minimum. Carbon dioixde was separated from the other gases in the GC column, and its amount determined with the quadrupole mass spetrometer. The analytical system consisted of four parts: the laser unit, GC-MS unit, gas caibration unit and inlet unit (Fig. 1).

Laser unit

A Nd-YAG laser with maximum power of 7 W (Model SL114L, NEC Corporation, Japan) was used to melt the glass samples. The wave length of this laser is 1.064 μm. There are two modes for laser beam generation; continuous wave (CW) and pulsed (Q switched) modes. The pluse frequency can be changed from 1 to 99 kHz by use of the Q switch. The laser beam was focused on the sample in the sample cell through the objective lens in the unit's mocriscope. The focal length of the focusing lens used was 18 mm. The diameter of the laser beam targeted on the sample was adjusted to 10 μm.

Inlet unit

The inlet unit consists of a sample cell made of stainless steel (Fig. 2), metal valves (N, O,

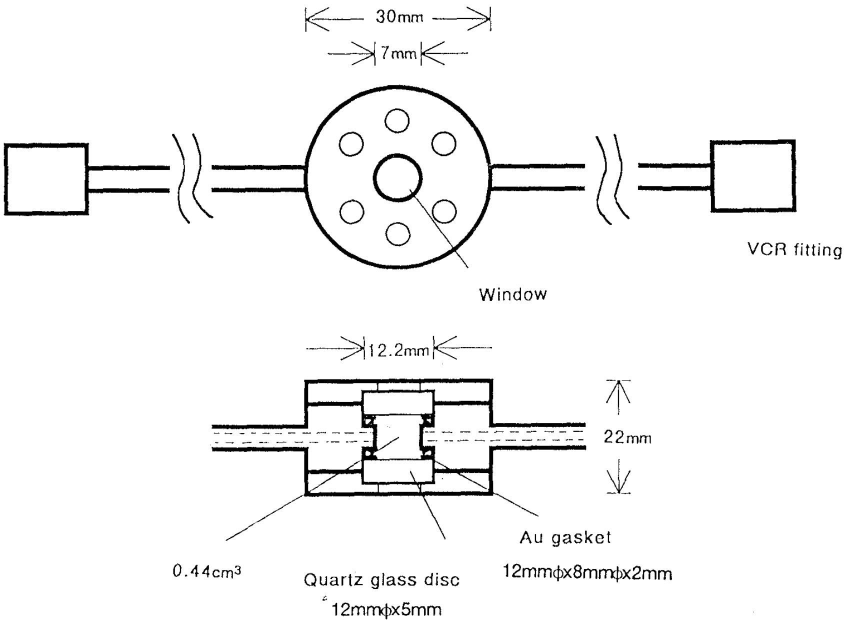

Fig. 2 Diagram of the sample cell.

P, Q, and R), cold traps (traps 1 to 3) and stainless steel tubing with an inner diameter of 3 mm. The sample cell has quartz glass windows and a 0.44 cm^3 capacity. The laser beam is focused on the sample through the upper window. A gold gasket is placed between the window and the cell body for vacuum sealing. Trap 1, which is made of stainless steel tubing, is for the collection of the H_2O and CO_2 extracted from the glass inclusions during laser heating. Trap 2, which consists of a GC capillary column, concentrates the extracted gases relased into the inlet volume by cooling them with liquid nitrogen. The concentrated gases are then introduced into the GC-MS unit by heating the trap 2 to 100°C. Concentration of the gases prior to analysis is essential in order to separate them and to obtain sharp, sensitive chromatograms. Trap 3, made of the same column as in trap 2, is used to reduce the background CO_2 contained in the He carrier gas.

GC-MS unit

The detection and quantitative determination of the CO_2 extracted from a sample glass were done with a gas chromatograph-quadrupole mass spectrometer (GC-MS, model QP300, Shimadzu Corporation, Japan). PoraPLOT-Q was used as the stationary phase of the column in order to separate the CO_2 from the other gases. The column temperature was 150°C. Helium was the carrier gas.

