

## A low-pressure–high-temperature technique for the piston-cylinder

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### ABSTRACT

A method for conducting successful low pressure (0.3–0.5 GPa) and high temperature (900–1200 °C) experiments in the 19 mm piston-cylinder is presented. The technique is capable of running high fluid/melt experiments with minimum hydrogen loss, attaining precise, reproducible pressures ( $\pm 10\%$ ), and has fast initial quench rates ( $>150$  °C/s). These abilities are invaluable when conducting low pressure, fluid-saturated experiments such as phase equilibria, volatile solubility, and dynamic degassing experiments that are relevant to sub-volcanic magma chamber processes. A double capsule construction is also described that uses a solid oxygen buffer, and minimizes both contamination of the sample by carbon and the loss of iron in the melt to the capsule walls.

**Keywords:** Piston-cylinder, volatile, solubility, experiment, calibration, fluid, carbon dioxide, H<sub>2</sub>O

### INTRODUCTION

The piston-cylinder (PC) technique has been in use in the experimental petrology community for nearly fifty years. Many studies have proven the capability of this apparatus and shown that it is well suited for experiments in the 0.5 to 2.5 GPa pressure range (e.g., Boyd and England 1960; Johannes et al. 1971; Holloway and Wood 1988). Its use, however, at pressures lower than 0.5 GPa has been questioned (e.g., Nelson and Montana 1992) due to assembly failure and the specter of friction and its effect on the translation of the measured hydraulic oil pressure to the actual experimental pressure felt by the sample.

Given these difficulties, the success of any low-pressure assembly design rests not only on the ability to successfully reach certain *P-T* conditions without assembly failure, but also on the accurate calibration between hydraulic oil pressure and the actual sample pressure. Achieving such a calibration, however, is problematic as there are few appropriate calibrants available to consider. Although the melting curves of various salts are well known and can be used (Clark 1959; Bohlen 1984) for this purpose, their melting points are low relative to the temperatures of interest for silicate melts, making them a poor choice. Also, because of these relatively low temperatures, there can be significant uncertainty in determining melting due to small temperature gradients within the assembly, and contaminants such as H<sub>2</sub>O can also introduce error. Solid-state reactions in systems such as the pure SiO<sub>2</sub> and aluminosilicate system (kyanite-sillimanite-andalusite) are also potential calibrants, but they are famously plagued by slow kinetics (e.g., Bohlen and Boettcher 1982) induced by their composition and their relatively low temperature (compared to igneous temperatures) of transformation. More recently, Baker (2004) has used the H<sub>2</sub>O-albite liquid solubility relations measured and empirically modeled by Behrens et

al. (2001) to calibrate pressure between 400 and 500 MPa in a non-end-loaded piston-cylinder apparatus. This study has shown the potential to successfully use solid media apparatus such as piston-cylinders at low pressure, although the presence of carbon contamination of the fluid-melt system from the graphite furnace (Brooker et al. 1998) was not assessed in their study (i.e., a pure H<sub>2</sub>O fluid was assumed), and no runs at high temperature ( $>800$  °C) below 392 MPa were attempted (Baker 2004).

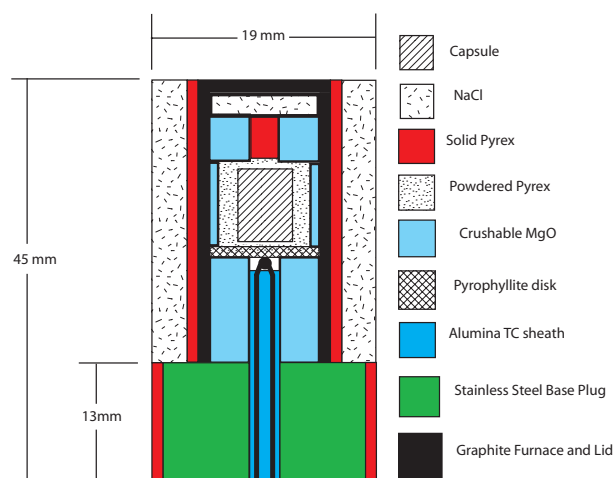
We present here a sample assembly and modified run method for use with the piston-cylinder at pressures as low as 300 MPa, and show the results of a calibration study using mixed CO<sub>2</sub>-H<sub>2</sub>O fluid solubility in rhyolite melt. A double-capsule technique, using a Pt outer capsule with an Au80-Pd20 alloy inner capsule, is also discussed that minimizes carbon contamination from the graphite furnace. The capsule design also allows the use of a solid oxygen buffer, as well as minimizing the loss of Fe from the inner capsule melt to the capsule wall. Mass balance constraints are also discussed that indicate no significant loss of any volatile component (H<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub>, O<sub>2</sub>) from the sample capsule assembly at high (1200 °C) temperatures.

