The solubility of carbon dioxide in rhyolitic melts: A quantitative FTIR study

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ABSTRACT

The solubility of CO₂ in rhyolite liquid has been determined using quantitative Fourier-transform infrared spectroscopy (FTIR). CO₂ saturation experiments were conducted along isotherms at 950 °C, 1050 °C, and 1150 °C at pressures between 500 and 6600 bars. The band at 2350 cm⁻¹, which represents the antisymmetric stretch of dissolved CO₂ molecules, was used for quantitative determinations of CO₂ concentration.

The isotherm at 1050 °C was investigated in greatest detail. Along this isotherm CO₂ solubility is ideal (in the Henrian sense) up to ≈ 2300 bars. Above this pressure deviations from ideality are prominent, with concentrations less than predicted by extrapolation of the linear form of Henry's Law. The effect of increasing temperature is to decrease the solubility of molecular CO₂. The water contents of these glasses were also monitored using the 3570 cm⁻¹ OH fundamental vibration. Maximum H₂O contents were 0.32 wt%.

The solubility of CO₂ in rhyolite has been modeled with a modified Henry's Law equation. The data were regressed to determine the partial molar volume (v = 33.04 ± 0.78 cm³/mol) and the heat of solution (Δh = -20.32 ± 3.18 kJ/mol) of dissolved CO₂ (reference T = 1323 K and P = 0 bars).

CO₂ diffusion profiles were present in several samples. The diffusion coefficient of CO₂ in rhyolite at 1050 °C was estimated in three samples to be 2.4 (±0.5) x 10⁻⁸ cm²/s, in close agreement with previous work.

A comparison of rhyolite and albite melts at low P and high T shows that the two compositions dissolve nearly identical amounts of molecular CO₂. This implies a CO₂ (molecular, hereafter Mol.) solubility mechanism that is comparable in both compositions. Divergence of CO₂(Mol.) solubility in albite and rhyolite at high P and low T is consistent with accentuated differences in melt structure at these conditions and differences in the sifting of CO₂(Mol.) at high CO₂ concentrations.

Infrared bands attributable to dissolved carbonate complexes were not detected. This is consistent with the general decrease in the ratio of CO₂⁻ to CO₂(Mol.) in the sequence basalt, andesite, rhyodacite, rhyolite observed in this study. Basalt dissolves CO₂ in the form of carbonate complexes, whereas rhyolite dissolves CO₂ in the molecular form. Somewhat more CO₂ dissolves in rhyolite than in basalt under similar conditions. The common contention that CO₂ is more soluble in mafic magmas than in more evolved compositions is incorrect.

INTRODUCTION

Magma genesis and evolution are often associated with a fluid phase in which CO₂ is an important component. This is particularly true of basaltic magmas, where CO₂ is generally the main component of the fluid phase (Dixon et al., 1988; Gerlach, 1986; Roedder, 1965). H₂O is an important volatile component in more silicic magmas, but CO₂ may be present in significant amounts and could play a critical role in the genesis, evolution, and eruption of high-silica magmas. The presence of CO₂ in silicic magmas has been confirmed by the analysis of melt inclusions trapped by phenocryst phases (Anderson et al., 1989; Sommer, 1977) and the analysis of obsidian fragments (Newman et al., 1988). Degassing, which accompanied the recent Mount Saint Helens eruptions, also indicates a significant fraction of CO₂ (1–10 mol%) in the magmatic fluid (Gerlach and Casadevall, 1986a, 1986b). Phase-equilibrium studies of the dacite pumice erupted from Mount Saint Helens on May 18, 1980 (Rutherford et al., 1985) and the Fish Canyon quartz latite (Johnson and Rutherford, 1989) are consistent with the magmas having been in equilibrium with an H₂O-CO₂ fluid. There is, therefore, ample evidence that CO₂ dissolves in silicic as well as basaltic magmas.

It is generally understood that CO₂ plays an important role in magmatic processes. Despite this recognition, current understanding of the physical and chemical effects
of CO₂ upon magma is still in its infancy. This appears to be an extension of the poor state of knowledge of the gaseous properties of CO₂, where the nonideality of CO₂ at high pressures and temperatures is still poorly known and the behavior of CO₂ in the presence of other magmatic fluid species is even less well understood.

With regard to magmatic evolution, the most important thermodynamic property of CO₂ is its solubility in silicate liquids. A detailed understanding of processes such as phase equilibrium, magma vesiculation, bubble growth, magma explosivity, and planetary atmospheric evolution all require reasonable estimates of CO₂ solubility. An understanding of CO₂ speciation within the silicate molecular structure is also of importance, as it leads to physically correct solution models and more accurate solubility predictions.

Although the significance of CO₂ solubility measurements has long been recognized, advances in this area were hindered by the lack of a reliable technique for measuring CO₂ concentrations. Most studies were consequently carried out at very high pressures (>10 kbar), where CO₂ solubility is appreciable, and the problems of CO₂ detection and analysis were less critical. Recently, Fine and Stolper (1985) made use of quantitative infrared spectroscopy (QIS) for determining CO₂ concentrations in liquid compositions of geological importance. QIS is a rapid, nondestructive technique that is capable of high spatial and compositional resolution. It has been used to study the solubility behavior of CO₂ in albite melt at 1450 °C-1625 °C and pressures of 15-30 kbar (Stolper et al., 1987), and the Henry's Law behavior of CO₂ in basaltic melt at 1200 °C and at pressures below 1500 bars (Stolper and Holloway, 1988).

The purpose of this study is to determine the solubility of CO₂ in rhyolite melt under a wide range of P and T. Our analytical method makes use of FTIR spectroscopy for determining both CO₂ solubility and speciation (molecular CO₂ vs. carbonate). Experiments were conducted at pressures between 500 and 6600 bars and at temperatures between 950 °C and 1150 °C. These experiments cover a pressure range that is governed by Henry's Law as well as higher pressure conditions where significant deviations from Henry's Law occur. The range in temperature allows extrapolation of the results to lower T as well as direct application to high-temperature rhyolitic volcanism. The temperature-pressure range investigated also allows a comparison of our work with that of Stolper and Holloway (1988) to address the common perception that CO₂ solubility is much greater in liquids of low silica activity (i.e., basalt), than liquids of high silica activity (i.e., rhyolite; e.g., Eggler and Rosenhauer, 1978; Carmichael et al., 1974).

### Experimental Techniques

#### Experimental procedure

Rhyolitic obsidian VNM50-15 from the Brown University collection was used in all experiments. VNM50-15 is an obsidian fragment from an unknown locality in the area of the Valles Caldera, New Mexico. It was chosen because its physical and chemical properties were ideal for this study. It is vitreous and free from vapor bubbles and silicate crystals (although occasional Fe-Ti oxide crystals are present). Its composition (Table 1) is similar to highly evolved rhyolites such as the Upper Bandelier Tuff (Fo- gel, 1989) and the Bishop Tuff (Anderson et al., 1989). Normalized to the granite ternary (quartz-albite-orthoclase), VNM50-15 falls close to the minimum melting point at 3000 bar for H₂O-saturated granite (Tuttle and Bowen, 1958). The H₂O content of VNM50-15 as determined by IR analyses is 1366 ± 67 ppm by weight (ppmw) based on six analyses on a sample ≈17 mm².

Rectangular chips of VNM50-15 glass were cut with a diamond saw, ground to a weight of between 50 and 150 mg, cleaned with water, rinsed in ethanol, and dried. Samples were weighed and placed in Ag₉₀Pd₁₀ tubes welded shut at the bottom. One chip was used per tube, the approximate dimensions of which were 2.5 × 2.5 × 5 mm. Silver oxide (Ag₂O) was added to the tube in an amount far in excess of that required to saturate the sample in CO₂. The tube was welded shut and tested for leaks by weighing the tube, heating to 112 °C for a few minutes, and then rapidly quenching in H₂O. Leakage of the tube was determined by weighing and checking for a H₂O weight gain.

Experiments were conducted in either TZM pressure vessels or an internally heated pressure vessel (IHPV). The TZM pressure vessels were used to investigate the low pressure region below 3000 bars and temperatures below 1100 °C. The internally heated pressure vessel was used for pressures greater than 3000 bars or temperatures in excess of 1100 °C. The pressurizing medium for both vessels was Ar. For the TZM experiments, pressure was measured on a bourdon tube Heise gauge (0-7000 bar) periodically calibrated at the factory. In the IHPV, experiments between 3000 and 6000 bars were measured on a THI transducer (0-6900 bar) calibrated at the factory. Experimental pressures in excess of 6000 bars were measured using a Harwood manganin cell (0-13800 bar).

