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Non-equilibrium and unsteady fluid degassing during slow decompression

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Abstract. Decompression experiments were performed on corn syrup-water solutions in order to investigate the effect of viscosity on processes of vesiculation and degassing at low to moderate degrees of volatile supersaturation. Repeat experiments demonstrated similar long term vesiculation behavior at moderate decompression rates despite highly variable initial nucleation styles. Results suggest that magmas may not necessarily achieve chemical equilibrium by vapor exsolution and may require viscosity-dependent critical supersaturations in order to vesiculate. Vesiculation also increased the ambient pressure and decreased supersaturations, resulting in unsteady degassing.

Introduction

The explosivity of a volcanic eruption is controlled by the initial volatile content and by the relative rates of volatile exsolution, gas escape, and magma ascent. Volatile exsolution, in turn, requires volatile supersaturation by an amount sufficient for bubble nucleation. Calculations of exsolution depth, bubble growth rate, magma acceleration and exit velocity typically assume that vesiculation occurs to the extent determined by H_2O solubility in magma [e.g., *Wilson et al.,* 1980; *Jaupart and Allègre,* 1991; *Papale and Dobran,* 1994]. Observations that magma can reach the surface supersaturated in dissolved volatiles [e.g., *Fink et al.,* 1992; *Hoblitt and Harmon,* 1993; *Hammer et al.,* in press] suggest that degassing may not be an equilibrium process. Noting that "the effect of supersaturation can even suppress fragmentation of the magma leading to venting of a vesicular lava", *Woods* [1995] emphasizes the need to determine the degree of supersaturation developed in decompressing magmas for improved understanding of transitions in eruptive style.

Experiments with natural magmas have characterized the initial stages of bubble nucleation and growth in response to variable rates and degrees of supersaturation [*Hurwitz and Navon,* 1994; *Bagdassarov et al.,* 1996]. Most studies using analog materials have explored the dynamic behavior of a very low viscosity (10^{-3} Pa s) vesiculating fluid decompressed over timescales of ~ 10 ms [*Mader et al.,* 1997; *Zhang et al.,* 1997]. One set of analog experiments involving a moderate range of fluid viscosities (0.5-20 Pa s) and decompression rates (over timescales of $\sim$10 ms to $\sim$ 10 s) produced both explosive and non-explosive degassing behavior [*Phillips et al.*, 1995]. The present study addresses the evolution of volatile saturation as a function of fluid viscosity in a gradually decompressing fluid. We examine the range of degassing behaviors that might be achieved at low to moderate decompression rates, such as those that prevail at many hazardous recent and ongoing eruptions, e.g., Mt. Unzen, Japan and Merapi Volcano, Indonesia.

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Experimental method

Corn syrup is a convenient analog material for vesiculation experiments because it has a Newtonian rheology over the relevant strain rates, and can be diluted to produce solutions having nearly constant surface tension while encompassing a range in viscosity of nearly six orders of magnitude [*Hammer*, 1998]. We combine the weight fraction of added water with that of pre-existing water (determined by mass loss upon desiccation) to obtain the total mass fraction of water, w_{H_2O}, of each prepared solution. Solutions ranged from undiluted syrup to pure tap water. Viscosity,

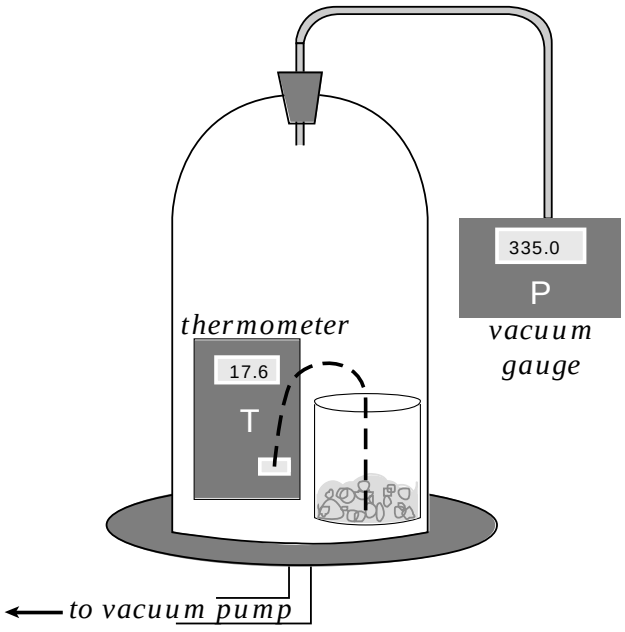

Figure 1. Experimental apparatus. A rotary vane vacuum pump evacuated a 4.4L bell jar containing the solution and digital thermometer with K-type thermocouple. Pressure in the bell jar was measured using a Pirani-type vacuum gauge with digital display. A video camera capturing 30 fps recorded all experiments. Fluid (liquid + gas) volume, pressure, and temperature were measured every 1-10 s during video playback. Uncertainties are thought to be $\pm$ 1 cm^3, $< 5\%$, and $\pm$ 0.1 ^oC, respectively. Temporal resolution is better than 2 s.

