Homogeneous bubble nucleation in rhyolitic melt: Experiments and nonclassical theory

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[1] The transfer of volatiles from the Earth’s interior to the atmosphere occurs through degassing of magma, the dynamics of which assert a significant control on volcanic eruptions. The first and most critical step in degassing is the nucleation of gas bubbles, which requires that a sufficient number of volatile molecules cluster together to overcome the free energy associated with the formation of a new interface between nucleus and surrounding melt. This free energy is a function of surface tension, typically assumed to equate to the macroscopically measurable value. Surface tension estimates inferred from bubble nucleation experiments in silicate melts are, however, lower than direct macroscopic measurements, making it difficult to accurately predict magma ascent and decompression rates from measured bubble number densities in pyroclasts. We provide a potential resolution to this problem through an integrated study of bubble nucleation experiments and modeling thereof, based on nonclassical nucleation theory. We find that surface tension between critical bubble nuclei and the surrounding melt depends on the degree of supersaturation and is lower than the macroscopically measured value. This is consistent with the view that far from equilibrium the interface between a nucleus and surrounding metastable bulk phase is diffuse instead of sharp. As a consequence, the increase in nucleation rate with supersaturation is significantly larger at high supersaturations than predicted by classical nucleation theory.

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1. Introduction

[1] Volcanism is the principal mechanism by which volatiles are transferred from the Earth’s interior to its surface. The underlying process is magma degassing, a consequence of pressure-dependent solubilities of volatiles, such as H$_2$O and CO$_2$, in silicate melts. As magma rises toward the surface, and pressure decreases, the melt becomes supersaturated in volatiles. As a result, volatile-bearing bubbles nucleate and grow [Toramaru, 1989, 1995; Gonnermann and Manga, 2007], with the rates of bubble nucleation and growth largely determining the style by which the magma erupts [Gonnermann and Manga, 2007; Houghton and Gonnermann, 2008].

[2] As bubbles nucleate, the distance between individual bubbles, and hence the characteristic diffusion time of volatiles, decrease. Consequently, continuous bubble nucleation during magma ascent will eventually cause the diffusion of volatiles to be sufficiently fast to decrease supersaturation, despite further magma decompression. Magma decompression and bubble nucleation are thus competing processes that cause and inhibit supersaturation, respectively [Toramaru, 1989, 1995, 2006]. It is therefore possible to constrain magma ascent and decompression rates from the number of bubbles that nucleated in a given volume of melt upon eruptive magma ascent. To this end, a substantial body of research has been aimed at characterizing the size and abundance of bubbles (vesicles) in pyroclasts [e.g., Sparks and Brazier, 1982; Toramaru, 1989, 1990; Mangan et al., 1993; Klug and Cashman, 1994; Gardner et al., 1996; Klug and Cashman, 1996; Mangan and Cashman, 1996; Blower et al., 2001; Polacci et al., 2001; Blower et al., 2002; Klug et al., 2002; Polacci et al., 2003; Gaonac’h et al., 1996a, 1996b, 2005; Polacci, 2005; Polacci et al., 2006, 2009; Gurioli et al., 2005; Adams et al., 2006; Lautze and Houghton, 2007; Piachi et al., 2008; Giachetti et al., 2010; Houghton et al., 2010; Alfano et al., 2012].

[3] Bubble nucleation in magmas can be homogeneous, heterogeneous, or a combination of both [e.g., Hurwitz and Navon, 1994; Mourtada-Bonnefoi and Laporte, 1999; Mangan and Sisson, 2000; Mourtada-Bonnefoi and Laporte, 2002; Gardner and Denis, 2004; Mourtada-Bonnefoi and Laporte, 2004; Mangan and Sisson, 2005; Gardner, 2007; Cluzel et al., 2008; Larsen, 2008; Hamada et al., 2010; Gardner and Ketcham, 2011; Gonde et al., 2011]. In the case of heterogeneous nucleation, the abundant presence of impurities, such as crystals, provide nucleation substrates of lower interfacial energy. In some cases, however, the number density of bubbles in pyroclasts far exceeds the abundance of crystals which could act as nucleation substrates, suggesting that bubbles may have nucleated within the bulk metastable melt phase through homogeneous nucleation [e.g., Debenedetti, 1996]. Because the moments of the bubble size distribution, which are used to infer eruption dynamics, are a function of the nucleation rate [e.g., Toramaru, 1995], the ability to predict bubble nucleation rates is of essence to the study of volcanic eruptions. In this study, we solely focus on homogeneous bubble nucleation, because it constitutes the most fundamental bubble nucleation process and, thus, the basis for understanding bubble nucleation in magmas.