### EXPERIMENTAL SAMPLE ASSEMBLY

The low-pressure 19 mm piston-cylinder assembly is shown in Figure 1. Overall, it is very similar to the high-pressure design (e.g., Holloway and Wood 1988), but has several modifications that address the two main concerns of running at low pressures: the effect of friction leading to a non-hydrostatic pressure within the sample assembly, and thermocouple and/or furnace failure.

Similar to the high-pressure assembly, use of a pyrex sleeve between the graphite furnace and the outer NaCl cell is necessary to reach temperatures higher than  $\sim 800$  °C (Holloway and Wood 1988). Crushable MgO is also used as the main support material within the furnace. A thin-walled sleeve of crushable MgO ceramic is placed around the sample capsule, with powdered pyrex packed between the MgO sleeve and the capsule. The MgO ceramic sleeve is necessary to provide support of the furnace during compression and minimizes furnace failures due to localized deformation due to the compression of the powdered pyrex placed around the sample capsule. The powdered pyrex is used as it provides a softer support medium around the capsule, and is easier to remove from the outer capsule walls after the run than crushable MgO or alumina. This is a desirable feature as it allows easier

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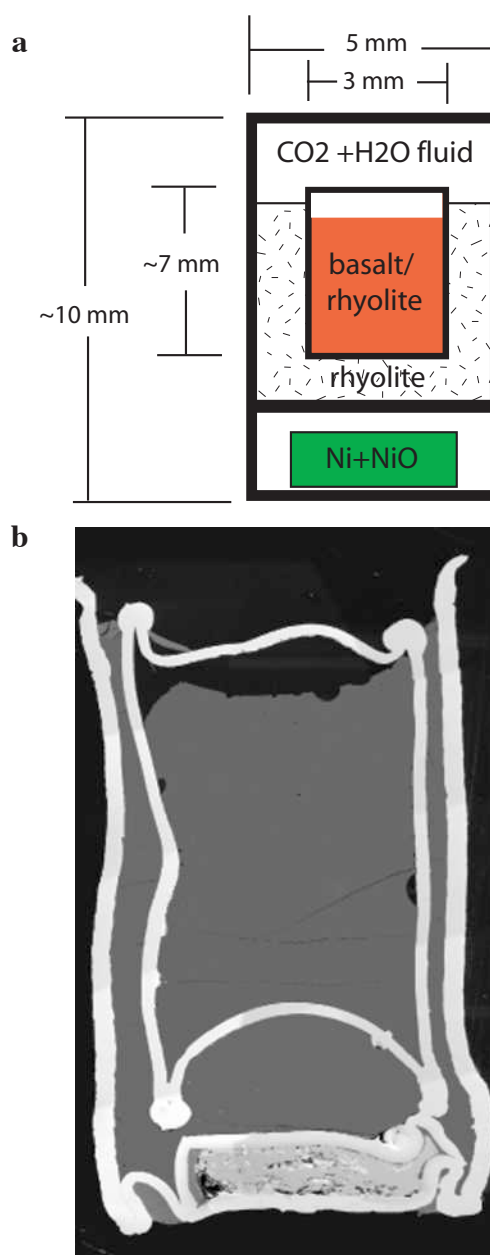
**FIGURE 1.** Schematic cross section of 19 mm experimental assembly for the piston-cylinder.

cleaning of the sample capsule after the run, and facilitates a more accurate post-run weight determination. The presence of soft borosilicate glass (pyrex) around the capsule at run temperature also allows the capsule to more easily stretch and deform, minimizing capsule failures in fluid-rich experiments where there is significant volume change during the initial run-up to final pressure and temperature. A borosilicate glass plug is also placed inside of an MgO sleeve above the capsule. This is done again to minimize the contact of the Pt capsule with the MgO, and to fill a hole in the drilled MgO ceramic rod. An unfired disk of pyrophyllite is also placed underneath the capsule to prevent contact of the capsule with the crushable MgO, and to aid in preventing diffusive hydrogen loss during the run.

