LASER MICROPROBE ANALYSIS OF CARBON DIOXIDE AND WATER IN GLASS INCLUSIONS: AN ATTEMPT TO DETERMINE THEIR CONCENTRATIONS IN PRE-ERUPTIVE Magma

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Genji Saito

The Graduate School of Natural Science and Technology (Doctor Course) OKAYAMA UNIVERSITY
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AN ATTEMPT TO DETERMINE THEIR CONCENTRATIONS
IN PRE-ERUPTIVE MAGMA

by

Genji Saito

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ABSTRACT

Volatile materials dissolved in magmas play an important role in the evolution of magmas and volcanic eruptions. During magma ascent, the magma may be saturated with the volatiles because of decrease in solubilities of the volatiles in silicate melts with pressure. Formation of a gas phase would lead to decrease in the bulk density of magma and thereby accelerate the magma ascent. Expansion of the resulting gas phase may induce a volcanic eruption.

The major volatile components in a magma are H₂O, CO₂, S and Cl. Glass inclusions in phenocrysts are the most suitable samples for measuring volatile concentrations in pre-eruptive magmas. However, it has been difficult to measure the H₂O and CO₂ concentrations in glass inclusions, mainly because the size of the glass inclusions is very small (50-200 µm) and the sensitivity of analytical methods is not sufficient. In this study, we have developed a laser microprobe technique for determining a minute amount of H₂O and CO₂ dissolved in glass inclusions.

The analytical system consisting of a Nd-YAG laser for selective heating of glass inclusions and a gas chromatograph-mass spectrometer for measuring a micro quantity of H₂O and CO₂ dissolved in glass inclusions. The H₂O and CO₂ were extracted from glass inclusions by laser heating under a vacuum. The extracted gas was collected in a cold trap and then introduced to GCMS by carrier gas. Gas concentration was calculated from the absolute amount of the extracted gas and the mass of glass melted. The optimum working conditions (lamp current, pulse frequency and shooting duration) of laser extraction were decided using a basaltic glass sample. A glass sample ground to less than 100 µm thick was pierced by a laser beam
and measured for diameter of the hole produced to obtain the accurate determination of the volume of the glass melted. The mass of the melted glass was calculated from its volume and density.

Efforts were made for reduction of background level of CO₂ and H₂O. High purity helium carrier gas was farther purified with cold traps to remove CO₂ and H₂O contained in the carrier gas. Analytical line was thoroughly baked out at 300°C before the analyses. With these procedures, the blank CO₂ was reduced to less than 0.07 ng and the blank H₂O to less than 6 ng. The detection limit of the present system was found to be 0.15 ng CO₂ and 15 ng H₂O, considering the confidence limit of the calibration. The repeated analyses of CO₂ in basaltic glass indicate that the present technique allows us to analyze CO₂ concentration of glass inclusions as small as 70 μm in diameter within an accuracy of ±60 ppm, assuming that the glass inclusion contains 300 ppm CO₂. The H₂O analyses of the glass by the present technique gave significantly lower H₂O concentration than the bulk analysis, suggesting incomplete degassing of H₂O from molten glass during laser irradiation due probably to its slow diffusion rate.

The glass inclusion samples from Kilauea volcano, Hawaii, and Izu-Oshima volcano, Japan, were analyzed to determine CO₂ concentrations of pre-eruptive magma. The CO₂ concentration of pre-eruptive magma in South-West Rift Zone of Kilauea volcano was 230 ppm. This suggests that the magma has been significantly degassed during its storage in the summit magma chamber and migration to the rift system. The depth of the magma chamber was estimated to be 2.8-4.0 km from the CO₂ concentration of the pre-eruptive magma, in good agreement with the geophysical estimation. Comparison of the volatile budget of Kilauea volcano based on the CO₂ analysis of glass inclusion with the observed CO₂ flux suggests
that parental magma contains 3000 ppm CO₂. The bulk density of magma containing exsolved gases is not small enough to ascend to the surface by its own buoyancy. This is consistent with the present settings of the Kilauean magma: the summit magma chamber and rift magma system extending from the summit caldera.

The CO₂ concentration of pre-eruptive magma of Izu-Oshima volcano was found to be 170 ppm. The measured CO₂ concentration indicates that the magma chamber exists at a depth of about 2 km beneath the volcano. At this depth, the magma should be saturated with CO₂. The estimated bulk densities of the magma (d=2.4-2.6 g/cm³) containing CO₂-rich gas phase are consistent with the density structure of the volcano, if the magma before degassing contains CO₂ more than 1700 ppm. The rate of magma supply was estimated from the CO₂ concentration of pre-eruptive magma and CO₂ fluxes based on measurements on surface volcanic gases. Assuming the primary magma contains 2500 ppm CO₂, the estimated rate of magma supply (6-19x10³ tons/day) is compatible with the observed rate of magma supply based on the total mass of ejecta of major eruptions during the last 1500 years.
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CHAPTER I

INTRODUCTION

I-1. Water in magma

The major volatile components in magma are H$_2$O, CO$_2$, S, F and Cl, of which water is generally the most abundant. The solubility of H$_2$O in silicate melts is relatively large, for example, 3 wt.% at 1 kbar and 8 wt.% 5 kbar both at 1100 °C in a basalt melt (Hamilton et al., 1964). Water exerts great effects on many aspects of the chemical and physical properties of a silicate melt. For example liquidus temperatures are lowered depending on H$_2$O concentration in magma, giving rise to different crystallization paths (Yoder, 1965, 1969). Changes in phenocryst mineral assemblages with H$_2$O concentration of a crystallizing magma were used to estimate the initial water concentration in magmas for some volcanoes (Eggler, 1972; Maaløe and Wyllie, 1975; Sakuyama, 1979; Sekine et al., 1979). Viscosity of a silicate melt decreases with increase in the H$_2$O concentration in the melt, because presence of H$_2$O modifies the structure of the silicate melt by depolymerization (Scarfe, 1986). Density of magma is also lowered when H$_2$O is dissolved (Scarfe, 1986). Decrease in both viscosity and density is considered to be due to the reaction between dissolved H$_2$O and oxygen ions in the melt, which breaks Si-O-Si bridges and produces OH$^-$ ions (Burnham and Davis, 1971). The viscosity and density of magma are important physical parameters which affect behaviors of magma such as magma ascent in the crust and magma mixing (Campbell
and Turner, 1985, 1986; Huppert et al., 1982, 1984; Koyaguchi and Blake, 1989). Because the solubility of H$_2$O in magma becomes smaller as pressure lowers, a H$_2$O-rich gas phase would form as the magma ascends to a depth which is shallow enough for the magma to be saturated with H$_2$O. Formation of the gas phase would lead to decrease in virtual magma density and thereby accelerate the magma ascent. In a cooling magma chamber, crystallization of volatile-free minerals would also cause volatile concentration (Harris and Anderson, 1984) followed by saturation. This gas phase would have a significant effect on volcanic eruption because formation of the gas phase would be accelerated as crystallization proceeds. Therefore the water-rich gas phase produced in a shallow magma chamber would grow and the increased pressure in the chamber may eventually trigger an explosive eruption (Eichelberger, 1980; Tait et al., 1989).

It has been suggested that H$_2$O is concentrated in an upper part of a pre-eruptive magma chamber (Kennedy, 1955). Sekine et al. (1979) observed that the H$_2$O contents of ejecta at an early stage of the 1783 Asama eruption and the 1914-1915 Sakurajima eruption were higher than those at later stages. Water contents in rhyolitic glass inclusions in quartz phenocrysts from the early stage airfall tephra of the 1 Ma eruption of Jemez Mountain, New Mexico, were higher than those from the later stage tephras (Sommer and Schramm, 1983). These findings seem to support an idea of vertical inhomogeneity of magma with respect to the water concentration. However, recent determinations of volatiles in the pre-eruptive magma which was responsible to the 2 ka great eruption of Taupo, New Zealand, do not show such a systematic trend. Accumulation of data on H$_2$O concentrations in pre-eruptive magma is highly required to generalize the problem.
I-2. Carbon dioxide in magma

Although the relevant data are still limited, carbon dioxide is known to have much lower solubilities in silicate melts than H$_2$O when compared at the same pressures (Stolper and Holloway, 1988; Fogel et al., 1990; Pan et al., 1991; Mattey, 1991). Consequently it is expected that a CO$_2$-rich gas phase may be initially formed in an ascending magma at much greater depths than the depth where H$_2$O saturation is reached. Formation of the CO$_2$-rich gas phase would reduce the bulk magma density and thereby accelerate the magma ascent, if a significant amount of CO$_2$ is present in the initial magma. For this reason, CO$_2$ is recently believed as an essential component that may drive a deep-seated magma to a shallow level of the Earth's crust and induce a volcanic eruption.

A large amount of CO$_2$-rich gases was emitted during the 1980 eruption of Mount St. Helens (Casadevall et al., 1981; Barnes et al., 1984). Phase equilibrium relations of the dacitic pumices erupted from the volcano indicated that CO$_2$ occupied 30-50% of the gas phase that was present in the pre-eruptive magma (Rutherford et al., 1985). In the 1986 disaster of Lake Nyos, Cameroon, almost pure CO$_2$ gas was suddenly released from the crater lake, killing more than 1700 people (Kusakabe et al., 1989). The CO$_2$ was most likely derived from the basaltic magma that was responsible for the formation of Lake Nyos maar (Kusakabe and Sano, 1991). Because CO$_2$ in magma can have such a direct or indirect relation to volcanic events, measurements of CO$_2$ content in pre-eruptive magmas are essential to understand the
behavior and effects of CO₂ during magma ascent and volcanic eruptions.

I-3. Volcanic gases

High temperature volcanic gases have been considered to represent the volatile materials originally dissolved in magma. This interpretation is correct only if the gases are collected directly from a magma, i.e., gases obtained from a lava lake (Jagger 1940; Sigvaldason and Elisson, 1968; Giggenbach and Le Guern, 1976; Greenland et al., 1985). Recent investigations on the behavior of volatiles at Kilauea volcano, Hawaii, indicate that degassing takes place during magma ascent from depths to a shallow magma reservoir (Gerlach and Graeber, 1985). In this respect, even lava lake gases may not represent truly primary magmatic volatiles. Moreover, in the case of explosive eruptions, it is almost impossible to collect gases that are jetting out of an exploding vent. The gases from such volcanoes are generally collected from accessible fumaroles after the explosive stage has been over. It is known that such fumarolic gases are variably contaminated by meteoric water and other surface materials (e.g., Mizutani and Sugiura, 1982, Kusakabe and Matsubaya, 1985), and that chemical compositions of fumarolic gases change greatly depending on temperature, pressure and a flow velocity of gases at the time of collection (Saito et al., 1988). Thus, it can be said that information on magmatic volatiles based on gas chemistry of volcanic gases is rather limited.

Concentrations of volatiles in quenched glasses in volcanic ashes and lavas are generally very low, because most of the volatiles dissolved
in magma is released to the atmosphere due to rapid reduction of pressure at the time of eruption. Therefore it is almost impossible to estimate the compositions and concentrations of volatiles in pre-eruptive magma from analysis of volcanic glasses in ashes and lavas.

1-4. Glass inclusions in phenocryst

The H$_2$O and CO$_2$ contents in magmas of mid ocean ridge basalts (MORB) have been measured using the quenched glass rim of MORBs which are believed to retain their original gas concentrations because of a huge hydrostatic pressure exerted to the sites of submarine eruptions (Moore and Schilling, 1973). However, glasses in volcanic rocks effused onto the surface of the Earth are not suitable for estimation of the gas concentrations of pre-eruptive magmas because they have most likely degassed before and/or during the eruption as described above.

The crystals may trap the surrounding silicate melt during their rapid growth in a magma chamber. Such melt is quenched at the time of eruption as glass inclusions in a phenocryst (Roedder, 1979). Protected by thick harness of the host crystal, degassing from the glass inclusions and the contamination by extraneous volatiles after trapping are kept negligible (Anderson, 1973). For this reason the glass inclusions in phenocrysts are the most suitable samples for measuring volatile concentrations in pre-eruptive magmas. Until recently, however, it has been difficult to measure H$_2$O and CO$_2$ concentrations in glass inclusions, mainly because the size of the glass inclusions is very small (50-200 µm) and the sensitivity of analytical methods is not sufficient (Saito and Kusakabe, 1989). The present study aims at
development of analytical techniques for determination of a micro quantity of gases in glass inclusions and its application to natural volcanic systems.

1.5. Previous studies on volatile analysis of glass inclusions

The analytical methods for the determination of H$_2$O and CO$_2$ concentrations in glass inclusions have been reviewed by Saito and Kusakabe (1989). They can be classified into mainly two groups; (A) a vacuum fusion technique for gas extraction followed by micro gas analysis, and (B) in situ measurement with infrared spectroscopy or ion microprobe analysis.

In the method (A), several analytical techniques have been applied; (1) extraction of volatiles by vacuum fusion of a phenocryst containing a glass inclusion followed by manometric measurements (Harris and Anderson, 1983, 1984; Sommer and Schramm, 1983), (2) the vacuum fusion technique combined with quadrupole mass spectrometry (Delaney et al., 1978; Garcia et al., 1979; Muenow et al., 1979), and (3) focused laser heating and subsequent mass spectrometric analysis (Franchi et al., 1986; Yonover et al., 1989; Gibson and Carr, 1989; Saito and Kusakabe, 1992). In these methods glass inclusions were melted in vacuum using an electrical furnace or a laser beam to extract H$_2$O and CO$_2$. Because in the vacuum fusion technique the host crystals and other materials that surround the glass inclusions are also heated, H$_2$O and CO$_2$ present in the materials other than the glass inclusions are also extracted to give a positive error in the H$_2$O and CO$_2$ concentrations of the glass inclusions. It was reported that, in the analysis of a glass
inclusion in a olivine crystal from Kilauea volcano, Hawaii, contribution of gases from the host olivine crystal to the total gases extracted from the sample was estimated to be about 6-14 % for H₂O and 5-50 % for CO₂ (Harris and Anderson, 1983). Consequently, a microprobe analysis has to be developed for the selective analysis of the glass inclusions. The laser probe technique is capable of selective heating of inclusion glasses as small as 10 µm in diameter and therefore promising if a high sensitive analytical system such as mass spectrometry is combined. Yonover et al. (1989) applied the laser probe extraction and a quadrupole mass spectrometer to MORB glasses, but unfortunately they presented only CO₂/H₂O ratios and no concentration of each component.

In the latter method (B), the in situ analytical techniques were applied; they are (4) "by-difference" electron-probe microanalysis (EPMA, Anderson, 1973; Devine and Sigurdsson, 1983), (5) Ion-probe microanalysis (IPMA, Dunber et al., 1989; Hervig et al., 1989), (6) Fourier transform infrared spectroscopy (FTIR, Anderson et al., 1989; Metrich et al., 1990). The pioneering work was performed by Anderson (1973) to measure the volatile concentrations in glass inclusions by EPMA. This method was apparently limited to determination of the total volatile concentration in glass inclusions because the volatile concentration was given by difference of an EPMA analysis of major constituents of the inclusion glass from 100%. Although this method could give a rough estimate how much total volatiles are contained in the inclusion, the actual H₂O and CO₂ concentrations cannot be known in principle. In the IPMA technique, the secondary ions produced by spattering a sample surface with the primary ion beam having a diameter of 20-30 µm are analyzed with a
high resolution mass spectrometer. The IPMA technique allows the analysis of H₂O in a glass inclusion with the precision of ±0.5 wt.% for samples containing H₂O between 1 and 6 wt.% (Hervig et al., 1989). Because there are large matrix effects in the IPMA technique, i.e., the production rate of the secondary ions varies extensively depending on the chemical composition of the material in which H₂O and CO₂ are dissolved, the relationship between the sensitivity of the ions to be measured and chemical composition of the matrix must be known before the glass inclusion analysis is made. The FTIR technique is a rapid, nondestructive and highly sensitive method that is characterized by high spatial resolution (Fine and Stolper, 1986). However, there is again the "matrix effects" in that the molar absorption coefficients of individual IR spectra are highly dependent on the chemical composition of the inclusion glass. For this reason, the FTIR technique has been applied only to glasses with a limited range of chemical compositions, i.e., basalts and rhyolites (Stolper et al., 1987; Dixon et al., 1988; Fogel and Rutherford, 1990).

I-6. This study

In this study, we attempt to develop a "quantitative" laser microprobe technique for determination of micro quantities of H₂O and CO₂ dissolved in glass inclusions, because this method is considered to have little drawbacks such as "matrix effects" that are pertinent to other methods mentioned above, still keeping a high sensitivity.

This dissertation describes mainly technical developments of the analytical methods using laser microprobe. In Chapter II, the analytical
techniques developed in the present study will be described. In Chapter III, analytical accuracies of the present techniques will be discussed taking examples of analyses of natural and homogenized glasses for which gas concentrations are known. In Chapter IV are presented the analytical results of some glass inclusion samples from Kilauea (Hawaii) and Izu-Oshima (Japan) volcanoes, and their implications of the effects of volatiles on volcanic eruptions, volatile budget, and the rate of magma supply.
CHAPTER II

DEVELOPMENT OF A LASERPROBE-GCMS SYSTEM FOR DETERMINATION OF A MICRO AMOUNT OF CO₂ AND H₂O IN GLASS INCLUSIONS

II-1. Laserprobe-GCMS system

II-1-1. Amount of H₂O and CO₂ in a glass inclusion

The concentrations of H₂O and CO₂ in magma can be calculated from the solubility data of H₂O and CO₂ (Hamilton et al., 1964; Stolper and Holloway, 1988; Fogel and Rutherford, 1990; Pan et al., 1991; Mattey, 1991), if the melt is saturated with these gases (Fig. II-1). If the depth of a magma chamber in which the melt is trapped as inclusions of phenocrysts is 1-7 km, or 0.3-2.1 kbar, the melt should have the H₂O concentration of 1.2-6.2 wt % and the CO₂ concentration of 100-1000 ppm. The absolute amounts of H₂O and CO₂ contained in a single spherical glass inclusion are then calculated from its volume, density and gas concentrations as shown in Fig. II-2. A spherical glass inclusion with the diameter of 100 μm is expected to contain 17-85 ng of H₂O and 0.14-1.4 ng of CO₂ (Fig. II-2). Therefore, a sensitive analytical system is required to measure these minute amounts of H₂O and CO₂. In addition, there is a possibility that the host phenocryst contains fluid inclusions consists of H₂O and/or CO₂ (Norman and Sawkins, 1987), so that a microprobe technique is needed to extract only the gases dissolved in the glass inclusion.
Figure II-1. (a) Solubilities of CO$_2$ in basaltic and rhyolitic melts at 1200°C. Solid lines are for the tholeiitic basalt melt (Stolper and Holloway, 1988; Pan et al., 1991) and a dashed line for the rhyolitic melt (Fogel and Rutherford, 1990). A solid circle represents the solubility in tholeiitic basalt melt by Mattey (1991). (b) Solubilities of H$_2$O in basaltic melt (solid curve) and andesitic melt (dashed curve) at 1100°C after Hamilton (1964).
Figure II-2. (a) Relationship between the absolute amount of CO$_2$ dissolved in a single glass inclusion and its diameter assuming that the CO$_2$ concentration of the glass inclusion ranges from 50 ppm to 5000 ppm. (b) Relationship between absolute amount of H$_2$O dissolved in a single glass inclusion and its diameter assuming that the H$_2$O concentration of the glass inclusion ranges from 0.5 wt.% to 5 wt.%.
II-1-2. Principle of a laserprobe-GCMS system

In preliminary experiments, a prototype laserprobe-quadrupole mass spectrometry system was set up to obtain various information on working conditions of laserprobe and the most suitable experimental conditions of micro-analysis of $\text{H}_2\text{O}$ and $\text{CO}_2$. (Appendix). In order to analyze a micro amount of $\text{H}_2\text{O}$ and $\text{CO}_2$ in glass inclusions, selective heating by laser probe to extract $\text{H}_2\text{O}$ and $\text{CO}_2$ was carried out and gas chromatography-mass spectrometry (GC-MS) was adopted as an analytical method (Fig. II-3). The volatile materials extracted in vacuum were quickly transferred to a GC column by a flow of helium carrier gas keeping minimum their adsorption on to the wall of the analytical line which was heated to 50-150 °C. Water and carbon dioxide were separated from the other gases in the GC column and determined for their amounts by the quadrupole mass spectrometer (QMS). It is expected that this analytical system allows us to measure the extracted $\text{H}_2\text{O}$ and $\text{CO}_2$ at the same time. The analytical system consists of four units; laser unit, GC-MS unit, gas calibration unit and inlet unit as shown in Fig. II-3.