[4] Bubble nucleation is a consequence of random fluctuations in the spatial distribution of molecules of dissolved volatiles within the melt, resulting in the spontaneous formation of small molecular clusters. The rate of cluster formation increases with the supersaturation of volatiles that are dissolved within the melt phase. Supersaturation, in turn, is a consequence of magma decompression at faster rates than the rate at which volatiles can diffuse through the melt into bubbles, if they exist [e.g., Toramaru, 1989, 1995; Navon et al., 1998; Navon and Lyakhovsky, 1998; Lensky et al., 2004; Toramaru, 2006; Gonnermann and Manga, 2007]. For a given supersaturation, the free work associated with cluster formation increases with cluster size and reaches a maximum at a critical size, after which it decreases. This critical cluster size strongly depends on the change in energy associated with the formation of the vapor-melt interface. In other words, the critical cluster size depends on surface tension, with clusters larger than the critical size growing into bubbles, whereas smaller ones will not. Because the critical cluster size decreases with decreasing surface tension, the probability of cluster formation, that is the bubble nucleation rate, increases as surface tension decreases. Thus, the surface tension between the nucleating volatiles and the surrounding melt phase is of critical importance to bubble nucleation, magma degassing, and the dynamics of volcanic eruptions.

[5] The conventional theoretical framework within which the nucleation rate of bubbles is predicted is classical nucleation theory (CNT). It is based on the approximations that there exists an equilibrium distribution of nuclei and that these nuclei have the properties of the bulk phase. These approximations allow nucleation to be treated within a
thermodynamic framework, as opposed to a kinetic one [Debenedetti, 1996]. It is thus assumed that the surface tension between bubble nuclei and surrounding melt is the same as the surface tension that can be measured macroscopically. Close to equilibrium, the work of formation of a critical nucleus is in reasonable agreement with predictions from CNT, in part because the surface tension of the newly formed interface approaches that of a flat interface [Kelton and Greer, 2010]. With increasing departure from equilibrium, however, the interface between the new and original phases departs from capillarity (a sharp interface) and becomes diffuse. In the spinodal limit, far from equilibrium, surface tension and the work of formation of the new phase vanish. Consequently, the approximation of CNT that macroscopic properties of the bulk phase, and in particular surface tension, can be used to predict nucleation rates is strictly valid only close to equilibrium [Kelton and Greer, 2010]. With increasing departure from equilibrium this approximation no longer holds and surface tension is no longer constant. Instead, it may depend on the degree of departure from equilibrium, that is on the degree of supersaturation.

One approach to studying bubble nucleation in magmas is the controlled decompression of silicate melt, which was equilibrated at some higher pressure with a volatile phase, usually H₂O [e.g., Hurwitz and Navon, 1994; Mourtada-Bonnefoi and Laporte, 1999, 2002, 2004; Mangan and Sisson, 2000, 2005; Gardner and Denis, 2004; Gardner, 2007; Larsen, 2008; Hamada et al., 2010; Gonde et al., 2011; Nowak et al., 2011; Gardner and Ketcham, 2011]. The resultant number of bubbles that nucleate within a volume of melt is then measured and divided by the duration of the experiment, typically of the order of 10–100 s, to obtain an average nucleation rate. Using CNT, together with the known supersaturation and other parameters, it is then possible to estimate the value of surface tension. As already pointed out, for example, by Hamada et al. [2010], typical values of surface tension thus obtained are significantly lower than those determined by direct measurements [Bagdassarov et al., 2000]. At the same time they are relatively high for producing the high bubble number densities observed in pyroclasts at magma decompression rates typically obtained from fluid dynamical modeling of magma ascent [Toramaru, 2006].