We discovered that in runs where the thermocouple failed at low pressures, the failure was caused by flow of softer assembly material (e.g., MgO or pyrex) into the open space present within the hard four-hole alumina thermocouple sheath. The flowing material ultimately sheared the thermocouple wire and thereby broke the thermocouple circuit. By vacuum-impregnating the four-hole alumina thermocouple sheath containing the W-Re thermocouple wire with a slurry of fine-grained alumina cement (Zircar Type AL-R/H) and water and then subsequently drying at  $\sim 60^\circ\text{C}$  prior to placement in the assembly, we have essentially eliminated thermocouple failure of this type. As this type of failure is rare at higher pressures (500 MPa and greater) we attribute it to the low-pressure conditions not deforming the assembly at low temperature (i.e., prior to heating) enough to effectively “seal” the thermocouple wire and prevent the softer ceramics from flowing into the open space present in the harder four hole alumina thermocouple sheath.

### Capsule design

The majority of rhyolite glass run products used in this study were taken from the outer capsule portion of a double-capsule design consisting of an inner capsule made from Au80-Pd20 alloy (3 mm O.D.) and an outer capsule (5 mm O.D.) made of platinum (Fig. 2). Both capsules are of the cylindrical “trash-can” design. The inner capsule usually contained 25 to 45 mg of a basaltic composition plus fluid (for a mixed-volatile solubility study, the results of which will be published later).  $\text{H}_2\text{O}$  was added as distilled water, and  $\text{H}_2\text{O}$  and  $\text{CO}_2$  were added as oxalic acid dihydrate. The outer capsule contained 80 to 100 mg of Los Posos rhyolite (Shaw 1963) plus mixed volatiles. The final fluid composition was varied from capsule to capsule by changing the ratio of added  $\text{H}_2\text{O}$  to oxalic acid. For the most  $\text{CO}_2$  rich fluids, only oxalic acid was added and in an amount to achieve a low fluid to rock ratio, and thus a low  $X_{\text{H}_2\text{O}}$  (fluid) value. A Ni-NiO solid oxygen buffer was also placed in the bottom portion of the outer capsule and physically separated from the rhyolite melt by a formed platinum disk (Fig. 3). Several runs, designed specifically for this study, included samples where both the inner and outer capsule contained rhyolite and differing fluid compositions (e.g., LoPcal-10, LoPcal-11, and LoPcal-22; see Table 1), and that effectively resulted in two calibration points for each run (i.e., both the inner and outer capsules contained rhyolite with a different  $\text{H}_2\text{O-CO}_2$  fluid composition).



**FIGURE 2.** (a) Schematic of double capsule design. (b) Back-scattered electron micrograph of double capsule design containing rhyolite in the inner and outer capsule, with a Ni-NiO buffer at the base.

### Experimental conditions, technique, and analysis

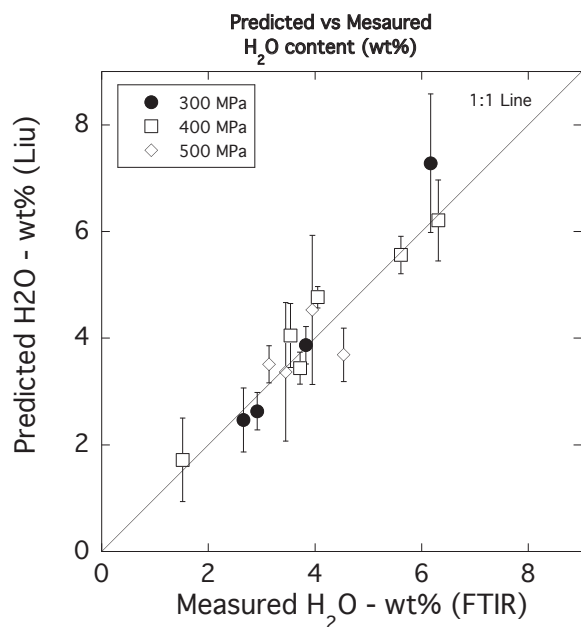
Experiments were conducted between 1080 and 1200  $^\circ\text{C}$ , and 0.3 to 0.5 GPa (Table 1) using a non-end-loaded piston cylinder with a 127 mm ram and a 19 mm piston. Both the piston and cylinder were lubricated with a thin film of molybdenum disulfide based, high-temperature grease, rather than using a thin Pb-foil wrapped around the assembly. All run temperatures were measured using a crossed wire (i.e., unwelded) C-type (W5Re-W26Re) thermocouple placed at the base of the sample capsule. Temperature was measured and controlled using an Omega CN-76000 PID controller in conjunction with an SCR-modulated power supply. Given the low-pressure conditions, no pressure correction to the e.m.f. of the thermocouple was applied. Oil pressures were measured using a Heise gauge precise to  $\pm 50$  psi. The  $P$ - $T$  path to final conditions consisted of applying  $\sim 100$  MPa of pressure at ambient temperature,