#### Table 1. Electron microprobe analyses and CIPW norm of VNM50-15 starting material

<table>
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<th>Oxide</th>
<th>Wt%</th>
<th>α</th>
<th>CIPW Norm</th>
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<td>di</td>
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<tr>
<td>K₂O</td>
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</tr>
<tr>
<td>Total</td>
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Note: Electron microprobe analysis of starting material VNM50-15 along with its CIPW Norm. All Fe is calculated as FeO. Parentheses indicate one standard deviation (1σ) on six microprobe analyses. N.D. = not determined.
and Foxboro gauge calibrated at the factory. Both IHPV pressure measuring devices were periodically checked against the Heise gauge for internal consistency. Reported pressures are accurate to better than 0.5% of full scale values.

Temperature was controlled by Eurotherm temperature controllers accurate to within \( \pm 3 \) °C. In the IHPV experiments, the sample sat in a cylindrical Pt container, the walls of which are 1 mm thick. Pt-Pt,Rh measuring and controlling thermocouples were inserted into a hole in the bottom of this container. This platinum-block assembly was used to minimize temperature gradients across the sample. Temperatures are considered to be within \( \pm 5 \) °C of that recorded. The TZM assembly consisted of a TZM alloy pressure vessel with an external inconel sheath. The charge sat at the bottom of the vessel and graphite rods took up most of the excess volume so as to minimize convection. A few bars of Ar pressure were constantly applied between the pressure vessel and the sheath to prevent oxidation of the TZM. As a consequence of this type of assembly, temperatures within the pressure vessel could not be measured during the experiments; temperatures within the vessel were calibrated at 1 atm of Ar pressure against the temperature in the sheath wall. The reproducibility of this calibration is \( \pm 5 \) °C. Temperatures in the TZM vessels are thought to be accurate to better than \( \pm 10 \) °C.

IHPV experiments were quenched by turning the power off and rotating the vessel 90° to disturb its thermal stability. Quench rates were on the order of 100 °C/s for the first 2–3 s of the quench. The TZM experiments were quenched by removing the vessel from the furnace and quenching in H₂O. TZM quench rates were on the order of 2–3 °C/s and produced glasses indistinguishable from those produced using the IHPV. After the experiment, the samples were weighed to check for weight loss. Upon cutting of the noble metal container, an audible hiss verified the presence of a CO₂ vapor phase and the integrity of the capsule. Experimental glasses were also examined under a binocular microscope for vapor bubbles, the presence of which lends support for the existence of a vapor phase during the run.

Vapor bubbles were present in almost all samples. Generally, these were a few micrometers in diameter, but bubbles on the order of hundreds of micrometers were sometimes present. Vesiculation occurred predominantly along the margins of the sample, and an examination of glass exteriors showed vapor bubble indentations. Vapor bubbles within the sample were most often found along planes, suggesting that bubble formation occurred along preexisting cracks in the glass sample. These observations suggest that the presence of vapor bubbles is mainly due to the physical incorporation of CO₂ vapor rather than vesiculation of the liquid upon the quench.

**FTIR sample preparation and analytical technique**

After preliminary examination, experimental glasses were cut into wafers and ground in a slurry of alumina and H₂O. Samples were generally ground to thicknesses of 100–300 μm and were polished on two parallel sides with alumina either 0.3 or 0.05 μm in diameter. FTIR sections were then examined under a microscope and a detailed sketch of the section made. Section thicknesses were mapped using a Mitutoyo digital dial indicator with a precision of roughly \( \pm 3 \) μm. This mapping was necessary because of the difficulty in making sections of uniform thickness. The fine spatial resolution of the micro-FTIR puts added emphasis on accurately determining sample thickness. An average thickness may lead to erroneous concentration determinations when spatial resolution is on the order of tens of micrometers.

FTIR spectra were performed on the Brown University IBM Instruments Model IR-98 (IFS-113v) FTIR spectrometer. All samples were analyzed with the micro-FTIR attachment. The microscope is equipped with an objective lens of 15× magnification. A set of apertures ranging in size from 1200–300 μm provided spatial resolution from 80–20 μm, respectively. Samples were positioned over apertures on a sample-holder slide. This assembly was placed on the microscope stage, and an area free from vesicles was chosen for analyses. In a few cases where micrometer-sized bubbles could not be avoided, spectra were taken of several areas relatively free from bubbles, and the CO₂ concentration was shown to be independent of bubble density. Spectra were taken using a globar source, a KBr beamsplitter, a HgCdTe detector, resolution of 4 cm⁻¹, a mirror velocity of 0.396 cm/s and either 128, 256, or 512 scans.

**Quantitative IR spectroscopy**

Theory

The relationship between concentration and IR band intensity is given by the Beer-Lambert law:

\[
C = \frac{10^6 MW \cdot Abs}{\rho \cdot e \cdot d}
\]

where \( C \) is concentration in ppm by weight, \( MW \) is the molecular weight of the IR active component in g/mol (\( CO_2 = 44.01 \), \( H_2O = 18.02 \)), \( Abs \) is the band intensity in dimensionless absorbance units, \( \rho \) is sample density in g/L, \( e \) is the molar absorptivity or extinction coefficient of the IR band in L/(mol·cm), and \( d \) is the thickness of sample under the IR beam in cm.

\( Abs \) is measured from peak to baseline where the baseline is interpolated from the surrounding spectral range. Baseline interpolation is accomplished by drawing a line tangential to the baseline on both the high- and low-energy side of the band. In cases where silicate network vibrations overlap the band of interest or interfere with the smooth interpolation of baseline, spectral subtraction of a reference sample devoid of the absorbing species is used; the spectra of the reference being first normalized to the thickness of the unknown. Since the bands of interest in this study have smooth, noncomplicated backgrounds, spectral subtraction was not employed.
The density of VNM50-15 was measured using a 25 mL pycnometer. H_2O was used as the liquid-density medium, being first boiled and set to cool to 25 °C to eliminate dissolved O. A density of 997.05 g/L (Weast and Astle, 1981) was taken as the density of deionized H_2O at 25 °C to which the glass densities were referenced. The density of seven chips of VNM50-15 cumulatively weighing 0.89083 g was determined to be 2348 ± 10 g/L. All CO_2 solubility measurements were determined with this value. Incorporation of CO_2 into the experimental glasses was assumed to have a negligible effect on densities.

Since concentration is inversely proportional to sample thickness, analyses of an experimental sample at several thicknesses should retrieve the same total concentration. A Beer’s Law test was conducted measuring CO_2 concentration (from the band at 2350 cm⁻¹) as a function of thickness and found to retrieve the same value consistently. The measured relative standard deviation on the concentration was 4%.

Band assignments

An example of a typical FTIR spectrum of a CO_2-bearing rhyolite is shown in Figure 1. The spectral range of interest is the area between 5000 cm⁻¹ and 1000 cm⁻¹. Several bands are present in this spectral region, each of which will be discussed individually.

The bands at 1375 and 1610 cm⁻¹. Newman et al. (1986) and Stolper et al. (1985) have investigated the speciation of CO_2 along the join NaAlO_2-SiO_2 studying the NaAlSi_3O_8 (jadeite), NaAlSiO_4 (albite), and NaAlSi_3O_8 glass compositions. A single value for ε in 945 ± 45 L/mol·cm) was determined for all three compositions.

The band at 2350 cm⁻¹. This band represents the ν_3 antisymmetric stretch of dissolved CO_2 molecules (Fine and Stolper, 1985). It is a sharp narrow band that is often the dominant spectral feature for glasses with moderate to high CO_2 concentrations. Its extinction coefficient in sodium aluminosilicate melts has been determined by Fine and Stolper (1985). They investigated the speciation of CO_2 along the join NaAlO_2-SiO_2 and found that within the portion of the sodium-aluminosilicate join they investigated, ε was independent of SiO_2 content. The band at 2350 cm⁻¹ is used in this study as the principal band for the determination of CO_2 solubility in rhyolitic glasses.

