

Supplemental information

I. Alternative version of figure 1

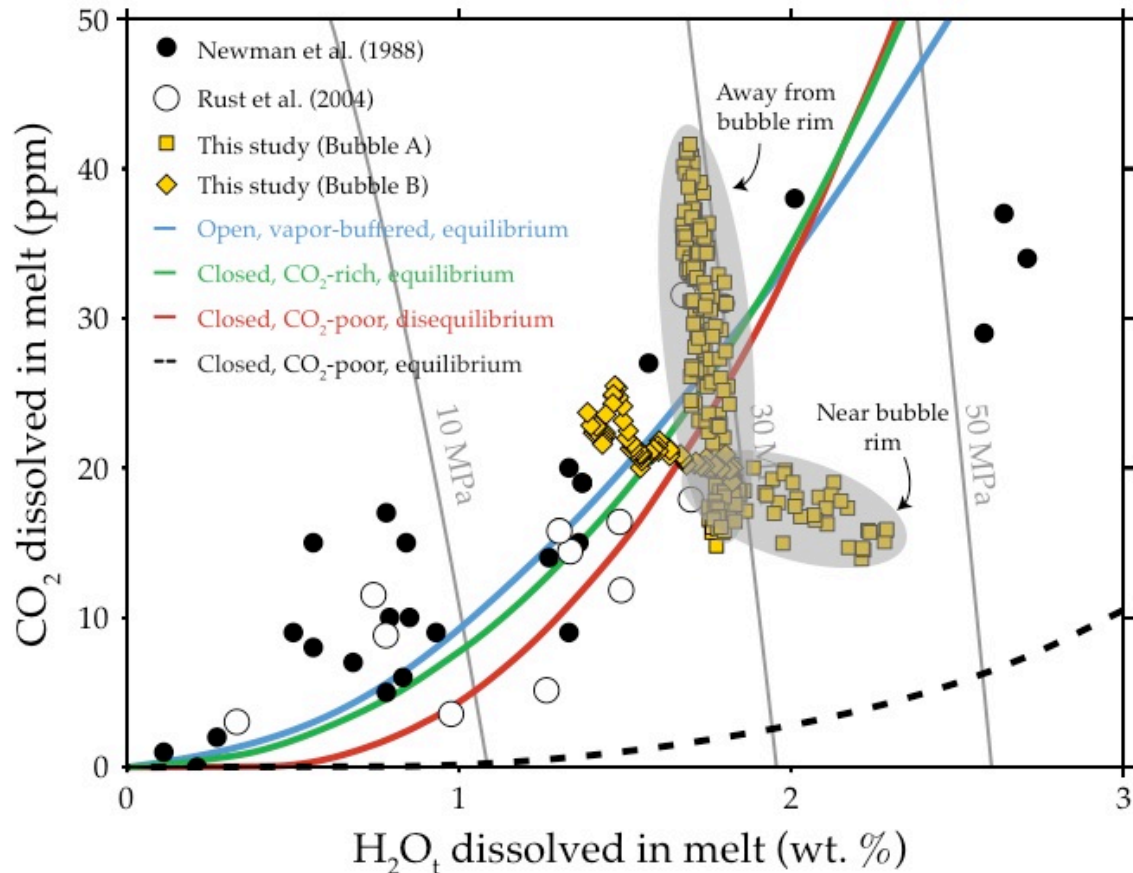


Figure A1. CO₂ versus H₂O for Mono Craters pyroclasts. Circles represent spot analyses on obsidian clasts. Squares and diamonds represent data from transects within individual clasts.

II. Sample preparation

Three obsidian clasts from beds 2 and 7 were selected for analysis. Doubly-polished thin sections (approximately 100-300 μm thick) were prepared following methods described in Watkins et al. (2008). Each wafer has at least one bubble with radius much greater than the wafer thickness so that effects of bubble curvature on volatile concentration measurements can be neglected. In addition to samples bearing at least one bubble, we determined that the glass should contain greater than about 20 ppm dissolved CO₂ to be

above detection limits for relatively thin (ca. 200 μm) wafers. Our sample selections were fortuitous in this respect since it is impossible to tell by visual inspection whether an individual clast will be volatile-rich.