**TABLE 1.** Experimental conditions and analytical results

Run no.	$T$ (°C)	P-MPa Oil pressure	Run duration hours	Added H <sub>2</sub> O mg	Added Oxalic acid mg	Added Rhyolite mg	Measured H <sub>2</sub> O (fluid) μmol	Measured CO <sub>2</sub> (fluid) μmol	X <sub>H<sub>2</sub>O</sub> (fluid)	Fluid mass difference mg	Dissolved H <sub>2</sub> O Rhyolite wt%
LoPcal-10 outer	1100	300	24	0	5.5	91.1	36.54	102.45	0.26 (0.10)	0.23	2.7
LoPcal-10 inner	1100	300	24	7.4	0	69.0	25.58	0	1.0 (0.15)	-0.06	6.2
LoPcal-11 outer	1100	350	46	0	6.0	104.8	36.88	102.35	0.26 (0.05)	-0.17	2.9
LoPcal-11 inner	1100	350	46	2.1	3.3	49.4	45.80	58.46	0.57 (0.05)	-0.50*	3.8
R-72	1200	415	24	1.2	2.6	76.7	36.62	47.09	0.44 (0.07)	-0.03	3.5
R-90	1200	400	24	0	7.4	79.5	65.48	111.49	0.37 (0.04)	0.12	3.7
R-91	1200	412	24	0	4.3	91.2	116.18	69.99	0.62 (0.04)	0.03	5.6
RLC-2	1150	440	24	8.1	0	100.9	62.67	31.66	0.66 (0.08)	-1.35*	6.3
RLC-7	1080	410	26	0	5.6	112.4	12.25	86.07	0.12 (0.10)	-0.63*	1.5
R28-3	1200	397	24	5.1	9.9	77.2	184.29	157.88	0.54 (0.02)	0.14	4.0
R-82	1200	510	24	1.9	5.2	84.1	58.50	112.96	0.34 (0.04)	0.48*	3.1
R-95	1200	510	24	2.9	5.5	63.4	41.76	72.95	0.36 (0.06)	0.54*	4.5
LoPcal-22 outer	1100	500	24	1.6	6.0	86.8	8.11	10.30	0.44 (0.25)	-0.10	4.0
LoPcal-22 inner	1100	500	24	1.7	2.4	52.5	16.32	36.84	0.31 (0.15)	-0.01	3.5

Notes: Pressure calculated from the nominal oil pressure using a 44.44 multiplier based on ratio of radii of the ram and piston. One sigma error is given in parentheses for X<sub>H<sub>2</sub>O</sub> (fluid) based on ±10 μmol precision in the manometric technique and the total mass of fluid recovered from the capsule. Fluid mass difference is the measured weight loss after fluid extraction minus the calculated weight of the total fluid recovered.

\* Runs where a small amount of glass from capsule was lost during fluid manometry procedure.



**FIGURE 3.** Predicted vs. measured H<sub>2</sub>O contents in rhyolitic glass. Predicted values calculated from empirical expression of Liu et al. (2005). Error bars estimated from error in the fluid manometry measurements. Note lack of variation from 1:1 line associated with pressure.

with subsequent heating to ~250 °C. This was then followed by incremental pressure increases of ~50–100 MPa with continuous temperature increase until the final temperature and pressure is reached. The approach to final  $P$ - $T$  conditions is always such that a hot piston-in situation is created. Run durations are between 24 and 48 h, depending on the goal of the run (i.e., solubility determination, phase equilibria, or pressure calibration). All runs were isobarically quenched (i.e., the oil pressure was held constant during cooling), with an initial quench rate of >150 °C/s.