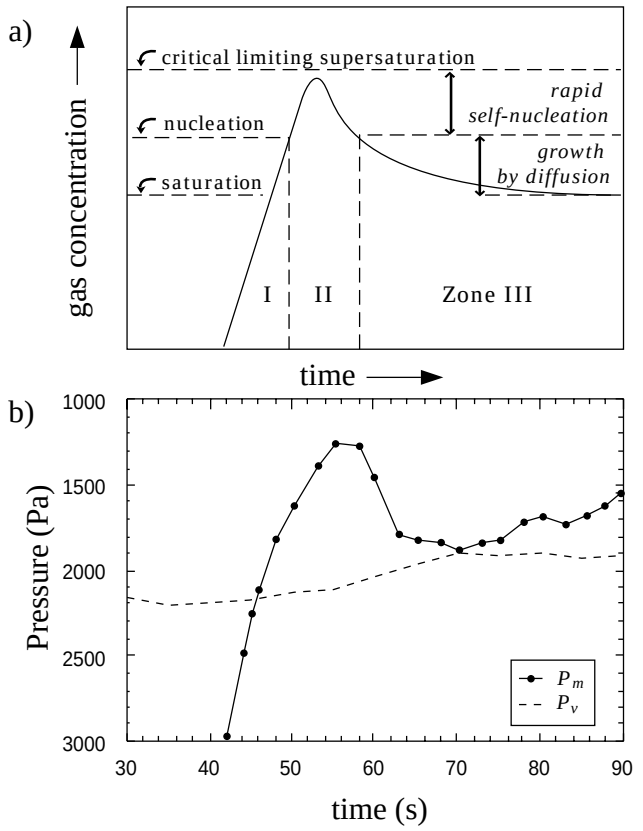

Figure 2. a) Classical nucleation sequence after *La Mer* [1952]. In Zone I, the solution becomes increasingly supersaturated. At a critical supersaturation, homogeneous nucleation begins (Zone II). Due to a lag time between saturation and the onset of nucleation, supersaturation increases to a maximum supersaturation. Below the saturation level required for nucleation (Zone III), bubbles no longer form, but diffusion into existing bubbles brings the system to equilibrium. b) Dashed line shows the saturation pressure which is a function of temperature. Solid line shows P_m.

measured with a rotational viscometer (error <5%), is an Arrhenian function of temperature over the relevant temperature range.

We measured vapor pressure, P_v, as a function of temperature and w_{H2O} as the pressure at which heterogeneous bubble nucleation began along a roughened wire under conditions of very slow decompression. Over the range in temperature (283-298 K) observed in the experiments, we fit measurements to the following phase relationship:

$$P_v = (aT + b)(\ln w_{\mathrm{H_2O}}) + (cT + d), \qquad (1)$$

where $a = 0.029737$ kPa K^{-1}, $b = -7.9523$ kPa, $c = 0.23592$ kPa K^{-1}, and $d = -65.789$ kPa. Using Eq. (1) to calculate P_v as a function of T during decompression, the degree of supersaturation ΔP (defined as the difference between P_v and measured pressure in the bell jar, P_m) was monitored over a 10-minute decompression interval. P_m, measured using a Pirani-type sensor, is a function of gas composition. However, for P_m less than a few thousand Pa, P_m should be close to the actual pressure. Moreover, measured P_v does not change as water is vaporized. Finally, as the phase relationship and P_m are determined using the same gauge, results are self-consistent.

An illustration of the experimental apparatus used for 55 decompression experiments is shown in Figure 1. A subset of the experiments examined the relationship between viscosity and style of bubble nucleation, growth, and coalescence [*Hammer*, 1998]. Moderate to high viscosity fluids (80 - 500 Pa s) maintained different degrees of supersaturation during vesiculation, and are the focus of this remainder of this paper.

Results

Pressure in the bell jar decreased exponentially from atmospheric during initial evacuation, and approached a steady lower limit controlled by vapor production by degassing solutions. Therefore, each experiment was composed of two decompression stages: an initial period ($\approx$ 2.5 min) of relatively high decompression rate, and a second stage ($\approx$ 7.5 min) of incremental decompression.