During the experiments all parameters were known or controlled, except surface tension of the nucleating bubble. We focused on a single rhyolitic melt, in order to eliminate compositional dependencies, and on experiments within a narrow range of temperatures (±25°C), in order to limit the effect of temperature [Walker and Mullins, 1981; Bagdassarov et al., 2000; Gardner and Ketcham, 2011]. The only parameters that varied significantly were dissolved H₂O content and decompression rate. From the modeling of our experiments, we find that surface tension of the nucleating bubble is strongly dependent on the degree of supersaturation and is of lower value than the macroscopically measurable surface tension. These results are consistent with the contemporary framework of nonclassical nucleation theory.

After a description of the experiments (section 2) we will, therefore, provide a discussion of nonclassical nucleation theory (section 3), as well as of our modeling approach for nonclassical bubble nucleation during the aforementioned experiments (section 4). This will be followed by a presentation of the results obtained from the modeling (section 5) and conclusions (section 6).

2. Bubble Nucleation Experiments

2.1. Samples and Experimental Techniques

All experiments used cylinders drilled from a high-silica rhyolitic obsidian that consists of clear rhyolitic glass and less than 1 vol.% microlites of Fe-Ti oxides (Table 1). The composition of the glasses was determined by electron microprobe and, normalized to 100%, was in weight percent: 76.53% SiO₂, 0.06% TiO₂, 13.01% Al₂O₃, 0.79% FeO, 0.08% MnO, 0.02% MgO, 0.74% CaO, 3.87% Na₂O, and 4.91% K₂O, with Fe reported as FeO. Most cores were 2.2 mm in diameter and 1.1–1.3 cm long. All sharp edges were ground with emery paper to avoid piercing the metal tubing in which the cores were held during experiments. The cylinders were washed after being ground.

Each experiment consisted of two steps: a sample was first hydrated with a given amount of water, and then decompressed to a lower pressure. For both hydration and decompression the pressure vessel was pressurized with water. For each hydration, a cylinder and distilled water were
Table 1. Experimental Conditions and Results

<table>
<thead>
<tr>
<th>Run</th>
<th>Starting Material</th>
<th>(p_{\text{initial}}) (MPa)</th>
<th>(T) (°C)</th>
<th>Time</th>
<th>([\text{H}_2\text{O}]) (wt.%</th>
<th>(N_m) (m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-1079</td>
<td>Rhyolite</td>
<td>120</td>
<td>900</td>
<td>144</td>
<td>4.27 ± 0.08</td>
<td>–</td>
</tr>
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<td>120</td>
<td>900</td>
<td>144</td>
<td>4.22 ± 0.01</td>
<td>–</td>
</tr>
<tr>
<td>G-1095</td>
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<td>140</td>
<td>900</td>
<td>120</td>
<td>4.71 ± 0.02</td>
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</tr>
<tr>
<td>G-1096</td>
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<td>900</td>
<td>120</td>
<td>4.77 ± 0.04</td>
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<td>120</td>
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</tr>
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<td>G-594*</td>
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<td>120</td>
<td>5.17 ± 0.50</td>
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<td>G-595*</td>
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<td>875</td>
<td>120</td>
<td>4.93 ± 0.13</td>
<td>–</td>
</tr>
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<td>G-610*</td>
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<td>120</td>
<td>5.00 ± 0.03</td>
<td>–</td>
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<td>120</td>
<td>4.81 ± 0.14</td>
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<td>4.90 ± 0.08</td>
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<td>120</td>
<td>4.95 ± 0.05</td>
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<td>875</td>
<td>120</td>
<td>5.03 ± 0.01</td>
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<td>120</td>
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<td>120</td>
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</tr>
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<tr>
<td>G-1221</td>
<td>Rhyolite</td>
<td>210</td>
<td>850</td>
<td>120</td>
<td>5.58 ± 0.02</td>
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Decompression experiments