After quench, the run assembly was extracted from the PC, and the double capsule recovered. The capsule was cleaned of as much residual pyrex and ceramic as possible by physical removal from the outer walls of the platinum capsule. If a large amount of this material was not removable and remained attached to the capsule, it was submerged in HF acid for up to 15 min. Once cleaned, the capsule was weighed to check against its pre-run weight. If the capsule did not leak (i.e., lose significant mass) during the course of the run, the outer capsule fluid composition was determined by puncturing the capsule in a vacuum line, with the CO<sub>2</sub>

and H<sub>2</sub>O amounts being measured by manometry. After this step, the outer capsule is peeled away from the inner capsule, recovering both the inner capsule and the rhyolite glass that surrounds it. The inner capsule is then weighed and the excess fluid measured in a similar manner to that of the outer capsule.

### Fluid manometry technique

All capsules were pierced under a static vacuum using a modified version of a standard Teflon bore stopcock, where the tip of the Teflon bore was removed and replaced with a tungsten electrode that had been sharpened to a point. The capsules were placed in a glass sleeve and pierced on end with the pointed tungsten electrode. All condensable gases were then cryogenically separated with a series of cold traps. A dry ice/isopropanol slush bath (−68 °C) was used to collect the water fraction while the remaining carbon dioxide was collected with a liquid nitrogen trap. Any non-condensable gases were noted and then pumped away. The number of moles of carbon dioxide was then measured using a mercury u-tube manometer. The remaining water was reduced over hot uranium and the resulting hydrogen measured using a calibrated Toepler pump. The resulting fluid compositions for all capsules are reported in terms of micromoles of H<sub>2</sub>O and CO<sub>2</sub>, with the mole fraction of H<sub>2</sub>O also given, in Table 1. The estimated sensitivity of the manometry determinations is ±10 μmol, and the calculated one sigma error for the mole fraction of H<sub>2</sub>O in the fluid is consequently dependent on the total mass of the fluid recovered, as well as the composition of the fluid.

### Major and volatile element compositions of rhyolite glasses

Aliquots of the glasses from both the outer capsule (always rhyolite) and the inner capsule (rhyolite or various basalt compositions) were collected after the fluid analysis procedure, and mounted and prepared for electron microprobe and FTIR spectrometry analysis. We present here the results for the rhyolite glasses only, as the basalt melts are not useful for pressure calibration as their solubilities of H<sub>2</sub>O and CO<sub>2</sub> are unknown, and are the focus of an ongoing solubility study to be published elsewhere.

The bulk compositions of the rhyolite glasses were determined using wavelength-dispersive spectrometry analysis on a JEOL 8600 Superprobe at A.S.U. to determine compositional homogeneity. A 10 μm de-focused beam, a 10 nA beam current, and an accelerating voltage of 15 kV were used to minimize alkali migration and beam damage in the hydrous glasses. The H<sub>2</sub>O contents of the glasses were determined using a Nicolet Magna IR spectrometer 750 and Spectra Tech IR plan analytical microscope at the U.S. Geological Survey in Menlo Park, courtesy of J. Lowenstern. Thicknesses of glass plates ranging between 100 to 280 μm were measured by digital micrometer. Absorption coefficients of 1.5 L·mol/cm for the OH peak at 4500 cm<sup>−1</sup> and 1.86 L·mol/cm for the H<sub>2</sub>O molecular peak at 5200 cm<sup>−1</sup>, respectively, are from Ihinger et al. (1994). During analysis the glass wafers were placed on a NaCl pellet and the light beam was restricted to a 100 to 200 μm square region using shutters above and below the sample. A total of 512 scans were collected for each sample. Baselines were hand-drawn using French curves and peak heights were measured using a Gerber scale.