III. SS-FTIR measurements

Concentrations of total water ($\text{H}_2\text{O}_\text{t}$) and CO_2 were determined by synchrotron radiation-source Fourier Transform Infrared Spectroscopy (SR-FTIR) at the Advanced Light Source beamline 1.4.3 using a Nicolet Magna 760 FTIR Spectrometer interfaced with a Nic-Plan IR microscope. Measurements were made using a 32x Refflachromat objective, MCT A detector and KBr beamsplitter. The spot size for the infrared beam is diffraction limited, about 2-4 μm in this spectral region, and the step size between individual measurements can be as low as 0.1 μm . Transects were oriented perpendicular to bubble rims and we collected 32 scans per spot and 128 scans for the background. A new background was collected every 5 minutes during each transect. Since CO_2 was found to be near detection limits, we performed several tests to ensure that contamination from the atmosphere was minimal, including repeated measurements on different days. From the baseline fitting used in FTIR spectroscopy, we estimate the relative uncertainty between adjacent points to be <10% for CO_2 , and <2% for water species (OH and $\text{H}_2\text{O}_\text{m}$). Figure A2 shows a picture of a typical background-subtracted absorbance spectrum for a relatively volatile-rich rhyolite glass.

Concentrations were determined using the Beer-Lambert law:

$$C_i = \frac{M_i A}{\rho d \epsilon_i}$$

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38 where M_i is the molecular weight (g/mol), A is the absorbance (height or area), ρ is the
 39 sample density (≈ 2300 g/L for rhyolite glass), d is the thickness of the wafer (cm), and ϵ_i
 40 is the molar absorption coefficient (L cm/mol). We used molar absorption coefficients for
 41 OH and H₂O_m from Zhang et al. (1997) and CO₂ from Behrens et al. (2004). The
 42 thickness of the wafer along each transect was measured using the method of Nichols and
 43 Wysoczanski (2007), which allows us to correct for non-uniform sample thickness using
 44 the wavelength of interference fringes in reflectance mode. We used an index of
 45 refraction for rhyolite glass of 1.49 (Tatlock et al., 1976).

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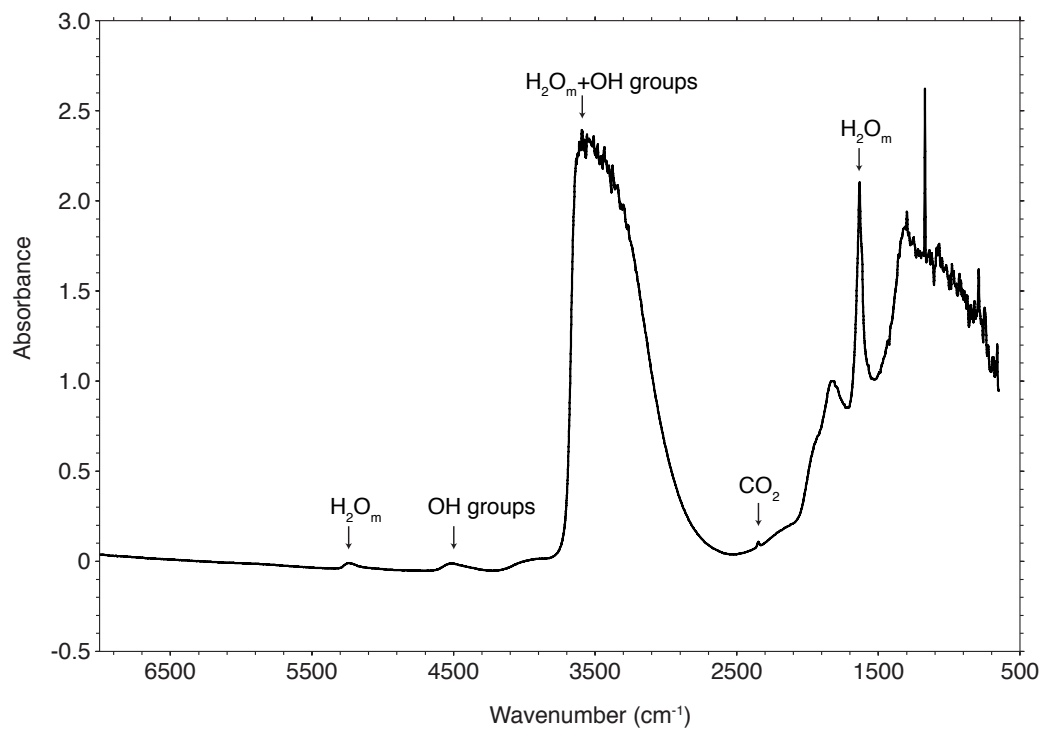


