ERUPTIVE DYNAMICS IN PLINIAN SILICIC ERUPTIONS

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ABSTRACT

Plinian eruptions are characterized by high magma discharge rates and pyroclastic material containing extraordinary large numbers of bubbles. Upon ascent to the surface magma decompresses and volatiles become supersaturated, causing bubbles to nucleate with a rate dependent on the degree of supersaturation. Thus, the conventional view is that the number of bubbles nucleating within the erupting magma depends on decompression rate, which is in turn a function of discharge rate. The interplay between decompression and bubble nucleation rates is of importance for the explosive nature of eruptions and thus provides an incentive for quantifying their dependency. Conventional approaches, however, predict unrealistically high decompression rates for the observed bubble number densities. Moreover, inferred pre-eruptive saturation pressures are often too low to overcome the surface energy barrier for homogeneous nucleation. To resolve these discrepancies, we simulated bubble nucleation in silica-rich magma under Plinian eruptive conditions. We demonstrate that bubble number densities and saturation pressures of Plinian silicic eruptions can be reconciled with heterogeneous nucleation, if facilitated by magnetite nanolites.

1 Introduction

Plinian eruptions are among Earth’s most explosive volcanic events and are typically associated with magmas of high silica content [1]. In the past 100 kyr, Plinian silicic eruptions have occurred around the globe, including in proximity to populated regions (Figure 1a). These eruptions have considerable destructive power and present extensive risks both locally and globally. The destructive potential of such eruptions derives from the myriad of gas bubbles within the erupting magma. These bubbles contain a highly compressible fluid mixture of exsolved magmatic volatiles, predominantly H2O [2], and provide the potential energy for explosive eruptions [3]. Magma explosivity results from fragmentation, thought to depend on the rate at which magma decompresses during ascent [4, 5]. Because eruptive processes are inaccessible to direct observation, understanding explosive volcanism is contingent upon reconstructing governing processes and controlling parameters from indirect observations. The number density of bubbles preserved in erupted pyroclasts is one such observation and of critical importance in elucidating the dynamical feedback between magma decompression, H2O exsolution, and explosive magma fragmentation.

Bubble nucleation rate, and the resultant bubble number density, are governed by the feedback between H2O exsolution and magma decompression. The latter is a consequence of the combination of decrease in static pressure, as magma rises toward the surface, and pressure loss from viscous resistance to flow [3]. Consequently, decompression rate depends dynamically on magma discharge rate, conduit dimensions, and magma viscosity. The latter increases as H2O, initially dissolved within the silicate melt, exsolves into bubbles by diffusion. The efficiency of diffusion, in turn, is rate limited by the number density of bubbles. Slow diffusion kinetics facilitate large supersaturations and subsequent high rates of bubble nucleation. The observed bubble number density in eruptions is thus governed by complex feedback between several physical processes. Reconstruction of these processes for a reliable estimation of magma decompression rate requires quantitative models of eruption dynamics that include bubble nucleation calibrated with experimental results.

Bubble number densities preserved in pyroclasts from Plinian silicic eruptions are high and span a narrow range of 1015−1 m−3, despite more than 3 wt% variation in pre-eruptive H2O concentration. Bubbles are thought to nucleate homogeneously within a disordered silicate melt structure [6, 7, 8, 9, 10]. Figure 1b compares the observed bubble number densities with experimental results of homogeneous nucleation in rhyolite. The data are presented in terms of potential maximum supersaturation pressure, which is the difference between H2O saturation pressure and final pressure in the case of experiments, or the difference between saturation pressure and atmospheric pressure for eruptions. Experiments suggest that homogeneous nucleation typically initiates at supersaturation pressures of ≈110 MPa, bubble number density increases with supersaturation pressure, and it reaches the range of bubble number density observed in pyroclasts at supersaturation pressures of >150 MPa. Such high pressures, however, are greater than the potential maximum supersaturation pressure for most eruptions. Moreover, the conventional estimates of decompression rate based on homogeneous nucleation are unrealistically high, ~100 MPa s−1, and are independent of magma discharge rate, Figure 1c. These estimates are substantially greater than decompression rate estimates, which are in the range of ~1 MPa s−1 or less, for independent methods [5]. These results present a quandary that Plinian eruptions are driven by bubbles, but the H2O saturation pressure and magma decompression rate are often insufficient to nucleate appreciable numbers of bubbles. The objective of the present work is to resolve some of these discrepancies and thereby advance our ability for quantitative assessment of Plinian volcanic eruptions and hazards.