The bands at 1600 and 1820 cm⁻¹. Newman et al. (1986) attributed these bands to aluminosilicate network vibrations. Their work involving rhyolitic compositions similar to that used in this study found these bands to correlate with H_2O content. This study shows no correlation of the intensity of these bands with CO_2 content. FTIR spectra of the compositional sequence basalt (49 wt% SiO_2), andesite (56 wt% SiO_2), rhyodacite (66 wt% SiO_2), and rhyolite (76 wt% SiO_2) show a clear growth of these bands. They are barely existent in basalt but grow in intensity and definition with increasing melt polymerization (SiO_2 content). Although most silicate network vibrations are present at energy levels below 1200 cm⁻¹, the combination of factors listed above tends to support the suggestion of Newman et al. (1986). We suggest, however, that because of the high energy levels of these bands, they may be combination or overtone bands of the aluminosilicate network.

The band at 2287 cm⁻¹. This band has been assigned to the ν_3 antisymmetric stretch of CO_2 molecules (Stolper et al., 1987; Fine and Stolper, 1985). It appears as a small band just off the shoulder of the high intensity band centered at 2350 cm⁻¹. Stolper et al. (1987) determined the extinction coefficient of this band (ε_{2287}) for molecular CO_2 in albite glass. Their value for ε_{2287} of 11.7 L/(mol·cm) was determined for the total CO_2 (Mol.) in albite melt instead of the molecular CO_2 it represents. At low CO_2 concentrations this band is not very intense, but it is generally useful for the determination of high CO_2 concentrations.

The bands at 1375 and 1610 cm⁻¹. The doublet bands centered on 1375 and 1610 cm⁻¹ are caused by the presence of dissolved carbonate (CO_3). CO_2 in the form of carbonate appears to be the dominant form of CO_2 solution in basalt, diopside, and akermanite melts (Fine and Stolper, 1986; Rai et al., 1983; Sharma et al. 1979). At high pressures, it has also been shown to be present in sodium aluminosilicate melts (Stolper et al., 1987; Fine and Stolper, 1985). Unpublished work from this laboratory shows it to be an important species in andesite melts.

The bands at 1375 and 1610 cm⁻¹. Stolper et al. (1987) determined the extinction coefficient of this band (ε_{1375}) for molecular CO_2 in albite glass. Their value for ε_{1375} of 11.7 L/(mol·cm) was determined for the total CO_2 (Mol.) in albite melt instead of the molecular CO_2 it represents. At low CO_2 concentrations this band is not very intense, but it is generally useful for the determination of high CO_2 concentrations.

Fig. 1. Typical FTIR spectrum of a CO_2-saturated experimental glass. Band assignments are indicated above the respective bands. The experimental glass (BF147) contains 2860 ppmw CO_2 and 1921 ppmw H_2O.
concentration. In addition, the composition NaAlSiO$_{10}$ in their study is roughly that of the albite-silica eutectic at 1 atm. The addition of orthoclase to the albite-silica system produces the granite ternary in which sample VNM50-15 projects with less than a 3% residual (Table 1). The combination of these factors suggests that the only influence, if any, on changing $\varepsilon_{2350}$ for rhyolitic compositions from that determined for the sodium-aluminosilicates is the substitution of K$_2$O for Na$_2$O in the silicate structure. The addition of minute amounts of FeO, MgO, MnO, TiO$_2$, and CaO that total to no more than 3% is unlikely to have an effect on $\varepsilon_{2350}$.

The broadly similar behavior of K$_2$O and Na$_2$O in silicate glasses and crystals as well as molecular similarities suggests that $\varepsilon_{2350}$ is little affected by the K$_2$O for Na$_2$O substitution. It is more intuitively satisfying, however, to note that the species under discussion is dissolved in the silicate melt in the molecular form—i.e., CO$_2$ appears to be trapped in holes in the melt and is not bonded to the aluminosilicate network. Although holes have potential fields, an alkali substitution is less likely to affect dissolved molecular species that would respond to changes in the size and shape of the holes they occupy than to affect species bonded to the network, which would respond to changes in composition and network structure. The extinction coefficients for the molecular and OH$^-$ forms of H$_2$O in albite (Silver and Stolper, 1989) and rhyolite (Newman et al., 1986) glasses support this idea. For rhyolite and albite glass, the extinction coefficients for OH$^-$ (4500 cm$^{-1}$) are 1.73 and 1.13 L/(mol·cm), whereas the extinction coefficients for the bands representing molecular H$_2$O are 1630 cm$^{-1}$ = 55 and 49 L/(mol·cm) and 5200 cm$^{-1}$ = 1.61 and 1.67 L/(mol·cm), respectively.

Ultimately, the value of the extinction coefficient used in the Beer-Lambert Law affects only the magnitude of CO$_2$ solubility. The ratio of two glasses of constant density with concentrations $C_1$ and $C_2$ yields

$$\frac{C_1}{C_2} = \frac{Abs_1/d_1}{Abs_2/d_2},$$

(2)

demonstrating that CO$_2$ concentrations determined relative to each other are not dependent upon $\varepsilon$ and can be used with confidence. If indeed $\varepsilon_{2350}$ is shown to be significantly different in rhyolite than in albite glass, absolute CO$_2$ concentrations can be reetermined with the Beer-Lambert law and the updated value of $\varepsilon_{2350}$.

The band at 3570 cm$^{-1}$. The fundamental OH$^-$ stretching vibration produces this broad band (Stolper 1982a). H$_2$O in the form of both H$_2$O(Mol.) and OH$^-$ contributes to the intensity of this band. It is highly asymmetric with the maximum peak intensity occurring around 3570 cm$^{-1}$. This band is used in this study as the fundamental band for the determination of H$_2$O contents of the experimental glasses. Since total H$_2$O contents of experimental samples in this study were less than 0.32 wt% and bands attributable solely to molecular H$_2$O (5200 cm$^{-1}$ and 1620 cm$^{-1}$) were not detected, the H$_2$O contents represented by the band at 3570 cm$^{-1}$ represent only OH$^-$ groups. The extinction coefficient in rhyolitic glasses for low H$_2$O contents representing only OH$^-$ groups is 88 ± 2 L/(mol·cm) (Dobson et al., 1989).

The band at 3710 cm$^{-1}$. Stolper et al. (1987) attributed this band to a combination of the $\nu_1$ and $\nu_2$ modes of $^{13}$CO$_2$. It is a low intensity band off the high energy shoulder of the OH$^-$ band at 3570 cm$^{-1}$. The extinction coefficient, $\varepsilon_{3710}$, was determined in their study to be 13.9 L/(mol·cm) in albite glass.

The band at 4500 cm$^{-1}$. This band was assigned to the combination mode of Si-OH groups by Stolper (1982a). Newman et al. (1986) determined a value of 1.73 L/(mol·cm) for $\varepsilon_{4500}$ in rhyolite glass. At low H$_2$O contents this band supplies the same information as does the band at 3570 cm$^{-1}$; the latter is used in this study because it is more intense.

The band at 4700 cm$^{-1}$. This band appears to be correlated to total CO$_2$ concentration. It is absent in the VNM50-15 starting material. At high CO$_2$ concentrations it appears as a roughly symmetric, narrow band beginning only a few wavenumbers from the high energy baseline of the 4500 cm$^{-1}$ band. To our knowledge this band has not been identified in IR spectra of geological melts. We tentatively assign it to the first overtone of the $^{12}$CO$_2$ band at 2350 cm$^{-1}$.

Evaluation of uncertainty

Precision. The Beer-Lambert law describes the relationships among species concentration, band intensity, density, and sample thickness. The effect of the uncertainty in each of these variables contributes to the cumulative analytical precision. An uncertainty of ±3 μm was assigned to the measured thickness, and a standard deviation of ±10 g/L was determined for the density measurements. To find the standard deviation $(\sigma)$ of band-intensity measurements, 12 spectra were taken on the same spot of sample BF-153C. A band intensity of 1.5032 was determined for the CO$_2$ peak at 2350 cm$^{-1}$ with an absolute standard deviation of ±0.0145 or a relative standard deviation of ±0.96%. Considering only the uncertainty in band intensity, these measurements translate into a CO$_2$ concentration of 2867 ± 28 ppmw. The precision of measured intensity is even better for the H$_2$O band at 3570 cm$^{-1}$, where for the 12 spectra an average band intensity of 0.21809 was determined with an absolute standard deviation of ±0.00152 or a relative standard deviation of 0.70%. This translates into an H$_2$O content of 1829 ± 13 ppmw.