Figure A2. FTIR spectrum from a single spot on a doubly-polished obsidian clast from bed 2. The absorbances at 2350, 4520 and 5230 cm^{-1} were used to determine concentrations of CO_2 , OH, and H_2O_m , respectively.

IV. Additional transects

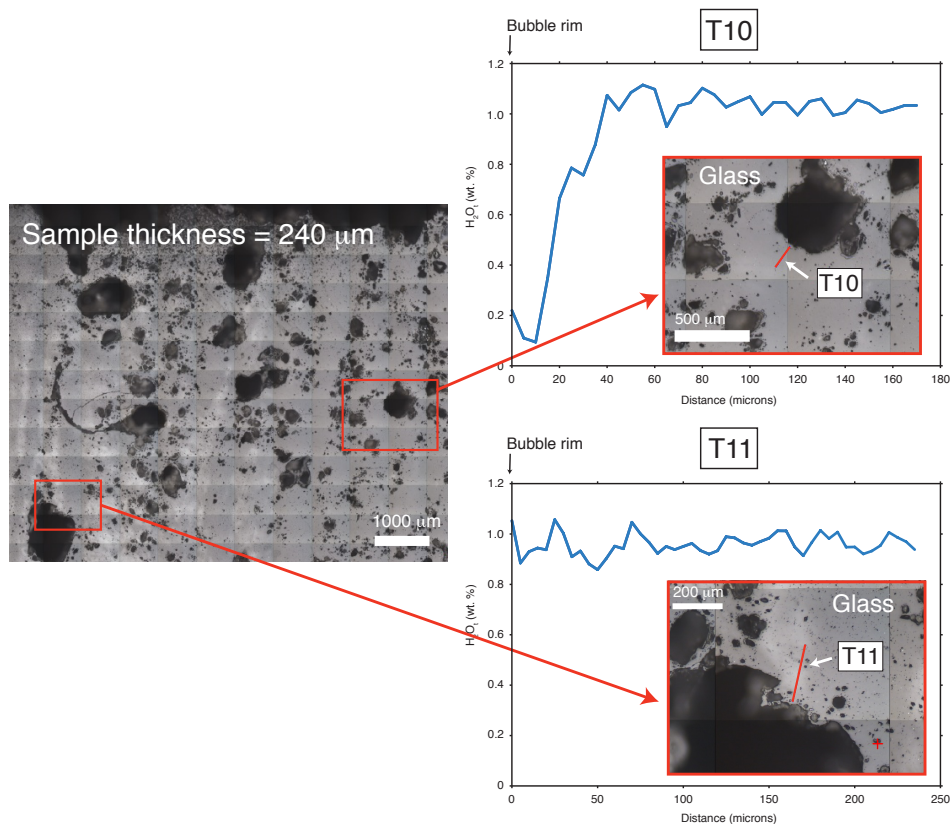


Figure A3. H₂O concentration profiles near two bubbles from a bubble-rich obsidian clast. Different clasts, and bubbles within clasts, record different *P-T-X* histories in the conduit. Within a single clast, some bubbles appear to be in chemical equilibrium with the melt (T11) while others are surrounded by a melt shell that is depleted in water, characteristic of disequilibrium bubble growth (T10). In these samples, CO₂ is below detection limits.

