

VOLCANISM ON MARS: EXPERIMENTS ON CO₂ SOLUBILITY IN SILICIC MAGMAS.

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Introduction: The driving force for explosive eruptions is now well recognized as largely coming from the exsolution of a fluid phase from the ascending magma (1, 2). Explosive volcanism occurs widely on Earth, primarily in the case of more evolved magmas, but explosive eruption of basalt is not uncommon. Recent studies of surface features on Mars have documented extensive basaltic volcanism (3, 4) but rhyolitic lava flows (5) silicic domes (6) and explosive volcanism deposits (7) have also been tentatively identified. H₂O and CO₂ are the most abundant magmatic volatiles on Earth. Available data from atmospheric measurements, surface geomorphology and sample analyses suggest that these two species are also the most abundant on Mars, although the present H₂O/CO₂ ratio appears to be much lower than it was earlier in Mars history. The initial volatile content and extent of degassing is not known, but clearly Mars volcanism was accompanied by an H₂O-CO₂ fluid.

The data that is most crucial to understanding the effect of a volatile species on the physical and chemical processes involved in terrestrial planet volcanism is its solubility in magma. The solubility of CO₂ has been determined in several types of melts, however, the reliability of certain analytical methods has been called into question (8). Quantitative FTIR spectroscopy is a reliable, reproducible and non-destructive method that has recently been applied to melts of geological importance.

Experimental Technique: In order to understand the role of CO₂ in silicic volcanism, we have conducted experiments on a natural rhyolite obsidian (76 wt%) from the Valles Caldera, New Mexico area. Experiments were performed in both an internally heated pressure vessel and in TZM bombs using Ar as the pressurizing medium. The experimental run conditions ranged from 500 to 6600 bars and 950°C to 1150°C. Run times were generally greater than 2 days. Experimental run products were cut and doubly polished for FTIR analyses. FTIR spectra were obtained on the Brown University IBM Instruments IFS 100 FTIR. These spectra were obtained using a globar source, HgCdTe detector, 4 cm⁻¹ resolution and between 128-512 scans. The 1050°C isotherm was determined most completely so that both the ideal (in the Henrian sense) and non-ideal portions of the solubility curve could be studied in detail.

Results: CO₂ was found to dissolve solely in the molecular form in the rhyolite melt. No IR peaks attributable to carbonate ions were found. This lack of dissolved carbonate ion follows the trend of decreasing carbonate to molecular CO₂ ratio with increasing silica content found by (9). This same trend has been found in this lab for the petrogenetic sequence basalt, andesite, rhyodacite, rhyolite. Basalts dissolve CO₂ in the form of carbonate, andesite and rhyodacite contain both molecular CO₂ and carbonate ion and rhyolite contains only molecular CO₂.