WORKING CONDITIONS OF THE LASER UNIT

The absolute amount of the extracted CO_2 and the mass of the glass melted by a laser beam must be known in order to determine the CO_2 concentration in the sample. We studied the relation between the conditions of the laser beam and the mass of the glass melted. Mariana Trough basalt (MTB) glass that had been ground to a thickness of about 300 μm was ued as the sample glass. Three factors affect the effective power of laser beam: the electric current applied to the krypton arc lamp, pulse frequency and duration. In our study, laser power was varied by changing the shooting duration. The pulse frequency was fixed at 10 kHz and the lamp current at 17 A. After the laser irradiation, the upper surface of the samlpe and a cross section of its laser pits were observed under an optical microscope and with a scanning electron microprobe (SEM). The pits produced had various shapes and werre covered by frothy secondary glasses which look like a dome (Fig. 3). A typical cross section of such a pit is shown in Fig. 4. The diameters and depths of the pits measured microscopically are roughly proportional to the laser energy applied. The volume of a pit was tentatively estimated from the area of its cross section, assuming that

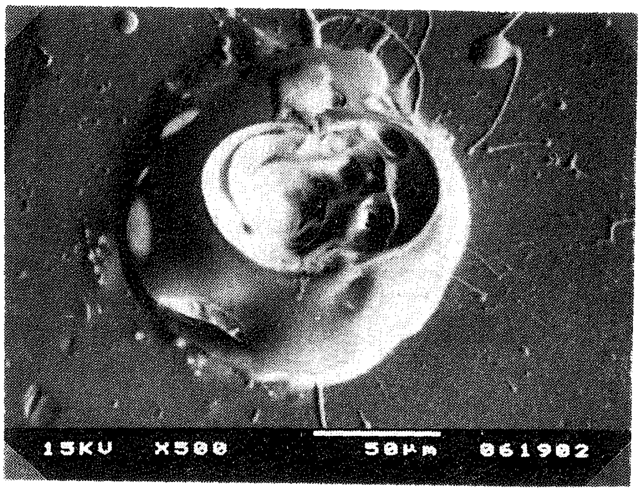

Fig. 3 SEM photomicrograph of a laser pit produced on the surface of MTB glass. Note that the pit is covered by a secondary frothy glass.

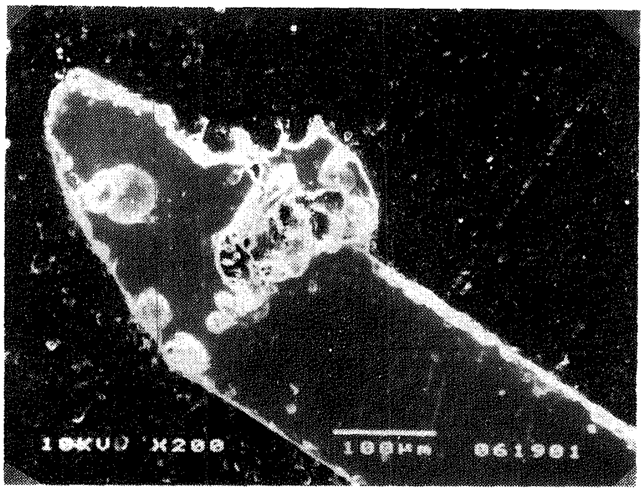

Fig. 4 SEM photomicrograph showing a cross section of a laser pit. Note that the diameter of the secondary frothy glass is larger than that of the pit.

its shape was approximated by a body of revolution. The mass of melted glass in the pits was calculated from the pit volume and the density of MTB glass (2.74 g/cm^3). A reasonable correlation was found between the mass of the melted glass and the laser energy applied (Fig. 5), which enabled us to estimate the laser energy needed to melt a glass inclsuion of a given size.

The secondary frothed glass covering the pits made it difficult to measure the pit dimeters accurately by microscopic observation. Depth estimations made through the secondary glass tend to result in underestimation of the pit depth. Consequently the pit depth must be measured by observations of the cross sectoin (Fig. 4), but the preparation of cross sections is tedious and time consuming. We therefore adopted the following procedures to estimate pit volume. The glass sample was ground to a wafer less than 100 μm thick, then the wafer was doubly polished. The prepared glass sample was pierced in a vacuum by a laser beam (Fig. 6). The volume of the