If the uncertainty assigned to the thickness is treated as a standard deviation, this value along with the standard deviation in measured absorbance and density can be used to evaluate a total precision for measured concentration. For all the experimental samples, the result is a precision between 1.3 and 3.2% for CO$_2$ and the precision on measured H$_2$O is essentially the same. The factors affecting precision in order of decreasing importance
are thickness, density, and absorbance; although the relative uncertainty in thickness changes dramatically with sample thickness. It is assumed that the uncertainties in measured absorbance of all other samples are identical to BF-153C. Although this is surely a simplification, it is probably a good approximation for most of the measured concentration range. Spectra of samples taken weeks apart fall within this range of precision.

**Accuracy.** The accuracy of these FTIR concentration measurements is difficult to evaluate. Contributing factors are the uncertainty in the extinction coefficient, sample heterogeneity, and the lack of suitable CO₂ standards of similar composition. The lack of rhyolite standards is a problem that cannot be addressed at this time, although if they were available, the current research would probably not be needed. As far as sample heterogeneity is concerned, almost all major heterogeneities were attributable to diffusion gradients. The procedure for determining equilibrium composition, including a more detailed description of sample heterogeneities, is outlined below (see Kinetics of CO₂ Solubility). Nevertheless, seven analyses were taken at seven places near the rim of sample BF-153 with sample thicknesses ranging from 97 to 106 μm. An average concentration of CO₂ at 2607 ± 92 ppmw (3.5%) and of H₂O at 1877 ± 68 ppmw (3.6%) was obtained. This is comparable to the standard deviation determined for multiple spot analyses of homogeneous samples.

The extinction coefficient of the band at 2350 cm⁻¹ has been assigned a value of 945 ± 45 L/(mol·cm) (Fine and Stolper, 1985). If the arguments presented previously for use of this extinction coefficient with rhyolitic composition are accepted, the accuracy of CO₂ concentrations due to the uncertainty in ε₂₃₅₀ is quantifiable. The ±45 L/(mol·cm) uncertainty in ε₂₃₅₀ is a standard error (Stolper et al., 1987). Conversion into standard deviation yields an absolute standard deviation of ±201 L/(mol·cm) or a relative standard deviation of ±21%. Similarly, the relative standard deviation of measured H₂O content resulting from the uncertainty in ε₂₃₅₀ is ±1% (Dobson et al., 1989).

### Experimental results

**The data.** Results of CO₂-rhyolite experiments tabulated for each isotherm are presented in Table 2. The isotherm at 1050 °C was the most extensively studied and gives the most detailed information on both the Henry’s Law region and the nonideal (in the Henrian sense) region. The isotherms at 950 °C and 1150 °C are most useful in delineating the effects of temperature on CO₂ solubility. In the diagrams that follow CO₂ concentrations are reported in ppm mole fraction (ppmm) or ppm weight fraction (ppmw). Fugacities of CO₂ were calculated with the hard-sphere modified Redlich-Kwong (HSMRK) equation of state of Kerrick and Jacobs (1981).

**Henry’s Law and nonideal regions.** The portion of the 1050 °C isotherm adhering to Henry’s Law is shown in Figure 2, where CO₂ concentration is plotted against f(CO₂) for experiments up to 3.5 kbar. The figure shows a highly correlated linear trend between f(CO₂) and dissolved CO₂ up to an f(CO₂) of roughly 3550 bars (P

### Table 2. Experimental results

<table>
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<tr>
<th>Experiment no.</th>
<th>Duration (h)</th>
<th>P (bars)</th>
<th>f(CO₂) (bars)</th>
<th>d (μm)</th>
<th>Abs (2350 cm⁻¹)</th>
<th>CO₂ (ppmm)</th>
<th>CO₂ (ppmw)</th>
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*Note: All concentrations calculated with a density of 2348 g/L.
* Calculated from the HSMRK equation of state (see text).
** d = thickness.
† T = TZM, I = HPV.
‡ Not included in thermodynamic calculations.
Fig. 2. Solubility of CO₂ in rhyolite melt as a function of \( f_{\text{CO}_2} \) for the low pressure region along the isotherm at 1050 °C. \( X_{\text{CO}_2} \) and \( W_{\text{CO}_2} \) are the mole and weight fractions of CO₂ in the melt in ppm, respectively. Error bars are 5% uncertainty encompassing precision of analyses and homogeneity. At low \( f_{\text{CO}_2} \), CO₂ solubility follows the linear form of Henry’s Law. This is shown on the diagram by a straight line going through the region that behaves ideally.

\( \approx 2050 \) bars). The first evidence of nonideality appears in the experiment with an \( f_{\text{CO}_2} \) of 4977 bars (\( P = 2490 \) bars), indicating that nonideality begins between 2050 and 2490 bars total pressure.

The nonideal region of CO₂ solubility is clearly distinguishable at pressures greater than \( \approx 2500 \) bars (\( f_{\text{CO}_2} \approx 5000 \) bars). This is shown in Figure 3, where \( f_{\text{CO}_2} \) is plotted against ppm CO₂ for the entire experimental pressure range. For the temperatures of this study, the overall pressure dependence is roughly linear at low \( P \) and somewhat less than the linear prediction at high \( P \) (Fig. 4).

The experiments confirm a decrease in CO₂ solubility with increasing temperature. This is portrayed in Figures 3 and 4, where \( f_{\text{CO}_2} \) and \( P \) vs. ppm CO₂ are contoured for temperature, respectively. This effect is similar to that observed for molecular CO₂ solubility in albite glass as determined by IR spectroscopy (Stolper et al., 1987). Sharma (1979) also reported a negative correlation between \( T \) and CO₂ solubility (in the form of CO₃⁻) in diopside and sodium melilitite glasses using relative carbonate solubility as determined by Raman spectroscopy.

**CO₂ solubility and H₂O concentration**

The H₂O concentrations of all experimental glasses produced in this study are low, ranging from 500 to 3200 ppmw. There appears to be a positive correlation between CO₂ and H₂O concentration (Fig. 5); however, the highest H₂O contents on the isotherm at 1050 °C may be partly caused by the crystallization of feldspar in two experiments. BF-145 and BF-148, the two highest \( P \) experiments, contain \( \approx 5 \) and 20% crystals concentrated on the
Fluid phase composition

As previously mentioned, the H₂O contents of the glasses indicate that the fluid phase contained only very small amounts of H₂O. It is possible, however, that conditions within the noble metal capsule were too reducing and produced substantial CO as well as CO₂. Several factors lead us to believe this was not a problem. First, some of the experimental glasses contained large bubbles of trapped fluid. FTIR spectra of these bubbles (accompanied by a computer-normalized subtracted spectra of a bubble-free portion of the glass) show a peak for gaseous CO. In contrast, spectra of bubbles in experimental rhyolitic glasses encapsulated with graphite and silver oxalate contain a peak centered about 2160 cm⁻¹ that we attribute to gaseous CO. This suggests the relative absence of substantial gaseous CO in the vapor phase of the CO₂ solubility experiments. Second, if f_{H₂O} conditions within the charge had been too low, graphite would have precipitated. Graphite has not been observed in any of our experimental products. Additionally, graphite-C-O fluid equilibria constrain the maximum amount of CO possibly present within the capsule. Figure 6 is a plot of the mol% CO₂ of the fluid in equilibrium with graphite for the three isotherms investigated in this study. Fluids in the graphite-C-O system become richer in CO₂ with increasing P and decreasing T. As illustrated, most of the experiments at 1050 °C have a minimum allowable molar CO₂ content of the gas in excess of 70%. Since graphite has not been found in any of the CO₂ solubility experiments, Figure 6 gives a minimum estimate of the concentration of CO₂ in the experimental fluids.

Kinetics of CO₂ solubility

With few exceptions, experimental glasses were removed from the capsules in the exact shape they were cut. This undoubtedly resulted from the very high viscosity of the rhyolitic melt. This observation implies that, other than mixing caused by vapor bubble infiltration, very little mixing of the melt occurred during the experiment and that the primary mechanism of equilibration was diffusion.