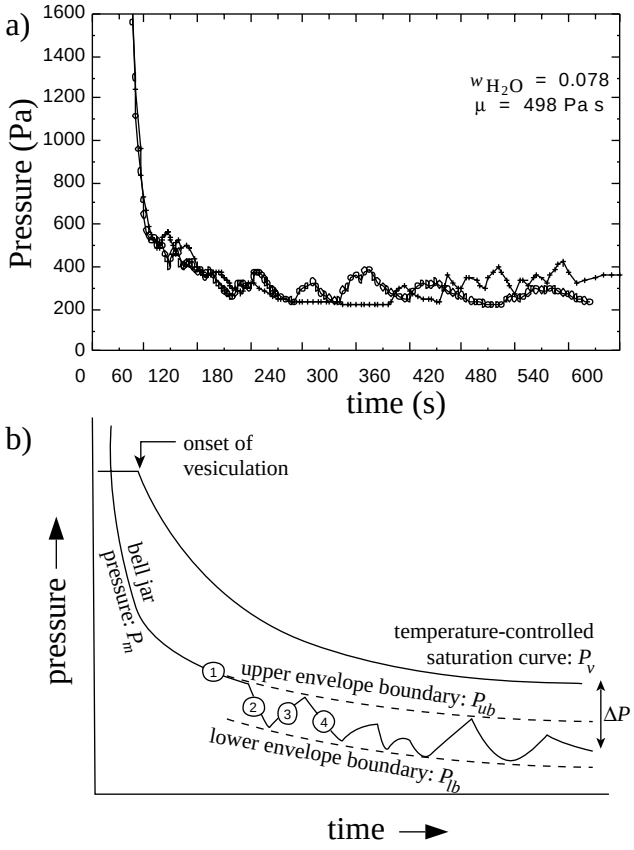

Figure 3. a) P_m for two runs of the same solution. b) Schematic diagram of decompression. (1) Moderate vesiculation and degassing. Pressure decreases gradually because degassing is less efficient than the vacuum pump. (2) Solution abruptly stops vesiculating and in response, pressure decreases. (3) At a lower pressure threshold, the solution resumes vesiculating and degassing; pressure increases in response. When the minimum degree of supersaturation required for bubble growth (P_{ub}) is attained, the solution again stops vesiculating (4).

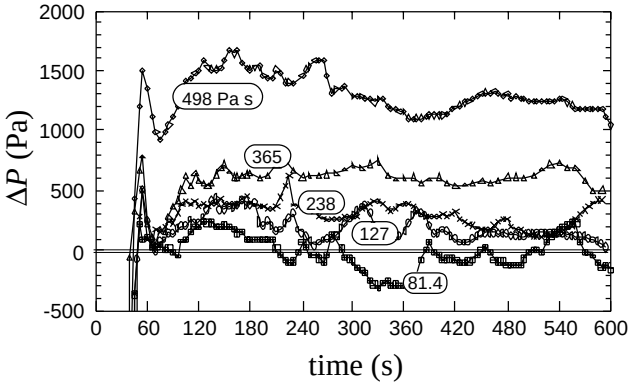

Figure 4. Supersaturation, $\Delta P = P_v - P_m$, shown versus time for 5 viscous solutions. Estimated uncertainty is 250 Pa. Double line represents saturation.

Processes of bubble nucleation and growth observed in these experiments are partially explained by classical descriptions of the response of sulfur solutions to a single rapid supersaturation event [*La Mer*, 1952]. This nucleation sequence, represented graphically in Figure 2a, provides a qualitative explanation for the characteristics of pressure-time trends during the initial stages of our experiments (Fig. 2b). Repeat experiments using the same solutions showed that the style of nucleation and vesiculation varied considerably during the initial decompression stage. Differences in the distribution of heterogeneous nucleation sites between the runs may have caused the disparity in the supersaturation required to initiate nucleation. In contrast, vesiculation styles and degassing histories for repeat runs were very similar during the latter experimental stage. For example, volume expansion histories were identical among repeat runs [see *Hammer,* 1998], and pressures oscillated between upper and lower limits characteristic to fluid composition (described below).

Measured pressure, P_m, reflects the combined effects of the vacuum pump, which lowers P_m, and vapor release by boiling, which increases P_m. Oscillations of P_m (Fig. 3a) demonstrate the unsteady vesiculation style characteristic of the most viscous solutions: rising pressure corresponds to vigorous vesiculation and degassing, while falling pressure represents the absence of degassing. Stages of degassing behavior of viscous solutions are described schematically in Figure 3b. Repeat experiments showed that pressure fluctuated between well-defined upper (P_{ub}) and lower bounds (P_{lb}).