II-1-3. Laser unit

A Nd-YAG laser with a maximum power of 7 W (Model SL114L, NEC Corporation, Japan) was used to melt sample glasses in this work. The wave length of the Nd-YAG laser was 1.064 μm. There are two modes for laser beam generation; a continuous wave (CW) mode and a
Figure II-3. Schematic diagram of the laserprobe-GCMS system for analysis of micro quantities of H₂O and CO₂ in glass inclusions.
pulsed (Q switched) mode. The pulse frequency can be changed from 1 to 99 kHz by means of the Q switch. As the pulse frequency increases, average power of the laser beam becomes larger and the output energy of a single pulse smaller. Maximum power can be attained in the CW mode. A schematic diagram of the laser system is shown in Figure II-4. The laser beam was reflected by a mirror in a microscope and focused on a sample held in the sample cell through an objective lens (20x) attached to the microscope. The focal length of the focusing lens used in this work was 18 mm. The diameter of the laser beam on the sample was adjusted to 10 μm. The same optics were used to view the sample to find a target for the laser shot. The sample was illuminated either by transmitted or reflected light. Because the laser housing and microscope were fixed in position, movement of the sample with respect to the focused beam was accomplished by adjusting the sample cell on a stage using three micrometers operating in the X, Y and Z directions.

II-1-4. Inlet unit

The inlet unit consists of a sample cell made of stainless steel, high-vacuum bellows valves (Nupro company, Ohio, USA) N, O, P, Q, R and S, cold traps (Traps 1 and 2), purification traps and stainless steel tubings with the inner diameter of 3 mm in Fig. II-3. These parts are connected with each other by gasketed vacuum fittings (VCR fittings) made of stainless steel (Cajon company, Ohio, USA). This system can be baked up to about 300 °C.

The sample cell has a capacity of 0.44 cm³ with quartz glass windows (Fig. II-5). The laser beam is focused on the sample through
Figure II-4. Schematic diagram of the laser extraction system. Sample on the stage can be observed with a microscope under both transmitted and reflected lights.
Figure II-5. Schematic presentation of the sample cell.
the top side of the window. A gold gasket or a teflon gasket is placed between the window and the cell body for vacuum sealing. Air leakage often took place due to uneven fastening of the flange, resulting in cracking of the quartz glass window when the gold gasket was used for vacuum sealing, although use of the gold gasket allows us to bake the cell at more than 300 °C. On the other hand, the teflon gasket gave better sealing, but the maximum baking temperature was 200 °C. The sample cell was connected to the vacuum line by VCR fittings (Fig. II-5). The flexibility of the stainless steel tubings of the inlet unit allows movement of the sample cell for focusing the laser beam.

The trap 1 which is made of stainless steel tubing is for collection of condensible gases, mainly H₂O and CO₂, extracted from a sample glass during laser heating in vacuum. Water and carbon dioxide after trapping in the trap 1 were transferred to the trap 2 by heating of the trap 1 and with a flow of helium carrier gas from valve P. The trap 2 which is made of a GC capillary column (coated with PoraPLOT-Q, inner diameter 0.32 mm) is to concentrate the extracted gases by cooling with liquid nitrogen. The concentrated gases are then introduced into the GCMS unit by heating the trap 2 to 100 °C. This concentration procedure of gases prior to analysis is essential to separate the gases and to yield sharp and sensitive chromatograms.

The purification trap 1, made of a Molecular Sieve 5A column, was used to reduce the level of background gases contained in the He carrier gas. In addition, the purification trap 2, which was made of the same material as trap 2 and has the total length of about 2 m, is used for the same reason. The purification trap 3 made of a stainless steel tubing with a diameter of 15 mm and the length of 100 mm was also used as a
cryopump to reduce the background level of H₂O and CO₂ in the inlet unit.

II-1-5. GCMS unit

Detection and quantitative determination of H₂O and CO₂ extracted from a sample glass were performed using a gas chromatograph-quadrupole mass spectrometer (GC-MS, model QP300, Shimadzu Corporation, Japan). High purity helium gas (99.9999%) was used as a carrier gas with the secondary pressure of 2 kgf/cm². PoraPLOT-Q (Chrompack, Netherlands) was used as a stationary phase in the fused silica capillary column to separate H₂O and CO₂ from the other gases. The capillary column which had the inner diameter of 0.32 mm and the length of 25 m was maintained at 150 °C in the GC oven to obtain the clear separation and a sharp chromatogram of the gases. The carrier gas which picked up the sample gas was led to the ionization source in the quadrupole mass spectrometer (QMS). The QMS was always evacuated to about 6x10⁻⁶ torr by two oil diffusion pumps with pumping capacities of 3200 l/sec and 700 l/sec. The neutral gas species entering the mass spectrometer were ionized by impact of thermal electrons with an energy of 70 eV from the filament in the ionization source. The quadrupole mass filter, which consisted of four molybdenum rods with precise hyperbolic configuration, separated positive ions having a given M/z (mass/charge) ratios out of ions having various M/z ratios. Detection of the positive ions extracted by the mass filter was accomplished by an electron multiplier. The computer-controlled mass spectrometer permitted us continuous and simultaneous
measurement of ion currents of four ionized species within the mass range of 1 to 300 (M/z) at a scanning rate of 5 times per second. In the present study, the masses (M/z) 18, 32, 40 and 44 were measured for the analysis because the masses 18 and 44 were the parental ions of H₂O and CO₂ respectively. The masses 32 (O₂) and 40 (Ar) were measured for monitoring a possible leakage of air in the line. The data obtained were processed by the data reduction system to give a gas chromatogram for each gas.

II-1-6. Calibration unit

The calibration unit was constructed for calibration of the GCMS system. The calibration unit consisted of vacuum pumps, vacuum gauges and Nupro high-vacuum bellows valves made from stainless steel (Fig. II-3), which were connected with VCR fittings for high vacuum sealing. The calibration unit was maintained at 150-200 °C by tape heaters during analyses. The oil diffusion pump (250 l/sec) backed up by a rotary pump was able to evacuate the calibration unit and the inlet unit. A cold trap kept at a liquid nitrogen temperature was used together with the diffusion pump to avoid possible back-diffusion of organic materials from the oil diffusion pump. An ion pump (20 l/sec) was also provided as an auxiliary pump. An ultimate pressure of about 2x10⁻⁵ torr in the inlet unit were attained. A capacitance manometer (MKS Instruments, Inc., USA), which enables us to measure an absolute pressure of gases ranging from 1 torr to 1x10⁻⁴ torr, was used for measuring the total pressure of the calibration gases inside the calibration unit. The sensor head of the capacitance manometer was
maintained at 150 °C to minimize adsorption of H₂O and other gases. A McLeod gauge was also used as a standard pressure gauge to measure gas pressure of more than 1 torr in the calibration experiments. Experiments for calibration of GCMS will be described in Chapter II-3.

II-2. Preliminary experiments of laser heating

II-2-1. Observation of laser pits

An absolute amount of the extracted H₂O and CO₂ and a mass of the glass melted by a laser beam have to be known to determine H₂O and CO₂ concentrations in the sample glass;

\[
\text{Gas concentration} = \frac{\text{The amount of gas}}{\text{Mass of the glass melted}}
\]

Estimation of a mass of the glass melted by a laser beam was the most difficult part of this study, because the shapes of laser-shot pits were variable. Consequently, the relationship between the working conditions of the laser unit and the mass of glass melted were studied. For this purpose, Mariana Trough basalt (MTB) glasses that had been wafered to about 300 μm thick were used as a sample. Laser beam with various working conditions was shot to the MTB glass. After the laser irradiation, the laser pit on the sample was observed by the following procedures.

At first, the sample wafer was glued horizontally on a slide glass by an epoxy resin adhesive agent (Rapid araldite, Ciba-Geigy limited, Switzerland). Then the upside surface of the pit was observed under an
optical microscope and a scanning electron microprobe (SEM). Secondly the sample was removed from the slide glass by soaking in boiling acetone for half an hour. The sample wafer was let stand vertically on a slide glass and fixed with the above adhesive agent, and the side of the wafer was ground until cross section of the laser pit was exposed using sand papers (No. 1200-No. 1500). Then the cross section of the laser pit was observed with an optical microscope and SEM.

The pits produced had various shapes and were often covered by frothy secondary glasses which looked like a dome as shown in Fig. II-6. Splashed fragments of the secondary glass can be observed, suggesting complete melting of the sample glass by laser irradiation. A typical example of the cross sections of pit craters is shown in Fig. II-7. The diameter of the frothed glass dome was significantly greater than the actual diameter of the laser pit. However, it was found that the secondary frothed glass covering the pit was easily filed away using fine sand papers (Nos. 1200-1500), and that the diameter of the exposed pit could be accurately measured by a microscope. In the preliminary experiments described in Appendix, it was attempted to measure the pit depth by changing focus of the optical microscope from the surface to the bottom of the laser pit. However, the depth estimation through the secondary glasses by an optical microscope was found to result in underestimation of the pit depth because the pit was also filled with the secondary glasses as shown in Fig. II-7. It was concluded that the pit depth had to be measured by observing the cross section.

There are three factors which affect the effective power of laser beam; electric current applied to the krypton arc lamp, pulse frequency and shooting duration. In order to know the relationship between the working conditions of the laser unit and shapes of laser pits produced,
Figure II-6. SEM photomicrograph of a laser pit on a MTB glass sample. Note that the pit is covered by a secondary frothed glass. A part of the melted glass was scattered around the pit forming hairs and droplets.
Figure II-7. SEM photomicrograph showing a cross section of a laser pit. Note that the diameter of the secondary frothed glass at the surface is larger than that of the pit. Secondary glass is also present in the pit.
the laser beam was shot to the MTB glass by varying the shooting duration and pulse frequency (Tables II-1 and II-2) at a fixed lamp current of 17 A. The lamp current can be changed from 14 A to 22 A. Too low lamp current make the power of laser beam unstable, and energy available was found optimum when the lamp current was 17 A. Considering these factors, the lamp current of 17 A was decided. Preliminary experiments indicated that the laser beam with pulse frequency less than 10 kHz often flicked the sample glass away and tended to produce irregular shaped pits because of a very large output energy available for a single pulse. Thus, the laser experiments were carried out using the pulse frequency higher than 10 kHz or CW mode.

After the laser irradiation, an upside surface and a cross section of the laser pit were observed as described previously. The upside surface of the pits after removal of the frothed glass cover was circular or elliptical. The cross sections of the pits were highly variable and it was difficult to express the pit shape with any geometrical approximation, for example, such as a paraboloid of revolution (Toyoda and Ozima, 1988).

In spite of these difficulties, the diameter and depth of the pits measured microscopically increase generally with the shooting duration and the pulse frequency (Tables II-1 and II-2). An average energy of a Nd-YAG laser shot in each run can be calculated from the monitored output energy per second and the shooting duration as;

$$\text{Average energy} = (\text{Output energy}) \times (\text{Shooting duration})$$

(mJ) (W) (msec)

The output energy per second (W) varies depending on the pulse frequency of the Nd-YAG laser beam. The average energy of the Nd-
Table II-1. The diameter (μm) of pits produced by laser beam with various working conditions.

<table>
<thead>
<tr>
<th>Pulse frequency (kHz)</th>
<th>Pit diameter under variable duration (μm)</th>
<th>5 msec</th>
<th>10 msec</th>
<th>50 msec</th>
<th>100 msec</th>
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<tbody>
<tr>
<td>10</td>
<td></td>
<td>44</td>
<td>53</td>
<td>133</td>
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<td>66</td>
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<td>71</td>
<td>94</td>
<td>184</td>
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<td>79</td>
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<td></td>
<td></td>
<td>81</td>
<td>28</td>
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<tr>
<td>CW*</td>
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<td>44</td>
<td>97</td>
<td>220</td>
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<td>74</td>
<td>133</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>77</td>
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</tbody>
</table>

* Continuous wave mode
Table II-2. The depth (μm) of pits produced by laser beam with various working conditions.

<table>
<thead>
<tr>
<th>Pulse frequency (kHz)</th>
<th>Pit depth under variable duration (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 msec</td>
</tr>
<tr>
<td>10</td>
<td>92</td>
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<tr>
<td></td>
<td>101</td>
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<tr>
<td>20</td>
<td>86</td>
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<tr>
<td>50</td>
<td>80</td>
</tr>
<tr>
<td>80</td>
<td>105</td>
</tr>
<tr>
<td>CW*</td>
<td>118</td>
</tr>
</tbody>
</table>

* Continuous wave mode
YAG laser with various shooting durations and pulse frequencies is shown in Table II-3. The variations of the diameter and depth of the pits with the laser energy applied are shown in Figs. II-8a and II-8b, respectively. When the pulse frequency is fixed, the diameter and depth of the pits increase with the laser energy or duration of laser irradiation. From these experimental results, the size of pits can be roughly controlled by changing of the duration.

The change in diameter of a pit with depth was measured by measuring diameters at different depths of a pit on the cross section as shown in Fig. II-9. The volume of the pit was obtained from the dimension of the cross section assuming that the pit shape was approximated by a body of revolution. The density of MTB glass was measured to be 2.74 g/cm³ using heavy liquids. The masses of melted glass given in Table II-4 were thus calculated from the pit volume and the density of MTB glass. A reasonable correlation was observed between the mass of the melted glass and the applied laser energy as shown in Fig. II-10. This diagram enables us to estimate the laser energy which is needed to melt a glass inclusion of a given size.

II-2-2. Improved methods for estimating mass of glass melted

The above method to measure the volume of a pit through observation of the cross section of a sample glass is very tedious and time consuming. For this reason the following procedures were adopted to estimate the pit volumes. A sample glass which had been laser-shot was ground to a less than 100 μm thick wafer. The wafer was doubly polished. The sample wafer thus prepared was then pierced
Table II-3. Total energy of Nd-YAG laser (mJ) with various working conditions.

<table>
<thead>
<tr>
<th>Pulse frequency (kHz)</th>
<th>Output energy per second** (W)</th>
<th>Total energy under various shooting duration (mJ) †</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5 msec</td>
</tr>
<tr>
<td>10</td>
<td>3.3</td>
<td>17</td>
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<td>50</td>
<td>4.0</td>
<td>20</td>
</tr>
<tr>
<td>80</td>
<td>4.3</td>
<td>22</td>
</tr>
<tr>
<td>CW*</td>
<td>4.3</td>
<td>22</td>
</tr>
</tbody>
</table>

* Continuous wave mode  
** Fluctuation of the output energy per second is within ±0.5 W.  
† Errors of the total energy due to the fluctuation of the output energy are estimated to be ±2.5 mJ for the duration of 5 msec, ±5.0 mJ for 10 msec, ±25 mJ for 50 msec and ±50 mJ for 100 msec.
Figure II-8. (a) Variation in the diameter of pits produced by a laser beam with the total laser energy which is a function of duration. (b) Variation in pit depths with the total laser energy. The working conditions of laser were set at constant lamp current of 17.0 A and pulse frequency of 10 kHz.
Figure II-9. Observation of a cross section of the pit. A pit area was integrated from the top to the bottom to obtain the pit volume.
Table II-4. Mass of glass melted by laser irradiation with various working conditions.

<table>
<thead>
<tr>
<th>Pulse frequency (kHz)</th>
<th>Mass of glass melted with various shooting duration (μg)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 msec</td>
<td>10 msec</td>
<td>50 msec</td>
<td>100 msec</td>
</tr>
<tr>
<td>10</td>
<td>0.24</td>
<td>0.17</td>
<td>5.50</td>
<td>5.00</td>
</tr>
<tr>
<td></td>
<td>0.39</td>
<td>0.52</td>
<td>2.76</td>
<td>4.69</td>
</tr>
<tr>
<td>20</td>
<td>0.40</td>
<td></td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.95</td>
<td>0.51</td>
<td>1.96</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>0.49</td>
<td>0.29</td>
<td>13.1</td>
<td></td>
</tr>
<tr>
<td>CW*</td>
<td></td>
<td>1.49</td>
<td>11.0</td>
<td></td>
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</tbody>
</table>

* Continuous wave mode
Figure II-10. Variation of the masses of glass melted by laser heating with laser energies applied. The working conditions of the laser unit were set at constant lamp current of 17.0 A and pulse frequency of 10 kHz. Laser energy needed to melt a glass inclusion of a given size can be estimated from this figure.
in a vacuum by a laser beam (Fig. II-11). The experiments on the working conditions of the laser unit indicate that the pit depth of more than 100 μm was obtainable with the pulse mode of 10 kHz or CW mode and the shooting duration of more than 50 msec (Table II-2 and Fig. II-8). The pit diameter could be easily controlled by changing the shooting duration under a constant pulse frequency of 10 kHz or CW mode as shown in Fig. II-8. Because the diameter of the hole can be easily measured after removal of the secondary glasses mentioned previously, the volume of a cylindrical hole is rather accurately estimated from the diameter of the hole and the wafer thickness (Fig. II-11). The mass of glass melted is then calculated from the volume and the glass density. We believe that this technique is the best way to estimate the amount of glass melted by a laser beam.