## RESULTS

### Observations of the rhyolite glasses

Visual observation of the rhyolitic glasses recovered from the outer capsules revealed a color change from amber to a white or clear appearance. Subsequent analysis by electron microprobe showed that the color differences are due to the loss of the small amount of iron initially present in the rhyolite ( $\sim 1$  wt% FeO\*) to the platinum outer capsule. This observation is consistent with the white or clear glasses being located between the walls of the inner and outer capsule where the melt forms a relatively thin layer, and the diffusion of iron into the outer capsule results in almost complete removal of the iron. This color change is also correlated to heterogeneity observed in the H<sub>2</sub>O content of the outer rhyolite glasses, with the white to clear glasses containing anomalously high and heterogeneous H<sub>2</sub>O concentrations. At this time, we cannot explain these high H<sub>2</sub>O contents, and only note that they appear to be correlated with Fe-loss. As a result of these observations, we report here only the H<sub>2</sub>O contents of glasses that have been shown by electron microprobe measurement not to suffer from significant iron loss to the platinum capsule, and that are shown by FTIR to be homogeneous in H<sub>2</sub>O content. In fact, if significant heterogeneity was measured in either the major or H<sub>2</sub>O concentrations of the rhyolite glasses, the data were not considered equilibrium solubility values and were subsequently not included.

### Analytical results

**Mass balance considerations.** As discussed in the technique section above, both the inner and outer capsules were carefully weighed before and after the run. If the capsule masses did not agree within estimated weighing error of the scale ( $\pm 0.0001$  g), the run was considered suspect and not included in this study. For runs that did not obviously lose their fluids due to a catastrophic leak, we did not detect any significant mass difference in the capsule assembly after the run. Mass balance considerations that assume a 1:1 molar breakdown of oxalic acid into CO<sub>2</sub> and H<sub>2</sub>O (Holloway and Wood 1988) however show that CO<sub>2</sub> diffusion into the capsule assembly possibly did occur in some runs, particularly those that were at high  $T$  (1200 °C) and had nominally H<sub>2</sub>O-rich fluids (e.g., RLC-2; Table 1). This observation is consistent with the work of Brooker et al. (1998), who observed carbon contamination in their high- $T$  PC runs. They convincingly related the presence of carbon in their samples to migration from the graphite furnace, and also showed that the closer the capsule was to the furnace during the run the more likely it was to be contaminated. Another possible explanation for the positive carbon gain in the capsules is that the carbon yield of the oxalic acid is not well known.

Previous work by Truckenbrodt and Johannes (1999) has also shown that there can be considerable loss of both oxygen and H<sub>2</sub>O from Pt capsules at 1100 °C and above with a six day run duration. In contrast, our mass balance data show that we do not lose either H<sub>2</sub> or H<sub>2</sub>O from our runs, and in fact almost always have a slightly positive result for H<sub>2</sub>O (i.e., more H<sub>2</sub>O is found than was loaded into the capsule). We attribute this very slight increase in water to the possibility of H<sub>2</sub>O addition to the capsule during the final welding step in an ice-water bath. It is also possible that the presence of pyrophyllite disk underneath

the sample capsule (Freda et al. 2001), and the shorter run times relative to Truckenbrodt and Johannes (1999) have minimized the potential loss of H<sub>2</sub> or H<sub>2</sub>O out of the capsule during our runs.

### Presence of dissolved carbonate species in rhyolite glasses.

The analysis of the volatile content of the experimental glasses by FTIR spectroscopy shows that this rhyolite composition can have dissolved carbonate species within it (Moore et al. 2006), as well as the expected molecular CO<sub>2</sub> species. To our knowledge, this is the first observation of dissolved carbonate species in a true rhyolitic melt. Typically, the speciation of the dissolved carbon in a rhyolite is that of molecular CO<sub>2</sub> units (Holloway and Blank 1994), while andesitic compositions contain both molecular and carbonate species (King and Holloway 2002), and basalts contain only carbonate (Blank and Brooker 1994). Behrens et al. (2004) also observed both types of carbon species in a dacitic melt, but our composition is significantly different and more rhyolitic than that of their study. While the reasons for the presence of carbonate in our rhyolite is under continuing study, the lack of knowledge about the absorption coefficients for the carbonate peaks in the rhyolite FTIR spectra (Behrens et al. 2004) makes quantifying the total dissolved CO<sub>2</sub> content impossible by using only a single measurement technique (e.g., FTIR spectroscopy). As a result, we cannot use the total dissolved CO<sub>2</sub> content as measured by FTIR as a pressure calibrant, and therefore only discuss here the measured dissolved H<sub>2</sub>O content, for which there is no ambiguity in interpreting the rhyolite FTIR spectra (Ihinger et al. 1994).