Many of the glasses from experiments of short duration contained diffusion profiles. Most experiment durations
TABLE 3. CO₂ diffusion in rhyolite at 1050 °C

<table>
<thead>
<tr>
<th>Experiment</th>
<th>P (bar)</th>
<th>t (s)</th>
<th>Rim CO₂ (ppm)</th>
<th>Core CO₂ (ppm)</th>
<th>a (cm)</th>
<th>Dtld</th>
<th>Log₁₀ D</th>
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<td></td>
<td></td>
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<td></td>
<td>-7.63</td>
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</table>

Note: Core and rim concentrations of CO₂ and relevant parameters for calculation of the diffusion coefficient of CO₂ in rhyolitic melt. Melt geometry is assumed to approximate a cylinder. The distance between measured rim and core concentrations = a, the duration of the experiment = t, and the dimensionless parameter Dtld is taken from Crank (1985).

Table 3 gives core and rim CO₂ concentrations of three experiments and other relevant information required for the calculation of $D_{1050°C}$; the diffusion coefficient of CO₂ in rhyolite at 1050 °C. The average value of $D_{1050°C}$ for the three experiments is $2.4 (±0.5) \times 10^{-4}$ cm²/s. These values compare favorably with that of Watson et al. (1982) for diffusion of CO₂ into a sodium aluminosilicate of composition 60% SiO₂, 30% Na₂O and 10% Al₂O₃ by weight. Their expression for $D$, uncorrected for pressure (negligible at P-T discussed here) yields $5.6 \times 10^{-4}$ cm²/s. In view of the approximations made to retrieve $D_{1050°C}$, the agreement between the two studies is excellent.

**Thermodynamics of CO₂ Solubility**

**Henry's Law solubility**

At extreme levels of dilution, the solubility of a volatile component within a liquid obeys Henry's Law. For the solubility of CO₂ in rhyolite liquid at constant $T$ it is given as

$$f_{CO₂} = X_{CO₂} \cdot k_H$$

where $f_{CO₂}$ is the fugacity of CO₂ in bars, $X_{CO₂}$ is the mole fraction of CO₂ in the liquid, and $k_H$ is the Henry's Law constant. This equation expresses a linear relationship between CO₂ solubility and fugacity. Figure 2 shows that CO₂ solubility in rhyolite obeys this law up to approximately 2300 bars total pressure; however, some concavity is apparent and results from the effect of pressure (see below). The Henry's Law constant determined with a least-squares regression of the data between 0 and 2000 bars for the isotherm at 1050 °C is $k_H = 1.393 (±0.074) \times 10^6$ bar.

Above 2300 bars the linear form of Henry's Law (Eq. 3) is no longer applicable and must be modified to account for the effect of pressure. This is accomplished with the thermodynamic equality

$$\left( \frac{\partial \ln f_{CO₂}}{\partial P} \right)_{P,X} = \frac{\tilde{v}}{RT}$$

(4)

to obtain the Krichevsky-Kasarnovsky equation (Prausnitz et al., 1986):
where $k_h$ is the Henry’s Law constant at reference pressure $P_r$, and $\bar{v}$ is the partial molar volume at infinite dilution of CO$_2$ in the liquid. Similarly, the following thermodynamic equality is used to modify Henry’s Law to account for changes in temperature:

$$\ln \left( \frac{f_{CO_2}}{X_{CO_2}} \right) = \ln k_h + \frac{\nu(P - P_r)}{RT}$$

(5)

where $h$ and $\bar{h}$ are the molar enthalpy of CO$_2$ in the ideal gas state and the partial molar enthalpy of CO$_2$ in rhyolite, respectively. Henry’s Law is then given by the expression:

$$\ln \left( \frac{f_{CO_2}}{X_{CO_2}} \right) = \ln k_h + \frac{\nu(P - P_r)}{RT} + \frac{h \ln (1 - \frac{1}{T})}{RT^2}$$

(6)

and can be rearranged to yield:

$$X_{CO_2} = \frac{f_{CO_2}}{k_h(P_r, T)} \exp \left[-\frac{\nu(P - P_r)}{RT} - \frac{\Delta h}{R} \left(1 - \frac{1}{T} \right)\right]$$

(7)

where $\Delta h$ is the heat of solution of CO$_2$ given by $\bar{h} - h$ at $P_r$ and $k_h(P_r, T)$ is the Henry’s Law constant at $P_r$ and $T_r$. At reference $P$ and $T$, $k_h$ is simply equal to $f_{CO_2}(P_r, T_r)/X_{CO_2}(P_r, T_r)$, making Equation 8 identical with that used by Stolper et al. (1987) for CO$_2$ solubility in albite melt.

Although the choice of $P$, $T$, and $T_r$ is somewhat arbitrary, there are factors that influence their selection. We select $P_r = 0$ for the following reasons: First, Prausnitz et al. (1986) pointed out that as $X_{CO_2} \to 0$, $P$ tends toward $P^*$, the saturation vapor pressure of the solvent. If we set $P_r = P^*$, Equation 8 is made more intuitively satisfying and directly expresses the functionality of the solubility process; the direct correlation of CO$_2$ solubility with $P$ in excess of $P^*$. The value of $P^*$ for rhyolite melt is unknown but is assumed to be close to 0 bars. Second, the selection of reference $P$ only affects the Henry’s Law constant and the enthalpy of solution. The partial molar volume of CO$_2$ in the melt is not affected by this selection. Although two of the constants change with $P$, the correlation coefficient, or the goodness of fit, does not change. $T_r$ was selected as 1323 K since the isotherm at 1050°C was investigated most thoroughly. For details and comments on the regression process see Appendix 1.

**Thermodynamic results**

Table 4 gives the values determined for $k_h$, $\nu$, and $\Delta h$. The uncertainties given are the standard error of the estimates. The partial molar volume at infinite dilution is determined to be 33.04 ± 0.78 cm$^3$/mol. This compares favorably with the work of Spera and Bergman (1980), who used the data of Mysen et al. (1976) and Mysen (1976) to determine the partial molar volume of CO$_2$ in albite, jadeite, and nepheline glasses to be 35–30 cm$^3$/mol. These partial molar volumes are not directly comparable since, in addition to being of different composition, the glasses were produced at high $T$ and $P$ ($1460°C < T < 1620°C$ and 10 kbar $< P < 30$ kbar), and contained large fractions of CO$_2$ dissolved as carbonate. A further complication is that the validity of the data presented by Mysen et al. (1976) has been called into question. Stolper et al. (1987) indicated problems with the experimental and analytical techniques of Mysen et al. (1976). The experiments of Mysen et al. (1976) were also shown to be inconsistent in the determination of CO$_2$ and CO$_3^-$ in albite with the Stolper et al. (1987) IR measurements. The partial molar volume presented here diverges somewhat from that of Stolper et al. (1987), who determined a value of 28.6 cm$^3$/mol for CO$_2$ in albite melt. This value was determined with a regression through their data obtained in roughly the same $P$ and $T$ range as that of Mysen et al. (1976) and using the same analytical techniques as that used in this study.

One of the assumptions of the CO$_2$ solubility model is that $\nu$ is not a function of $P$. Krichevsky and Kasarnovsky (1935) suggested that $\nu$ may follow a simple relation with $P$ such as

$$\nu = \nu^0 - \beta P$$

(9)

where $\nu^0$ is the partial molar volume at 0 pressure and $\beta$ is the coefficient of compressibility. Incorporation of this expression did little to improve the model and verified the initial assumption of the constancy of $\nu$ with $P$.

Strictly speaking, the use of oxide mole fraction as the basis for calculating CO$_2$ concentration implies within the context of the solution model that all oxide components mix ideally in the melt. Although this implicit assumption is probably incorrect, the use of a more reasonable model does not significantly change the thermodynamic results. In accordance with the model of Stolper et al. (1987), the melt can be envisioned as an ideal mixture of O atoms, molecular CO$_2$, and carbonate molecules. Since carbonate complexes were not detected in this study,
CO\textsuperscript{3−} need not be included; however, H\textsubscript{2}O in the form of OH\textsuperscript{−} ions should be included. This model assumes that melt O atoms, and molecular CO\textsubscript{2} molecules are each indistinguishable and that, in addition, OH\textsuperscript{−} ions are indistinguishable and mix ideally with both melt O atoms and CO\textsubscript{2} molecules. Stolper et al. (1987) pointed out some drawbacks of these assumptions, one of which is that in actuality there are probably many types of distinguishable O atoms in the melt. The advantage of this type of model is that the number of components is diminished, making the ideal mixing assumption more realistic.