47 **V. Mechanisms for bubble resorption**

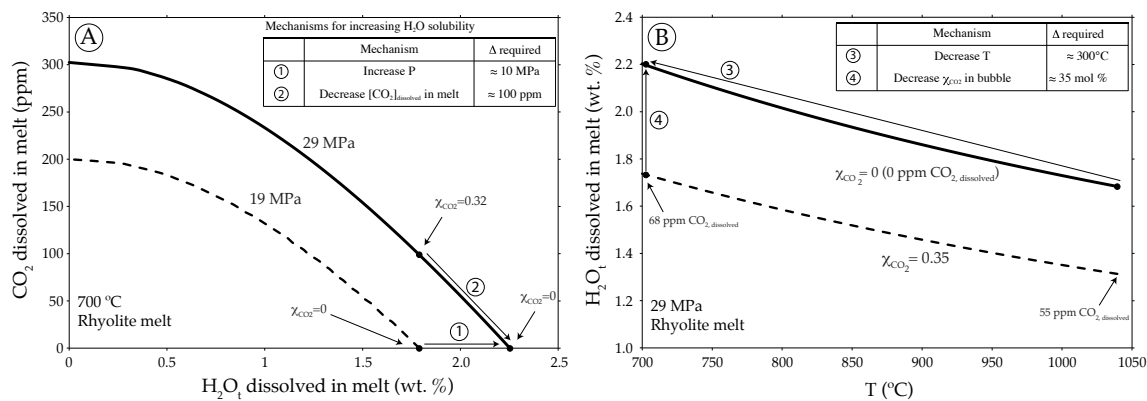
48 Table A1 summarizes the possible mechanisms for resorbing bubbles in the conduit.
 49 Figures A3 and A4 show how we estimate the magnitude of physical and/or chemical
 50 changes in the conduit necessary to increase the solubility of water in rhyolite melt from
 51 about 1.7 to 2.2 wt. %.

Mechanisms for increasing H₂O solubility

	Mechanism	Δ required
1	Increase P	≈ 10 MPa
2	Decrease $[\text{CO}_2]_{\text{dissolved}}$ in melt	≈ 100 ppm
3	Decrease T	$\approx 300^\circ\text{C}$
4	Vapor fluxing	-

Table A1. Mechanisms for resorbing bubbles. For 1, 2, and 3 the magnitudes correspond to an increase in H₂O solubility from about 1.7 to 2.2 wt. %. Vapor fluxing, on the other hand, causes a reduction in H₂O solubility; bubbles resorb as water is lost from the melt to fluid-filled fractures.

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Figure A4. Mechanisms for increasing H₂O solubility. (a) Equilibrium concentrations of CO₂ and H₂O dissolved in silicic melt at 700°C (Newman and Lowenstern, 2002). Each line is an isobar and each point on an isobar corresponds to a specific vapor phase composition. At any pressure, a decrease in the CO₂ content of the melt (or vapor) phase results in a decrease in CO₂ solubility and increase in H₂O solubility. At the same time, the solubilities of both CO₂ and H₂O increase with increasing pressure. (b) Equilibrium concentration of H₂O dissolved in silicic melt at 29 MPa (Liu et al., 2005). At any temperature, a decrease in the CO₂ content of the melt (or vapor)

phase results in a decrease in CO₂ solubility and increase in H₂O solubility. At the same time, the solubilities of both CO₂ and H₂O increase with decreasing temperature.