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<th>Run</th>
<th>Starting Material</th>
<th>(p_{\text{initial}}) (MPa)</th>
<th>(T) (°C)</th>
<th>(p_{\text{final}}) (MPa)</th>
<th>Time</th>
<th>([\text{H}_2\text{O}]) (wt.%</th>
<th>(N_m) (m(^{-3}))</th>
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<td>161</td>
<td>825</td>
<td>10/50</td>
<td>–</td>
<td>0</td>
<td>7.35 × 10(^6)</td>
</tr>
<tr>
<td>G-938*</td>
<td>G-931</td>
<td>161</td>
<td>825</td>
<td>10/50</td>
<td>–</td>
<td>0</td>
<td>2.26 × 10(^6)</td>
</tr>
<tr>
<td>G-890*</td>
<td>G-882</td>
<td>161</td>
<td>825</td>
<td>16/44</td>
<td>–</td>
<td>0</td>
<td>4.95 × 10(^6)</td>
</tr>
<tr>
<td>G-907*</td>
<td>G-885</td>
<td>161</td>
<td>825</td>
<td>10/50</td>
<td>–</td>
<td>0</td>
<td>7.84 × 10(^6)</td>
</tr>
<tr>
<td>G-889*</td>
<td>G-876</td>
<td>161</td>
<td>825</td>
<td>10/50</td>
<td>–</td>
<td>0</td>
<td>4.4 × 10(^{13})</td>
</tr>
<tr>
<td>G-1233</td>
<td>G-1231</td>
<td>211</td>
<td>825</td>
<td>10/20</td>
<td>–</td>
<td>0</td>
<td>6.8 × 10(^{13})</td>
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<tr>
<td>G-1234</td>
<td>G-1231</td>
<td>211</td>
<td>825</td>
<td>8/52</td>
<td>–</td>
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<td>4.23 ± 0.03</td>
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<tr>
<td>G-1089</td>
<td>G-1079</td>
<td>121</td>
<td>875</td>
<td>22/38</td>
<td>–</td>
<td>0</td>
<td>5.52 ± 0.02</td>
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<td>G-1149</td>
<td>1108</td>
<td>121</td>
<td>875</td>
<td>20/40</td>
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<td>5.58 ± 0.02</td>
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<tr>
<td>G-1110</td>
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<td>141</td>
<td>875</td>
<td>20/40</td>
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<td>141</td>
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<td>20/40</td>
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<td>G-630</td>
<td>161</td>
<td>850</td>
<td>5/55</td>
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<td>G-591</td>
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<td>875</td>
<td>5/55</td>
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<td>G-658*</td>
<td>G-610</td>
<td>161</td>
<td>875</td>
<td>5/55</td>
<td>–</td>
<td>0</td>
<td>5.52 ± 0.02</td>
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<td>G-594</td>
<td>161</td>
<td>875</td>
<td>5/55</td>
<td>–</td>
<td>0</td>
<td>5.52 ± 0.02</td>
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<tr>
<td>G-665*</td>
<td>G-644</td>
<td>161</td>
<td>875</td>
<td>5/55</td>
<td>–</td>
<td>0</td>
<td>5.52 ± 0.02</td>
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<tr>
<td>G-608*</td>
<td>G-595</td>
<td>161</td>
<td>875</td>
<td>5/55</td>
<td>–</td>
<td>0</td>
<td>5.52 ± 0.02</td>
</tr>
</tbody>
</table>

\(p_{\text{initial}}\) and \(p_{\text{final}}\) are the initial and final pressures of the experiment; Times are either hours at hydration pressure, or number of seconds it took to lower pressure to \(p_{\text{final}}\) (± 1 s) and number of seconds the sample remained at \(p_{\text{final}}\); \([\text{H}_2\text{O}]\) is total water content (± 1%); \(N_m\) is the number density of bubbles nucleated, determined by counting numbers of bubbles in given volumes of the sample, except \(6\) for which \(N_m\) was determined from measured bubbles sizes and porosity (see text for discussion). Experiments indicated by * were also reported in Gardner and Ketcham [2011].

added to a 4 mm O.D. Au capsule, which had been welded at one end. Enough water, usually ca. 10\% by weight of the cylinder, was added to ensure that a fluid existed throughout the hydration. Then, the capsule was crimped, weighed, and welded shut. The sealed capsule was then heated on a hotplate for 10–15 min and weighed again to check for leaks. All hydrations were carried out in externally heated, cold-seal pressure vessels, made of a Nickel-based alloy, and were run at 850°C, 875°C, or 900°C and various pressures for 5 days (Table 1). The samples were absolutely crystal free after this hydration step.