\( X_{CO2} \) was recalculated on this new basis by first putting all the melt-oxide components (excluding CO\textsubscript{2}) on an equal O basis (multiplying the moles of each melt-oxide component by \( r \), where \( r \) is the number of O atoms in the component, e.g., 2 for SiO\textsubscript{2}, 3 for Al\textsubscript{2}O\textsubscript{3}). One half of the moles of H\textsubscript{2}O (representing OH\textsuperscript{−}) was subtracted from the total moles of melt O atoms (Stolper, 1982b). The mole fraction of CO\textsubscript{2} was then recalculated and the model parameters redetermined. These are given in Table 4 along with the first set of parameters. A comparison of the two parameter sets shows that \( \varphi \) and \( \Delta h \) are so slightly affected by this coordinate change that the standard errors of the two sets overlap. The main change is in the Henry’s constant, which nearly doubles. From a mathematical perspective the differences in the parameter sets are straightforward. The basis change of components mainly affects the magnitude of \( X_{CO2} \), whereas the variation of \( X_{CO2} \) with changes in \( P \) and \( T \) remains unaffected. It is the exponential term that controls these progressions, implying that the two data sets should give approximately the same \( \varphi \) and \( \Delta h \). The Henry’s constant, however, is defined by \( f_{CO2}(P, T)/X_{CO2}(P, T) \) and should be directly affected by changes in component selection. With the case at hand, recasting of the oxide components on an equal O basis results in a decrease in \( X_{CO2} \), which demands an increase in \( k_{in} \). From a thermodynamic standpoint, the Henry’s constant is directly related to the activity coefficient of the component, and activity coefficients must change with changes in basis components.

Equation 8 makes use of the \( f_{CO2} \) as well as the solubility data reported in Table 2 to determine the thermodynamic constants \( k_{in}, \varphi, \) and \( \Delta h \). Obviously then, the least-squares values determined for these constants depend upon the correct determination of \( f_{CO2} \), as well as the solubility data. Although the HSMRK equation of state (EOS) of Kerrick and Jacobs (1981) was used for this purpose, it is important to investigate the effects of a different \( f_{CO2} \) on the thermodynamic constants. For this purpose we redetermined \( k_{in}, \varphi, \) and \( \Delta h \) using the \( f_{CO2} \) calculated with the Modified Redlich Kwong (MRK) equation of state of Holloway (1977). These results (Table 3) show that the three constants are somewhat different, although not radically, from those calculated previously. Interestingly, \( \varphi \) (30.4 cm\textsuperscript{3}/mol) is now much closer to \( \varphi \) in albite (28.6 cm\textsuperscript{3}/mol) and results from the fact that the latter was determined with the MRK EOS (Stolper et al., 1987). The HSMRK model is considered to retrieve \( f_{CO2} \) values superior to those obtained from the MRK model; Kerrick and Jacobs (1981) compared the two models.

Two other points concerning the use of this model are pertinent to this discussion. First, since different equations of state yield different \( f_{CO2} \) and, hence, different CO\textsubscript{2} solubility constants, the use of Equation 8 is restricted to CO\textsubscript{2} solubility determinations with either one of these equations of state. Use of Equation 8 with \( f_{CO2} \) determined with a third EOS may yield erroneous CO\textsubscript{2} solubilities. The solubility constants must be redetermined when the EOS of the fluid is changed because different fugacities are obtained from different equations of state. This situation exists because the lack of accurate \( PVT \) data at high \( P \) and \( T \) for CO\textsubscript{2} necessitates the use of an EOS with extrapolation capabilities. Second, since it is difficult to place an error on the \( f_{CO2} \) calculations, the reported uncertainties on the model constants do not reflect errors in \( f_{CO2} \).

**DISCUSSION**

The absence of carbonate

The lack of detectable CO\textsuperscript{3−} species in CO\textsubscript{2}-saturated rhyolite glasses at pressures of up to 6.6 kbar is consistent with a trend of a decreasing ratio of CO\textsuperscript{3−} to CO\textsubscript{2}(Mol.) with increasing silica activity (\( a_{SiO2} \)) observed by Fine and Stolper (1985) for glasses along the NaAl\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} join. Unpublished data from this laboratory on basalt, andesite, and rhyodacite melts equilibrated with a graphite-CO\textsubscript{2} fluid show the same relationship between CO\textsuperscript{3−}/CO\textsubscript{2}(Mol.) and activity of silica (\( a_{SiO2} \)). The basaltic glasses contain dissolved carbonate with no detectable CO\textsuperscript{3−}(Mol.), whereas the andesite and rhyodacite contain both CO\textsuperscript{3−} and molecular CO\textsubscript{2}, with the latter increasing at the expense of the former in the more evolved liquids.

Because the basalt-rhyolite petrogenetic sequence involves numerous chemical trends, it is uncertain whether the apparent correlation between \( a_{SiO2} \) and CO\textsuperscript{3−}/CO\textsubscript{2}(Mol.) simply masks a more direct correlation of other cations such as Na\textsuperscript{+} and Ca\textsuperscript{2+} with CO\textsuperscript{3−}/CO\textsubscript{2}(Mol.). The speciation data for the sodium-aluminosilicate system (Fine and Stolper, 1985) are also ambiguous in this respect, since the correlation of decreased CO\textsuperscript{3−}/CO\textsubscript{2}(Mol.) with increased SiO\textsubscript{2} activity demonstrated in this system could equally well be due to decreases in Na\textsubscript{2}O, Al\textsubscript{2}O\textsubscript{3}, or NaAl\textsubscript{2}O\textsubscript{5} activity.

The ratio of CO\textsuperscript{3−} to CO\textsubscript{2}(Mol.) may also be a function of the competition between CO\textsuperscript{3−} and Al\textsuperscript{3+} for charge balancing cations such as Na\textsuperscript{+} (Brearley and Monta, 1989). If this paradigm is correct, it suggests that the ratio of CO\textsuperscript{3−} to CO\textsubscript{2}(Mol.) is sensitive to the agpaitic index \( K^* (K_2O + Na_2O/Al_2O_3) \) of the melt. For \( K^* < 1 \) (peraluminous region) aluminum is in excess of alkalis, a condition that favors low ratios of CO\textsuperscript{3−} to CO\textsubscript{2}(Mol.) because of stiff competition between CO\textsuperscript{3−} and Al\textsuperscript{3+} for charge-balancing cations. When \( K^* \) is greater than unity (peralkaline region), charge-balancing alkalis are in excess of aluminum, implying higher ratios of CO\textsuperscript{3−} to CO\textsubscript{2}(Mol.)
resulting from free alkali cations not used by Al\(^{3+}\) for charge balancing. This idea is supported by the CO\(_2\) solubility data in the system Na\(_2\)O-SiO\(_2\) (Eitel and Weyl, 1932), which show high concentrations of CO\(_2\) in solution at low pressures (8 wt% at 1250 atm and 1100 °C) in sodium-metasilicate glasses. The dominant form of CO\(_2\) in these glasses is presumably carbonate and can reasonably be attributed to the absence of aluminum (K* = ∞) which frees up Na for complex formation. This reasoning suggests that measurable quantities of carbonate would be present in peralkaline rhyolites of high K*.

Irrespective of the mechanism, these observations clearly indicate that the forward reactions in the equilibria

\[
\begin{align*}
\text{CO}_3^{2-} & \rightarrow \text{CO}_2(\text{Mol.}) + \text{O}_2^{2-} \quad (10) \\
\text{O}_2^{2-} + \text{CO}_3^{2-} & \rightarrow \text{CO}_2(\text{Mol.}) + 2\text{O}_2^{2-} \quad (11)
\end{align*}
\]

are favored with progressive evolution in the basalt-rhyolite petrogenetic sequence. [O\(^{2-}\), O\(^{2-}\), and O\(^{-}\) represent bridging, nonbridging, and free melt O atoms, respectively (Hess, 1980).]

The experiments presented here were all carried out at pressures below 6.6 kbar. We have no doubt that carbonate is present in these experimental glasses; albeit at levels below FTIR detection (roughly 50–100 ppmw for the techniques presented here). A progressive increase in pressure above 6.6 kbar should eventually bring carbonate levels above IR detectability limits. This contention is supported by the data of Fine and Stolper (1985), which indicate the presence of carbonate in CO\(_2\)-undersaturated experiments on Na\(_2\)Si\(_2\)O\(_6\) glass at 25 kbar.