In panel A of figure A4, the ΔP is a minimum estimate because we assume there is no CO₂ in the system. In figure A5 we consider the effect of a pressure increase when CO₂ is present. The figure is modified from Rust et al. (2004) and illustrates the importance of the gas/melt mass ratio on the content of dissolved volatiles in the melt phase. For low gas/melt ratios, consistent with the formation of obsidian, a pressure increase of about 14 MPa is needed to change the water content of the melt from 1.7 to 2.2 wt. %. Interestingly, in this scenario the increase in the CO₂ content of the melt is relatively minor.

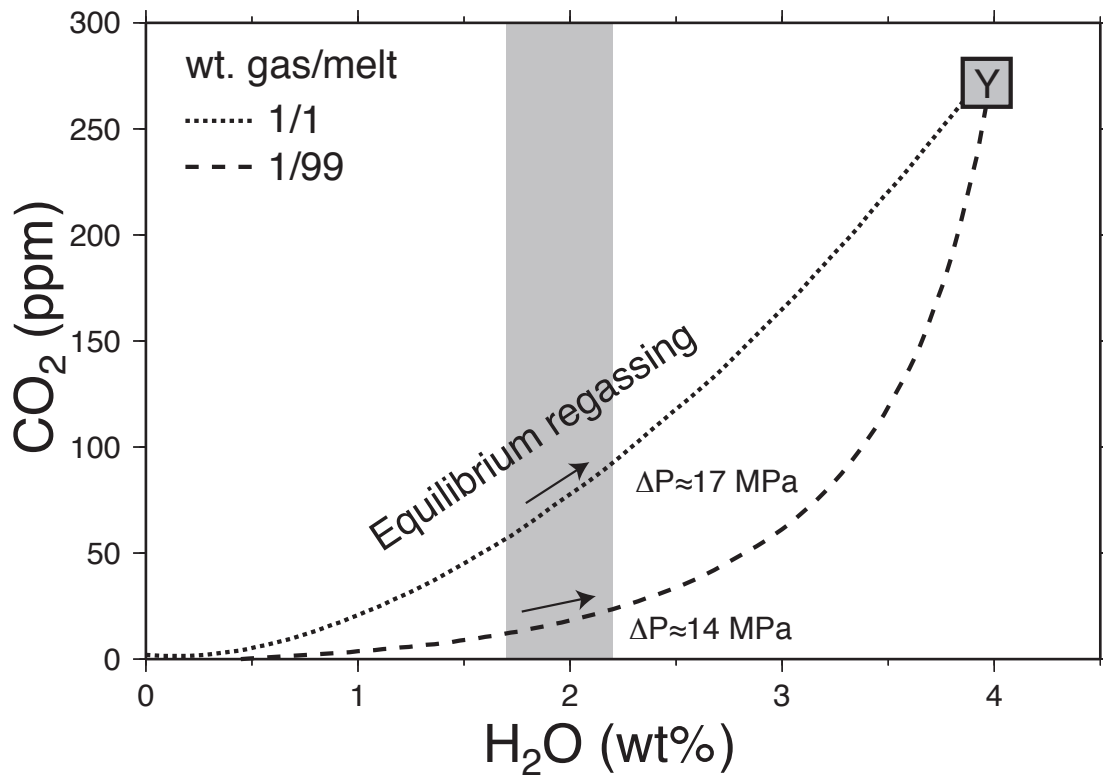


Figure A5. Equilibrium degassing and regassing of a vapor-saturated parent melt (composition Y) in a closed system (modified from Rust et al., 2004). Curves show degassing trajectories for two cases that differ in the amount of vapor initially. Dashed curve: During decompression-driven degassing, the melt has 2.2 wt. % H₂O at P ≈ 37 MPa and 1.7 wt. % H₂O P ≈ 23 MPa.

VI. Model for bubble resorption

We model the isothermal resorption of a spherical bubble caused by an instantaneous change in pressure and concomitant increase in water solubility.