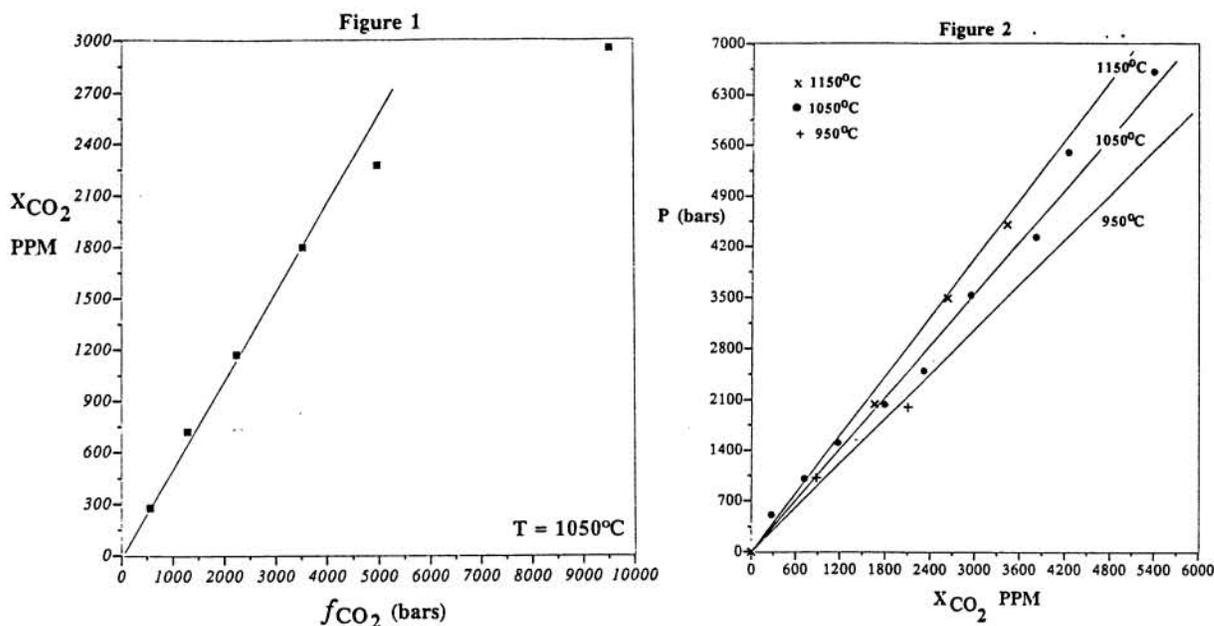
The molecular CO₂ peak centered about 2350 cm⁻¹ was used as the primary IR peak for the determination of dissolved CO₂. The extinction coefficient (ϵ) of 945 L/(cm²mol) determined by Fine and Stolper (1985) for glasses along the NaAlO₂-SiO₂ join was used. The use of this value is justified by the invariance of ϵ with SiO₂ content found in their study, the similarity of the cations Na and K, and the low concentrations of cations other than Na, K, Al and Si in the rhyolite (FeO + CaO + MgO + MnO < 1.5 wt %).

The solubility of CO₂ in rhyolite ranges from 188 ppmw at 504 bars to 3,711 ppmw at 6,612 bars. Two distinct regions of CO₂ solubility can be discerned. Figure 1 is a plot of mole fraction CO₂ (ppm) in the melt versus CO₂ fugacity for the low pressure experiments at 1050°C. Between f CO₂ of 0 and 3500 bars (P=0-2000 bars) CO₂ solubility obeys the linear form of Henry's Law (f CO₂=XCO₂H where H is the Henry's Law constant). For the 1050°C isotherm, the Henry's Law constant is 1.94 x 10⁸ bar. Experiments conducted above P=2000 bars show a strong deviation from Henry's Law linearity. This is shown at high f CO₂ in Figure 1, and is confirmed by additional experiments as high as 43 kbars f CO₂.

Figure 2 is a plot of P versus mole fraction CO₂ (ppm) for the entire pressure range, contoured for T. CO₂ solubility is roughly linear with P over the 6600 bar range. With increasing T there is a decrease in CO₂ solubility. This negative temperature dependence of molecular CO₂ solubility has also been found in albite melts by (10).

A comparison of CO₂ solubility in basalt (11) with that shown here shows that CO₂ solubility is somewhat greater in rhyolite than in basalt (on a wt % and mole % basis). This is contrary to that which has generally been assumed. These data show that the most significant difference between CO₂ solubility in these two liquids is the mode of speciation. Whereas CO₂ dissolves in basalt solely in the carbonate form, in rhyolite it dissolves exclusively in the molecular form.

The solubility of CO₂ at saturation is small at these pressures (<10 kbars) relative to that of H₂O, and therefore its potential as a physical driving force for explosive volcanic eruptions is much less than water. Furthermore, sufficient experiments have been done to recognize that small amounts of H₂O are not likely to affect the CO₂ dissolved in these melts. All samples initially contained 1300 ppmw H₂O and the final H₂O concentration ranged from 988 to 2,758 ppmw. In contrast, the role of CO on CO₂ solubility in rhyolite melts remains unclear. The results of these experiments is a new understanding of the role of C-O species in silicate melts, and if natural glass samples become available (melt inclusions), estimates of f_{CO_2} could be made for volcanic source magmas.



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