**Rhyolite vs. albite**

A comparison of CO\(_2\) solubility in rhyolite and albite melts sheds some light on the solubility mechanism of CO\(_2\) (Mol.) in silicate melts. Figure 7 shows the solubility of CO\(_2\) (Mol.) in albite and rhyolite as a function of P contoured for T. The solution model of Stolper et al. (1987) was used to extrapolate their high P-T data down to the regions of this study. (CO\(_2\) concentrations are compared on an equal O basis.) The CO\(_2\) (Mol.) solubility in the two compositions is remarkably similar; no significant departures exist up to 5 kbar. Departures in CO\(_2\) (Mol.) solubility between the two compositions become more acute with decreasing T and increasing P. Interestingly, total CO\(_2\) solubility in albite is only slightly higher than CO\(_2\) (Mol.) solubility, with CO\(_2\)\(^{-}\) composing only 2–3 mol% of total CO\(_2\) at these pressures and temperatures.

The uniformity of CO\(_2\) (Mol.) solubility in rhyolite and albite melt at low pressures implies a similar, if not identical, solubility mechanism in the two compositions. This is probably the result of similarities in rhyolite and albite melt structures. Although rhyolite is more SiO\(_2\)-rich than albite, as far as CO\(_2\) (Mol.) solubility is concerned the basic melt structures are the same. This is supported by the data of Taylor and Brown (1979), who determined the radial distribution functions (RDF) for albite, anorthite, and orthoclase glasses and compared them with the RDF of pure SiO\(_2\) glass. They showed that the RDF of albite and orthoclase melts are quite similar to SiO\(_2\) melt, indicating that their basic melt structures are comparable. Rhyolite should also share this basic melt structure, since it falls within the SiO\(_2\)-Na\(_2\)Si\(_2\)O\(_6\)-KAl\(_2\)Si\(_3\)O\(_8\) system.

The similarity in albite and rhyolite CO\(_2\) solubility suggests that molecular CO\(_2\) occupies the same sites in the two melts and that the solution mechanisms for these sites are comparable. Deviations from this behavior would be expected at high P and low T, conditions that tend to accentuate differences between melt structures and could lead to differences in solubility. This is exactly what is predicted for the two compositions (Fig. 7). These deviations could also be attributed to increased CO\(_2\) (Mol.) solubility at high P and low T. At high CO\(_2\) (Mol.) melt concentrations the siting of CO\(_2\) (Mol.) may differ in the two compositions, manifesting itself as differences in solubility.

**Rhyolite vs. basalt**

The data presented here and those of Stolper and Holloway (1988) can be used to compare the relative solubilities of CO\(_2\) in rhyolite and basalt. The solubility of CO\(_2\) in basalt at 1200 °C and 1000 and 1500 bars of total CO\(_2\) gas pressure is 390 and 577 ppmw, respectively (Stolper and Holloway, 1988). This translates into 565 and 836 ppmw. With the solubility model presented here, the corresponding CO\(_2\) solubility in rhyolite is 731 and 1100 ppmw, respectively. This contrast between CO\(_2\) solubility in basalt and rhyolite is shown in Figure 8, where...
CO₂ solubility is plotted against \( P_{\text{CO}_2} \) for 1200 °C. This demonstrates that on a molar basis \( \text{CO}_2 \) solubility in rhyolite is somewhat greater than in basalt, a situation that is true on a weight percent basis as well. Considering the uncertainty in the two data sets, the solubility of CO₂ in basalt and rhyolite is, at the least, comparable.

The comparison of CO₂ solubility data for basaltic and rhyolitic melts (Fig. 8) illustrates the two main differences in the behavior of CO₂ in these diverse liquids. First, the difference in CO₂ solubility between rhyolite and basalt is manifested in its mode of speciation. At low pressure, CO₂ dissolves in basalt as carbonate, whereas in rhyolite it dissolves in the molecular form. Second, the solubility of CO₂ in rhyolite is comparable to and somewhat greater than that in basalt at the same \( P \) and \( T \). This demonstrates that the decrease in silica activity between rhyolite and basalt does not cause an increase in CO₂ solubility. This contrasts with the conclusions of many workers that CO₂ solubility decreases with increasing silica content (Eggler and Rosenhauer, 1978; Holloway et al., 1976; Mysen et al., 1976; Carmichael et al., 1974; Eggler, 1973).

We reach this conclusion in spite of the conflict with some earlier works since (1) our analytical technique for rhyolite solubility is essentially identical to that of Stolper and Holloway (1988), who made the latest basalt solubility measurements, (2) the new data are based upon measured CO₂ concentrations and not implied from phase equilibria or other information, and (3) the accuracy of beta track autoradiography for CO₂ concentration measurements (Tingle and Aines, 1988) casts doubt on conclusions based upon data generated by this technique (e.g., Mysen et al., 1976). At this time, however, we can only make this comparison between basalt and rhyolite at pressures below 1500 bars.

**Application to rhyolitic volcanism**

The experimental data reported in this study is to our knowledge the first low-pressure solubility data for CO₂ in rhyolite melts. With the aid of the CO₂ solubility model, it is possible to extrapolate the results of this study to temperatures of rhyolitic volcanism in order to make estimates of magmatic CO₂ concentrations. The model can also be inverted to retrieve intensive parameters from known concentrations of CO₂ in rhyolite melt.

Our CO₂ solubility data have great potential for deciphering the evolution of rhyolitic magmas if the volatile contents of melt inclusions can be determined. In this vein, the relationship describing CO₂ solubility as a function of \( T \) and \( P \) is quite significant. The relationship between \( P_{\text{CO}_2} \) and CO₂ concentration is roughly linear at low \( P \) (Fig. 4). An a priori knowledge of magmatic \( P_{\text{CO}_2} \) and CO₂ concentration can yield magmatic \( T \); however, a very accurate estimate of \( P \) would be required since the magnitude of the CO₂ solubility temperature effect is not large (Fig. 4). Unfortunately, magmatic \( P \) is rarely known with such accuracy. Conversely, knowledge of magmatic \( T \) and CO₂ concentration can yield \( P \). Although the effect of \( T \) on CO₂ solubility is not drastic, it is still sufficiently great to require temperature estimates of high quality. Figure 9 shows the relationship between \( X_{\text{CO}_2} \) (Melt) and temperature as a function of \( P \). At high \( T \) and low \( P \) (\( \partial X_{\text{CO}_2}/\partial T \)) is close to 0. At moderate to high \( P \) and low \( T \) (\( \partial X_{\text{CO}_2}/\partial T \)) is quite significant.
The fluid phase associated with rhyolitic magmatism usually contains a large, if not dominant, fraction of H$_2$O. At a given $P$ and $T$ H$_2$O will dissolve preferentially to CO$_2$ in rhyolite melt. The heterogeneous equilibria between fluid and magma with respect to CO$_2$ and H$_2$O are:

$$\text{CO}_2(\text{fluid}) = \text{CO}_2(\text{Mol.})(\text{melt})$$

$$\text{H}_2\text{O}(\text{fluid}) = \text{H}_2\text{O}(\text{Mol.})(\text{melt})$$

and the homogeneous equilibria within the melt are:

$$\text{CO}_2(\text{Mol.}) + \text{O}^{2-}(\text{melt}) = \text{CO}_3^-$$

$$\text{H}_2\text{O}(\text{Mol.}) + \text{O}^{2-}(\text{melt}) = 2\text{OH}^-.$$ 

The two basic unknowns in the formulation of these equilibria are the extent of ideality of CO$_2$-H$_2$O mixing in the fluid phase, and the effect of dissolved H$_2$O and CO$_2$ on their mutual solubilities in the silicate melt. The lack of thermochemical data on CO$_2$-H$_2$O fluid mixtures at high $P$ and $T$ necessitates reliance on the predictive capacities of reasonably formulated equations of state. The HSMRK EOS of Kerrick and Jacobs (1981) predicts an extreme degree of nonideality between mixtures of these two gases. For small $X_{\text{CO}_2}$ the activity coefficient of CO$_2$ is predicted to be quite high. The same is true for the activity coefficient of H$_2$O for small $X_{\text{H}_2\text{O}}$. This further complicates the situation since CO$_2$ can reach high degrees of dilution ($X_{\text{CO}_2} < X_{\text{H}_2\text{O}}$) at magmatic conditions.