II-2-3. Degassing from periphery of pits

One possible source of error associated with the present analytical method may be outgassing of volatiles from the periphery of the laser pit. Peripheral extraction of volatiles would result in overestimation of the volatile concentration in a sample glass. In order to assess the possibility of degassing from the pit periphery, distribution of relative concentrations of sulfur, chroline and sodium in the areas surrounding the laser pit was measured with electron microprobe analysis. These elements were selected because they must have greater volatility than the other elements in the sample glass, although H2O and CO2 could not be measured with EPMA. Electron microprobe analyses with a beam diameter of 3 μm were made for a cross section of a laser pit produced
Figure II-11. Photomicrograph of a MTB glass wafer (70 μm thick) pierced by a laser beam. The volume of melted glass is calculated from the diameter of the cylindrical hole and wafer thickness.
on MTB glass. Distributions of the X-ray counts per 20 sec from sulfur, chlorine and sodium in the glass surrounding the pit are shown in Figs. II-12, II-13 and II-14, respectively. An average value of 21±4 (1σ) was obtained for sulfur in the immediate neighborhood of the pit, in good agreement with the average value of 20±5 (1σ) for the other part of the glass which was 50-150 μm away from the pit (Fig. II-12). It should be noted that there was no recognizable concentration gradient away from the pit. A similar result was obtained for chlorine (Fig. II-13); 16±2 (1σ) counts/20 sec for the immediate neighborhood and exactly the same value for the rest of the glass. It is known that sodium migrates away from the spot where electron beam concentrates to produce local high temperature (Nielsen and Sigurdsson, 1981). Consequently it is expected that sodium present near the laser pit may be affected by laser irradiation. However, Figure II-14 indicates that this is not the case; 48±7 (1σ) counts/20 sec for the 0-10 μm region, 48±7 for the 10-20 μm region, 49±8 for the 20-50 μm region and 53±8 for the >50 μm region. These observations indicate that outgassing of sulfur and chlorine from the immediate neighborhood of the laser pit is negligible. Sulfur depletion in periphery of the laser pits was observed when Nd-YAG laser was shot to sulfide mineral (Crowe et al., 1990). In their experiments, a larger laser power (about 10 W) and longer shooting duration (more than 2 sec) were used, which could be the reasons why sulfur depletion in periphery of the pits was induced. From the foregoing, we assume that degassing of carbon dioxide and water from the pit periphery at the time of laser irradiation is negligible, although we must keep in mind that the assumption may not be 100 % guaranteed.
Figure II-12. Distribution of relative sulfur concentrations in the pit periphery. Underscored numbers represent X-ray counts of sulfur per 20 seconds for the points nearest to the rim.
Figure II-13. Distribution of relative chlorine concentrations in the pit periphery. Underlined numbers represent X-ray counts of chlorine per 20 seconds for the points nearest to the rim.
Figure II-14. Distribution of relative sodium concentrations in the pit periphery. Underlined numbers represent X-ray counts of sodium per 20 seconds for the points in the 0-10 \( \mu \text{m} \) region from the rim.
II-3. Micro-gas-analysis of CO₂ and H₂O by GCMS

II-3-1. Background of CO₂

The absolute amount of CO₂ contained in a glass inclusion with a diameter of 100 μm is expected to range from 0.1 to 1 ng as shown in Fig. II-2. When this small amount of CO₂ is to be analyzed, evaluation of background CO₂ is essential to obtain a reliable result. The CO₂ background in our system can arise from the two sources; the CO₂ adhered in the inlet tubings and metal valves and CO₂ contained in the helium carrier gas used for GCMS.

To reduce CO₂ contribution from the first source, the stainless steel tubings and metal valves were initially cleaned with acetone, dilute nitric acid and distilled water, followed by repeated baking at 300 °C in vacuum. To reduce CO₂ contribution from the second source, high purity helium gas (99.9999%) was used as a carrier gas for GCMS analysis. The helium carrier gas was further purified by passing through the purification trap 1 made of a Molecular Sieve 5A column and the purification trap 2 coated with PoraPLOT-Q, both immersed in liquid nitrogen, before entering the inlet unit (Fig. II-3). This purification was able to reduce the CO₂ background by about 1/20 compared with the runs without these traps. It was found that baking of the purification trap 1 at 300 °C for >24 hrs before blank analysis was very effective to reduce the CO₂ background. The baking procedure of the purification trap 1 was found to be recommended repeat every two weeks in the present study.
Table II-5 gives the repeated analyses of the CO$_2$ background at different times of this study. The amount of CO$_2$ background was measured at the line temperatures from 50°C to 200°C with and without the baking procedure of the purification trap 1. The CO$_2$ analyses without baking procedure of the purification trap 1 indicated that the CO$_2$ background at 50°C was by 1/4-1/5 lower than that at 150°C (Table II-5). Reproducibility of CO$_2$ background in terms of a standard deviation for each day was also better at 50°C than at 150°C. The CO$_2$ background of the system increased linearly with temperature of the inlet unit as shown in Fig. II-15 for both cases where measurements were made before and after the baking procedure of the purification trap 1. Therefore, the source of this CO$_2$ is most likely organic materials adsorbed on the inner surface of the tubing and the metal valves. These results indicate that the line temperature of 50°C should be taken as the condition when CO$_2$ less than 1 ng is to be analyzed, because a signal from such a small amount of CO$_2$ becomes smaller.

The CO$_2$ background and reproducibility at 50°C and 200°C after baking of the purification trap 1 are also shown in Table II-5. The level of CO$_2$ background after the baking procedure was drastically smaller than that without the baking procedure, resulting in overall reduction of CO$_2$ background to 1/200 (Fig. II-15). It is important to note that the standard deviations became also smaller after the baking procedure. It was found essential that the purification trap 1 should be baked at 300°C before CO$_2$ analysis is made, because capacity of the purification trap 1 filled with Molecular Sieve 5A is readily exceeded by impurities in helium carrier gas.
Table II-5. Repeated measurements of blank CO$_2$ at line temperatures of 50 °C, 150 °C and 200 °C at different times of experiments.

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* The purification trap 1 baked at 300 °C was used (Fig. II-3).
Figure II-15. Variation in peak areas of background CO₂ with line temperatures. Open squares represent the results of experiments made before baking of the purification trap 1. Solid symbols represent those after baking of the trap 1.
Based on the above results, the line temperature of 50 °C with the above precautions should be adopted for analysis of less than 1 ng CO\textsubscript{2} to obtain good S/N ratios.

II-3-2. Background of H\textsubscript{2}O

In the GCMS analysis of water, the peak height rather than the peak area of the chromatogram was used because a H\textsubscript{2}O signal has typically a long tail (Fig. II-16) which is not suitable for data processing by a computer. In order to evaluate the background level and reproducibility of H\textsubscript{2}O analysis in this system, the measurements of H\textsubscript{2}O background at the line temperature of 150 °C and 200 °C were repeated at different times during the whole experimental period. The background analyses were carried out both before and after baking procedures of the purification unit as in the same way for measurements of CO\textsubscript{2} background. The results are shown in Table II-6. Before baking of the purification trap 1, the average value of the H\textsubscript{2}O background for each day ranged from 16000 to 46000. The standard deviation of the H\textsubscript{2}O background within a day was highly variable, but less than ±9300 at maximum for runs without baking procedures of purification trap 1. After baking of the purification trap 1 at 300 °C for >24 hrs, the average values of the H\textsubscript{2}O background for each day were again drastically reduced to 1400 to 6500 (Table II-6). The standard deviation of H\textsubscript{2}O background in each day with the baking procedure was less than 1100. Thus the level of H\textsubscript{2}O background and its reproducibility were reduced by about 1/10 compared to those without baking of the purification trap 1 (Fig. II-17). These results
Figure II-16. Gas chromatograms of H$_2$O (M/e=18) and CO$_2$ (M/e=44).

Note that it takes two minutes for the H$_2$O peak to return to a background level.
Table II-6. Repeated measurements of blank H$_2$O at different times of experiments.

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|                     | 2   | 200           | 20982       |                     | 2   | 200           | 2224        |
|                     | 3   | 200           | 23885       |                     | 3   | 200           | 1585        |
|                     | Av. |               | 23152       |                     | Av. |               | Range ±640  |
|                     | 1σ  |               | ±3203       |                     | 1σ  |               | ±415        |

| October 25, 1991    | 1   | 200           | 18179       | *November 22, 1991 | 1   | 200           | 3294        |
|                     | 2   | 200           | 16760       |                     | 2   | 200           | 3574        |
|                     | 3   | 200           | 12214       |                     | 3   | 200           | 3920        |
|                     | Av. |               | 15718       |                     | Av. |               | 3506        |
|                     | 1σ  |               | ±3116       |                     | 1σ  |               | ±314        |

|                     | 2   | 200           | 36955       |                     | 2   | 200           | 541         |
|                     | 3   | 200           | 38919       |                     | 3   | 200           | 1560        |
|                     | 4   | 200           | 24298       |                     | Av. |               | 1365        |
|                     |     |               | 34189       |                     | 1σ  |               | ±746        |
|                     |     |               | ±6673       |                     | 1σ  |               | ±1102       |

* The purification trap 1 was baked at 300 °C before analysis (Fig. II-3)
Figure II-17. Variation in peak heights of background H$_2$O with run numbers which correspond to the dates of experiments (see Table II-6). Open squares represent the results of experiments made before baking of the purification trap 1. Solid circles represent those after baking of the trap 1.
indicate that the cleaning of the purification trap 1 was very necessary for the reduction of H₂O background as was the case for the CO₂ analysis. Fluctuation of the average H₂O background may be due to variations in efficiency of the baking procedures of the inlet line and purification trap 1 before the blank analysis.

II-3-3. Calibration of CO₂

II-3-3-1. Methods of calibration

For CO₂ calibration of the GCMS system, a He-CO₂ gas mixture with CO₂ concentration of 1050 ppm was used as the standard gas. This He-CO₂ mixture enables us to obtain a very minute amount of CO₂ (0.1-1 ng) in the inlet unit where the gas pressure can be accurately measured down to 10⁻⁴ torr using a capacitance manometer (Fig. II-3). The He-CO₂ mixture was introduced into the calibration unit (B-C-D-F-G-K) from valve J (Fig. II-3) at various pressures from 0.03 torr to 0.004 torr. The amount of the He-CO₂ gas mixture to be introduced to the GCMS was adjusted by repeating expansion and evacuation of the gas in the calibration unit. The gas with an appropriate pressure was then introduced to the volume between L, O and Q. The amount of CO₂ gas in the inlet unit was calculated from the total pressure, CO₂ concentration of the gas mixture, temperature and the volume of the inlet unit (volume between N-O-Q=13.0±0.4 cm³) using the ideal gas law. The gas mixture was then carried into the trap 2 by the carrier gas introduced from valve P to concentrate CO₂ in a small volume. The trap 2 was maintained at liquid nitrogen temperature for 15 minutes to
collect all CO₂ in the inlet unit. Carbon dioxide in the trap 2 was instantaneously released by heating rapidly the trap 2 to 100 °C and introduced to the GCMS unit to measure the peak area of a CO₂ chromatogram. A series of calibrations were made by changing the pressure of the He-CO₂ mixture.

II-3-3-2. Results of CO₂ calibration

Two calibration curves were prepared; one to cover the range from 0 to 1 ng of CO₂ (Fig. II-18) and the other from 0 to 20 ng (Fig. II-19). A linear relationship was obtained between 0.15 and 0.9 ng CO₂ for which the inlet unit temperature was kept at 50 °C. The calibration line with the slope of 47202 (peak area/ng) was approximated by a least square method assuming that the calibration line starts from the point of origin. As already shown in Table II-5, the level of background and the standard deviation of CO₂ at the line temperature of 50 °C are small, so that it is able to analyze CO₂ as small as 0.15 - 0.9 ng CO₂ using this calibration line. The dashed curves drawn at both sides of the calibration line in Fig. II-18 indicate the 95 % confidence limit of the calibration line. For example, when a peak area corrected for blank is 20000, a value of 0.42 ng CO₂ is obtained from the calibration line with the allowable maximum and minimum values of 0.52 and 0.31 ng CO₂, respectively. The smallest amount of CO₂ which can be analyzed using this system is about 0.15 ng CO₂. Our analytical system is more than 20 times as sensitive as the analytical method developed by Harris and Anderson (1983), who were able to measure the absolute amount of more than 4 ng CO₂. With the present technique it is possible to
Figure II-18. Peak areas of CO₂ (corrected for blank) versus the absolute amount of CO₂ carried into GCMS at a line temperature of 50 °C. The calibration line was drawn through the data points from the point of origin by the least square method. The dashed curves indicate the 95 % confidence limits of the calibration line.
Figure II-19. Peak areas of CO₂ (corrected for blank) versus the absolute amount of CO₂ carried into GCMS at line temperatures of 200 °C. The calibration line was drawn through the data points from the point of origin by the least square method. The dashed curves indicate the 95 % confidence limits of the calibration line.
analyze a glass inclusion as small as 70 μm in diameter assuming that the glass inclusion contains 300 ppm CO₂ (Fig. II-2).

When the inlet unit temperature was kept at 200 °C, a linear relationship was also obtained between 2 and 17 ng CO₂ (Fig. II-19). The calibration line with the slope of 29085 (peak area/ng) was approximated by a least square method assuming that the calibration line starts from the point of origin. The 95% confidence limits of the calibration line are also shown in Fig. II-19. This calibration line can be used for analysis of glass inclusions with high CO₂ concentrations (>1500 ppm).

II-3-4. Calibration of H₂O

II-3-4-1. Preparation of the standard gas

For calibration of H₂O for GCMS analysis, helium-H₂O gas mixtures with H₂O being 1.2 to 2.6 % were used as the standard gases. The standard gases were prepared by mixing water vapor from a saturated KOH solution with He gas containing 1050 ppm CO₂ in a stainless steel bottle. The saturated KOH solution has a water vapor pressure of 2.2 torr that is less than saturated water vapor pressure (23 torr) of pure water at 25 °C. The mixing procedure was carried out using a vacuum line as shown in Fig. II-20. At first, after complete evacuation of the bottle, water vapor from the saturated KOH solution was introduced into the bottle. At least 5 minutes were required to attain equilibrium. After closing valve U, the water vapor in the bottle was frozen at Dry-ice temperature. Secondly the CO₂-containing He
Figure II-20. Schematic presentation of the vacuum line used for the preparation of a He-H$_2$O gas mixture.
gas was introduced into the bottle. The amount of helium gas in the bottle was calculated from the total pressure (about 250 torr) of the gas measured with a Hg manometer on the line, the temperature of the gas and the volume of the bottle (328 cm³). With these procedures, the standard gases containing about 1.2-2.6% of H₂O were prepared. Only a fraction of this gas mixture was used in calibration of H₂O for GCMS, and the rest was used to determine the exact H₂O concentration of the gas mixture as described below.

The H₂O concentrations of the standard gases were determined using a vacuum line consisting of cold traps, an uranium furnace and a Toepler pump (Fig. II-21). Water in the bottle was recovered by pumping the gas slowly through two cold traps immersed in liquid nitrogen. The evacuation was carried out at a pressure less than 2 torr (Craig, 1953) to collect all water vapor in the bottle. Water was then transferred to a heated uranium furnace (750 °C) to reduce it to hydrogen. The hydrogen gas was quantitatively recovered using the Toepler pump and its volume was measured manometrically. The concentration of water in the gas mixture was calculated from the amounts of water and helium in the stainless steel bottle.

II-3-4-2. Methods of calibration

The stainless steel bottle was set to the calibration unit at valve J (Fig. II-3). The calibration unit, the inlet unit and the metal bottle were heated to 200°C during operation using tape heaters to avoid adsorption of H₂O onto the inner wall of the line and bottle. After evacuation of air between valves J and U (Fig. II-3 and Fig. II-20), the gas mixture
Figure II-21. Schematic diagram of the vacuum line used for determination of H₂O concentration of a He-H₂O gas mixture.
was expanded up to valve T and a fraction of the gas between valves T and U was introduced to the calibration unit for H₂O calibration.

To obtain a desired amount of H₂O in the inlet unit, a part of the gas mixture in the calibration unit was discarded stepwisely in the following way. The gas mixture expanded to the calibration unit (B-C-D-F-G-K) was evacuated except the gas remaining between the two valves T and U of the metal bottle. These expansion and evacuation procedures were repeated until the desired gas pressure was obtained. Finally the gas mixture remaining between the two valves T and U was expanded to the inlet unit (K-O-Q). In this procedure, it took more than 3 minutes for the expanded gas to attain equilibrium with respect to concentration distribution of H₂O in the calibration unit and inlet unit. It also took more than 1 minute for complete evacuation of the H₂O-containing gas from the line. Details of the experimental determination for optimum conditions are given in the next section. The absolute amount of H₂O in the inlet unit was calculated using the ideal gas law from the gas pressure measured with a capacitance manometer, the line temperature (200 °C), the volume of the inlet unit (N-O-Q, 13.0±0.4 cm³ ) and H₂O concentration of the gas mixture. The gas mixture in the inlet unit was then carried into the GCMS unit by the purified helium carrier gas in the same way as was for the CO₂ calibration. The peak height of mass 18 (H₂O) was measured with GCMS.

II-3-4-3. Time necessary for expansion and evacuation

In order to obtain a minute amount of H₂O in the inlet unit, a part of the gas mixture between the two valves T and U of the metal bottle
was discarded by expansion and evacuation procedures as mentioned above. Because H₂O is more adsorptive than He and CO₂ due to a polar nature of H₂O molecules, a longer time is needed for expansion and evacuation of H₂O than for the other gases. Short expansion time would induce a gradient of H₂O concentration in the line, and the H₂O concentration of the gas mixture in the inlet unit would be smaller than that in the original gas. This would lead underestimation of the amount of H₂O in the inlet unit. On the other hand, if time for evacuation of the calibration unit is not long enough, it would leave a part of H₂O in the calibration unit unevacuated and induce a positive error in the H₂O calibration. Thus, the optimum expansion and evacuation times were decided experimentally.

Repeated analyses of H₂O in the gas mixture were carried out by changing the expansion time ranging from 0.5 to 6 minutes (Fig. II-22). The peak height of H₂O increased with the expansion time up to 3 minutes and became constant after 3 minutes. These results indicate that at least 3 minutes are required for expansion of the H₂O-containing gas to attain equilibrium in the calibration and inlet units.

Similar to the expansion experiments, repeated analyses of H₂O in the gas mixture were carried out by changing the evacuation time from 1 to 5 minutes. There was no change in the peak height of H₂O regardless of the evacuation time as shown in Fig. II-23. These results indicate that the evacuation time of more than 1 minute can give sufficient evacuation of H₂O from the calibration unit.
Figure II-22. Variation with expansion time in the peak height of H$_2$O expanded in the inlet system. At least three minutes are required to attain uniform distribution of water in the inlet system.
Figure II-23. Variation with evacuation time in the peak height of H$_2$O remaining in the inlet unit. No change was recognized from 1 to 5 minutes.
II-3-4-4. Results of H₂O calibration

The results of the H₂O calibration are shown in Fig. II-24. A linear relationship was obtained between 8 and 103 ng H₂O. The variation of the data points is most likely caused by fluctuation of the background. Because this calibration was carried out without baking of the purification trap 1, the maximum experimental error was expected to be ±9300 in terms of the peak height (see Table II-6). The calibration line with a slope of 1069 (peak height/ng) was obtained by a least square method assuming that the calibration line started from the point of origin. The dashed curves in Fig. II-24 mean the 95 % confidence limits for the calibration line. For example, if a peak height corrected for blank is 40000, a value of 37 ng H₂O is obtained from the calibration line and the maximum and minimum values of 47 and 24 ng are estimated from the confidence limits respectively. With this technique it is possible to analyze a glass inclusion as small as 110 μm in diameter assuming that the glass inclusion contains 1 wt.% H₂O (see Fig. II-2).
Figure II-24. Peak heights of H$_2$O (corrected for blank) versus the absolute amount of H$_2$O carried into GCMS at line temperature of 200 °C. The calibration line was drawn through the data points from the point of origin by the least square method. The dashed curves indicate the 95 % confidence limits of the calibration line.
CHAPTER III

ANALYTICAL PROCEDURE, REPRODUCIBILITY AND ACCURACY OF THE LASERPROBE-GCMS SYSTEM

III-1. Bulk analysis of MTB glass

The standard material used in this study is a fragment of the quenched glass rim of submarine pillow basalt which was collected from the Mariana Trough back-arc basin at 18°N during the "1987 U.S.-Japan DSIRV ALVIN investigations of western Pacific back-arc and fore-arc regions" (see Special Section "The Mariana Trough" in Earth. Planet. Sci. Lett., Vol. 100, No. 1/3, 1990). The Mariana Trough basalt (MTB) glass was chosen because it contained relatively high H₂O (0.5-2.1 wt.%, Mayeda, 1989) and CO₂ concentrations similar to those of mid-oceanic ridge basalts (0-300 ppm) (Mayeda, 1989; Hochstaedter et al., 1990). It looked homogeneous under a microscope, although other glass samples contained a small amount of phenocrysts such as olivine, pyroxene and plagioclase. The phenocryst-free MTB glass which will be simply "MTB glass" hereafter was subjected to CO₂ and H₂O analysis to test our analytical techniques. This MTB glass was later found to be inhomogeneous as far as the CO₂ concentration is concerned, so that it was remelted at 1300°C and 10 kbar to obtain a homogeneous glass which was used as the standard for CO₂ analysis.