Gardner et al. [1999] showed that samples hydrated at superliquidus conditions for 5 days result in homogeneous nucleation, whereas samples hydrated for 3 or less days resulted in heterogeneous nucleation, despite the apparent absence of any crystals suitable as bubble nucleation sites. We thus conclude that our sample preparation resulted in experiments where bubbles nucleated homogeneously within the bulk of the melt.

[12] Pressure was measured to ±0.1 MPa, and the K-type thermocouples used have been found to be
precise to ±5°C. The use of a Ni filler rod in the pressure vessel ensured that the sample hydrated at an oxygen fugacity similar to the Ni-NiO oxygen buffer [Gardner et al., 1995]. Samples were quenched by removing the pressure vessel from the furnace and, after blowing on the vessel with compressed air until it stopped glowing red, immersing it into a bucket of water. The hydrated glass cylinder was then extracted from the capsule and split; one piece was used to measure dissolved water contents by Fourier transform infrared spectroscopy (see below), the other in a decompression experiment.

Decompression experiments consisted of hydrated cylinders inside Au capsules welded shut. Each capsule was placed into a cup on the end of an Inconel rod and inserted into an externally heated, cold-seal pressure vessel fitted with a rapid-quench extension. The sample was held in the water-cooled region of the vessel while the pressure vessel heated to 825–875°C. Because the pressurizing medium was water, the adiabatic temperature drop during depressurization is smaller than in experiments that are pressurized by compressed gas [e.g., Hamada et al., 2010], with the difference in temperature between initial hydration and decompression corresponding in all cases to a solubility difference of <0.1 wt.% [e.g., Liu et al., 2005]. We thus expect a negligible effect on the experimental results.

Once the pressure vessel thermally equilibrated, the sample rod was raised with a magnet to insert the sample into the hot zone of the pressure vessel. The pressure was quickly adjusted using a hand-operated intensifier to 1 MPa above the hydration pressure to discourage water loss from the melt during heating. After the sample heated for 5 min, pressure was released manually within 3–35 s to a lower final pressure (Table 1). After samples reached their final pressures, most of them were held at that pressure until a total of 60 s had elapsed, including the time during which pressure was decreased. Samples were then quenched rapidly by lowering the magnet, which brought the sample back into the water-cooled jacket. One experiment (G-1234) was quenched after only a total of 30 s had elapsed, whereas G-608 was quenched only after 120 s had elapsed.

After being quenched, each capsule was removed from its pressure vessel, checked that it had remained sealed, and then the sample was removed and sectioned for analysis. The number density of bubbles, \( N_{m,\text{obs}} \), that nucleated was determined by selecting 4–5 areas (40 \( \mu \text{m} \times 40 \mu \text{m} \)) of a sample and counting all bubbles that appear as the field of view is moved through the sample using the focusing knob of the microscope. If bubbles had a shape indicative of two bubbles quenched in the act of merging, then we counted the two separately. The depth viewed was usually between 800 \( \mu \text{m} \) and 2000 \( \mu \text{m} \), and measured using a Heidenhain focus drive linear encoder. The average error is ±0.6 \( \mu \text{m} \), determined by repeatedly focusing through a sample. In two cases, bubbles were too numerous to count individually. In those cases, number densities were calculated from porosity and bubble sizes in the experiments, modified from Gardner et al. [1999]

\[
N_m = \frac{\phi N_{\text{tot}}}{(1 - \phi) \sum (n_i V_i)},
\]

in which \( n_i \) and \( V_i \) are the number and volume of bubbles of diameter \( i \), respectively, \( N_{\text{tot}} \) is the total number of bubbles measured, and \( \phi \) is the volume fraction of bubbles.

All hydration samples were analyzed for dissolved water contents by Fourier transform infrared (FTIR) spectroscopy, using a Thermo Electron Nicolet 6700 spectrometer and Continuum IR microscope. Three to six spectra were collected, with each spectrum consisting of 60 scans at a resolution of 4 cm\(^{-1}\), and measured in transmittance mode in the near-IR region (7800–4000 cm\(^{-1}\)) with white light and a CaF\(_2\) beam splitter. Contents of molecular water (H\(_2\)O\(_m\)) and hydroxyl water (OH\(^-\)) were determined from absorbances at \( \approx 5250 \text{ cm}^{-1} \) and \( \approx 4500 \text{ cm}^{-1} \), respectively, using the model of Zhang et al. [1997], and the thickness where each spectrum was collected measured with the method described above. Water contents reported are the averaged sums of H\(_2\)O\(_m\) and OH\(^-\) contents (Table 1). Water contents in one decompression sample were measured at various positions through the sample.