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2 BUBBLE NUCLEATION

Bubble nucleation is formation of molecular clusters which are larger than a critical size, and hence are stable and grow into bubbles. Nucleation is driven by thermodynamic disequilibrium, in volcanic eruptions, by supersaturation of dissolved volatiles when magma decompresses to a pressure below their saturation pressure. Classical nucleation theory quantifies the change in free energy, \( W \), associated with and the rate of formation of bubble nuclei. \( W \) derives from the balance between a reduction in free energy, caused by the clustering of volatile molecules, and an increase in free energy, caused by the formation of a new interface that separates volatile molecules within the cluster from the surrounding melt. The bubble nucleation rate, in turn, depends exponentially on \( W \) [32]. Bubble nuclei are of the order of a few nanometers in size [25, 32] and will grow into micro- to milli-meter size bubbles by diffusion of volatiles. Diffusion thus tends to bring dissolved volatiles back to the thermodynamic equilibrium.

To examine the conditions under which bubbles in Plinian pyroclasts may have nucleated we simulate bubble nucleation and growth during magma decompression (see methods for details on the numerical simulation). We consider \( H_2O \) as the dominant volatile phase because it is the most abundant [2], and it primarily controls the final bubble number density [33]. Our simulations predict nucleation rate during decompression from an initial saturation pressure until magma fragmentation. Decompression rate is estimated for flow of magma within a cylindrical conduit with a constant cross-sectional area using the Darcy-Weisbach relation [3]. Dependent parameters are: the pressure inside bubbles and in the surrounding melt, the average concentration of dissolved \( H_2O \) in the melt, nucleation rate, bubble number density, and the average bubble size. We use the nucleation model of Hajimirza et al. [25], which has been calibrated against homogeneous bubble nucleation experiments in rhyolite and reliably predicts experimental results under a wide range of saturation pressures and decompression rates.

The homogeneous nucleation energy, \( W_{\text{hom}} \), is large and a high supersaturation pressure is required to overcome the surface...
Figure 2: (a) The maximum value of the nucleation factor as a function of homogeneous nucleation energy and bubble number density. The measured bubble number densities can be reconciled with model simulations if homogeneous nucleation energy is scaled with $\alpha \leq \alpha_{\text{max}}$. Only Pinatubo can be reconciled with homogeneous nucleation, whereas all other eruptions require $\alpha < 1$. The red shaded area shows the range of $\alpha$ that can match observed bubble number densities in all eruptions. (b) Heterogeneous nucleation factor, $\alpha_{\text{het}}$, versus contact angle, $\theta$, for different minerals. Estimates are for magnetite [34, 35], hematite [34, 36], and feldspar [35]. Magnetite is the only mineral phase that allows heterogeneous nucleation to simultaneously match observed bubble number densities in all eruptions.

energy barrier for nucleus formation [25, 27]. In our simulations we first examined whether the observed bubble number density in each eruption can be produced by homogeneous nucleation. If homogeneous nucleation did not match the observed values, we determined a maximum nucleation factor, $\alpha_{\text{max}} \leq 1$, such that the simulation can match the observed bubble number density if nucleation energy is reduced through scaling by $\alpha$, such that $W = \alpha W_{\text{Hom}}$ and $0 < \alpha \leq \alpha_{\text{max}}$. We find that the 1991 eruption of Pinatubo (Philippines) is the only eruption where homogeneous nucleation ($\alpha_{\text{max}} = 1$) can result in the observed bubble number density. In all other eruptions $\alpha_{\text{max}} < 1$ (Figure 2a) which may represent several potential mechanisms. The presence of solid heterogeneities, for instance, scales $W_{\text{Hom}}$ with $\alpha_{\text{het}} \leq 1$ by providing low surface energy sites for bubble nucleation [32]. An alternative to scaling $W_{\text{Hom}}$ are halogens. Gardner et al. [22] demonstrated that the presence of 1 wt% fluorine results in $W = W_{\text{Hom}}/4$. The amount of fluorine in most eruptions is, however, in the order of 200-1500 ppm [2]. In what follows we thus only focus on heterogeneous nucleation.