Currently, there is no consensus as to the effects of dissolved CO$_2$ and H$_2$O on their mutual solubilities in silicate melts. As a first approximation these effects can be assumed to be negligible. In actuality, since total dissolved CO$_2$ is quite low, both in an absolute sense as well as relative to H$_2$O, it is more likely that the effects of H$_2$O upon CO$_2$ will be more profound than the effects of CO$_2$ upon H$_2$O.

The solubility model describes the behavior of CO$_2$ solubility in rhyolite for all coexisting fluid-phase compositions that contain CO$_2$. When the fluid phase is pure CO$_2$, the solubility of CO$_2$ in rhyolite follows the behavior described by the model lines, shown as a function of $P$, $T$, and $f_{\text{CO}_2}$ in the preceding diagrams. When the fluid phase is a mixture of CO$_2$ and some other species, CO$_2$ does not follow these curves. At constant $T$ and $P$ Equation 8 simplifies to

$$X_{\text{CO}_2} = \frac{f_{\text{CO}_2}}{k_0(P, T)}$$

where $k_0(P, T)$ is the Henry's constant at the specific $P$ and $T$ of interest and is given by

$$k_0(P, T) = k_0(P, T)\exp\left[\frac{\delta h(P - P_s)}{RT} + \frac{\Delta h}{R}\left(\frac{1}{T} - \frac{1}{T_s}\right)\right].$$

$X_{\text{CO}_2}$ is linear with changes in $f_{\text{CO}_2}$ with the slope equal to $1/k_0(P, T)$. At constant $T$ and $P$, the dilution of CO$_2$ fluid with another fluid species causes $f_{\text{CO}_2}$ to be lowered and in a strict sense is given by

$$f_{\text{CO}_2}^{\text{Mix}} = a_{\text{CO}_2}f_{\text{CO}_2}^{\text{pure}}$$

where $a_{\text{CO}_2}$ is the activity of CO$_2$ in the fluid phase; thus, the accuracy of CO$_2$ solubility predictions under mixed fluid conditions is severely constrained by our ability to determine $a_{\text{CO}_2}$. The replacement of $a_{\text{CO}_2}^{\text{pure}}$ with $X_{\text{CO}_2}^{\text{pure}}$ as in the ideal mixing rule of Lewis and Randall can lead to questionable results.

The above discussion is illustrated in Figure 10, where both the CO$_2$ saturation curve and the 3 kbar CO$_2$ mixing line are plotted as a function of $f_{\text{CO}_2}$ for $T = 700$ °C. At these conditions the dilution of fluid CO$_2$ with another fluid species such as H$_2$O displaces CO$_2$ contents down along the 3 kbar mixing line and not along the pure CO$_2$ saturation curve. Assuming ideal mixing, the predicted CO$_2$ solubility of a fluid containing 30% CO$_2$-70% H$_2$O (mol%) is 1316 ppm (point I: $f_{\text{CO}_2}^{\text{pure}} = 2384$ bars). Assuming HSMRK behavior for the same fluid composition, the predicted CO$_2$ solubility would be 1594 ppm (point R: $f_{\text{CO}_2}^{\text{pure}} = 2887$ bars) or 21% higher. The disparity becomes even greater with decreasing $X_{\text{CO}_2}$, increasing $P$, and decreasing $T$. Of course, the HSMRK EOS uses empirical mixing rules, and as such adds an element of uncertainty to these calculations. Additionally, if the solubility of H$_2$O affects the activity coefficient of CO$_2$ in the melt, the 3 kbar mixing line is distorted and would no
longer accurately represent CO₂ mixing conditions at 3 kbar. Clearly, the extent of ideality of the fluid mixing properties is a crucial element in the determination of CO₂ solubility under mixed volatile conditions and is a major consideration in the application of volatile solubility estimates to determine magmatic intensive parameters.

CONCLUSIONS

1. CO₂ solubility in rhyolite at 1050 °C follows a linear Henry’s Law behavior to pressures of ~2300 bars. Above this pressure CO₂ solubility rapidly becomes nonideal and deviates from the linear form of Henry’s Law.

2. Results of experiments along the 950 °C, 1050 °C, and 1150 °C isotherms show a decrease in CO₂ solubility with increasing temperature.

3. H₂O concentrations below 0.32 wt% do not affect the speciation of CO₂ in rhyolite melt. A positive correlation between CO₂ solubility and H₂O content cannot be ruled out; however, the lack of fH₂O control during the experiments, including other factors, makes this correlation suspect.

4. The diffusion of CO₂ into rhyolite appears to be the main mechanism for CO₂(fluid)-rhyolite equilibration. Diffusion of CO₂ into rhyolite is slow; the diffusion coefficient at 1050 °C is ≈2.4 (±0.5) × 10⁻⁸ cm²/s.

5. CO₂ solubility data can be described by an extended Henry’s Law model that considers the effects of pressure and temperature. These are related to the partial molar volume at infinite dilution and the heat of solution of molecular CO₂ in rhyolite melt. The values of v and Δh were determined to be 33.04 ± 0.78 cm³ and −20.32 ± 3.18 kJ/mol, respectively.

6. CO₂ dissolves in rhyolite melt in the molecular form; CO₂⁺ was not detected in any of the experimental products. This observation follows the general trend of an increasing ratio of CO₂(Mol.) to CO₂ in the sequence basalt, andesite, rhyodacite, rhyolite, with basalt showing no detectable molecular CO₂.

7. CO₂(Mol.) solubility in rhyolite and albite appear to be identical at low P and high T. This implies a similar solubility mechanism in the two compositions. Divergence of CO₂(Mol.) solubility in albite and rhyolite at high P and low T is consistent with accentuated differences in melt structure at these conditions and differences in the siting of CO₂(Mol.) at high CO₂ concentrations.

8. A comparison of CO₂ solubility in rhyolite and basalt at low pressures and 1200 °C shows that CO₂ is somewhat more soluble in rhyolite than in basalt. Solubility differences between the two magma types are primarily differences in speciation: CO₂ dissolves in basalt as carbonate complexes and in rhyolite as molecular CO₂.

9. CO₂ solubility data, along with H₂O solubility data and T estimates, can be used to make magmatic intensive parameter estimates from melt inclusion volatile determinations. For a given P and T, if rhyolite is in equilibrium with a CO₂ fluid mixture, CO₂ solubility is described by a cord extending from 0 solubility at fCO₂ = 0 bars to the pure CO₂ saturation surface on an XCO₂=fCO₂ diagram. The solubility is found along this cord by determining the correct fCO₂ of the fluid mixture.

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Equation 7 is the linearized form of Equation 8 and could serve as the basis for a linear least-squares regression of ln(f_{CO₂}/X_{CO₂}) vs. P for the entire data set in a manner similar to that used by Spera and Bergman (1980). The problem with this technique is the difficulty in fitting the data in the low pressure region, since the quantity ln(f_{CO₂}/X_{CO₂}) is quite sensitive to small errors in X_{CO₂}. Deviations from linearity are accentuated in this region, and since the low pressure region is an end point of the ln(f_{CO₂}/X_{CO₂}) vs. P line, it has a dominating effect upon the regression. This leads to a poor correlation of all the data and an underestimation of the partial molar volume term. In point of


**APPENDIX I. LEAST-SQUARES REGRESSION**

The experimental data were fitted to Equation 8 with the SAS procedure NLIN, a nonlinear least-squares routine (since Equation 8 is nonlinear) allowing constants kₙ, P, and ΔH to vary so as to produce optimized values. P, and T, could have been chosen to be one of the experimental conditions and kₙ determined as f_{CO₂}/X_{CO₂} from the data, a procedure that forces the least-squares regression through the reference conditions. Considering the error associated with any one point, or even a series of experimental points, leads to the conclusion that this type of fitting process does not produced optimum results.

Equation 7 is the linearized form of Equation 8 and could serve as the basis for a linear least-squares regression of ln(f_{CO₂}/X_{CO₂}) vs. P for the entire data set in a manner similar to that used by Spera and Bergman (1980). The problem with this technique is the difficulty in fitting the data in the low pressure region, since the quantity ln(f_{CO₂}/X_{CO₂}) is quite sensitive to small errors in X_{CO₂}. Deviations from linearity are accentuated in this region, and since the low pressure region is an end point of the ln(f_{CO₂}/X_{CO₂}) vs. P line, it has a dominating effect upon the regression. This leads to a poor correlation of all the data and an underestimation of the partial molar volume term. In point of