

## 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

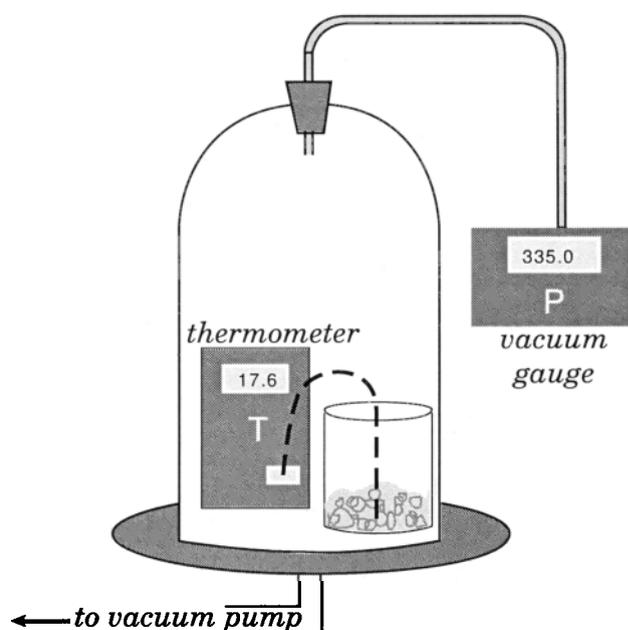
The explosivity of a volcanic eruption is controlled by the initial volatile content and by the relative rates of volatile exsolution, gas escape, and magma ascent. Volatile exsolution, in turn, requires volatile supersaturation by an amount sufficient for bubble nucleation. Calculations of exsolution 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  $\sim 10$  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.

### Experimental method

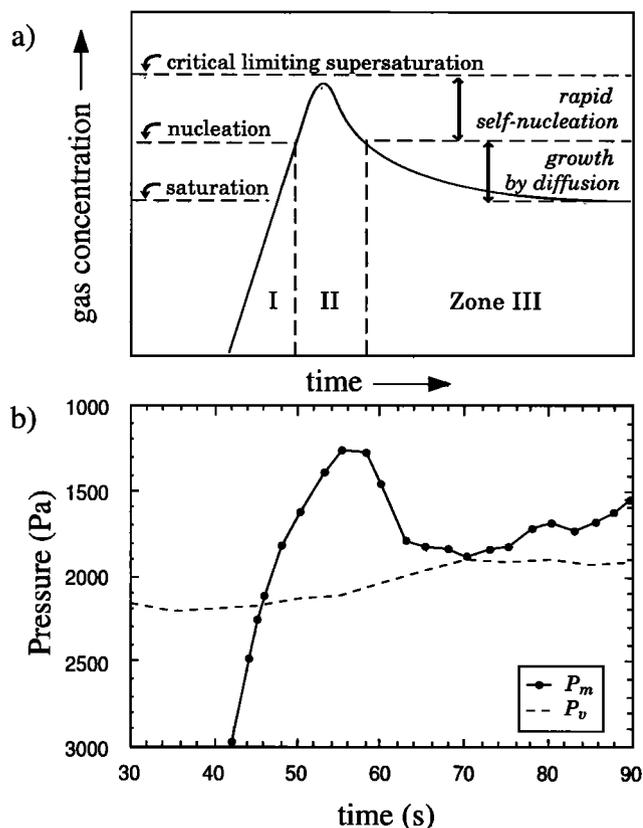
Corn syrup is a convenient analog material for vesiculation experiments because it has a Newtonian rheology over the relevant strain rates, and can be diluted to produce solutions having nearly constant surface tension while encompassing a range in viscosity of nearly six orders of magnitude [*Hammer*, 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  $\pm 0.1$   $^{\circ}C$ , respectively. Temporal resolution is better than 2 s.

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**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  $w_{H_2O}$  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:

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

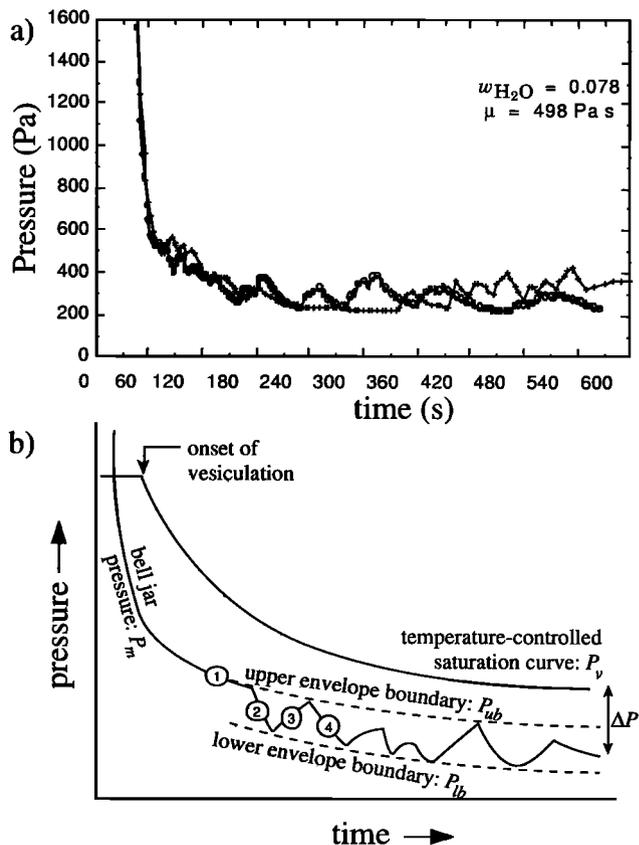
where  $a = 0.029737 \text{ kPa K}^{-1}$ ,  $b = -7.9523 \text{ kPa}$ ,  $c = 0.23592 \text{ kPa K}^{-1}$ , and  $d = -65.789 \text{ kPa}$ . Using Eq. (1) to calculate  $P_v$  as a function of  $T$  during decompression, the degree of supersaturation  $\Delta P$  (defined as the difference between  $P_v$  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 re-

lationship and  $P_m$  are determined using the same gauge, results are self-consistent.

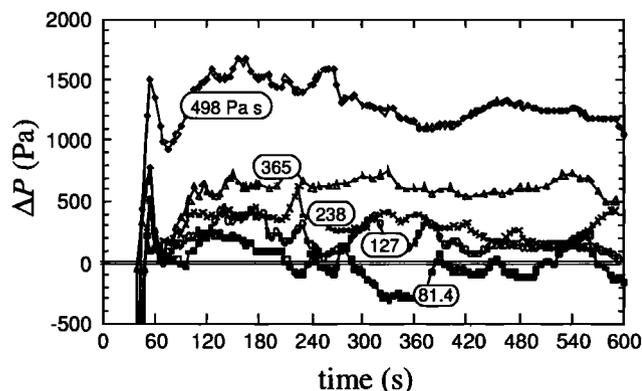
An illustration of the experimental apparatus used for 55 decompression experiments is shown in Figure 1. A subset of the experiments examined the relationship between viscosity and style of bubble nucleation, growth, and coalescence [Hammer, 1998]. Moderate to high viscosity fluids (80–500 Pa s) maintained 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 ( $\approx 2.5 \text{ min}$ ) of relatively high decompression rate, and a second stage ( $\approx 7.5 \text{ min}$ ) 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 ( $\Delta P$ ) 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

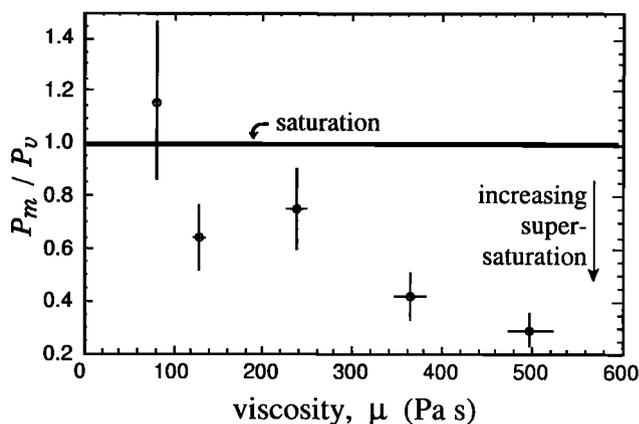
Several observations are a consequence of the limitations of the decompression equipment or specific to the analog material used. For example, the minimum pressure observed during decompression depended on the vacuum

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 crystallization 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,  $\Delta P$ , and fluid viscosity,  $\mu$ , 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; Lyakhovskiy 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 ( $0.5\text{--}10$  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  $\Delta P$ .