The bulk CO₂ concentration of the MTB glass was determined by a stepwise heating under vacuum followed by manometric analysis using about 1 g of the MTB glass. Carbon extracted at temperatures higher
than 800°C is considered to represent indigenous carbon present in basaltic glass (Exley et al., 1986; Mattey, 1991). The determination yielded a bulk CO$_2$ concentration of 326±7 ppm. FTIR analysis of MTB glasses that were collected from almost the same localities gave the CO$_2$ concentrations ranging from 60 to 200 ppm (Stolper and Newman, 1991). Discrepancy of the CO$_2$ concentrations obtained by the two different methods will be discussed below in more detail.

The bulk H$_2$O concentration of the MTB glass was determined by dehydration under vacuum at about 1300 °C. The extracted water was quantitatively converted to H$_2$ gas, the volume of which was measured manometrically. About 0.2-1 g of the MTB glass was used for the bulk H$_2$O determination. The bulk H$_2$O concentration of the MTB glass thus determined was 1.35±0.04 (1σ) wt.%. Using 0.051 g and 0.086 g of the homogenized glass, the bulk H$_2$O concentrations of 1.22 wt.% and 1.24 wt.% were obtained. FTIR analysis of MTB glasses by Stolper and Newman (1991) gave the H$_2$O concentrations ranging from 0.5 to 1.9 wt.%.

III-2. Analytical procedures

III-2-1. Sample preparation

A glassy rim of the MTB pillow lava was coarsely crushed into about 10 mesh fragments by a mortar. Glass sample was handpicked from the fragments under a stereo-microscope. The glass sample was cleaned by the ultrasonic washing in acetone and in deionized water. The glass sample was glued on a slide glass by epoxy resin or an acetone
soluble adhesive (Crystalbond No. 509, Aremco products, USA). The glass sample was initially ground with sand paper until surface of the sample became flat, and then polished with a diamond paste. Next, the glass sample was removed from the slide glass by warming it in acetone. It was reversed and glued again on a slide glass with the adhesive. The glass sample was again ground to a thickness typically less than 100 μm. We call it as a glass wafer. The glass wafer was carefully detached from the slide glass in an warm acetone bath. The wafer was cleaned by the ultrasonic washing in acetone and in deionized water followed by drying at 90 °C in the oven.

III-2-2. Sample loading

The glass wafer was so light that it was easily displaced by an impact of a laser beam or the flow of the carrier gas, which made the sample disappear out of a field of microscopic view. When more than two wafers were placed in the cell, one of them was displaced and sometimes overlapping of the wafers took place upon laser irradiation. In order to avoid such inconvenience the sample wafer has to be fixed in the sample cell. Two methods were adopted; (1) a brass ring was placed on the cell to confine the sample wafers, and (2) a ceramic adhesive was used to fix the wafer position. In the first method, the sample wafers were confined in the brass ring with an inner diameter of 4 mm as shown in Fig. III-1 (a). Also tested was a brass plate having several small holes (φ=0.5-3 mm) in which the wafers with variable sizes were placed (Fig. III-1 (b)). Because only a single sample was placed in a hole, overlapping of the wafers could be avoided. However, "moving
Figure III-1. Schematic diagrams of (a) brass ring, (b) brass plate and (c) quartz glass plate for setting sample wafers (shaded area) in a sample cell. Numbers indicate the size in mm.
around" of a sample wafer in the hole was still possible by an impact of a laser beam, so that the pits that had irregular shapes of melting were occasionally produced. This induced difficulties in measuring the pit volumes, leading to the unreliable results.

In the second method, the sample wafers were fixed using a ceramic adhesive (Ceramabond, No. 503, Aremco products, USA) on a quartz glass plate placed in the cell. Major constituent of this adhesive is aluminium oxide and the temperature limit of this adhesive is 1650°C. A drop of the adhesive was placed in a small depression at the center of the quartz glass plate (Fig. III-1 (c)). Typically four to five wafers were glued at their corners in a radial fashion. The samples on the plate were preliminarily heated to 230 °C on a hot plate (or in an oven) to remove water from the adhesive and to obtain maximum adhesion. Care was taken not to shoot the adhesive with the laser beam. This method worked quite good, and no displacement of the sample wafers was observed upon laser irradiation. Possible degassing from the adhesive was tested by shooting the dried adhesive with laser. It was found that neither H₂O nor CO₂ was extracted from the adhesive when it was shot by the laser beam, and the H₂O and CO₂ backgrounds from the inlet unit with the adhesive in it remained unchanged. These tests indicate that the adhesive can be used to fix tiny wafers in the cell.

III-2-3. Preheating

After the sample wafers prepared were loaded in the cell, the inlet unit was evacuated with a diffusion pump. The inlet unit was baked overnight at 300 °C except the sample cell. The sample cell and the
calibration unit were also baked overnight at 200 °C that was maximum temperature permitted by the output power of the heating apparatus used.

III-2-4. Sample analysis

When H$_2$O analysis was carried out, the whole analytical system (Fig. II-3) was maintained at 200°C. In the case of CO$_2$ analysis, the sample cell and the inlet unit were kept at 50 °C or 200 °C depending on the amount of CO$_2$ to be measured. The calibration unit was always kept at 150°C. Before the gas analysis, helium carrier gas was let flow through the inlet unit from valve P in order to wash away any H$_2$O and CO$_2$ adsorbed in the inlet unit. This procedure effectively reduced the background level of H$_2$O and CO$_2$. Then, after valves P and Q were closed, the inlet unit was evacuated to a pressure of about 10$^{-5}$ torr by means of a diffusion pump and an ion pump. A purification trap 3 was immersed in liquid nitrogen for cryo-pumping. After the valves N and S were closed, H$_2$O and CO$_2$ were extracted from the sample wafer by laser irradiation. The extracted gases were collected in the trap 1 with liquid nitrogen. After helium carrier gas was introduced into the inlet unit, the trap 1 was heated to the same temperature as the surrounding inlet unit for vaporization of H$_2$O and CO$_2$ in the trap 1. The helium carrier gas transferred the sample gas from the trap 1 to the trap 2. The analytical procedures after concentration of the extracted gases in the trap 2 were identical to the calibration procedures described in Chapter II-3.
Blank analyses were carried out before and after the sample analysis. The procedures for the blank analysis were the same as those for the sample analysis except that laser irradiation was not applied. The peak area \((\text{CO}_2)\) or peak height \((\text{H}_2\text{O})\) corrected for blank was obtained by subtracting the measured signals of the sample analysis from the average value of the signals for the two blank analyses. The absolute amount of the extracted \(\text{H}_2\text{O}\) or \(\text{CO}_2\) was determined using the calibration lines given in Chapter II-3.

III-2-5. Calculation of gas concentration

After the gas analysis, the diameter of the pit produced by a laser beam and the wafer thickness were measured by the procedures of described in Chapter II-2 to calculate the volume of the laser pit. The mass of melted glass in the pit was obtained from the pit volume and the density of the sample glass. Finally the concentration of \(\text{H}_2\text{O}\) or \(\text{CO}_2\) in the sample was calculated by dividing the absolute amount of the extracted \(\text{H}_2\text{O}\) or \(\text{CO}_2\) gas by the mass of glass melted.

III-3. \(\text{CO}_2\) analysis

The analytical results of MTB glasses and the homogenized glasses are shown in Tables III-1 and III-2. These results, together with the bulk analyses and FTIR analyses by Stolper and Newman (1991), are summarized in Fig. III-2.
Table III-1. Laser microprobe analyses of CO$_2$ of Mariana Trough basalt glasses.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Diameter of laser pit (µm)</th>
<th>Wafer thickness (µm)</th>
<th>Mass of melted glass (µg)</th>
<th>Extracted CO$_2$ content (ng)</th>
<th>CO$_2$ content (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>128</td>
<td>58</td>
<td>2.00</td>
<td>0.53±0.10</td>
<td>270±50</td>
</tr>
<tr>
<td>2</td>
<td>125</td>
<td>47</td>
<td>1.60</td>
<td>0.88±0.21</td>
<td>560±140</td>
</tr>
<tr>
<td>3</td>
<td>88</td>
<td>47</td>
<td>0.63</td>
<td>0.54±0.10</td>
<td>860±160</td>
</tr>
<tr>
<td>4</td>
<td>87</td>
<td>47</td>
<td>0.67</td>
<td>0.77±0.16</td>
<td>1100±290</td>
</tr>
</tbody>
</table>

Errors for extracted CO$_2$ (ng) and CO$_2$ content (ppm) were estimated from the 95% confidence limit of the calibration line.
Table III-2. Laser microprobe analyses of CO$_2$ of homogenized MTB glasses.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Diameter of laser pit (μm)</th>
<th>Wafer thickness (μm)</th>
<th>Mass of melted glass (μg)</th>
<th>Extracted CO$_2$ (ng)</th>
<th>CO$_2$ content (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line temperature $=50 , ^\circ$C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>190</td>
<td>73</td>
<td>4.60</td>
<td>1.24±0.34</td>
<td>270±70</td>
</tr>
<tr>
<td>6</td>
<td>120</td>
<td>73</td>
<td>2.33</td>
<td>0.60±0.11</td>
<td>260±50</td>
</tr>
<tr>
<td>7</td>
<td>90</td>
<td>73</td>
<td>1.37</td>
<td>0.19±0.14</td>
<td>140±100</td>
</tr>
<tr>
<td>8</td>
<td>65</td>
<td>73</td>
<td>0.72</td>
<td>(+0.19, -0.07)</td>
<td>$&lt;360$</td>
</tr>
<tr>
<td>Line temperature $=200 , ^\circ$C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>270±260</td>
<td>130</td>
<td>39.3</td>
<td>10.1±0.9</td>
<td>260±30</td>
</tr>
<tr>
<td>10</td>
<td>240</td>
<td>140</td>
<td>17.4</td>
<td>4.1±1.6</td>
<td>240±100</td>
</tr>
<tr>
<td>11</td>
<td>370</td>
<td>190</td>
<td>56.0</td>
<td>8.3±0.8</td>
<td>150±20</td>
</tr>
<tr>
<td>12</td>
<td>700</td>
<td>140</td>
<td>158</td>
<td>10.2±0.8</td>
<td>65±5</td>
</tr>
<tr>
<td>13</td>
<td>130</td>
<td>190</td>
<td>6.9</td>
<td>1.2±1.2</td>
<td>$&lt;350$</td>
</tr>
</tbody>
</table>

Errors for extracted CO$_2$ (ng) and CO$_2$ content (ppm) were estimated from the 95% confidence limit of the calibration line.
Figure III-2. The CO₂ analyses of Mariana Trough basalt glass by the present study. Open circles represent the analyses of the natural glass. Solid circles represent the analyses of the homogenized glass at a line temperature of 50 °C. Open squares represent the analyses of the homogenized glass at 200°C. Dashed line denotes the bulk CO₂ analysis. Shaded area represents the CO₂ analyses of bubble free region of MTB glass using FTIR by Stolper and Newman (1991).
The CO₂ analysis of the MTB glass by the present study is highly variable: Run 1 gave a CO₂ content of 270 ppm, similar to the value obtained from the bulk analysis. The other runs (runs 2, 3 and 4), however, gave variable and much higher CO₂ concentrations than the bulk analysis. The variation of the data may reflect (1) a surface contamination during sample preparation or (2) inhomogeneity of dissolved CO₂ in the glass which may include tiny vesicles filled with CO₂-rich gases. For runs 1 through 4, the sample glasses were glued on a slide glass with epoxy resin and then ground to a thickness of 40-60 μm. The glue was removed from the sample glasses in acetone at about 50°C, followed by ultrasonic washings in acetone and deionized water. A source of the background CO₂ could be carbonaceous materials in the glue that remained on the surface of the sample glass. The sample glasses used for runs 3 and 4 were further cleaned with acetone repeatedly. However, the runs 3 and 4 gave even higher CO₂ concentrations than the runs 1 and 2. Therefore it is unlikely that the variation in the CO₂ concentrations of the MTB glass resulted from the surface contamination of organic materials, although the possibility that the organic materials on the surface were insoluble in acetone can not be ruled out.

The Mariana Trough basalt used here was dredged from the seafloor with a depth of 3600 m. In other words, the melt was quenched at about 360 bar. Saturated CO₂ concentration in basaltic melt at 360 bar and 1200 °C are 140-200 ppm (Stolper and Holloway, 1988; Pan et al., 1991). The measured CO₂ concentration of 326 ppm by the step-wise heating technique on a large size sample (1 g) indicates that the melt was supersaturated with CO₂ at the time of eruption. Supersaturation of CO₂ would produce vesiculation of CO₂ and
inhomogeneous distribution of dissolved CO$_2$ in the glass due to rather slow diffusion rate of CO$_2$ in the melt. Microscopic observation indicates that the MTB glass contains vesicles with a diameter ranging up to 200 µm (Fig. III-3). Runs 3 and 4 were performed on vesicle-free regions after careful observation of the sample glass with a microscope. Therefore, it is unlikely that high CO$_2$ content was caused by CO$_2$ gas from the vesicles in the glass. Large variations of dissolved CO$_2$ concentrations have been reported for the submarine basalt glasses which contain CO$_2$ concentrations higher than the saturated value (Fine and Stolper, 1986; Dixon et al., 1988). For example, even vesicle free regions of the MORB glasses from East Pacific Rise collected at 2600 m deep exhibited the dissolved CO$_2$ concentrations by 3-4 times as much as the saturated CO$_2$ concentration of 110 ppm at 260 bar. A highly variable nature of CO$_2$ concentrations as shown in Fig. III-2 suggests that inhomogeneity of dissolved CO$_2$ exists in the MTB glass.

In order to test the accuracy and precision of the present analytical techniques, it is essential to obtain a glass sample which is homogeneous in a microscopic scale with respect to CO$_2$ distribution. The MTB glass, sealed in a Pt capsule, was melted using a piston-cylinder apparatus under the conditions of 1300°C and 10 kbar for two hours and then quenched to obtain a homogenized glass. Because the solubility of CO$_2$ in basaltic melt is 7500 ppm under these conditions, this material should be well undersaturated with CO$_2$. To avoid the surface contamination by organic materials during sample preparation as mentioned above, an acetone-soluble adhesive agent (Crystalbond No. 509, Aremco products, USA) was used to glue the sample glass on a slide glass.
Figure III-3. Photograph of Mariana Trough basalt glass containing two large vesicles at an upper part of the photograph. The diameter of vesicle is about 200 μm. Small dark spots represent aggregates of growing tiny crystals of plagioclase.
The CO₂ analyses of this homogenized glass were carried out by changing the mass of glass melted which ranged from 0.72 μg to 158 μg (Table III-3). The analyses were performed at the line temperature of 50 ºC when less than 1 ng of CO₂ gas was expected for the extraction. On the other hand, the analyses of more than 1 ng CO₂ was carried out at the line temperature of 200 ºC that allowed us to analyze H₂O simultaneously. The results from runs 5, 6, 9 and 10 agreed well with each other (270, 260, 260 and 240 ppm, respectively) and the results from runs 8 and 13 were also compatible with these results. Runs 7 and 11 gave CO₂ concentrations of 140 and 150 ppm, respectively, which were lower than the other values, although they still agreed with the results for runs 5, 6, 9, and 10 within the large analytical errors assigned. Run 12 gave a CO₂ concentration of 65 ppm much lower than the other values. This result may be caused by the overestimation of the mass of the glass melted because the pit in run 12 had the irregular shape unlike those in the other runs.

Because only a small amount (< 0.3 g) of the homogenized glass was available from the piston-cylinder experiment due to a small capacity of the Pt capsule used, it was not possible to make a bulk CO₂ analysis using the step-wise heating technique which is believed to give a reliable result (Exley et al., 1986; Mattey, 1991). The maximum and minimum values of the CO₂ concentration of the homogenized MTB glass can be estimated in the following way. It is likely that the natural MTB glass contained the CO₂-rich vesicles as mentioned above, and that CO₂ in the vesicles may have contributed to the bulk CO₂ concentration of 326 ppm determined by the step-wise heating technique for which the coarsely crushed MTB glasses with the size of 20-60 mesh were used. This interpretation is compatible with the FTIR analysis by Stolper and
Newman (1991) that vesicle-free regions in the natural MTB glass had the CO$_2$ concentration of 60-200 ppm. The homogenized MTB glass was prepared by re-melting both the coarse fragments (20-60 mesh) and the pulverized MTB glass (<200 mesh) in the proportion of about 1:1. Assuming that negligible amounts of the CO$_2$-rich vesicles were contained in the pulverized sample, the actual CO$_2$ concentration of the homogenized glass is considered to be lower than 326 ppm. If the powdered MTB glass had the CO$_2$ concentration of 60 ppm which is the minimum value of the natural MTB glasses measured by the FTIR analysis (Stolper and Newman, 1991), the CO$_2$ concentration of the homogenized MTB glass can be calculated to be 193 ppm as the minimum CO$_2$ concentration. Therefore the actual homogenized MTB glass is expected to have the CO$_2$ concentration between 193 ppm and 326 ppm (average value was 260 ppm). As given in Table III-2, most of the analytical values of the homogenized glass in this study cluster in this range. Six runs (Nos. 5, 6, 7, 9, 10 and 11) except No.12 gave the average CO$_2$ concentration of 220±60 (1σ) ppm. Considering the possible range of the CO$_2$ concentrations of the homogenized glass (193-326 ppm), our technique allows us to analyze a micro quantity of CO$_2$ in glasses within the error of ±60 ppm, provided that the extracted CO$_2$ is more than 0.2 ng.

When carbon is extracted in vacuum as CO$_2$ from the MTB glass at high temperature, there is a possibility that a part of the CO$_2$ is thermally decomposed to CO and O at the time of laser irradiation. In our system, the instrumental background of mass 28 (mainly CO) was fairly high, so that it was difficult to measure with confidence the signal of the CO which may have been produced from CO$_2$ decomposition. Yonover et al. (1989) measured the ratio of CO$_2$ and CO of gases
extracted in vacuum from the basaltic glass inclusions at high temperatures using a Nd-glass laser (wave length of 0.6943 µm). The proportion of measured CO₂ to the total carbon (CO₂+CO) was 0.74±0.14 (1σ) on the average. Their laser system gave an output energy per pulse above 400 kW, that was more than 160 times as high as our laser system (2.5 kW). The total energy of laser beam shot on a sample in their experiments was also larger than that in the present study. Thus, it is questionable to assume that the decomposition of CO₂ to CO on laser heating took place to the same degree as the case of Yonover et al. (1989) in our experiments, because the thermal decomposition of CO₂ would be promoted with the increase in the laser energy applied to the sample. Further investigation is necessary to solve this problem.