Heterogeneous nucleation in magmatic systems is facilitated by the presence of crystalline molecular aggregates that provide nucleation sites for bubbles. The value of $\alpha_{\text{het}}$ depends on the contact angle, $\theta$, between the melt-bubble interface and the pre-existing crystal (Figure 2b). Direct measurements of $\theta$ for bubble nuclei are impossible because nuclei are too small and ephemeral. Some studies have attempted to estimate $\theta$ from contact angle between microscopically observed bubbles and crystals [35]. It is, however, unlikely that the contact angle is the same for nuclei and microscopically observable bubbles, because their thermodynamic properties are different [25, 32]. Instead, $\theta$ has been inferred from the difference in pressure, $\Delta P$, at which bubbles first nucleate during decompression in homogeneous and heterogeneous nucleation experiments with $\alpha_{\text{het}} = (\Delta P_{\text{Het}}/\Delta P_{\text{Hom}})^2$ [32, 34]. Based on such experiments it has been shown that the contact angle is dependent on the substrate’s mineralogical structure (Figure 2b). For example, the contact angle for feldspar is approximately 20° [35], whereas for hematite it is approximately 90°-100° [36, 34], and for magnetite it is approximately 145°-160° [35, 34]. Magnetite is thus the most efficient mineral phase in facilitating bubble nucleation. A comparison between $\alpha_{\text{max}}$ and $\alpha_{\text{het}}$ in Figure 2. In fact, illustrates that magnetite is the only mineral phase that can facilitate nucleation of the observed bubbles in all seven eruptions.

3 RECONSTRUCTING ERUPTION DYNAMICS

For each eruption we ran simulations wherein $W = \alpha_{\text{Het}} W_{\text{Hom}}$ and $\alpha_{\text{Het}}$ spanning the range associated with contact angles for magnetite. For each value of $\theta$ we determined the average decompression rate at which the magma would be predicted to fragment at a bubble number density equal to the observed value. The resultant average decompression rates range between 0.1 MPa/s and 1 MPa/s (Figure 3). Decompression rates are correlated with magma ascent rate, which varies between 10 m/s to 100 m/s at fragmentation. Our average decompression rate estimates are substantially lower than conventional estimates based on homogeneous nucleation and are consistent with independent estimates from melt embayments [37], and from conduit models [38, 39]. Decompression rate estimates from ground mass crystallization and from crystal rims tend to be low. <0.01 MPa/s [40, 41, 20]. It has been suggested that these techniques may provide a potential lower bound, rather than a defined estimate, on decompression rates of fast ascending explosive eruptions [42].

Heterogeneous nucleation exerts a complex feedback between $\text{H}_2\text{O}$ exsolution, decompression rate, and explosive fragmentation. Figure 4 provides a representative example of such feedback for $\theta = 145°$. Heterogeneous nucleation energy is low...
enough that nucleation peaks at supersaturation pressure of 15 MPa. After nucleation, H$_2$O diffuses into existing bubbles, as magma continues to decompress. Because of the nucleated bubbles from the first nucleation event the characteristic diffusion length is small and H$_2$O efficiently diffuses into the existing bubbles as the magma continues to decompress. Consequently, the average dissolved H$_2$O concentration remains close to equilibrium. At the same time supersaturation increases gradually which leads to a second nucleation event, followed by magma fragmentation.