There are three timescales of importance for bubble growth (Gonnermann and Manga, 2007): (1) the timescale for solubility changes due to pressure changes (τ_{dec}), (2) the timescale for viscous relaxation of the melt around a bubble ($\tau_\eta = \eta/\Delta P$), and (3) the timescale for volatile diffusion into a bubble ($\tau_d = R^2/D$). In our problem, we assume the bubble begins to dissolve after it is compressed, which is valid since the timescale for viscous relaxation relative to diffusion is effectively instantaneous:

$$Pe = \frac{\tau_d}{\tau_\eta} = \frac{\Delta P R^2}{\eta D} \approx \frac{(10^7 \text{ Pa}) (10^{-3} \text{ m})^2}{(10^8 \text{ Pa s}) (10^{-12} \text{ m}^2 \text{ s}^{-1})} = 10^5$$

The viscosity of 10⁸ Pa s corresponds to Mono Craters rhyolite (Newman et al., 1988) with 1.7 wt.% H₂O_t at 700°C and was calculated using the model of Hui and Zhang (2007). For simplicity, and since we do not know the initial or final vapor composition, we neglect CO₂ altogether and assume the bubble is made entirely of water vapor.

We begin with a bubble that has grown under equilibrium conditions with respect to H₂O so that the concentration of H₂O in the melt is initially homogeneous. The pressure increases, the bubble is compressed to a radius of 1 mm, and H₂O diffuses into the melt. The concentration of H₂O in the melt shell evolves according to the one-dimensional advection-diffusion equation in spherical coordinates:

$$\frac{\partial c_i}{\partial t} + u_r \frac{\partial c_i}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D_i r^2 \frac{\partial c_i}{\partial r} \right)$$

where c_i is concentration (moles/m³) of component i (i =H₂O in this case), u_r (equal to dR/dt where R is the radius of the bubble) is the velocity of vapor-melt interface, and D_i is the diffusivity of H₂O given by (Zhang et al., 2007):

$$D_{H_2O} = 10^{-12} X \exp(m) \left\{ 1 + \exp \left[56 + m + X \left(-34.1 + \frac{44620}{T} + \frac{57.3P}{T} \right) - \sqrt{X} \left(0.091 + \frac{4.77 \times 10^6}{T^2} \right) \right] \right\}.$$

Units of D_i are m² s⁻¹, $m = -20.79 - 5030/T - 1.4P/T$, P is in MPa, T is in Kelvin, and X is the mole fraction of water on a single-oxygen basis (Stolper, 1982; Zhang, 2008). As a further simplification, we approximate the diffusivity of H₂O as being constant (i.e., X corresponds to 1.7 wt. % H₂O). The boundary conditions for this problem are:

$$\left(\frac{\partial c_i}{\partial r} \right)_{r=\infty} = 0$$

and

$$c_i(r = R) = \text{constant}$$

where *constant* refers to the temperature- and pressure-dependent solubility of H₂O_t, which we calculate using the formulation of Liu et al. (2005). At each timestep, the change in bubble mass is calculated from the flux at the bubble-melt interface using Fick's first law:

$$dn_i = 4\pi R^2 \left(D_i \frac{\partial c_i}{\partial r} \right)_{r=R} dt$$

where n_i refers to the moles of water in the bubble. The radius of the bubble is updated assuming ideal gas behavior inside the bubble, which is appropriate for bubbles at shallow depths (Newman et al., 1988).

We choose $T=700^\circ\text{C}$, within the range for the glass transition temperature (T_g) of anhydrous rhyolite (Wright et al., 2007). For comparison, Newman et al. (1988) chose to model the Mono Craters dataset using 850°C , Rust et al. (2004) chose 800°C , and Gonnermann and Manga (2005) chose 850°C . The time scales we calculate decrease by about a factor of 4 in going from 700°C to 850°C .

Appendix references not cited elsewhere

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