III-4. H₂O analysis

The H₂O results of the MTB glasses and the homogenized glasses are shown in Tables III-3 and III-4. The numbers in the parentheses for the extracted H₂O and the H₂O concentration indicate the errors estimated from the confidence limits of the calibration (Fig. II-24). The H₂O analyses of the MTB glasses were carried out for the mass of glass melted ranging from 1.8 µg to 152 µg (Table III-3). In run 2, only minimum concentration was obtained because the extracted H₂O was larger than the range of detection. In runs 3 to 8, the amount of the extracted H₂O were close to or below the detection limit regardless the masses of glass melted. All the analytical results of the MTB glass except for run 2 are significantly lower than the bulk H₂O concentration
Table III-3. Laser microprobe analyses of H$_2$O of Mariana Trough basalt glasses.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Pit diameter ($\mu$m)</th>
<th>Wafer thickness ($\mu$m)</th>
<th>Mass of melted glass ($\mu$g)</th>
<th>Extracted H$_2$O (ng)</th>
<th>H$_2$O concentration (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>360</td>
<td>60</td>
<td>13</td>
<td>37</td>
<td>0.29</td>
</tr>
<tr>
<td>2</td>
<td>700*</td>
<td>138</td>
<td>152</td>
<td>&gt;290</td>
<td>&gt;0.19</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>60</td>
<td>5.4</td>
<td>&lt;18</td>
<td>&lt;0.31</td>
</tr>
<tr>
<td>4</td>
<td>400</td>
<td>103</td>
<td>43.4</td>
<td>&lt;18</td>
<td>&lt;0.041</td>
</tr>
<tr>
<td>5</td>
<td>380</td>
<td>47</td>
<td>1.5</td>
<td>n.d.</td>
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</tr>
<tr>
<td>6</td>
<td>140</td>
<td>103</td>
<td>3.67</td>
<td>n.d.</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>140</td>
<td>47</td>
<td>1.8</td>
<td>n.d.</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>140</td>
<td>43</td>
<td>1.8</td>
<td>n.d.</td>
<td>0</td>
</tr>
</tbody>
</table>

Errors for extracted H$_2$O (ng) and H$_2$O concentration (wt.%) were estimated from the confidence limit of the calibration line.

* Shape of the pit was irregular.
Table III-4. Laser microprobe analyses of H$_2$O of homogenized MTB glasses.

<table>
<thead>
<tr>
<th>Run No</th>
<th>Pit diameter (μm)</th>
<th>Wafer thickness (μm)</th>
<th>Mass of melted glass (μg)</th>
<th>Extracted H$_2$O (ng)</th>
<th>H$_2$O concentration (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>190</td>
<td>34</td>
<td>2.9</td>
<td>19.7</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(+13.3, -17.7)</td>
<td>(+0.43, -0.60)</td>
</tr>
<tr>
<td>10</td>
<td>300*</td>
<td>39</td>
<td>4.8</td>
<td>20.6</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(+13.4, -17.6)</td>
<td>(+0.28, -0.37)</td>
</tr>
<tr>
<td>11</td>
<td>240+150*</td>
<td>65</td>
<td>12</td>
<td>40.3</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(+10.7, -12.3)</td>
<td>(+0.07, -0.11)</td>
</tr>
<tr>
<td>12</td>
<td>270+260</td>
<td>130</td>
<td>39.3</td>
<td>58.9</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(+9.1, -9.9)</td>
<td>(+0.02, -0.03)</td>
</tr>
<tr>
<td>13</td>
<td>330</td>
<td>99</td>
<td>28</td>
<td>183.4</td>
<td>0.66</td>
</tr>
<tr>
<td>14</td>
<td>700*</td>
<td>140</td>
<td>158</td>
<td>261.5</td>
<td>0.17</td>
</tr>
<tr>
<td>15</td>
<td>110</td>
<td>34</td>
<td>0.91</td>
<td>&lt;21</td>
<td>&lt;2.3</td>
</tr>
<tr>
<td>16</td>
<td>49+32</td>
<td>73</td>
<td>0.55</td>
<td>&lt;24</td>
<td>&lt;1.4</td>
</tr>
<tr>
<td>17</td>
<td>160</td>
<td>34</td>
<td>1.5</td>
<td>&lt;22</td>
<td>&lt;1.4</td>
</tr>
<tr>
<td>18</td>
<td>140</td>
<td>56</td>
<td>2.4</td>
<td>&lt;23</td>
<td>&lt;0.97</td>
</tr>
<tr>
<td>19</td>
<td>180</td>
<td>34</td>
<td>2.5</td>
<td>&lt;24</td>
<td>&lt;0.95</td>
</tr>
<tr>
<td>20</td>
<td>150</td>
<td>65</td>
<td>3.1</td>
<td>&lt;22</td>
<td>&lt;0.71</td>
</tr>
<tr>
<td>21</td>
<td>130+160</td>
<td>82</td>
<td>6.8</td>
<td>&lt;28</td>
<td>&lt;0.41</td>
</tr>
<tr>
<td>22</td>
<td>240</td>
<td>140</td>
<td>17.4</td>
<td>&lt;25</td>
<td>&lt;0.14</td>
</tr>
<tr>
<td>23</td>
<td>370</td>
<td>190</td>
<td>56</td>
<td>&lt;32</td>
<td>&lt;0.057</td>
</tr>
<tr>
<td>24</td>
<td>130</td>
<td>190</td>
<td>6.91</td>
<td>n.d.</td>
<td>0</td>
</tr>
</tbody>
</table>

Errors for extracted H$_2$O (ng) and H$_2$O concentration (ppm) were estimated from the 95% confidence limit of the calibration line.

* Shapes of pits were irregular.
(1.35 wt.%). These results are summarized in Fig. III-4 together with the bulk analyses and FTIR analyses by Stolper and Newman (1991).

The H₂O analyses of the homogenized glasses were carried out for the mass of glass melted ranging from 0.55 μg to 158 μg (Table III-4). In runs 13 and 14, the errors of the extracted H₂O could not be estimated because the amounts of the extracted H₂O were larger than range of the calibration line (Fig. II-24). Runs 15 to 24 gave only maximum concentrations because of their large errors in the extracted H₂O. The analytical values of the homogenized MTB glass are also lower than the bulk H₂O concentration except for three runs (Nos. 15, 16 and 17) for which only maximum values are given.

Inhomogeneity of H₂O may also exist in glasses collected from a single locality in Mariana Trough because the H₂O concentrations determined for vesicle-free region of MTB glasses by the FTIR technique range from 0.5 to 1.9 wt.% (Stolper and Newman, 1991). Our results are similar to the above range of variation (Fig. III-4). However, the variation of our results is most likely caused by the artifacts that are peculiar to our analytical techniques, because we have analyzed a single tip of the homogenized MTB glass having 1.23 wt.% H₂O.

The possible sources of the variation are (1) adsorption of the extracted H₂O on to the wall of the analytical line, (2) overestimation of the mass of glass melted, (3) thermal decomposition and/or reduction of H₂O to H₂ at the time of extraction by laser irradiation, and (4) incomplete degassing of H₂O from the glass melted. The possibility (1) is unlikely for the reasons mentioned below. Firstly, even if the extracted H₂O was adsorbed on the inner wall of the inlet unit heated to 200°C, it would be flushed to the GCMS system by a sufficient flow of
Figure III-4. The H$_2$O analyses of MTB glass by the present study. Open circles represent the analyses of the natural glass. Solid circles represent the analyses of the homogenized glass. Horizontal line indicates the bulk analysis of H$_2$O for the natural glass. Shaded area represents the analyses of the bubble free region of the MTB glass using FTIR by Stolper and Newman (1991).
the helium carrier gas. Secondly, the calibration experiments for H$_2$O described in Chapter II-3 indicate that adsorption of water on the inlet is kept minimum because good linearity has been obtained for H$_2$O calibration regardless of the amount of water introduced to the inlet-GCMS system (Fig. II-24). The possibility (2) is also unlikely because H$_2$O concentrations do not correlate with irregularity in the shape of pits, and because the CO$_2$ analysis performed at the same time gave reasonable results (see Table III-2). As for the possibility (3), we have found it in preliminary experiments that H$_2$ gas extracted from the MTB glass did not exceed 3% of the total H$_2$O at most (see Appendix). Yonover et al. (1989) also stated that no free hydrogen was released from the basaltic glass by laser irradiation.

Diffusivity of H$_2$O in a silicate melt would have a great effect on the degree of extraction of H$_2$O from the melt. There is a possibility that H$_2$O in the melt can not be completely extracted within the short period of time (<1000 msec) of laser irradiation due to its low diffusivity. The diffusivity of H$_2$O in a rhyolitic melt has been measured at 700 bars pressure and temperatures from 650° to 950°C (Delaney and Karsten, 1981; Karsten et al., 1982). Holloway et al. (1984) presented the following equation for diffusion of water in granitic melts containing less than 6.0 wt.% H$_2$O based on the compilation of recent studies on the diffusion of water in granitic melts;

\[ \ln D = 0.75 \times C_{H_2O} - 9.75 - 9683/T \]

where $C_{H_2O}$ is a concentration of H$_2$O in the melt (wt.%), T is the temperature of the melt in K and D is the diffusivity of the H$_2$O cm$^2$/s. Assuming that this equation is applicable to basaltic melt, the diffusivity
of H$_2$O at higher temperatures in the basaltic melt containing 1 and 2 wt.% H$_2$O can be estimated by extrapolation of this equation as shown in Fig. III-5. It ranges from $2.5 \times 10^{-7}$ to $3.7 \times 10^{-6}$ (cm$^2$/sec) at 1300-2000 °C. The diffusivity of CO$_2$ in a sodium aluminosilicate melt and "iron-free" basalt melt was measured at pressures from 0.5 to 18 kbar and temperatures from 800 °C to 1350°C by Watson et al. (1982) (Fig. III-5). Diffusivity of CO$_2$ does not change much with the melt compositions. Although the temperature of the basaltic melt during the laser heating in this study is not certain, it is estimated well above 1300°C. The diffusivity of H$_2$O in a silicate melt with the H$_2$O concentrations of 1-2 wt.% is similar or greater than that of CO$_2$ at temperatures lower than 1300 °C. At temperatures higher than 1300°C, however, the diffusivity of H$_2$O becomes smaller than that of CO$_2$. The characteristic diffusion distance (L) of H$_2$O and CO$_2$ in the melt is given by $L = (2Dt)^{1/2}$, where t is time (sec). At 1300°C and the shooting duration of 100 msec, the characteristic diffusion distance L of CO$_2$ is 4.9 μm that is only slightly greater than that of H$_2$O; 2.3 μm for 1 wt.% H$_2$O and 3.3 μm for 2 wt.% H$_2$O. At 2000°C, the value of L for CO$_2$ is 48 μm that is more than 6 times as large as that of H$_2$O; 5.9 and 8.6 μm for 1 and 2 wt.% H$_2$O, respectively. These calculation suggest that CO$_2$ would be more easily be extracted from the basaltic melt than H$_2$O at the time of laser heating. This is consistent with the results that our analytical method gave lower H$_2$O concentrations than the bulk analysis, while CO$_2$ concentrations close to the bulk concentration were obtained.
Figure III-5. Variations in diffusivities of H$_2$O and CO$_2$ in silicate melt as a function of temperature. Diffusivities of H$_2$O were taken from Holloway et al. (1984), and that of CO$_2$ from Watson et al. (1982).
CHAPTER IV

APPLICATION OF THE LASERPROBE-GCMS TECHNIQUE FOR DETERMINATION OF CO₂ CONCENTRATIONS IN PRE-ERUPTIVE MAGMAS OF KILAUEA AND IZU-OISHIMA VOLCANOES

IV-1. Analysis of glass inclusions from Kilauea volcano

IV-1-1. Kilauea volcano

Kilauea volcano sits on the southeastern flank of Mauna Loa volcano, Hawaii. In its southern flank, the East Rift Zone (ERZ) and South-West Rift Zone (SWRZ) extend from the summit caldera. The summit area and ERZ are the most active sites of eruption and intrusion. It is considered that the primary magma generated in the upper mantle about 30-60 km below Kilauea volcano ascends to depths of 2-6 km beneath the caldera floor to form a summit magma chamber consisting of a sill-dike complex (Fiske and Kinoshita, 1969; Ryan et al., 1981). The top of the magma chamber sometimes appears to the Earth’s surface to form a temporal lava lake in the Halemaumau crater. Magma in the summit magma chamber migrates along the ERZ and SWRZ where eruptions often take place in recent years.

Gerlach and Graeber (1985) proposed an interesting model that parts of the volatiles (mainly H₂O, CO₂ and S) dissolved in the primary magma are released while residing in the summit chamber due to degassing caused by reduction in pressure (Fig. IV-1). Their model is based on gas compositions of lava lake gases collected from the Halemaumau crater and the ERZ eruptions and on the estimated volatile
Figure IV-1. Schematic diagram of the magma system of Kilauea volcano. The parental magma from the depths is stored in the summit chamber and rifts as reservoir equilibrated magmas, and degasses during storage and migration to the rifts. Adapted from Gerlach and Graeber (1985).
concentrations in the primary and summit chamber magmas. Determination of H$_2$O and CO$_2$ concentrations in the glass inclusions representing such magmas certainly gives a basis to examine the model by Gerlach and Graeber (1985).

IV-1-2. Experimental methods

We have analyzed CO$_2$ concentrations in glass inclusions in olivine phenocryst which was contained in picritic basalt from the SWRZ, Kilauea volcano, Hawaii. Fortunately, these olivine phenocrysts contained abundant glass inclusions, some of which were as large as 200 $\mu$m in diameter (Fig. IV-2).

A rock sample was coarsely crushed into the fragments with the size smaller than 10 mesh. The fragments were grouped into different sizes (10-20, 20-32, 32-60 and >60 mesh). The fragments with the sizes of 10-20 mesh (0.8-1.7 mm) were usually used in the present study. They were cleaned by the ultrasonic washing in acetone and in deionized water. Then phenocrysts containing glass inclusions were handpicked from the fragments under a stereo-microscope. The selected phenocryst was glued on a slide glass by an acetone soluble adhesive (Crystalbond No. 509, Aremco products, USA), and ground initially with sand paper until the glass inclusion inside was exposed to the surface of the phenocryst. After polishing with a diamond paste, the exposure of the glass inclusion was confirmed by microscopic observation using both transmitted and reflected light. Next, the phenocryst was removed from the slide glass by soaking it in acetone. It was reversed and re-glued on a slide glass with the adhesive. The phenocryst was again ground to a
Figure IV-2. Photomicrograph showing two large glass inclusions in olivine phenocryst in picritic basalt from SWRZ, Kilauea.
thickness typically less than 100 μm until the glass inclusion was exposed to the new side. We call it as a wafer. The new polished surface of the wafer was again observed through the microscope. The thin section of the wafer containing the doubly polished glass inclusion was carefully detached from the slide glass by soaking in an acetone bath. Extreme care has to be taken to handle this very fragile material. The wafer was gently cleaned both in acetone and deionized water followed by drying at 90 °C in an oven. The sample wafer thus prepared was fixed on a quartz glass plate by an adhesive as mentioned in Chapter III-2. The sample position in the cell was finally adjusted so as for the sample wafer to sit just on the spot of laser beam. This procedure allows us to heat only a glass inclusion by laser beam. The procedures for loading the sample into the cell were described in Chapter III-2.

IV-1-3. Results

The results of CO₂ analysis are shown in Table IV-1. A single glass inclusion was analyzed in each run except run 7 in which two glass inclusions were analyzed together. The lamp current of 17 A, pulse frequency of 10 kHz or CW mode (only run 7) and shooting duration of 100-200 msec were used as the working conditions of the laser unit. The diameter of the pits by the laser beam ranged from 32 to 78 μm except run 7. Laser was repeatedly shot at several different spots of a single inclusion to get as much gases as possible. Care was taken not to melt the host olivine phenocryst. Carbon dioxide extracted from repeated shots on a single inclusion was combined for analysis. Mass of
Table IV-1. Carbon dioxide analyses of glass inclusions in olivine phenocrysts from South-West Rift Zone, Kilauea.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Inclusion diameter</th>
<th>Pit diameter (μm)</th>
<th>Wafer thickness (μm)</th>
<th>Mass of glass melted (μg)</th>
<th>CO₂ extracted (ng)</th>
<th>CO₂ concentration (ppm)</th>
<th>S/N ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>160x220</td>
<td>50</td>
<td>95</td>
<td>1.83</td>
<td>0.42±0.10</td>
<td>230±50</td>
<td>6.8</td>
</tr>
<tr>
<td>2</td>
<td>190x280</td>
<td>40</td>
<td>112</td>
<td>1.04</td>
<td>0.14±0.12</td>
<td>130±120</td>
<td>2.2</td>
</tr>
<tr>
<td>3*</td>
<td>280</td>
<td>69+45+43</td>
<td>34</td>
<td>0.85</td>
<td>0.14±0.12</td>
<td>160±140</td>
<td>4.0</td>
</tr>
<tr>
<td>4</td>
<td>200x400</td>
<td>54+47</td>
<td>56</td>
<td>0.62</td>
<td>0.13±0.12</td>
<td>210±190</td>
<td>3.2</td>
</tr>
<tr>
<td>5</td>
<td>120x340</td>
<td>60+39+34</td>
<td>56</td>
<td>0.99</td>
<td>0.10±0.14</td>
<td>100±140</td>
<td>2.6</td>
</tr>
<tr>
<td>6*</td>
<td>240</td>
<td>78</td>
<td>34</td>
<td>0.46</td>
<td>0.08±0.14</td>
<td>190±300</td>
<td>2.3</td>
</tr>
<tr>
<td>7†</td>
<td>280, 280</td>
<td>130+120</td>
<td>86</td>
<td>4.32</td>
<td>0.03±0.15</td>
<td>7+ 35</td>
<td>0.7</td>
</tr>
</tbody>
</table>

* These inclusions were contained in a same host phenocryst.
† Two glass inclusion in a host phenocryst were analyzed together.
the glass melted of each pit was summed up to obtain the total mass of the glass melted.

The run 1 gave a CO$_2$ concentration of 230±50 ppm. In runs 2 to 7, the amount of extracted CO$_2$ in each run was so small that the large error was assigned based on the 95% confidence limits of the calibration line (Fig. II-18). Only maximum CO$_2$ concentrations were given for the runs 2 to 7. The results of runs 2 to 6, however, agree with that of run 1 within the analytical errors. The level of CO$_2$ background was drastically reduced after the experiments for the calibration line given in Chapter II-3. Therefore the actual analytical errors for CO$_2$ analysis would be smaller than those shown in Table IV-1. Although they have large analytical errors, the CO$_2$ concentrations obtained from runs 2-6 are consistent with the result for run 1, i.e., 230±50 ppm, which has the highest S/N ratio (Table IV-1). Based on these results, we conclude that CO$_2$ concentration of the pre-eruptive magma in SWRZ was about 230 ppm. A very low CO$_2$ concentration of run 7 may indicate that the host olivine may have trapped a melt that experienced significant degassing.

IV-1-4. Summit discharge of CO$_2$ at Kilauea

Water and CO$_2$ concentrations of the pre-eruptive magma responsible for the Kilauea summit eruption in 1959 were estimated to be 0.23±0.04 wt.% and 800±500 ppm, respectively, (Harris and Anderson, 1983) using glass inclusions in olivine phenocrysts which were contained in the ejecta of the 1959 summit eruption. Recent analyses of glass inclusions in olivine phenocrysts from the summit
eruption provide direct evidence of a minimum CO$_2$ content for the Kilauean parental magma which is 3000 ppm (Gerlach and Taylor, 1990). The CO$_2$ concentration of 230 ppm estimated for the SWRZ pre-eruptive magma is lower than that of the pre-eruptive magma responsible for the 1959 summit eruption. This means that the SWRZ pre-eruptive magma has degassed and lost a significant proportion of CO$_2$ originally retained in the primary magma during its migration to the rift system. Carbon isotopic ratios of CO$_2$ ($\delta^{13}C$=-3.7±0.1‰) in fumarolic gases collected from the summit area are significantly higher than those in volcanic gases collected from the ERZ ($\delta^{13}C$=-8±1‰) (Gerlach and Taylor, 1990). The difference in $\delta^{13}C$ values of CO$_2$ from the different volcanic settings is consistent with the model that the rift magma retains only a small fraction of CO$_2$ that was originally present in the primary magma. The degassed magma of the rift zone is thus estimated to contain the CO$_2$ concentration of 200 ppm based on the above carbon isotopic results on volcanic gases and rocks (Gerlach and Taylor, 1990). The results of our study is consistent with the above conclusion.