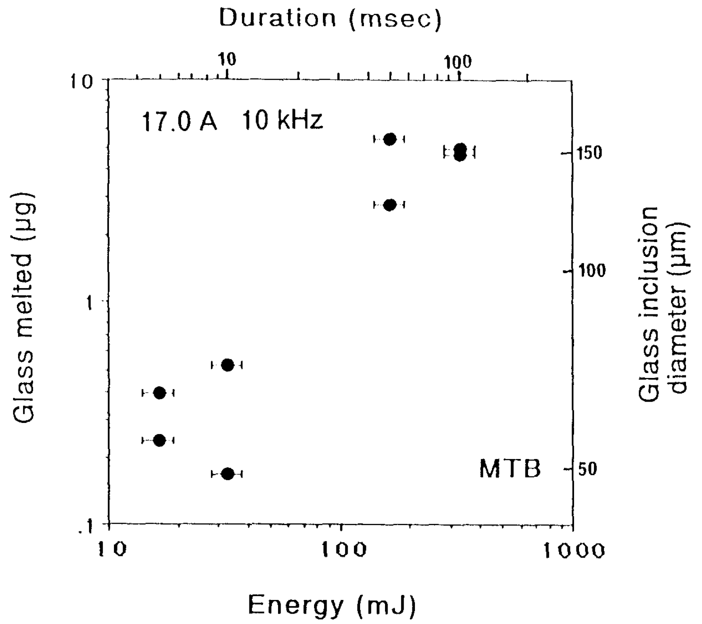

Fig. 5 Variation in the masses of glass samples melted by laser heating at various laser energies.

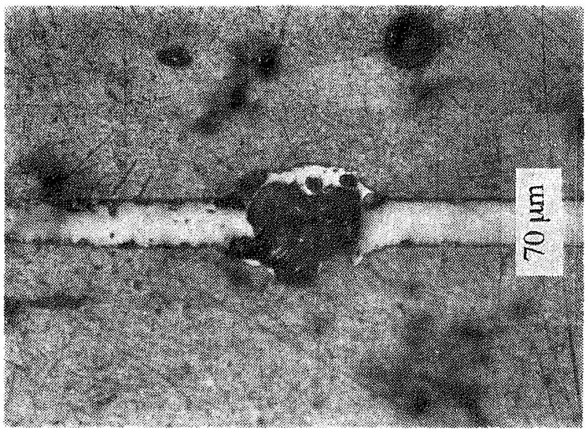

Fig. 6 Photomicrograph of a MTB glass wafer (about 70 μm thick) pierced by a laser beam. The volume of the melted glass is calculated from the diameter of the cylindrical hole and the wafer thickness.

cylindrical hole produced is easily estimated from the diameter of the hole and the thickness of the wafer. The mass of the melted glass is calculated from its volume and density. We believe that this technique is the best way to estimate the amount of glass melted by the laser irradiation.

CO_2 ANALYSIS

Background

The absolute amount of CO_2 present in a glass inclusion with a diameter of 100 μm is believed to range from 0.1 to 1 ng. When such a small amount of CO_2 is to be analyzed, evaluation of the backgorund CO_2 is very important if we are to obtain reliable results. The background CO_2 in our system is produced from two sources; the CO_2 contained in the He carrier gas and the CO_2 that adheres to the inlet tubing and metal valves.

High purity helium (99.9999%) was used as the carrier gas to avoid the first source of the background. It was further pruified by passing through a Molecular Sieve 5A column and trap

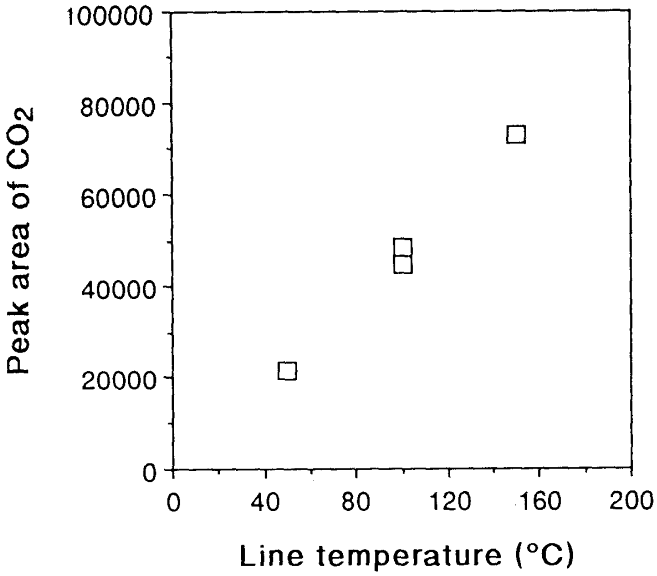

Fig. 7 Variation in peak areas of background CO_2 with line temperature. The extraction line was baked at 300°C before each background run.

3 which was coated with PoraPLOT-Q (both the column and trap being immersed in liquid nitrogen) before entering the inlet unit. This purification step reduced the CO_2 background to about 1/20.