Our simulation results suggest that the discrepancies between homogeneous nucleation experiments and observed bubble number densities in Plinian silicic eruptions can be resolved by heterogeneous nucleation on magnetite. Our findings are in agreement with the heterogeneous nucleation hypothesis by Shea [44]. For none of the eruptions studied here, however, magnetite crystals have been reported at number densities similar to or greater than bubble number density. Tephra samples for which bubble number density have been measured were analyzed using scanning electron microscopy at a resolution down to approximately 1 micron. Much smaller magnetite crystals in the range of 1-100 nm have, however, been documented within the glassy groundmass of pyroclasts from several explosive eruptions. For example, Schlinger et al. [45] reported magnetite nanolites as small as 20 nm in samples from Paintbrush Tuff (USA), whereas Di Genova et al. [46, 47] documented magnetite nanolites in samples from Green Tuff (Italy) and Yellowstone (USA) using Raman spectroscopy. Mujin et al. [48] observed magnetite nanolites in samples from Shinmoedake Volcano (Japan) with sizes down to 1 nm and number densities of up to $\sim 10^{23}$ m$^{-3}$ using transmission electron microscopy. Moreover, several experimental studies have produced heterogeneous nucleation without detecting crystals, suggesting magnetite were present at the nano scale [35, 49]. Our simulation results together with these observations and experiments suggest that magnetite may present at the nanoscale within Plinian silicic samples.

Our analysis has been based on the hypothesis that heterogeneous nucleation sites exist at the nano-scale. Although nanolites probably form by rapid undercooling during water exsolution [48], to avoid assumptions about poorly constrained crystal nucleation rates [50], we did not attempt to simulate concurrent nanolite formation and bubble nucleation. Instead we assumed nanolites are present prior to magma decompression. Our sim-
ulation results, however, serve to illustrate the possibility of syn-eruptive water exsolution and nanolite formation. Prior to an eruption magma is thought to contain exsolved volatile phases of predominantly H$_2$O, CO$_2$ and SO$_2$ [2]. Upon decompression H$_2$O may exsolve into these pre-existing bubbles without further bubble nucleation. This may result in sufficient undercooling for formation of magmatic nanolites [48], ultimately leading to a shallow bubble nucleation event near fragmentation.

In summary, we find that bubbles at number densities observed in pyroclastic samples from a wide range of Plinian silicic eruptions are consistent with heterogeneous nucleation on magmatic nanolites, if they are present at number densities similar to those discovered in several explosive eruptions. Such heterogeneous bubble nucleation can resolve the discrepancy between the inferred water saturation for many eruptions and that required to nucleate bubbles homogeneously. Heterogeneous nucleation would also resolve the long-standing controversy about the unrealistically high decompression rates required for homogeneous nucleation, relative to values predicted by melt embayments and conduit models. We thus conclude that heterogeneous bubble nucleation during Plinian silicic eruptions, facilitated by mag-netite nanolites, is a viable hypothesis that provides impetus for future investigations, in particular, a systematic search for the presence of magmatic nanolites in pyroclasts from Plinian silicic eruptions.

4 Methods

4.1 Bubble nucleation

We used classical nucleation theory to estimate nucleation rate of critical bubble nuclei at a given supersaturation pressure. Volatiles molecular clusters are stable and grow into bubbles if they are larger than the critical nucleus size, $R_c$, given by [32]

$$R_c = \frac{2\gamma}{P_n - P_m},$$

(1)

where $\gamma$ is surface tension of bubble nuclei, $P_n$ is pressure inside a bubble nucleus, and $P_m$ is pressure in the surrounding melt. $P_m$ is related to the saturation pressure of volatiles, $P_{sat}$, through [36]

$$f(P_m, T)P_n = f(P_{sat}, T)P_{sat}^{(2P_{sat} - P_m)/4\Omega},$$

(2)

where $T$ is temperature, $f(P, T)$ is fugacity coefficient of the super-saturated volatile phase, $\Omega$ is the volume of volatile molecules, and $k_B$ is the Boltzmann constant. The homogeneous nucleation energy, $W_{Hom}$, is estimated from

$$W_{Hom} = \frac{16\pi \gamma^3}{3(P_n - P_m)T},$$

(3)

and the nucleation rate is

$$J = J_0 \exp \left( -\frac{W_{Hom}}{k_BT} \right),$$

(4)

with

$$J_0 = \frac{2\Omega n_v^3 D}{a_0^2} \sqrt{\gamma \frac{k_BT}{k_B}},$$

(5)