According to the model by Gerlach and Graeber (1985), parental magma from mantle is injected into the summit magma chamber and is equilibrated with the chamber conditions releasing excess dissolved volatiles while residing in the summit chamber. The summit-lava lake is interpreted to emit "Type I" volcanic gases derived from the parental magma. The degassed magma, or reservoir equilibrated magma, migrates to the rift system emitting "Type II" volcanic gases when it erupts. Gerlach and Graeber named the volatiles remaining in the reservoir equilibrated magma "stored volatiles". They estimated concentrations of volatiles (H$_2$O, CO$_2$, S, Cl and F) in the parental
magma based on a sulfur concentration of glass inclusions in olivine phenocrysts from the summit eruption by scaling it to the Type I gas composition. The volatile concentrations in the reservoir equilibrated magma were similarly estimated using the Type II gas composition scaled by a sulfur concentration in the glassy rim of submarine ERZ lava (Sakai et al., 1982). Their results are summarized in Table IV-2. They calculated the CO$_2$ concentrations of parental and reservoir equilibrated magmas to be 6500 ppm and 340 ppm, respectively. This CO$_2$ concentration of the parental magma is two times higher than that of a glass inclusion in the summit olivine phenocrysts which is 3000 ppm (Gerlach and Taylor, 1990). The CO$_2$ concentration in the reservoir equilibrated magma is also higher than that in a glass inclusion (230 ppm) in an olivine phenocrysts from SWRZ which is considered to represent the reservoir equilibrated magma.

If the CO$_2$ concentrations of 3000 and 230 ppm are taken to represent those of the parental and reservoir equilibrated magmas, respectively, then a new set of volatile compositions of the magmas can be calculated. The results of this calculation is also shown in Table IV-2. The calculated H$_2$O concentration of the parental magma is 0.19 wt.%, closer to the value (0.23 wt.%) of glass inclusion data than that assigned by Gerlach and Graeber (1985). The sulfur concentration of the parental magma, however, becomes half as much as the glass inclusion analysis.

Volatile fluxes from Kilauea volcano were estimated in the same way as Gerlach and Graeber (1985), based on the revised volatile concentrations of the magma, as shown in Table IV-3. The mean magma supply rate to the summit chamber from July 1956 to April 1983 has been estimated to be $5.9 \times 10^{11}$ g/day (Dzurisin et al., 1984).
Table IV-2. Parental, stored and residual volatile concentrations of Kilauea volcano.

<table>
<thead>
<tr>
<th>Volatile class</th>
<th>H$_2$O (wt.%)</th>
<th>CO$_2$ (wt.%)</th>
<th>S (wt.%)</th>
<th>Cl (wt.%)</th>
<th>F (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GG</td>
<td>PS</td>
<td>GG</td>
<td>PS</td>
<td>GG</td>
</tr>
<tr>
<td>Parental</td>
<td>0.30</td>
<td>0.19</td>
<td>0.65</td>
<td>0.30</td>
<td>0.130</td>
</tr>
<tr>
<td>Stored</td>
<td>0.27</td>
<td>0.17</td>
<td>0.034</td>
<td>0.023</td>
<td>0.070</td>
</tr>
<tr>
<td>Residual</td>
<td>0.10</td>
<td>0.10</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
</tr>
</tbody>
</table>

PS: Calculation by present study.
Table IV-3. Volatile fluxes from Kilauea volcano (x10^8 g/day).

<table>
<thead>
<tr>
<th>Volatile class</th>
<th>H_2O</th>
<th>CO_2</th>
<th>S</th>
<th>Cl</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GG</td>
<td>PS</td>
<td>GG</td>
<td>PS</td>
<td>GG</td>
</tr>
<tr>
<td>Parental volatiles</td>
<td>18</td>
<td>11</td>
<td>39</td>
<td>18</td>
<td>7.7</td>
</tr>
<tr>
<td>Chamber gas</td>
<td>2</td>
<td>1</td>
<td>37</td>
<td>17</td>
<td>3.6</td>
</tr>
<tr>
<td>Stored volatiles</td>
<td>16</td>
<td>10</td>
<td>2</td>
<td>1.4</td>
<td>4.2</td>
</tr>
<tr>
<td>Volcanic gas</td>
<td>3.6</td>
<td>1.4</td>
<td>0.40</td>
<td>0.17</td>
<td>1.1</td>
</tr>
<tr>
<td>Residual</td>
<td>2.1</td>
<td>2.1</td>
<td>0.31</td>
<td>0.32</td>
<td>0.31</td>
</tr>
<tr>
<td>Nonerupted</td>
<td>10</td>
<td>6.5</td>
<td>1.3</td>
<td>0.91</td>
<td>2.7</td>
</tr>
</tbody>
</table>

GG: Results by Gerlach and Graeber (1985).
PS: Present study.
Parental volatile flux can be obtained by multiplying the volatile concentrations of the parental magma with the rate of magma supply. Because chamber gas is released from the parental magma in the summit magma chamber, its gas composition can be calculated from the differences in volatile concentrations between the parental and reservoir equilibrated magmas. The volatile fluxes from the reservoir equilibrated magma can be obtained by subtracting the chamber gas fluxes from the parental volatile fluxes. It is known that approximately 35 % of the total magma supply during July 1956 to April 1983 has erupted and the remaining 65 % is still in the rifts (Dzurisin et al., 1984). Using this magma distribution and the volatile concentrations still remaining in spatters and lavas, the stored volatile fluxes can be subdivided into fluxes of volcanic gases, residual volatiles and non-erupted volatiles remaining in the rifts.

The chamber gas flux of CO$_2$ is $37 \times 10^8$ g/day in Gerlach and Graeber's estimate, whereas it is $17 \times 10^8$ g/day in our estimate. Both estimates agree reasonably well with the measured CO$_2$ emissions of $20-40 \times 10^8$ g/day from the summit region (Greenland et al., 1985). The SO$_2$ flux of the chamber gas ($7.2 \times 10^8$ g/day) by Gerlach and Graeber (1985) is greater than the measured SO$_2$ emission by COSPEC ($1.5-3.0 \times 10^8$ g/day) in the summit plume at various times since 1975 (Stoiber and Malone, 1975; Casadevall and Hazlett, 1983), while our SO$_2$ flux ($4.4 \times 10^8$ g/day) is close to the COSPEC measurements. The above comparisons of the estimated fluxes by Gerlach and Graeber (1985) and by us with the measured fluxes suggest that the budget calculations on volatiles are more accurately made when the measured CO$_2$ concentrations in glass inclusions from the different volcanic settings are used.
Assuming that the CO$_2$-saturated melt was trapped in a growing phenocryst in a magma chamber, a minimum depth of the magma chamber may be estimated from the CO$_2$ concentration of glass inclusions and the solubility of CO$_2$ in the melt. The temperature of magma responsible for the 1956 summit eruption is reported to be 1150-1250 °C (Macdonald, 1968; Thompson and Tilley, 1969; Murata and Richter, 1966). We assume that the temperature of the picritic basalt we used for the glass inclusion measurements was 1200°C when the olivine phenocrysts were crystallized. At 1200 °C and P$_{CO2}$=0.6 kbar, the saturated CO$_2$ concentration in basaltic melt is 230 ppm (Stolper and Holloway, 1988; Pan et al., 1991). Note that this is a minimum pressure, because the gas phase coexisting with the melt is likely to contain the other volatile species like water.

Composition of the H$_2$O-CO$_2$ gas phase coexisting with a basaltic melt of given H$_2$O and CO$_2$ concentrations can be calculated in the following procedures (Kazahaya and Shinohara, 1992). The solubilities of H$_2$O ($S_h$, wt.%) and CO$_2$ ($S_c$, ppm) in basaltic melt are given as:

\[
S_h = k_h P_h^{\gamma_h} \\
S_c = k_c P_c^{\gamma_c}
\]  

where, $k$ is Henry's constant, $P$ denotes partial pressure (kbar) of H$_2$O or CO$_2$ and $\gamma$ is a pressure dependency parameter. Subscripts $h$ and $c$ denote H$_2$O and CO$_2$, respectively. The $k$ and $\gamma$ values can be found in Hamilton et al. (1964) for H$_2$O and in Stolper and Holloway (1988) for
CO₂. They are \( k_h = 2.864 \) (wt. \%/kbar), \( k_c = 384 \) (ppm/kbar), \( \gamma_h = 0.665 \) and \( \gamma_c = 1 \). For a gas mixture of H₂O and CO₂, partial pressures are given as:

\[
P_h = X_h^g P_t \tag{3}
\]
\[
P_c = X_c^g P_t \tag{4}
\]

where \( P_t \) is total pressure of the mixture, and \( X^g \) is a mole fraction of H₂O or CO₂ in gas phase. The \( S_h \) and \( S_c \) values of the melt are calculated from equations (1) through (4) for various \( P_t \) and \( X_h^g \) values. The results of the calculation for the total pressure from 0.1 to 1 kbar are shown in Fig. IV-3 taking \( X_h^g \) as a parameter. The solid line represents isobaric H₂O and CO₂ concentrations of the melt at a given total pressure, and the dashed line represents a constant mole fraction of H₂O \( (X_h^g) \) in the gas phase.

The chamber gas composition has already been estimated as shown in Table IV-3. If the concentrations of sulfur, chlorine and fluorine in gas phase are ignored, the mole fraction of H₂O (and CO₂) in gas phase in equilibrium with a melt of a given composition can be obtained. From Table IV-3, the chamber gas composition can be calculated to be \( X_h^g = 0.15 \). From this value and the CO₂ concentration (230 ppm) of the reservoir equilibrated magma which has been estimated from a glass inclusion analysis (Table IV-2), the total pressure of the magma chamber (0.70 kbar) can be estimated (Fig. IV-3). This estimation is more realistic than the estimation of the total pressure based only on the CO₂ concentration of the reservoir equilibrated magma, because existence of H₂O in gas phase has been taken into account. When the chamber gas composition \( (X_h^g = 0.07) \) and CO₂ concentration (340 ppm)
Figure IV-3. Relationship between $\text{H}_2\text{O}$ and $\text{CO}_2$ concentrations in basaltic melt coexisting $\text{H}_2\text{O}-\text{CO}_2$ gas mixture with various total pressure (0.1-1.0 kbar). Dashed curves indicate mole fraction of $\text{H}_2\text{O}$ in the gas phase ($X_h^g$).
obtained by Gerlach and Graeber (Tables IV-2 and IV-3) are taken, the total pressure of 0.99 kbar is obtained. Assuming that the density of the rocks above the magma chamber to be 2.5 g/cm³, these pressures correspond to the depths of 2.8 and 4.0 km, which are in good agreement with the depth of the magma chamber estimated to be 2-6 km from the seismic evidence (Fiske and Kinoshita, 1969; Ryan et al., 1981).

IV-1-6. Effects of bubble formation on the bulk density of magma

The CO₂ and H₂O concentrations of the parental magma and the reservoir equilibrated magma have been given in Table IV-2. Assuming that the reservoir equilibrated magma is a degassed product of the parental magma, the amount of H₂O and CO₂ exsolved from a unit mass of the parental magma can be calculated from difference of the volatile concentrations between the parental and reservoir equilibrated magmas. The results of such calculations are shown in Table IV-4. The same calculations were carried out for the parental magma containing 6500 ppm CO₂ and 0.30 wt% H₂O as suggested by Gerlach and Graeber (1985). The amounts of gases exsolved from 1 g of the parental magma are 11 μmol H₂O and 65 μmol CO₂ in our case, whereas they are 17 μmol H₂O and 140 μmol CO₂ in the case where the Gerlach and Graeber's model is taken.

When CO₂ exsolves from a melt to form a gas phase, water in the melt will also be partitioned into the gas phase, even if the H₂O concentration in the melt is well below the saturation level. This means that the gas bubbles consist of a mixture of mainly CO₂ and H₂O as
Table IV-4. Estimation of bulk density of reservoir equilibrated magma.

<table>
<thead>
<tr>
<th></th>
<th>Amount of gas exsolved from 1 g of magma (μmol)</th>
<th>Pressure (kbar)</th>
<th>Volume of H₂O-CO₂ gas (cm³/mol)</th>
<th>Bulk density* (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂O</td>
<td>CO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS</td>
<td>11</td>
<td>65</td>
<td>0.70</td>
<td>196</td>
</tr>
<tr>
<td>GG</td>
<td>17</td>
<td>140</td>
<td>0.99</td>
<td>147</td>
</tr>
</tbody>
</table>

PS: Calculated using volatile concentrations obtained by present study (Table IV-2).
GG: Calculated using parental and stored volatile concentrations obtained by Gerlach and Graeber (1985, Table IV-2).

* The density of parental magma is assumed to be 2.75 g/cm³.
discussed in the previous section. Once gas bubbles have been formed, the bulk density of the melt would decrease depending on the total volume of the bubbles in the melt. The volume of the H$_2$O-CO$_2$ gas mixture per mole at a given temperature and pressure can be calculated from the mole fractions of H$_2$O and CO$_2$ in the gas mixture using the modified Redlich-Kwong (MRK) equation (Holloway, 1977; de Santis et al., 1974; Kazahaya and Shinohara, 1992). The MRK equation of state is written as:

$$P_t = \frac{RT}{(V-b_m)} - \frac{a_m}{((V+b_m)VT^{1/2})}$$

(5)

where $P_t$ is the total pressure, $V$ the volume per mole of the real gas mixture, and $R$ the gas constant. The constant $a_m$ is a measure of the cohesion due to the attractive forces between the molecules and constant $b_m$ is a measure of the volume of the molecules which limits how closely two molecules can approach one another before repulsive forces become significant (Redlich and Kwong, 1949). The constants $a_m$ and $b_m$ for the mixture of H$_2$O and CO$_2$ are given as:

$$a_m = X_h^2 a_h + X_c^2 a_c + 2X_hX_c a_{hc}$$

(6)

$$b_m = X_h b_h + X_c b_c$$

(7)

where $a_h$ and $a_c$ are the temperature dependent constants $a$ of the MRK equation for pure H$_2$O or CO$_2$ fluids, $b_h$ and $b_c$ are also the constants $b$ for the pure fluids, and $a_{hc}$ the cross coefficient for H$_2$O and CO$_2$. The values for these constants can be found in Holloway (1977). In equations (6) and (7), $X_h$ and $X_c$ denote the mole fraction of H$_2$O and
\( CO_2 \) in the gas mixture. After de Santis et al. (1974), the \( a_{hc} \) term can be given as;

\[
a_{hc} = \sqrt{a_h a_c} + \frac{R^2 T^{5/2} Q}{2}
\]

where \( a_h = 35 \times 10^6, a_c = 46 \times 10^6 \) and

\[
Q = \exp \left[ -11.07 + \frac{5953}{T} - \frac{2746 \times 10^3}{T^2} + \frac{464.6 \times 10^6}{T^3} \right]
\]

By substituting equations (6) through (9) to (5), the volume per mole of the real gas mixture can be calculated at any given temperature and pressure.

The amounts of gases exsolved from 1 g of the parental magma (\( v, \mu \text{mol} \)) are listed in Table IV-4. Assuming the density of the parental magma \( d_o \) to be 2.75 g/cm\(^3\), the densities of the reservoir equilibrated magma \( d \) can be calculated from,

\[
d = \frac{1}{d_o + v \times 10^{-6}}
\]

The bulk density of the magma in which \( \text{CO}_2-\text{H}_2\text{O} \) bubbles are present is calculated in this way and shown in Table IV-4. The assumed initial density \( d_o = 2.75 \text{ g/cm}^3 \) for the bubble-free magma would be reduced to 2.59-2.64 g/cm\(^3\) upon formation of bubbles, depending on the initial concentrations of volatiles. The density of the volcanic piles to the depth of 2 km beneath Mauna Loa is considered to be 2.3 g/cm\(^3\) (Ryan, 1987). Thus, decrease in the bulk density due to formation of
the CO₂-rich gas bubbles is not sufficient enough for the reservoir equilibrated magma to ascend to the Earth’s surface by its own buoyancy. The reservoir equilibrated magma will have to stay in the summit magma chamber or to migrate towards the rift systems at depths greater than 2 km along the iso-density depth. In order for the magma to rise, it is necessary to consider different mechanisms to induce further reduction of the bulk density of the magma such as concentration of bubbles into the upper part of the magma chamber (Shinohara, 1990).

IV-2. Analysis of glass inclusions from Izu-Oshima volcano

IV-2-1. Izu-Oshima volcano

Izu-Oshima is an island of an active basaltic stratovolcano in Sagami Bay, about 100 km south-southwest from Tokyo. Izu-Oshima volcano has a collapsed summit caldera (3 km x 4 km) which was formed some 1300 years ago after violent steam explosions from the summit crater. There is an active central cone, Mihara-yama, on the southern floor of the caldera. Mihara-yama as we see today was formed by the 1777-1778 eruption (the great An’ei eruption) with a large-scale fire fountaining which showered a large amount of scoria and ash over the outer slopes of the caldera.

Volcanic activity of Izu-Oshima volcano is estimated to have started more than 40,000 years ago when the proto-island (Senzu Group) which now covers Tertiary pre-Oshima volcanic basements was formed (Issiki, 1984). Formation of the stratovolcano (Oshima Group)
which covers the Senzu Group started more than 10,000 years ago (Tazawa, 1980), and activity of the volcano has continued up to the present. Activity of the volcano during formation of the Oshima Group was divided into the Older Oshima Group and the Younger Oshima Group from a formation of the summit caldera about 1500 years ago (Nakamura, 1964). During the formation of the Younger Oshima Group (late 1500 years), a large eruption effusing more than $10^8$ m$^3$ of lavas and scoria occurred with a constant interval of 130±50 years (Nakamura, 1964). This characterizes a periodic nature of the volcanic activities at Izu-Oshima volcano.

The latest eruption of 1986 began with splendid fire fountaining at the pit crater of Mihara-yama followed by the two fissure eruptions; one on the caldera floor and the other on the flank outside the caldera rim. These eruptions ejected 5.8-7.9x$10^7$ tons of lava and pyroclasts (Hayakawa, 1987; Endo et al., 1988). It is presumed from the petrographic study that there are two magma chambers under the volcano; the main chamber at a depth of less than 10 km, where extensive crystal fractionation of parent tholeiitic magma has taken place, and a subsidiary magma chamber in a shallower depth of less than 6 km (Fig. IV-4, Aramaki and Fujii, 1988). The depth of the magma chamber is also estimated to be 2-10 km based on geophysical observations (seismicity, crustal tilt, ground surface deformation, the gravity and elevation changes, Yamaoka et al., 1988; Yamamoto et al., 1988; Endo et al., 1988; Okubo et al., 1988; Ida et al., 1988).

It has been demonstrated that volatiles in magma play an important role on the periodic volcanic activity at Izu-Oshima volcano (Kazahaya and Shinohara, 1992). According to their model, the density contrast between the crust and magma is the most important driving force of
Izu-Oshima volcano

Figure IV-4. Schematic diagram of the magma system of Izu-Oshima volcano. In deep main chamber, tholeiitic parental magma was differentiated by 50% fractionational crystallization. In shallow magma chamber, plagioclase phenocrysts were concentrated to its upper part due to their relatively small densities.
eruption. They emphasize that the density change of magma is mainly induced by degassing followed by vesiculation and accumulation of gas bubbles. In this respect information on the volatile concentrations in pre-eruptive magma available from glass inclusion analysis is very interesting to test their model.