### 2.2. Experimental Results

All hydrations produced crystal- and bubble-free glasses. Samples that were hydrated at 120–210 MPa, producing initial water contents that range from 4.2 to 5.7 wt.% (Table 1). At a given pressure, H\(_2\)O contents differ by only a few percent and agree well with those predicted by the solubility models of Gardner et al. [1999] and Liu et al. [2005], with an average difference of <2% between measured and model amounts. All
decompressed samples contained numerous small “fringe” bubbles at or very near the contact of the sample with the capsule wall, which result from heterogeneous nucleation along the contact [Mangan and Sisson, 2000]. We ignore those and measured only bubbles that nucleated in the interiors for our analysis. Because bubble nucleation depends on the degree of supersaturation, which is quantified as the difference between saturation pressure and actual pressure, we must calculate the saturation pressure, $p_{\text{sat}}$, of each sample. It is equal to the pressure at which the melt is saturated with the measured concentration of H$_2$O, according to the solubility model of Liu et al. [2005]. Similarly, we used the model of Liu et al. [2005] to estimate H$_2$O contents expected at final pressures, $p_f$. Water contents were measured in one decompressed sample that did not nucleate bubbles and found to match those of the hydrated sample used. We conclude that no water diffused out of the samples during the 60 s at low pressure.

Final pressures, $p_f$, ranged from 8.5 MPa to 100 MPa (Table 1). Decompression rates ranged between approximately 4 MPa s$^{-1}$ and 32 MPa s$^{-1}$ (Figure 1) and are defined as the difference between initial and final pressures divided by the time required to reach final pressure after the onset of decompression. Within the range of examined decompression rates, there was no significant correlation between decompression rate and whether bubbles nucleated or not during a given experiment. Similarly, whether bubbles nucleated did not significantly depend on $p_{\text{sat}}$, but rather appears to first-order dependent on the dif-

Figure 1. Difference of saturation pressure, $p_{\text{sat}}$, and final pressure, $p_f$, as a function of decompression rate, $dp/dt$. The threshold between homogeneous bubble nucleation (solid symbols) and no nucleation (open symbols) approximately correlates with $p_{\text{sat}}-p_f$, as indicated by the dashed line.

Figure 2. Difference of saturation pressure, $p_{\text{sat}}$, and final pressure, $p_f$, as a function of $p_{\text{sat}}-p_f$. The threshold between homogeneous bubble nucleation (solid symbols) and no nucleation (open symbols) approximately correlates with $p_{\text{sat}}-p_f$, as indicated by the dashed line. Symbols are the same as in Figure 1.

Figure 3. Bubble number density, $N_m$, as a function of supersaturation pressure, $p_{\text{sat}}-p_f$, indicating the $N_m$ is to first-order dependent on $p_{\text{sat}}-p_f$. Symbols are the same as in Figure 1.
Mourtada-Bonnefoi and Laporte, 2004; Hamada et al., 2010] because of the higher and more narrow range of initial water contents used.

3. Nucleation Theory

3.1. Classical Theory of Stationary Nucleation

[20] The spontaneous formation of molecular clusters is associated with a decrease in free energy, resulting from cluster formation and an increase in free energy, caused by the creation of an interface between the nucleus and the metastable liquid phase. The sum of these changes in free energy is energetically favorable.

[21] In classical nucleation theory, the spontaneous rate of cluster formation of critical size is based on an assumed steady state, obtained from the dimensionless Zeldovitch factor, $Z$, and the frequency, $\omega$, of formation of nuclei, is larger than the critical size [e.g., Hirth et al., 1970; Hurwitz and Navon, 1994; Debenedetti, 1996; Mourtada-Bonnefoi and Laporte, 2002]. They are given by

$$Z = \frac{\Omega_L (p_b - p)^2}{8\pi\sigma^{1/2} k_BT}$$

(2)

and

$$\omega = \frac{16\pi\sigma^2 n_0 D}{a_0 (p_b - p)}$$

(3)

where $\Omega_L$ is the molecular volume of water, $k_B = 1.38 \times 10^{-23}$ J K$^{-1}$ is the Boltzmann constant and $T$ is an absolute temperature. $n_0$ is the number of water molecules per unit volume, $a_0 \approx (n_0)^{-1/3}$ is the distance between molecule centers, and $\sigma$ is the interfacial tension between bubble nucleus and melt phase, assumed to be a constant and equal to the value at equilibrium conditions, $\sigma_\infty$.