To reduce the CO_2 contribution from the second source, the stainless steel tubing and metal valves initially were cleaned sequentially with acetone, dilute nitric acid and distilled water, then repeatedly baked at 300°C in a vacuum. After these treatments, the amount of background CO_2 was measured by varying the line temperature. As shown in Fig. 7, the background CO_2 in the system increased with the temperature of the inlet unit. Figure 7 and Table 1 indicate that the background CO_2 at 50°C is 1/4–1/5 that at 150°C and that better reproducibility also was obtained at 50°C (Table 1). The peak area of the background CO_2 fluctuated depending on the experimental period (Table 1). This fluctuation probably is the result of variations in the ef-

Table 1 Repeated measurements of blank CO_2 at the line temperatures of 50° and 150°C on different days.

Date of experiment	Run	Line temp. (°C)	Peak area
April 23, 1991	1	50	13381
	2	50	15719
	3	50	15144
	4	50	14548
	5	50	13604
	6	50	13930
	Av.		14388
	1σ		±917
	Rel. variation		6.4 %
May 21, 1991	1	50	21460
	2	50	20953
	3	50	19699
	Av.		20704
	1σ		±907
	Rel. variation		4.4 %
June 19, 1991	1	50	20488
	2	50	19485
	3	50	21805
	Av.		20593
	1σ		±1164
	Rel. variation		5.7 %
April 18, 1991	1	150	76553
	2	150	86353
	3	150	72285
	4	150	73545
	5	150	72798
	6	150	70787
	7	150	69760
	Av.		74583
	1σ		±5622
	Rel. variation		7.5 %
April 22, 1991	1	150	71780
	2	150	77589
	3	150	68071
	4	150	68329
	5	150	58103
	Av.		68774
	1σ		±7094
	Rel. variation		10.3 %

ficiency of the baking of the inlet line before the blank analysis and in the trapping efficiency of the cold trap used to purify the He carrier gas. The source of CO_2 in the inlet unit most likely is the organic materials adsorbed on the inner surface of the tubing and metal valves.

CO_2 calibration

For the CO_2 calibration of the GC-MS system, we used a He-CO_2 gas mixture with a CO_2 concentration of 1050 ppm as the standard gas. This mixture was introduced into the inlet unit (N-O-P-R-Q) through valve J (Fig. 1) at various pressures, the absolute total gas pressure being measured with a capacitance manometer (CM). The amount of CO_2 gas in the inlet unit was calculated from the total pressure, CO_2 concentration of the gas mixture, temperature and the volume of the inlet unit on the basis of the ideal gas law. The gas mixture then was carried into the GC-MS unit by the purified He carrier gas, after which the peak area of the CO_2 chromatogram was measured. A series of calibrations was made by changing the pressure of the He-CO_2 mixture and the temperature of the inlet unit. The calibration curves at 150°C and 50°C are shown in Fig. 8.

A linear relation was obtained in the CO/ range from 0.15 to 1.2 ng when the inlet unit was heated to 150°C (Fig. 8a) and in the range from 0.15 to 0.9 ng with a line temperature at 50°C (Fig. 8b). The broken-line curves drawn at both sides of the calibration lines show the 95% confidence limits of the calibration lines from which the analytical unceratinties can be estimated. It was difficult, however, to analyze less than 0.3 ng CO_2 with the 150°C calibration line because of the high blank contribution and poor blank reproducibility (Table 1). In contrast, when the inlet unit temperature was kept at 50°C, the relative standard deviation (1σ) of the background CO_2 ($<6\%$ of the mean of several blank signals, Table 1) was smaller than at 150°C ($<10\%$); therefore, as little as 0.15 ng CO_2 could be analyzed with the calibration line obtained at 50°C. With this technique it is possible to analyze glass inclusions as small as 70 μm in diameter, assuming that these inclusions contain 300 ppm CO_2.