The supersaturation pressure (ΔP) as a function of time is shown in Figure 4. All solutions vesiculated unsteadily, and maintained pressures between distinct upper and lower bounds throughout decompression. Only one of these solutions (viscosity $\approx$ 80 Pa s) hovered around equilibrium ($\Delta P \approx 0$) during decompression. In fact, the average P_m/P_v ratio decreased with increasing viscosity (Fig. 5).

Discussion

Several observations are a consequence of the limitations of the decompression equipment or specific to the analog material used. For example, the minimum pressure observed during decompression depended on the vacuum pump's evacuation rate and efficiency compared to the rate of vapor production by the degassing fluid. Therefore, both the rate of imposed supersaturation ($d\Delta P/dt$) and minimum experimental pressure, P_{lb}, were experiment-specific. Bubble nucleation occurred heterogeneously at fluid-glass or fluid-vapor interfaces in all experiments, and varied significantly in rate and style among repeat experiments. Furthermore, the density of heterogeneous nucleation sites in the corn syrup solutions probably differs from that of natural magmas containing crystals. The use of Newtonian fluids also precludes us from studying the effects of crytallization and more complex rheologies. However, several observations suggest that findings from this study are transferable to general degassing behavior of viscous liquids. Because P_{ub} defined the pressure at which vesiculation stopped, it did not rely on the pumping rate. For this reason, the relationship between supersaturation, ΔP, and fluid viscosity, μ, is not an experimental artifact.

Periodic vesiculation behavior resulted from the interplay between the pumping efficiency and fluid degassing, and might be analogous to natural magma ascent processes if magmas can "significantly" increase the ambient pressure by degassing. Indeed, pressure oscillations in volcanic conduits are inferred from seismo-acoustic measurements [e.g., *Chouet*, 1996].

A result of our experiments relevant to eruption models is that solutions did not necessarily achieve or maintain equilibrium by degassing during decompression. Theoretical treatments of diffusion-limited bubble growth during decompression predict that supersaturations can develop in the liquid between bubbles for various reasons: (1) a "shell" of liquid surrounding bubbles dries out and becomes more viscous, reducing the diffusion rate of volatile species [*Anderson et al.*, 1995; *Lyakhovsky et al.,* 1996]; (2) the shell cools due to the heat of vaporization and expansion work [*Sahagian and Proussevitch*, 1996]; (3) volatile solubility decreases with decompression [*Burnham and Davis*, 1974,]. The viscosities and volatile diffusion rates of both silicic magmas [*Zhang et al.,* 1991] and corn syrup solutions depend on w_{H_2O} and temperature, suggesting that the qualitative physico-chemical response to supersaturation may be comparable.

The low experimental decompression rates (0.5-10 Pa s^{-1}) would correspond to magma ascent velocities of 2.3 to

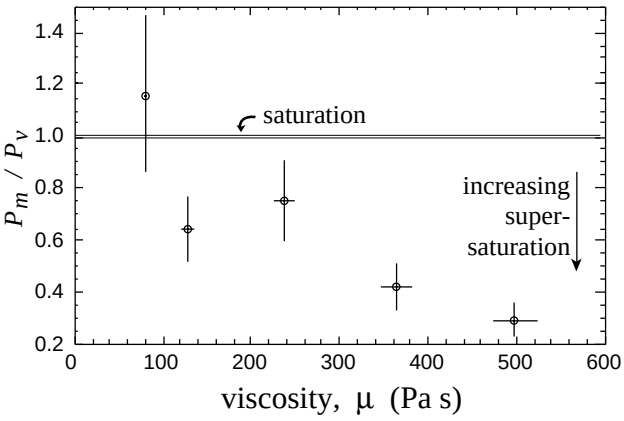

Figure 5. Ratio of average P_m to average P_v versus viscosity. Error bars are one standard deviation of ΔP.

37 m d^{-1} *if* dP/dt measured in the laboratory is equivalent to that for ascending magmas. Similar rates are estimated for the 1991-1994 dome extrusion at Mt. Unzen (13 - 40 m d^{-1}; *Nakada and Motomura,* 1995) and the 100-year average magma ascent rate at Merapi volcano (1.7 m d^{-1}; *Siswowidjoyo et al.,* 1995), although it is not yet clear how vesiculation phenomena scale with pressure. Overpressures generated in slow-ascending magmas may supply energy for pyroclastic flows following dome collapse [*Sato et al.,* 1992; *Navon et al.,* 1998].

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