$n_v$ is the concentration of volatiles molecules in melt, $D$ is the diffusion coefficient, $a_0$ is the average distance between volatiles molecules, and $\alpha$ is the nucleation factor. Here we use the heterogeneous nucleation factor, $\alpha = \alpha_{Het}$, which depends on the contact angle, $\theta$, between bubble nuclei and crystals as

$$\alpha_{Het} = \frac{(2 - \cos \theta)(1 + \cos \theta)^2}{4},$$

(6)

The nucleation rate is strongly controlled by surface tension, $\gamma$, such that a few percent variations in $\gamma$ can change $J$ by $>10$ orders of magnitude [38]. A reliable prediction of nucleation rate and consequently bubble number density thus requires a firm constraint on surface tension. Here we use the surface tension formulation defined by Hajimirza et al. [25] which has been shown to predict observed bubble number density in homogeneous nucleation experiments reliably. $\gamma$ is given by

$$\gamma = \frac{0.49 \gamma_{ni}}{1 + 20/R},$$

(7)

where $\gamma_{ni}$ is the surface tension measurements for macroscopic bubbles [51], and $\delta \approx 0.32$ nm is the Tolman length for bubble nuclei in rhyolite [25, 32].

4.2 Bubble growth

When a bubble nucleus forms the H$_2$O concentration at the bubble-melt interface is determined by the solubility of H$_2$O at the pressure inside the bubble. This concentration is lower than the concentration in the surrounding water, resulting in a concentration gradient which drives diffusion of H$_2$O molecules toward bubble nuclei. The resultant mass flux of H$_2$O into a bubble, $q$, is approximated using the mean-field approximation [33],

$$q = D \left( \frac{C_m - C_k}{R} \right),$$

(8)

where $C_m$ and $C_k$ are the average H$_2$O concentrations in the melt and at the bubble-melt interface, respectively. The mass of H$_2$O inside the bubble, $m_b$, will increase at the rate

$$\frac{dm_b}{dt} = 4\pi R^2 \rho_{H2O} q,$$

(9)

and the bubble will grow in size at a rate

$$\frac{dR}{dt} = \frac{R}{4\mu} \left( P_b - P_m - 2\gamma \right).$$

(10)

Here $\mu$ is viscosity of melt surrounding the bubble, and $P_b$ is pressure inside the bubble, estimated using the equation of state of H$_2$O. Inertial terms in equation 10 are neglected given that they are considerably lower than the viscous terms [33].

The above equations describe growth rate of a single bubble. Because the number of bubbles in the magma are too high to track growth rates for each bubble individually, we use the method of moments, which calculates the moments of size distributions, defined as [33]

$$M_k(t) = \int_0^\infty R^k f(R, t) dR,$$

(11)

with the subscript $k$ determining the order of the moment. Each moment refers to a measurable characteristic quantity [33]: $M_0$ is bubble number density, $M_1/M_b$ is mean bubble radius, and $M_2/(M_1 + 3/(4\pi))$ is the volume fraction of bubbles. The evolution of the zeroth moment through time is given by

$$\frac{dM_0}{dt} = J,$$

(12)

and the evolution of the higher order moments are

$$\frac{dM_k}{dt} = k \frac{dR}{dt} M_{k-1} + \frac{dM_0}{dt} R^k,$$

(13)

where $k \geq 1$.

The concentration of H$_2$O dissolved within the melt decreases as a result of the diffusion of water into bubbles. Based on the conservation of water molecules in magma, the rate of change in the concentration of dissolved H$_2$O is given by

$$\frac{dC_m}{dt} = -\frac{1}{\rho_m} \left( M_0 \frac{dm_b}{dt} + \frac{dm_b}{dt} m_b \right),$$

(14)

where $\rho_m$ is the melt density, assumed to be constant throughout magma decompression.
4.3 Decompression