IV-2-2. Sample description

Glass inclusions in phenocrysts in scoria discharged by the 1986 eruption are rare and, small in size when found occasionally.

Large glass inclusions (ca. 200 µm) in plagioclase phenocrysts (2 mm) in scoria discharged during the 1777-1778 activity (Y1) were used as the samples representing the pre-eruptive magma (Fig. IV-5). In these scoria samples, other phenocrysts are rare and small in size.

IV-2-3. Results

The results of CO₂ analysis are shown in Table IV-5. Where more than two inclusions were found in a single host phenocryst, the extracted CO₂ was combined before analysis (runs 1 and 2 in Table IV-5). For large inclusions (>200 µm) several laser shots were made on the same inclusion, for which the extracted CO₂ was also combined. The working conditions of the laser unit were similar to those given in Chapter III; the lamp current of 17 A, pulse frequency of 10 kHz or CW mode (only runs 1 and 3) and shooting duration of 100 msec.
Figure IV-5. Photomicrograph showing several angular glass inclusions in plagioclase phenocryst in basaltic scoria from the 1777 Izu-Oshima eruption.
Table IV-5. Carbon dioxide analyses of glass inclusions in plagioclase from Izu-Oshima volcano.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Inclusion diameter (µm)</th>
<th>Number of analyzed inclusions</th>
<th>Pit diameter (µm)</th>
<th>Wafer thickness (µm)</th>
<th>Mass of glass melted (µg)</th>
<th>CO₂ extracted (ng)</th>
<th>CO₂ concentration (ppm)</th>
<th>S/N ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1*</td>
<td>260x200 300x120</td>
<td>2</td>
<td>82+67+65</td>
<td>60</td>
<td>2.53</td>
<td>0.44±0.11</td>
<td>170±50</td>
<td>11.1</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>+52+22</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>+22+22</td>
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<tr>
<td>2</td>
<td>180x100 160x100 140x60</td>
<td>3</td>
<td>73+39+67</td>
<td>129</td>
<td>4.50</td>
<td>0.38±0.14</td>
<td>80±30</td>
<td>9.4</td>
</tr>
<tr>
<td>3**</td>
<td>280x140</td>
<td>1</td>
<td>150</td>
<td>95</td>
<td>3.67</td>
<td>0.18±0.11</td>
<td>48+32</td>
<td>4.5</td>
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<tr>
<td>4**</td>
<td>220x120</td>
<td>1</td>
<td>200</td>
<td>95</td>
<td>5.45</td>
<td>0.12±0.13</td>
<td>22+28</td>
<td>3.1</td>
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<tr>
<td>5</td>
<td>280x220</td>
<td>1</td>
<td>61</td>
<td>52</td>
<td>0.42</td>
<td>0.062±0.14</td>
<td>150+330</td>
<td>1.5</td>
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<tr>
<td>6*</td>
<td>140x100</td>
<td>1</td>
<td>61</td>
<td>60</td>
<td>0.48</td>
<td>0.060±0.14</td>
<td>120+300</td>
<td>1.5</td>
</tr>
</tbody>
</table>

* These glass inclusions were contained in a single host phenocryst.
** These glass inclusions were contained in a single but different host phenocryst.
The CO₂ concentrations of 170±50 ppm and 80±30 ppm were obtained for runs 1 and 2 with high S/N ratios (11.1 and 9.4). However, only maximum CO₂ concentrations are given for the other runs, because the amounts of the extracted CO₂ were not large enough. If the 95% confidence limit of the CO₂ calibration line is much smaller than that shown in Fig. II-18 (this is fairly likely because the background level was drastically reduced for the runs in Table IV-5), then the values estimated without considering the error can be taken as the CO₂ concentrations for runs 3 to 6 (Table IV-5). In runs 3 and 4, glass inclusions contained in the same host crystal were separately analyzed. The CO₂ concentrations of runs 3 and 4 are lower than those of the other runs. This suggests that this host crystal trapped the melt which had degassed more extensively than the other crystals. The analyses of runs 5 and 6 was comparable with those of runs 1 and 2, although runs 5 and 6 were assigned large analytical errors due to small amounts of CO₂ extracted. The CO₂ concentration estimated by run 2 is a half of the concentration estimated by run 1. This indicates that the host crystal of run 2 may have trapped magma which experienced more degassing than that for run 1. Based on these results, we conclude that CO₂ concentration of the pre-eruptive magma responsible for the 1777 eruption was about 170 ppm.

Here, we assume that the CO₂ concentration of melt in the shallow magma chamber responsible for the 1986 Izu-Oshima eruption was also 170 ppm in the following discussions.
Assuming that the host crystal containing the glass inclusions crystallized in a magma chamber, a minimum depth of the magma chamber is estimated from the CO$_2$ concentration of the inclusions and the solubility of CO$_2$ in basaltic melt (Fig. II-1). Because the CO$_2$ solubility changes with temperature only slightly for basaltic melts, the saturation pressure for the CO$_2$ concentration of 170 ppm is 0.44 kbar or 1.8 km deep assuming that the gas phase consists of only CO$_2$ and that the density of the rocks at a depth to 2 km beneath the volcano is 2.4 g/cm$^3$ (Hasegawa et al., 1987). Note that this is a minimum pressure, because the gas phase coexisting with the melt is likely to contain water when water is dissolved in the melt.

If the H$_2$O and CO$_2$ concentrations of the basaltic melt which is saturated with the gas mixture of H$_2$O and CO$_2$ are known, the total pressure of the melt can be estimated using Fig. IV-3. Our glass inclusion analyses indicated that the CO$_2$ concentration of the basaltic melt in the magma chamber is 170 ppm (Table IV-5). The H$_2$O concentration of basaltic magma responsible for the 1986 eruption was estimated to be less than 0.7 wt.% based on comparison of the petrologic and chemical properties of ejecta with phase relation experiments (Fujii et al., 1988). If we assume that the H$_2$O concentration of the basaltic melt is 0.7 wt.%, the pressure of the magma chamber is estimated to be 0.57 kbar from Fig. IV-3. This is a maximum pressure of the magma chamber because the H$_2$O concentration of 0.7 wt.% is the maximum value. Thus, the pressure of the melt in which phenocrysts containing our glass inclusions were
crystallized can be estimated to be between 0.44 and 0.57 kbar or 1.8 and 2.4 km in depth.

These depths correspond to the top of the magma chamber (2-10 km) estimated by geophysical evidence. This may be explained by an idea that the phenocrysts which trapped the melt crystallized in a conduit or the topmost of the shallow magma chamber. This explanation is consistent with the petrologic view that plagioclase phenocrysts were concentrated in the upper part of the magma chamber or the conduit above the chamber due to their relatively small densities (d=2.65 g/cm³) (Fujii et al., 1988).

IV-2-5. Formation of gas phase in pre-eruptive magma

There is no information regarding the CO₂ concentration in the primary magma which is supplied beneath Izu-Oshima volcano. Here we assume that the primary magma contained 1700-5000 ppm of CO₂. This assumption comes from the analysis made by Harris and Anderson (1984) on CO₂ determination of glass inclusions in olivine from the 1974 eruption of Fuego volcano, a subduction zone volcano in Guatemala. They found that the concentration of CO₂ in the melt ranged from 1700 ppm to 5000 ppm regardless of the differentiation of the liquid from SiO₂=50.7 wt.% to SiO₂=53.8 wt.% . In the following discussion we assume that the primary magma before degassing had the CO₂ concentration of 1700-5000 ppm at Izu-Oshima volcano.

The temperature of the pre-eruptive basaltic magma responsible for the 1986 eruption was considered to be 1100-1150 °C (Fujii et al., 1988). If the 1150°C magma containing 1700-5000 ppm CO₂ ascends to
a depth of 1.8-2.4 km, CO\textsubscript{2} would be exsolved to make the CO\textsubscript{2} concentration in the melt 170 ppm, forming a CO\textsubscript{2}-rich gas phase. If water is also dissolved in the melt, water would be partitioned into the gas phase depending on the partition factor of H\textsubscript{2}O and CO\textsubscript{2} between the gas phase and silicate melt, even if the H\textsubscript{2}O concentration is well below the saturation level (1.7 wt.% at 0.44 kbar).

The minimum pressure of 0.44 kbar has been estimated for the shallow magma chamber in the case where no H\textsubscript{2}O is assumed in the gas phase. If the primary magma with 1700 ppm CO\textsubscript{2} and no water ascends to a depth of 1.8 km or 0.44 kbar, 35 \( \mu \)mol (=\((1700-170)\times10^{-6}/44\)) of CO\textsubscript{2} exsolves from 1 g of the magma leaving 170 ppm of CO\textsubscript{2} in the melt (Table IV-6). If the primary magma contains 5000 ppm CO\textsubscript{2}, 110 \( \mu \)mol of CO\textsubscript{2} would exsolve from 1 g of the magma.

Maximum water concentration and pressure of the shallow magma chamber were estimated to be 0.7 wt\% and 0.57 kbar, respectively (Section IV-2-4). If the primary magma containing 1700 ppm CO\textsubscript{2} and more than 0.7 wt\% H\textsubscript{2}O ascends to a depth of 2.4 km or 0.57 kbar resulting in 170 ppm CO\textsubscript{2} in the melt, 35 \( \mu \)mol of CO\textsubscript{2} would again exsolve from 1 g of the magma. Once a vapor phase is produced, water dissolved in the melt will be partitioned between the vapor and melt phases. The mole fraction of H\textsubscript{2}O in the gas phase coexisting with the melt is 0.22 when the melt has 0.7 wt.\% H\textsubscript{2}O and 170 ppm CO\textsubscript{2} (Fig. IV-3). The amount of water partitioned into the vapor phase is readily calculated to be 9.8 \( \mu \)mol. The total amount of CO\textsubscript{2} and H\textsubscript{2}O in the vapor phase is thus 45 \( \mu \)mol/g-magma. Similarly, if the initial magma contains 5000 ppm CO\textsubscript{2}, then the total amount of the vapor phase is 141 \( \mu \)mol (Table IV-6). These calculations suggest that water comprises a
Table IV-6. Estimation of bulk density of pre-eruptive magma beneath Izu-Oshima volcano

<table>
<thead>
<tr>
<th>Initial CO₂ concentration (wt.%)</th>
<th>Retained volatile concentration</th>
<th>Pressure (kbar)</th>
<th>Amount of gas exsolved from 1 g of magma (μmol)</th>
<th>Volume of exsolved gas (cm³/mol)</th>
<th>Bulk density* (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O 0.17</td>
<td>CO₂ 0.017</td>
<td>0.44</td>
<td>H₂O 0</td>
<td>35</td>
<td>293 2.58</td>
</tr>
<tr>
<td>H₂O 0.17</td>
<td>CO₂ 0.017</td>
<td>0.57</td>
<td>H₂O 9.8</td>
<td>35</td>
<td>224 2.58</td>
</tr>
<tr>
<td>H₂O 0.50</td>
<td>CO₂ 0.017</td>
<td>0.44</td>
<td>H₂O 0</td>
<td>110</td>
<td>293 2.44</td>
</tr>
<tr>
<td>H₂O 0.50</td>
<td>CO₂ 0.017</td>
<td>0.57</td>
<td>H₂O 31</td>
<td>110</td>
<td>224 2.45</td>
</tr>
</tbody>
</table>

* The magma density before degassing is assumed to be 2.65 g/cm³.
significant proportion of the gas phase, regardless of the situation that
the magma is undersaturated with respect to water at that pressure.

The volume of the gas phase can be calculated from the amount of
CO₂ and H₂O using the MRK equation (see the similar calculations in
Chapter IV-1-5). If the initial melt contains no water, the gas phase
coexisting with the melt consists of only CO₂. In this extreme case, the
volume of the gas is 293 cm³/mol at 0.44 kbar and 1150°C (Table IV-6).
On the other hand, if the initial melt contains more than 0.7 wt.%
H₂O, the gas phase coexisting with the melt should contain 22% of H₂O
as shown in Fig. IV-3. In this case, the volume of the gas phase is 224
cm³/mol at 0.57 kbar and 1150°C (Table IV-6). Density of bubble-free
basaltic magma of Izu-Oshima volcano was estimated to be 2.65 to 2.70
g/cm³ at 1150 °C and <1 kbar (Aramaki and Fujii, 1988) based on
density calculation given by Bottinga and Weill (1970). Taking the
values of 2.65 g/cm³ for the bubble-free melt, the volume per gram of
the two-phase magma would be
$$\frac{1}{2.65} + 34 \times 10^{-6} \times 292 = 0.388 \text{ cm}^3/\text{g}$$
for the initially 1700 ppm CO₂ containing magma and similarly 0.409
cm³/g for the initially 5000 ppm CO₂ containing magma. These values
are equivalent to the bulk magma densities of 2.58 and 2.44 g/cm³,
respectively (Table IV-6). For the primary magma initially containing
H₂O more than 0.7 wt.%, similar calculation give the volume per gram
of the two-phase magma to be
$$\frac{1}{2.65} + 45 \times 10^{-6} \times 224 = 0.387 \text{ cm}^3/\text{g}$$
for the 1700 ppm CO₂ magma and 0.409 cm³/g for the 5000 ppm CO₂
magma. These values are equivalent to the bulk magma densities of
2.58 and 2.45 g/cm³, respectively (Table IV-6). Because 9.8-31 μmol-
H₂O /g-melt is present in the gas phase, the initial H₂O content of the
primary magma is calculated to range from 0.72-0.76 wt.%; only 2.8-
7.9 wt.% of the initial H₂O content is partitioned into the CO₂-rich gas phase.

A density model of the crust beneath the Izu-Oshima volcano indicates the densities of 2.4 g/cm³ at the depth of 1-2 km and 2.7 g/cm³ at the depth of more than 2 km, which are based on explosion seismography (Hasegawa et al., 1987). The bulk densities of the two-phase magma calculated above (2.44-2.58 g/cm³) are greater than the densities of the crust of 1-2 km deep but smaller than the density of the crust of deeper than 2 km. Our calculations suggest that the shallow magma chamber is located at the depth of about 2 km beneath Izu-Oshima volcano.

IV-2-6. Estimation of the rate of magma supply at Izu-Oshima volcano

The flux of SO₂ from the central pit crater of Izu-Oshima volcano has been repeatedly measured by COSPEC. It was 345 tons/day on the average in April, 1971 (Okita and Shimozuru, 1975), and similarly 350 tons/day from December 1987 to March 1990 (Ohta et al., 1988; Kazahaya et al., 1992). From March 1990, the flux decreased to less than 100 tons/day (Hirabayashi pers. commun.). We can now estimate the flux of CO₂ from the central pit crater by multiplying these SO₂ fluxes by CO₂/SO₂ ratios in the fumarolic gases in the crater. The molar ratios of CO₂ to SO₂ in the fumarolic gases varied from 0.39 to 11.7 between February 1987 and July 1987 with smaller values at the earlier period (Table IV-7, adapted from Hirabayashi et al., 1988). Using the earliest and smallest CO₂/SO₂ ratio for the fumarolic gases, the CO₂ fluxes of 27-94 tons/day are calculated. In this calculation, the
Table IV-7. Chemical composition of fumarolic gases from the central crater collected after the 1986 eruption of Izu-Oshima volcano.

<table>
<thead>
<tr>
<th>Date</th>
<th>Locality</th>
<th>Temp. (°C)</th>
<th>CO₂ (vol.%)</th>
<th>SO₂ (vol.%)</th>
<th>H₂S (vol.%)</th>
<th>HCl (vol.%)</th>
<th>HF (vol.%)</th>
<th>CO₂/SO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1987.2.20</td>
<td>M-1</td>
<td>630</td>
<td>20.7</td>
<td>52.8</td>
<td>0.2</td>
<td>21.1</td>
<td>5.3</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>844</td>
<td>26.7</td>
<td>16.4</td>
<td>1.6</td>
<td>41.2</td>
<td>14.1</td>
<td>1.63</td>
</tr>
<tr>
<td>1987.3.21</td>
<td>M-1</td>
<td>502</td>
<td>34.0</td>
<td>34.8</td>
<td>0.1</td>
<td>12.8</td>
<td>12.3</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>578</td>
<td>82.2</td>
<td>7.0</td>
<td>6.2</td>
<td>4.6</td>
<td>11.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>M-3</td>
<td>501</td>
<td>26.2</td>
<td>15.8</td>
<td>0.1</td>
<td>53.2</td>
<td>5.6</td>
<td>1.66</td>
</tr>
<tr>
<td>1987.7.4</td>
<td>M-2</td>
<td>397</td>
<td>80.5</td>
<td>8.6</td>
<td>1.3</td>
<td>9.0</td>
<td>0.6</td>
<td>9.36</td>
</tr>
</tbody>
</table>
SO₂ flux was assumed to be within the range of 100-350 tons/day when
gas measurements were made.

Given the CO₂ fluxes, it is possible to calculate the rate of magma
supply which can account for the CO₂ fluxes. Assuming that Izu-
Oshima volcano has steadily released CO₂ at the same rate as the above
estimated CO₂ fluxes and that the shallow magma chamber has existed
for the last 1500 years, the rate of magma supply to the shallow magma
chamber can be obtained by dividing the CO₂ fluxes by the amount of
CO₂ released from unit mass of the magma. Results of the calculation
are shown in Table IV-8. Because the magma initially carrying 1700
ppm CO₂ can release 35 μmol (1.53 μg) per gram of the magma, 18-
61×10³ tons/day of the magma has to be supplied to the shallow magma
chamber where degassing takes place. For the magma initially carrying
5000 ppm CO₂, 6-19×10³ tons/day has to be supplied. These values are
much smaller than the rate of magma supply (590×10³ tons/day)
reported for Kilauea volcano (Dzurisin et al., 1984).

The amounts of ejecta released by the major eruptions of Izu-
Oshima in the last 1500 years (Younger Oshima Group) are
summarized in Fig. IV-6 (after Nakamura, 1964). It is clearly indicated
that the eruptions occurred periodically with an interval of 130±50
years. The mass of ejecta in each eruption ranged from 24×10⁷ to
92×10⁷ tons except for the 1986 eruption which released only 6-8×10⁷
tons. The ejecta by eruptions between 500 A. D. and 1986 A. D. is
summed up to 640×10⁷ tons. Assuming that this total amount of ejecta
is equivalent to the amount of the primary magma supplied into the
shallow magma chamber from the main magma chamber, the rate of
magma supply becomes 12×10³ tons/day. The rate of magma supply
(6-19×10³ tons/day) estimated from the calculated CO₂ flux is in good
Table IV-8. Estimation of magma supply rate to the shallow magma chamber.