### Comparison of the measured H<sub>2</sub>O contents to predicted values

The solubility of H<sub>2</sub>O in rhyolitic melts as a function of pressure, temperature, and fluid composition, has been successfully modeled over a wide range of conditions by Liu et al. (2005). Given the measured  $P$ - $T$  conditions of our runs, plus the manometrically measured fluid compositions, we can use the expression in Liu et al. (2005) to directly calculate a predicted dissolved H<sub>2</sub>O content for each experiment. These values are plotted vs. the measured FTIR H<sub>2</sub>O determinations in Figure 3. The differing amount of error reflected in the error bars for the predicted values is calculated using the estimated error in the measured fluid composition (i.e., there is less error for those runs with higher fluid masses). The error bars shown do not account for any fit error in the expression of Liu et al. (2005), nor is there any attempt to account for the effect of a thermal gradient across the capsule. The assumption of a small thermal gradient across our relatively large capsule is justified by the observation of Watson et al. (2002) of a 10 mm isothermal area at a temperature of 1300 °C in the piston cylinder that appears to get larger at lower temperatures. The presence of the noble metal capsule will also have a damping effect on any thermal gradient in the assembly as well. It is also true that the temperature dependence of the Liu et al. model on the H<sub>2</sub>O content is relatively small (with a fluid composition of  $X_{\text{H}_2\text{O}} = 0.5$ , at 300 MPa, 1200 °C, a 50 °C decrease leads to  $\sim 0.1$  wt% increase in H<sub>2</sub>O), particularly compared to the effect of pressure.

Statistical analysis of the data shows that there is no significant deviation of the data set from the model of Liu et al. (2005) taken as a whole (slope of regression line =  $1.03 \pm 0.03$ ; rms error of the regression = 0.49), nor is there any measurable dependence of the variation of the measured data from the model on the

total oil pressure. This result indicates that there is not a detectable difference between the sample pressure and the nominal measured oil pressure. Inversion of the Liu et al. expression for H<sub>2</sub>O to estimate pressure was also done to investigate whether an estimate for the deviation of the sample pressure from the nominal oil pressure could be calculated. Unfortunately, due to the exponential nature of the Liu et al. model, the estimated error in fluid measurement, and the narrow range of pressures covered by our study (300–500 MPa), it was not possible to extract a statistically meaningful number using this method. To accomplish this, further calibration experiments would be necessary that maximized the amount of H<sub>2</sub>O–CO<sub>2</sub> fluid in the run, as well as an increase in the range of pressures investigated (i.e., conduct runs at even lower sample pressures than 300 MPa). Given the physical and geometrical constraints of the piston-cylinder apparatus, and the volumetric properties of H<sub>2</sub>O–CO<sub>2</sub> fluids, such experiments would most likely have a low probability of success, and were not pursued in this study.

### CONCLUDING REMARKS

This study highlights the efficacy of using the 19 mm piston-cylinder at the pressure conditions important to studying sub-volcanic, pre-eruptive magmatic properties such as volatile solubilities, phase equilibria, and crystal and bubble nucleation behavior. The advantages of piston-cylinders over other experimental apparatus that are generally used to reach such conditions (e.g., cold seal vessels, internally heated pressure vessels) include faster quench rates, simpler sample assembly construction, and significantly lower maintenance costs. These advantages make the effort necessary to develop and calibrate low-pressure assemblies and operational methods worthwhile, and make a new regime of experimental conditions available that were previously thought to be inaccessible with existing piston-cylinder apparatus.