CO_2 analysis of glass from Mariana Trough basalt

To test our analytical techniques, we subjected a small fragment of a quenched glass rim from Mariana Trough basalt (MTB) to CO_2 analysis by the techniques described. Results are shown in Table 2. Step-wise heating under a vacuum followed by manometric analysis (Exley

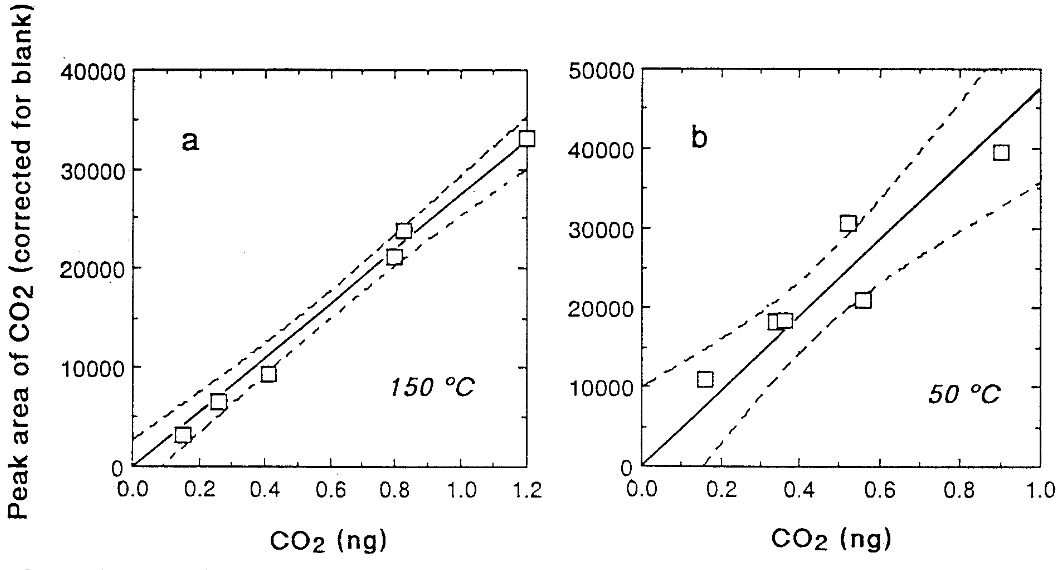

Fig. 8 Peak areas of CO_2 (corrected for blank) versus the absolute amount of CO_2 carried into the GCMS at the line temperatures of 150°C (a) and 50°C (b). The calibration lines were drawn by the least square method. The broken-line curves show the 95% confidence limits of the calibration lines.

Table 2 Laser microprobe analyses of CO_2 of Mariana trough basalt glasses.

Run No.	Diameter of laser pit (μm)	Wafer thickness (μm)	Mass of melted glass (μg)	Extracted CO_2 (ng)	CO_2 content (ppm)
1	128	58	2.00	0.53±0.10	270±50
2	125	47	1.60	0.88±0.21	560±140
3	88	47	0.63	0.54±0.10	860±160
4	87	47	0.67	0.77±0.16	1100±290

Errors for extracted CO_2 (ng) and CO_2 content (ppm) were estimated from variations in the calibration experiments.

et al., 1986) with about 1 g of the MTB glass yielded a bulk CO_2 concentration of 326 ppm. The CO_2 concentration of the MTB glass is highly variable (Table 2): run 1 gave a CO_2 content of 270 ppm, similar to the value obtained from the bulk analysis. The other runs (2,3 and 4) gave variable and much higher CO_2 concentrations than the bulk analysis. This variation may reflect (1) surface contamination that occurred during preparation of the small sample or (2) the non-homogeneity of the dissolved CO_2 in the natural glass which may include tiny vesicles filled with CO_2-rich gases.

The glass sample was glued on a slide glass with epoxy resin, then ground to a thickness of 40–60 μm. The glue was removed by placing the sample in acetone at about 50°C, then washing it ultrasonically in acetone and deionized water. The source of the background CO_2 could be carbonaceous materials present in the glue that remained on the surface of the glass sample. The glass samples used for runs 3 and 4 were repeatedly cleaned with acetone; but they gave even higher CO_2 concentrations than runs 1 and 2. Therefore it is unlikely that the variation in the CO_2 concentrations of the MTB glass was due to surface contamination by organic materials, although the possibility that organic materials on the surface were insoluble in aceone can not be ruled out.