<table>
<thead>
<tr>
<th>CO₂ conc. before degassing (wt.%)</th>
<th>CO₂ flux* (tons/day)</th>
<th>Amount of gas exsolved from 1 g of magma (x10⁻³ g)</th>
<th>Magma supply rate (x10³ tons/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.17</td>
<td>27-94</td>
<td>1.53</td>
<td>18-61</td>
</tr>
<tr>
<td>0.50</td>
<td>27-94</td>
<td>4.83</td>
<td>6-19</td>
</tr>
</tbody>
</table>

* CO₂ flux is estimated by multiplying the measured SO₂ flux (100-350 tons/day) by CO₂/SO₂ ratio (0.39) of fumarolic gas in the central crater.
Figure IV-6. Masses of ejecta discharged by the major eruptions in the last 1500 years at Izu-Oshima volcano. Note the periodic nature of the eruptions. Data taken from Nakamura (1964).
agreement with the observed rate of magma supply, although we must assume that the CO$_2$ flux estimated from the observed SO$_2$ fluxes and SO$_2$/CO$_2$ ratios of the fumarolic gases released during 1971-1990 can be applied to the 1777-1778 eruption. The above agreement may suggest that the CO$_2$ concentration of the basaltic magma in the main chamber is 5000 ppm. Aramaki and Fujii (1988) suggested that the magma supplied to the shallow magma chamber was a melt fraction after 50% crystallization of the primary tholeiitic magma in the deep main magma chamber. If this is the case, the CO$_2$ concentration of the primary tholeiitic magma is 2500 ppm before fractional crystallization.
CONCLUSIONS

The analytical system consisting of a laser probe extraction unit and a GC-MS detection unit was constructed to determine a micro quantity of H$_2$O and CO$_2$ dissolved in glass inclusions. The optimum working conditions (lamp current, pulse frequency and duration) of laser extraction were decided using a Mariana Trough submarine basalt glass as a sample because a gas concentration in a glass is calculated from the measured amount of the extracted H$_2$O and CO$_2$ and the mass of glass melted. It is essential to make accurate measurements of the mass of glass melted. This was accomplished by grinding a glass sample to a wafer with a typical thickness of about 100 μm which was then pierced by a laser beam. The mass of glass melted was fairly accurately measured under a microscope from the wafer thickness and the diameter of a laser pit. The detection limit of the present system is 0.15 ng CO$_2$ and 15 ng H$_2$O. Based on the analyses of homogeneous glass, it was concluded that the present technique allows us to analyze CO$_2$ concentration of glass inclusions as small as 70 μm in diameter within an accuracy of ±60 ppm. Complete degassing of H$_2$O in glass by the present technique was found difficult, probably due to slow diffusion of H$_2$O in basaltic melt at high temperatures.

Using this analytical system, CO$_2$ analyses of glass inclusions from Kilauea volcano, Hawaii, and Izu-Oshima volcano, Japan, were carried out to determine CO$_2$ concentration of pre-eruptive magma. The CO$_2$ concentration of pre-eruptive magma in South-West Rift Zone of Kilauea volcano was 230 ppm. This suggests that the magma has been significantly degassed during its storage in the summit magma chamber and migration to the rift system. The depth of the magma chamber and the volatile budget of Kilauea volcano based on the CO$_2$ analysis of glass
inclusion are consistent with the model on the volatile behaviors in the Kilauean magmatic system. The CO$_2$ concentration of pre-eruptive magma of Izu-Oshima volcano was 170 ppm. The measured CO$_2$ concentration and estimated bulk density of the magma containing gas phase indicate that the magma chamber exists at the depth of about 2 km beneath the volcano. The rate of magma supply estimated from the glass inclusion analysis, SO$_2$ fluxes and CO$_2$/SO$_2$ ratios of fumarolic gases is compatible with the average production rate of magma in the last 1500 years. Thus the determination of volatile concentrations in pre-eruptive magma through analysis of glass inclusions in phenocrysts has a great potential to model magma ascent and volcanic eruption processes, although it is obvious that much more data should be accumulated.
REFERENCES


APPENDIX

PRELIMINARY RESULTS ON PROTOTYPE LASERPROBE-QUADRUPOLE MASS SPECTROMETRY SYSTEM

A-1. Laserprobe-QMS system

For construction of a laserprobe-GCMS system, fundamental knowledge of laserprobe and micro-gas-analysis was necessary. A prototype laserprobe-quadrupole mass spectrometry system was set up to obtain various information on working conditions of laserprobe and the most suitable experimental conditions of micro-analysis of H$_2$O and CO$_2$. This system, as shown in Fig. A-1, consists of the gas extraction unit, the gas purification unit and the gas analysis unit.

A-1-1. Gas extraction unit

As shown in Fig. A-1, the gas extraction unit consists of Nd-YAG laser system, microscope, sample cell and X-Y-Z stage. The laser beam was reflected by a mirror in the microscope and focused on the sample in a sample cell through an objective lens. The sample cell made of Pyrex glass transparent to the defocused laser beam was connected to the gas purification unit with a flexible tubing. The sample cell and connecting tubing were heated to 150 °C during operation to avoid adsorption of H$_2$O on the inner wall of the vacuum line.
Figure A-1. Schematic diagram of the laserprobe-QMS system constructed for the preliminary experiments.
A-1.2. Gas purification unit

This unit consists of cold traps and a "uranium finger". The extracted H$_2$O and CO$_2$ were collected in a cold trap and purified by trap work. To avoid loss of the extracted water due to adsorption onto the inner surface of the line, quantitative conversion of the water to hydrogen was attempted and the QMS analysis was made for H$_2$ and not for H$_2$O. Reduction of H$_2$O to H$_2$ was accomplished by reaction of water with heated uranium (650°C) after separating CO$_2$ from water.

Gas purification unit was constructed with metal valves, stainless steel tubings, a trap 1 and a trap 2 (Fig. A-1). The metal valves and stainless steel tubing were also maintained at 150 °C to avoid adsorption of the extracted H$_2$O. The trap 1 is made of a Pyrex glass tube. The trap 2 is a quartz glass tube containing fragments of uranium metal for water reduction. The trap 1 cooled with liquid nitrogen was used to collect the condensible gases, mainly H$_2$O and CO$_2$, extracted from the sample by the laser irradiation. Because there was a possibility that a part of dissolved water in the sample glass was extracted as H$_2$ by either thermal decomposition of H$_2$O on laser irradiation or reduction of H$_2$O with ferrous iron in the sample glass, the hydrogen gas was expanded to the gas analysis unit for measurement of its amount by QMS while the H$_2$O and CO$_2$ was frozen in the cold trap. After the hydrogen gas was analyzed, the extracted CO$_2$ was separated from H$_2$O in the trap 1 by "warming" to the Dry-ice temperature and expanded to the gas analysis unit for measurement of its amount by QMS. Carbon dioxide should not be introduced to the trap 2 because CO$_2$ reacts with uranium at 650 °C. The extracted H$_2$O was transferred to the trap 2 followed by quantitative...
reduction of H₂O to H₂ with heated uranium at 650 °C for 10 minutes. The hydrogen gas thus produced was also expanded to the QMS for determination of the amount of H₂O extracted from the sample.

A-1-3. Gas analysis unit

The gas analysis unit consisted of vacuum pumps, three pressure gauges (Pirani gauge, ion gauge and McLeod gauge), a quadrupole mass spectrometer, metal valves and stainless steel tubings (Fig. A-1). Hydrogen gas or CO₂ gas in the gas purification unit was expanded to the volume up to the valve k. Then the hydrogen gas in the space between the valves j and k was introduced to the valve m to measure its amount by the static operated QMS. In the case of CO₂ analysis, the gas present in the space closed by the valves of b, c, e, f, h, i and k was used for measurement. The static operated QMS was necessary for analysis of a minute amount of gas because of its high sensitivity. After introduction of the sample gas into the QMS, ion current due to the sample gas was measured. Because a life time of ionized gas molecules except for rare gases in the ion source of the QMS is very short, the ion current decreases very rapidly to the base level immediately. For example, CO₂⁺ ions react with hot filament to decompose into CO, resulting in increase of M/e=28 signal (CO). The ion current of H₂⁺ ions also decreased rapidly, indicating very rapid degradation on the filament (Gardiner and Pillinger, 1979). In an attempt to measure carbon isotopic ratios of CO₂ using a static operation mass spectrometer, Gardiner and Pillinger (1979) used CD₄ which has a longer life time than CO₂.
The calibration of QMS was carried out for pure H$_2$ and CO$_2$. After each gas was introduced up to the valve k of the gas analysis unit, the absolute pressure of the gas was measured by the McLeod gauge. The amount of the gas present between the valves j and k (or b and k for CO$_2$ analysis) was calculated from the pressure, the volume of its space and the line temperature using the ideal gas law. The gas between the valves was introduced to the QMS and the ion current was monitored. The maximum ion current was plotted against the absolute amount of gas introduced to the QMS. A linear relationship for H$_2$ was obtained in a range from 0.01 nmol to 1.5 nmol that corresponded to a range from 0.18 ng to 27 ng of H$_2$O (Fig. A-2). Because only a fraction (about 1/14) of the gas in the purification-analysis units was introduced to the QMS as mentioned above, the actual detection limit of this system was 2.5 ng H$_2$O. A linear calibration line with a slope of 0.3136 (A/mol) was obtained from the data points using a least square method. The dash curves indicate the 95% confidence limits of the calibration line.

An excellent linear relationship for CO$_2$ was also obtained in a range from 0.001 nmol to 0.06 nmol that corresponded to a range from 0.044 ng to 2.6 ng CO$_2$ (Fig. A-3). Because only a fraction (about 4/5) of the gas in the purification-analysis units was introduced to the QMS as mentioned above, the actual detection limit of this system was 0.055 ng CO$_2$. The CO$_2$ calibration line with a slope of 0.1897 (A/mol) was obtained from the calibration data points using a least square method. The dash curves indicate the 95% confidence limits of the calibration line.
Figure A-2. Ion currents of $\text{H}_2$ versus the absolute amounts of $\text{H}_2$ introduced to the QMS. A linear calibration line has a slope of 0.3136 A/mol. Dashed curves indicate the 95% confidence limits of the calibration line.
Figure A-3. Ion currents of CO₂ versus the absolute amounts of CO₂ introduced to the QMS. A linear calibration line has a slope of 0.1897 A/mol. Dashed curves indicate the 95% confidence limits of the calibration line.
A-2. Analysis of glass samples

A-2-1. Analytical procedure

The glassy rim of the Mariana Trough basalt (MTB) was used to test the present analytical system. The sample glass was ground to a wafer of about 300 μm thick. After the sample wafer was placed in the cell, the cell was evacuated to less than 1x10⁻⁵ torr by vacuum pumps. The flexible tubing and the gas purification unit were also evacuated at 150-170 °C to minimize contribution from the adsorbed H₂O and CO₂. The uranium furnace was evacuated at 750 °C for 10 minutes and then at 650 °C just before the sample analysis.

In this preliminary experiment, the working conditions of the laser unit were; lamp current of 15.5-15.8 A and various pulse frequency ranging from 80 kHz to continuous wave mode. The duration for the laser irradiation in each run was less than one second but it could not be measured accurately because the duration was manually adjusted in this preliminary experiment.

The gas concentration of the sample glass was calculated by dividing the amount of the analyzed gas by the mass of the glass melted by a laser beam. The volume of a pit produced by a laser beam was estimated from microscopic observation of the pit diameter and depth. The pit depth was measured by changing focus of an optical microscope from the surface to the bottom of the laser pit. The volume of the laser pit was calculated assuming that the shape of the pit was approximated by the paraboloid of revolution (Toyoda and Ozima, 1988). The validity of this assumption was been examined in Chapter III-2. The pit volume
thus calculated was multiplied by the density of the glass to obtain the mass of glass melted.

The glassy rim of the Mariana Trough basalt (MTB) was used to test the present analytical system. Bulk analyses of the MTB glass indicate that it contains $1.35\pm0.04$ wt.% $\text{H}_2\text{O}$ and $326\pm7$ ppm $\text{CO}_2$ (see Chapter III). Blank analyses were carried out immediately before and/or after the sample analysis. The net amount of the $\text{H}_2\text{O}$ and $\text{CO}_2$ gas extracted from the sample by the laser irradiation was obtained by subtracting the blank analysis from the sample analysis. The gas concentration of the sample glass was calculated by dividing the amount of the analyzed gas by the mass of the glass melted by laser irradiation.

A-2-2. Results

The pits produced for the $\text{H}_2\text{O}$ analysis had the various shapes resulting in the masses of glass melted ranging variably from $1.7\ \mu\text{g}$ to $49.3\ \mu\text{g}$ (Table A-1). The relationship between the absolute amounts of $\text{H}_2\text{O}$ extracted and the masses of glass melted is shown in Fig. A-4 (a). The absolute amounts of the extracted $\text{H}_2\text{O}$ increased roughly with the mass of glass melted except for one analysis. The errors of the extracted amount of $\text{H}_2\text{O}$ and the $\text{H}_2\text{O}$ concentrations were estimated from the 95% confidence limit of the calibration line (Fig. A-2). Although runs 4 and 5 gave the $\text{H}_2\text{O}$ concentrations close to the bulk $\text{H}_2\text{O}$ concentration ($1.35$ wt.%), results from the other runs differed greatly from the value of the bulk analysis even if the error range was taken into consideration (Fig. A-4 (a)).
Table A-1. Results of H$_2$O analysis of MTB glasses

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Pit diameter</th>
<th>Pit depth</th>
<th>Mass of glass melted</th>
<th>Extracted H$_2$O</th>
<th>H$_2$O concentration</th>
<th>S/N ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(μm)</td>
<td>(μm)</td>
<td>(μg)</td>
<td>(ng)</td>
<td>(wt%)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>190</td>
<td>40</td>
<td>1.7</td>
<td>33.2±14.5</td>
<td>2.0±0.9</td>
<td>0.33</td>
</tr>
<tr>
<td>2</td>
<td>180</td>
<td>70</td>
<td>2.4</td>
<td>57.1±13.7</td>
<td>2.4±0.6</td>
<td>0.53</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>100</td>
<td>4.6</td>
<td>41.3±13.8</td>
<td>0.90±0.30</td>
<td>0.37</td>
</tr>
<tr>
<td>4</td>
<td>180+130+130</td>
<td>90+70</td>
<td>5.8</td>
<td>96.8±14.8</td>
<td>1.7±0.3</td>
<td>1.35</td>
</tr>
<tr>
<td></td>
<td>+130</td>
<td>+80</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>260</td>
<td>110</td>
<td>7.8</td>
<td>97.5±15.5</td>
<td>1.2±0.2</td>
<td>1.39</td>
</tr>
<tr>
<td>6</td>
<td>300</td>
<td>110</td>
<td>10.2</td>
<td>102.7±27.6</td>
<td>1.01±0.27</td>
<td>5.97</td>
</tr>
<tr>
<td>7</td>
<td>400</td>
<td>280</td>
<td>49.3</td>
<td>82.6±31.7</td>
<td>0.17±0.06</td>
<td>4.51</td>
</tr>
</tbody>
</table>
Figure A-4. (a) Relationship between the extracted H$_2$O (ng) and the mass of glass melted (μg) in H$_2$O analyses of MTB glass. The solid line shows the bulk analyses of MTB glass that is 1.35 wt.%. (b) The absolute amounts of the extracted H$_2$O and the blank H$_2$O in each run.
The possible sources of this discrepancy were most likely due to fluctuation of the blank H$_2$O and the method of estimation of the pit volume, or the mass of glass melted. Firstly, the blank H$_2$O analyzed before (or after) the sample analysis was highly variable ranging from 18 ng to 112 ng as shown in Fig. A-4 (b). The high values of the blank H$_2$O were likely caused by insufficient removal of H$_2$O adhering on the inner wall of the line, indicating that baking conditions of the line at a maximum temperature of 170 °C for 3 hours were not sufficient enough. The largest source of the blank H$_2$O was likely from the flexible bellow tubing (Fig. A-1) which had a large surface area. In addition, it was found that the background hydrogen gas which corresponded to about 30 ng H$_2$O was produced from the heated uranium even after preheating at 750 °C.

The second source of the discrepancy was in the estimation of the pit volumes. Because there is no guarantee that the shape of the pit can be approximated by the paraboloid of revolution, there should be large errors involved in the estimation of the pit volume. A low value of the H$_2$O concentration (0.17±0.06 wt%) was obtained in spite of the high S/N ratio (4.5) as given in Table A-1 suggesting the most likely cause of the low value to be overestimation of the pit volume.

The results of CO$_2$ analysis are given in Table A-2. The mass of glass melted ranged from 0.10 µg to 15.6 µg. The relationship between the absolute amount of extracted CO$_2$ and the mass of glass melted is shown in Fig. A-5 (a). The analytical errors of the extracted CO$_2$ were very small because the calibration data had a very small variation as shown in Fig. A-3. However, most of the analytical values differed from the bulk CO$_2$ concentration (326 ppm) of the MTB glass (Fig. A-5 (a)). This discrepancy is probably due to fluctuation of the blank CO$_2$
Table A-2. Results of CO₂ analysis of MTB glass.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Pit diameter (µm)</th>
<th>Pit depth (µm)</th>
<th>Mass of glass melted (µg)</th>
<th>Extracted CO₂ (ng)</th>
<th>CO₂ concentration (ppm)</th>
<th>S/N ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>94</td>
<td>11</td>
<td>0.10</td>
<td>0.08±0.03</td>
<td>800±300</td>
<td>0.30</td>
</tr>
<tr>
<td>9</td>
<td>86</td>
<td>15</td>
<td>0.12</td>
<td>0.05±0.03</td>
<td>400±300</td>
<td>0.30</td>
</tr>
<tr>
<td>10</td>
<td>140</td>
<td>42</td>
<td>0.94</td>
<td>0.59±0.02</td>
<td>630±30</td>
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Figure A-5. (a) Relationship between the extracted CO\(_2\) (ng) and the mass of glass melted (\(\mu\)g) in CO\(_2\) analyses of MTB glass. The solid line shows the bulk analyses of MTB glass that is 326 ppm. (b) The absolute amounts of the extracted CO\(_2\) and the blank CO\(_2\) in each run.
and the impertinent estimation of the pit volume, similar to the case for 
\text{H}_2\text{O} \text{ analysis}. The average value of the blank analyses just before and 
after the each sample analysis was used to calculate the net amount of the 
extracted \text{CO}_2. The blank \text{CO}_2 \text{ of the each run fluctuated from 0.20 ng} 
to 0.64 ng (Fig. A-5 (b)), but the range of the two blank analyses before 
and after each sample analysis was within less than 40\%. Thus, 
fluctuation of the blank \text{CO}_2 \text{ can explain the the discrepancy between the} 
analyzed values and the bulk analysis in the case where the analysis was 
made with low S/N ratios. However fluctuation of the blank \text{CO}_2 \text{ can} 
not explain the discrepancy in the case where the analysis was made with 
high S/N ratios. This means that the variation was produced by erratic 
estimation of the pit volume, rather than by the the fluctuation of the 
blank \text{CO}_2. Establishment of the method to accurately estimate the pit 
volume is important factor for micro-gas-analysis of glass inclusions.

\textbf{A-3. Preliminary experiments for low background level}

The background levels of \text{H}_2\text{O} and \text{CO}_2 of the present system were 
found comparable to the signals of the extracted gases from a single glass 
inclusion. High background levels of \text{H}_2\text{O} and \text{CO}_2 \text{ analyses and their} 
fluctuation have to be overcome. For reduction of the background level, 
additional experiments were attempted; baking of the gas purification 
unit for longer periods and at higher temperatures before sample 
analysis. Baking of the cell and flexible tubing was carried out 
overnight at 300 °C except for the gas purification and gas analysis units 
which were baked at 250°C. In addition to the baking procedure, the 
trap 1 was used as a cryopump. The water and carbon dioxide coming
from the cell and flexible tubing while baking were collected in the trap 1 with liquid nitrogen. After this procedure, the trap 1 was evacuated with heating at 250 °C. These procedures of baking and cryopump were able to reduce the background level of CO₂ to 0.02 ng. This CO₂ background was one tenth smaller than the minimum level without baking and cryopumping procedures. However the background level of H₂O was only a little smaller than the previous minimum level. This indicates that most of the H₂O background arises from the uranium furnace, not from water adsorbed onto the inner wall of the vacuum line.

The preliminary experiments suggest that it is necessary to make thorough baking of the vacuum line at 300 °C and that a cryopump close to the sample cell is very effective for reduction of the level of CO₂ background. Use of the uranium furnace has a disadvantage in that significant hydrogen background is produced from uranium furnace itself, although it has an advantage of avoiding the adsorption of H₂O on to the inner wall of the vacuum line during the H₂O analysis.