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### REFERENCES CITED

- Baker, D.R. (2004) Piston-cylinder calibration at 400–500 MPa: A comparison of using water solubility in albite melt and NaCl melting. *American Mineralogist*, 89, 1553–1556.
- Behrens, H., Meyer, M., Holtz, F., Benne, D., and Nowak, M. (2001) The effect of alkali ionic radius, temperature, and pressure on the solubility of water in MAISi<sub>3</sub>O<sub>8</sub> melts (M = Li, Na, K, Rb). *Chemical Geology*, 174, 275–289.
- Behrens, H., Ohlhorst, S., Holtz, F., and Champenois, M. (2004) CO<sub>2</sub> solubility in dacitic melts equilibrated with H<sub>2</sub>O–CO<sub>2</sub> fluids: Implications for modeling the solubility of CO<sub>2</sub> in silicic melts. *Geochimica et Cosmochimica Acta*, 68, 4687–4703.
- Blank, J. and Brooker, R. (1994) Experimental studies of carbon dioxide in silicate melts: Solubility, speciation, and stable carbon isotope behavior. In M.R. Carroll and J.R. Holloway, Eds., *Volatiles in Magmas*, 30, p.157–186. Reviews in Mineralogy, Mineralogical Society of America, Chantilly, Virginia.
- Bohlen, S.R. (1984) Equilibria for precise pressure calibration and a frictionless furnace assembly for the piston-cylinder apparatus. *Neues Jahrbuch für Mineralogie Monatshefte*, 9, 404–412.
- Bohlen, S.R. and Boettcher, A.L. (1982) The quartz-coesite transformation: a precise determination and the effects of other components. *Journal of Geophysical Research*, 87, 7073–7078.
- Boyd, J.R. and England, J.L. (1960) Apparatus for phase-equilibrium measurements at pressures up to 50 kbar and temperatures up to 1750 °C. *Journal of Geophysical Research*, 65, 741–748.
- Brooker, R., Holloway, J.R., and Hervig, R. (1998) Reduction in piston-cylinder experiments: The detection of carbon infiltration into platinum capsules. *American Mineralogist*, 83, 985–994.
- Clark, S.P. (1959) Effect of pressure on the melting points of eight alkali halides. *Journal of Chemistry and Physics*, 31, 1526–1531.
- Freda, C., Baker, D.R., and Ottolini, L. (2001) Reduction of water loss from gold-palladium capsules during piston-cylinder experiments by use of pyrophyllite powder. *American Mineralogist*, 86, 234–237.
- Holloway, J.R. and Blank, J. (1994) Application of experimental results to C–O–H species in natural melts. In M.R. Carroll and J.R. Holloway, Eds., *Volatiles in Magmas*, 30, p. 187–225. Reviews in Mineralogy, Mineralogical Society of America, Chantilly, Virginia.
- Holloway, J.R. and Wood, B.J. (1988) *Simulating the Earth: Experimental geochemistry*, 196 p. Unwin Hyman, Massachusetts.
- Ihinger, P.D., Hervig, R.L., and McMillan, P.F. (1994) Analytical methods for volatiles in glasses. In M.R. Carroll and J.R. Holloway, Eds., *Volatiles in Magmas*, 30, p. 67–121. Reviews in Mineralogy, Mineralogical Society of America, Chantilly, Virginia.
- Johannes, W., Bell, P.M., Mao, H.K., Boettcher, A.L., Chipman, D.W., Hays, J.F., Newton, R.C., and Seifert, F. (1971) An interlaboratory comparison of piston-cylinder pressure calibration using the albite-breakdown reaction. *Contributions to Mineralogy and Petrology*, 32, 24–38.
- King, P.L. and Holloway, J.R. (2002) CO<sub>2</sub> solubility and speciation in intermediate (andesitic) melts: The role of H<sub>2</sub>O and composition. *Geochimica et Cosmochimica Acta*, 66, 1627–1640.
- Liu, Y., Zhang, Y., and Behrens, H. (2005) Solubility of H<sub>2</sub>O in rhyolitic melts at low pressures and a new empirical model for mixed H<sub>2</sub>O–CO<sub>2</sub> solubility in rhyolitic glasses. *Journal of Volcanology and Geothermal Research*, 143, 219–235.
- Moore, G., Roggensack, K., and Holloway, J. (2006) Dissolved carbonate species in mixed volatile rhyolitic melts: Carbon speciation correlates with dissolved H<sub>2</sub>O content. *Transactions, American Geophysical Union Joint Assembly, San Francisco*, Abstract V23C-0621.
- Nelson, S.T. and Montana, A. (1992) Sieve-textured plagioclase in volcanic rocks produced by rapid decompression. *American Mineralogist*, 77, 1242–1249.
- Shaw, H.R. (1963) Obsidian–H<sub>2</sub>O viscosities at 1000 and 2000 bars in the temperature range 700 to 900 °C. *Journal of Geophysical Research*, 68, 6337–6343.
- Truckenbrodt, J. and Johannes, W. (1999) H<sub>2</sub>O loss during piston-cylinder experiments. *American Mineralogist*, 84, 1333–1335.
- Watson, E.B., Wark, D., Price, J., and Van Orman, J. (2002) Mapping the thermal structure of solid-media assemblies. *Contributions to Mineralogy and Petrology*, 142, 640–652.

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