37 m d<sup>-1</sup> 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<sup>-1</sup>; Nakada and Motomura, 1995) and the 100-year average magma ascent rate at Merapi volcano (1.7 m d<sup>-1</sup>; Siswowardjojo 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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## References

- Anderson, S.W., J.H. Fink, and W.I. Rose, Mount St. Helens and Santiaguito lava domes: The effect of short term eruption rate on surface texture and degassing processes, *J. Volc. Geotherm. Res.*, **69**, 105-116, 1995.
- Bagdassarov, N.S., D.B. Dingwell, and M.C. Wilding, Rhyolite magma degassing: an experimental study of melt vesiculation, *Bull. Volc.*, **57**, 587-601, 1996.
- Burnham, C.W., and N.F. Davis, The role of H<sub>2</sub>O in silicate melts: II. Thermodynamic and phase relations in the system NaAlSi<sub>3</sub>O<sub>8</sub> - H<sub>2</sub>O to 10 kilobars, 700 C - 1100°C, *Am. J. Sci.*, **274**, 902-940, 1974.
- Chouet, B.A., Long-period volcano seismicity: It's source and use in eruption forecasting, *Nature*, **380**, 309-316, 1996.
- Fink, J.H., S.W. Anderson, and C.R. Manley, Textural constraints on effusive silicic volcanism: Beyond the permeable foam model, *J. Geophys. Res.*, **97**, 9073-9083, 1992.
- Hammer, J., Magma vesiculation and crystallization: case studies and results from analog experiments, Ph.D. dissertation, 344 pp., Univ. of Oregon, June 1998.
- Hammer, J.E., K.V. Cashman, R.P. Hoblitt, and S. Newman, Degassing and microlite crystallization during pre-climactic events of the 1991 eruption of Mt. Pinatubo, Philippines, *Bull. Volc.*, in press.
- Hoblitt, R.P., and R.S. Harmon, Bimodal density distribution of cryptodome dacite from the 1980 eruption of Mount St. Helens, Washington, *Bull. Volc.*, **55**, 421-437, 1993.
- Hurwitz, S., and O. Navon, Bubble nucleation in rhyolitic melts: Experiments at high pressure, temperature, and water content, *Earth Planet. Sci. Lett.*, **122**, 267-280, 1994.
- Jaupart, C., and C. Allègre, Gas content, eruption rate and instabilities of eruption regime in silicic volcanoes, *Earth Planet. Sci. Lett.*, **102**, 413-429, 1991.
- La Mer, V., Nucleation in phase transitions, *Ind. Eng. Chem.*, **44**, 1270-1277, 1952.
- Lyakhovskiy, V., S. Hurwitz, and O. Navon, Bubble growth in rhyolitic melts: experimental and numerical investigation, *Bull. Volc.*, **58**, 19-32, 1996.
- Mader, M., E. Brodsky, D. Howard, and B. Sturtevant, Laboratory simulations of sustained volcanic eruptions, *Nature*, **388**, 462-464, 1997.
- Nakada, S., and Y. Motomura, Manner of magma ascent at Unzen volcano (Japan), *Geophys. Res. Lett.*, **22**, 567-570, 1995.
- Navon, O., A. Chekmir, and V. Lyakhovskiy, Bubble growth in highly viscous melts: Theory, experiments, and autoexplosivity of dome lavas, *Earth Planet. Sci. Lett.*, **160**, 763-776, 1998.
- Papale, P., and F. Dobran, Magma flow along the volcanic conduit during the Plinian and pyroclastic flow phases of the May 18, 1980, Mount St. Helens eruption, *J. Geophys. Res.*, **99**, 4355-4373, 1994.
- Phillips, J., S. Lane, A.-M. Lejeune, and M. Hilton, Gum rosin-acetone system as an analogue to the degassing behaviour of hydrated magmas, *Bull. Volc.*, **57**, 263-268, 1995.
- Sahagian, D., and A. Proussevitch, Thermal effects of magma degassing, *J. Volc. Geotherm. Res.*, **74**, 19-38, 1996.
- Sato, H., T. Fujii, and S. Nakada, Crumbling of dacite dome lava and generation of pyroclastic flows at Unzen volcano, *Nature*, **360**, 664-666, 1992.
- Siswowardjojo, S., I. Suryo, and I. Yokoyama, Magma eruption rates of Merapi volcano, Central Java, Indonesia during one century (1890-1992), *Bull. Volc.*, **57**, 111-116, 1995.
- Wilson, L., R.S.J. Sparks, and G.P.L. Walker, Explosive volcanic eruptions, IV. The control of magma properties and conduit geometry on eruption column behaviour., *Geophys. J. Roy. Astr. Soc.*, **63**, 117-148, 1980.
- Woods, A.W., The dynamics of explosive volcanic eruptions, *Rev. Geophys.*, **33**, 495-530, 1995.
- Zhang, Y., E.M. Stolper, G.J. Wasserburg, Diffusion of water in rhyolitic glasses, *Geochim. Cosmochim. Acta*, **55**, 441-456, 1991.
- Zhang, Y., B. Sturtevant, and E. Stolper, Dynamics of gas-driven eruptions: experimental simulations using CO<sub>2</sub>-H<sub>2</sub>O polymer system, *J. Geophys. Res.*, **102**, 3077-3096, 1997.

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