The decompression rate of erupting magma is not constant, but depends on a complex feedback between water exsolution and viscous resisting forces [3, 53]. We only simulate nucleation up to fragmentation because at fragmentation the decompression rate becomes small and the nucleation rate becomes negligible [53]. Decompression rate below fragmentation is estimated from the equation of motion for two phase flow, with variables averaged over the cross-sectional area of the conduit [3]. Conservation of mass and momentum are given by

$$\frac{d(\rho U a)}{dz} = 0,$$

and

$$\frac{dP_m}{dt} = -U \left( \rho U \frac{dU}{dz} + \rho g + F_{\text{fric}} \right),$$

respectively. Here $\rho$ is magma density, averaged over melt and gas phases,

$$\rho = \phi \rho_2 + (1 - \phi) \rho_m,$$

$\phi$ is the volume fraction of bubbles, $\rho_2$ and $\rho_m$ are gas and melt densities respectively, $U$ is magma ascent rate, $g$ is the gravitational acceleration, $A$ is the cross sectional area of conduit, and $F_{\text{fric}}$ is the friction force. The latter is calculated from the Darcy-Weisbach relation, $F = f_D U^2 / a$, where $f = 16/Re = (8\phi)/(\rho U a)$ is friction factor. $a$ is the conduit radius, and $\mu$ is the magma viscosity, given by $\mu_m(1 - \phi_{\text{crystal}}/0.6)^{6/5}$. Here $\mu_m$ is the melt viscosity and $\phi_{\text{crystal}}$ is the volume fraction of microlites. Substituting equation 15 into equation 16, and replacing $U$ with $Q/(\rho a^2)$ gives decompression rate as

$$\frac{dP_m}{dt} = -Q \rho a^2 \left[ \rho g + Q \rho a^2 \left( \frac{8\mu}{a^2} - \frac{d\rho}{dt} \right) \right],$$

where $Q$ is the mass discharge rate.

4.4 Model simulation

We integrated equations 12, 13, 14, and 18 using the ode15s function of MATLAB®. For each eruption simulations initiate at the known saturation pressure, and with additional initial conditions

$$M_i = 0, \quad P_m = P_{H_2O} \quad \text{and} \quad C_m = C_{H_2O},$$

where $C_{H_2O}$ is a function of $P_{H_2O}$ [57]. A given simulation ends when the fragmentation criterion of Spieler et al. [58] is reached.

The objective of our model simulation is to estimate decompression rate conditional on the observational constraints, observed bubble number density and the magma fragmentation. All parameters in the governing system of equations are either specified or calculated from existing formulations: $H_2O$ solubility [57], diffusion coefficient [59], equation of state [60], fugacity coefficient [60], surface tension [25], melt viscosity [61], and the molecular volume of $H_2O$ [62]. Conduit radius, which is related to decompression rate through equation 18, is the only parameter that is not constraint. For each eruption, the model simulations predict a conduit radius and subsequently decompression rate conditional on the observational constraints.

4.5 Maximum heterogeneous factor

To estimate the maximum heterogeneous factor, $a_{\text{max}}$, that allows model simulations to match the observed bubble number density for a given eruption, we simulated bubble nucleation under an instantaneous decompression from saturation pressure to atmospheric pressure. If homogeneous nucleation can match or exceed the observed bubble number density, then $a_{\text{max}} = 1$. If not, we determined maximum value of $a$ at which the observed bubble number density can be reached. An empirical fit to the $a_{\text{max}}$ as a function of homogeneous nucleation energy, $W_{\text{Hom}}$, is calculated as

$$a_{\text{max}} = \min \left\{ \left( \frac{\log_{10}(N_m) - k_1}{k_2} \right) \frac{k_3 T}{W_{\text{Hom}}}, 1 \right\}.$$

Here $k_1 = 26.5$ and $k_2 = 0.26$ are constants, and $N_m$ is the observed bubble number density. The empirical fit for $N_m$ over the range of $10^{14}$ m$^{-3}$ to $10^{16}$ m$^{-3}$, and for $T=850^\circ$C is shown by the blue shaded region in Figure 2.

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AUTHOR CONTRIBUTION

S.H. conducted the numerical simulation. All authors participated in interpretations of the results and preparation of the manuscript.

DATA AVAILABILITY

The data used are listed in the references. All equations in the numerical simulation are presented in the Methods.

COMPETING INTERESTS

The authors declare no competing interests.

REFERENCES