The Mariana Trough basalt used here was dredged from the seafloor at a depth of 3600 m, which means the melt was quenched at about 360 bar. The saturated CO_2 concentration in a basaltic melt at 360 bar and 1200°C ranges from 140 to 200 ppm (Stolper and Holloway, 1988; Pan et al., 1991). The CO_2 content of 326 ppm obtained by step-wise heating of a large sample (1 g) indicates that the melt was supersaturated with CO_2 at the time of eruption. Supersaturation with CO_2 would produce vesiculation and the non-homogeneous distribution of dissolved CO_2 in the glass would be due to the rather slow diffusion of the CO_2 in the mlet (Watson et al., 1982). Microscopic observations indicate that the MTB glass contains vesicles with diameters of up to 200 μm. Runs 3 and 4 were made on vesicle-free regions after careful microscopic observation of the glass sample; therefore, it is unlikely that the high CO_2 content was produced by CO_2 gas derived from vesicles in the glass. Large variations in dissolved CO_2 concentrations have been reported for submarine basalt glasses, with CO_2 concentrations higher than the saturated value (Fine and Stolper, 1986; Dixon et al., 1988). Even viscle-free regions of the MORB glasses from the East Pacific Rise collected at a depth of 2600 m had the dissolved CO_2 concentrations that were 3–4 times the saturated CO_2 concentration of 110 ppm at 260 bar. The highly variable nature of the CO_2 concentrations (Table 2) suggests the non-homogeneity of the dissolved CO_2 in MTB glass.

To test the accuracy and precision of the proposed analytical techniques, it was necessary to obtain a glass sample that was microscopically homogeneous with respect to CO_2 distribution. Such a homogeneous glass sample was prepared by remelting the MTB glass in a piston-cylinder apparatus. The sample glass was sealed in a Pt capsule and melted at 1300°C and 10 kbar for two hours, after which it was quenched to obtain a homogenized sample. Because the solubility of CO_2 in the basalitic melt is 7500 ppm under these conditions, the sample should be undersaturated with CO_2. Although no bulk analysis is available for this homogenized glass because of its very small size, the CO_2 concentration should be close to 326 ppm, the concentration for the

Table 3 Laser microprobe analyses of the CO_2 of homogenized MTB glasses.

Run No.	Diameter of laser pit (μm)	Wafer thickness (μm)	Mass of melted glass (μg)	Extracted CO_2 (ng)	CO_2 content (ppm)
5	190	73	4.60	1.24±0.34	270±70
6	120	73	2.33	0.60±0.11	260±50
7	90	73	1.37	0.19±0.14	140±100
8	65	73	0.72	0.07±0.19	100±260

Errors for extracted CO_2 (ng) and CO_2 content (ppm) were estimated from variation in the calibration data.

original MTB glass. The CO_2 analysis of this glass is shown in Table 3. To avoid surface contamination by organic materilas during sample preparation, we used an acetone-soluble adhesive agent (Crystalbond No. 509, Aremco products, USA) to glue the sample on a slide glass. Results from runs 5 and 6 agreed well (260 and 270 ppm, respectively), whereas, runs 7 and 8 gave CO_2 contents of 100 and 140 ppm (much lower than the other values), although they sitll agreed with the results of runs 5 and 6 within large analytical errors. The value for run 7, which is lower than the bulk MTB CO_2 concentration of 326 ppm, may be due to an overstimation of the mass of the melted glass. The result of run 8 cannot be considered important because the amount of CO_2 was almost one third of the analytical uncertainty, and because a large error was made in esitmating the mass of the melted glass due to its irregular shape. Runs 5 and 6 gave CO_2 concentrations (260 and 270 ppm) smaller by ca. 60 ppm than the value for the bulk MTB. During extraction of the CO_2 from a sample, thermal decomposition of CO_2 to CO and O may take place. According to the results of Yonover et al. (1989), who used a similar analytical system for gas analysis in MORB glasses, the CO fraction produced by the thermal decomposition of the extracted CO_2 was estimated as about 0.25. If this factor is considered, the average CO_2 concentration of runs 5 and 6 would be 350 ppm, which is in fairly good agreement with the bulk analytical result. The applicability of the factor obtained by Yonover et al. (1989) to our system is uncertain because they used much higher laser energy. On the basis of the foregoing discussion, we conclude that our technique produces an accurate analysis of a micro quanitity of CO_2 in basalt galss within an error of ± 70 ppm, provided that the CO_2 extracted is more than 0.60 ng.

CONCLUSIONS

A new analytical system consisting of a laser probe extraction unit and a GC-MS unit was constructed. With this system we can analyze the CO_2 present in glass inclusions as small as 100 μm in diameter within an accuracy of ± 70 ppm, assuming that the glass inclusions contain at least 300 ppm CO_2.

Knowledge of the volatile concentrations (mainly CO_2 and H_2O) in preeruptive magma gained ihrough gas analysis of glass inclusions should make it possible to better understand the behavior of the volatiles present during the ascent of magma and in eruption processes. This will lead to the accumulation of basic knowledge that can be used to mitigate volcanic hazards.

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