[22] The supersaturation pressure $(p_b - p)$ describes the degree of disequilibrium, where $p_b$ is the internal pressure of the critical nucleus and $p$ is the ambient pressure of the melt phase. In general, $p_b$ will be smaller than the saturation pressure of the melt, $p_{sat}$, and can be calculated from [Debenedetti, 1996; Cluzel et al., 2008]

$$\Gamma(p_b, T) p_b = \Gamma(p_{sat}, T) p_{sat} e^{(\Delta p_{sat})/k_BT},$$

(4)

where $\Gamma(p_b, T)$ and $\Gamma(p_{sat}, T)$ are the fugacity coefficients of the volatile phase at the specified pressure and temperature.

[23] Based on the above definitions, the stationary nucleation rate, based on the classical theory, can be written as [Hirth et al., 1970; Hurwitz and Navon, 1994; Mourtada-Bonnefoi and Laporte, 2002]

$$J_{cls} = A e^{-W_{cl}/k_BT}.$$  

(5)

[24] Here, $W_{cl}$ is the classical work of nucleus formation, first derived by Gibbs [1961]. The coefficient, $A$, is defined as

$$A = \frac{2\Omega_L D}{a_0} \left(\frac{\sigma_\infty}{k_BT}\right)^{1/2},$$

(6)

where in our case $D$ is the diffusivity of H$_2$O in the metastable melt phase.

[25] $W_{cl}$ depends on a single unknown quantity, the surface tension between bubble nucleus and melt phase, and is given by

$$W_{cl} = \frac{16\pi\sigma^3}{3(p_b - p)}.$$  

(7)

[26] It is important to note that in this definition surface tension between bubble nucleus and melt phase is considered equivalent to the macroscopically measurable interfacial tension between the magmatic vapor phase and the melt phase, $\sigma_\infty$, where the subscript $\infty$ denotes an interface of large radius of curvature, compared to a critical nucleus.

3.2. Nonstationary Nucleation

3.2.1. Nucleation Time Lag

[27] The finite time required for nucleation to reach steady state can be characterized by $\tau_{l}$, the nucleation time lag [e.g., Debenedetti, 1996; Kashchiev, 2000; Mourtada-Bonnefoi and Laporte, 2002]. The value of $\tau_{l}$ can be calculated as

$$\tau_{l} = \frac{4}{\pi^3 \omega Z^2}.$$  

(8)

[28] The nonstationary nucleation rate, $J_{clt}(t)$, is given by [Debenedetti, 1996]
\[ J_{cl} (t) = J_{cl} [1 - \exp(-t/\tau_i)], \]  
\[ J_{cl} (t) = J_{cl} \left[ 1 + 2 \sum_{i=1}^{\infty} (-1)^i \exp(-i^2 t/\tau_i) \right]. \]

where \( t \) is the time. An alternate formulation yielding similar results is given by Kashchiev [2000] as

\[ J_{cl} (t) = J_{cl} \left[ 1 + 2 \sum_{i=1}^{\infty} (-1)^i \exp(-i^2 t/\tau_i) \right]. \]

[29] For hydrated rhyolitic melt \( \tau_i \sim 10^{-6} \) s implying that steady state is reached after \( <10 \) \( \tau_i \sim 10^{-5} \) s. Consequently, \( J_{cl} \approx J_{cl} \) is a valid approximation and we shall use \( J_{cl} \) as the classical nucleation rate throughout the remainder of this discussion, in lieu of \( J_{cl} \) or \( J_{cl} \).

3.2.2. Induction Time

[30] The induction time, \( \tau_i \), also referred to as induction period, is the time that elapses until an appreciable number of bubbles are experimentally observable [Kashchiev, 2000]. A practical estimate of \( \tau_i \) is [Kashchiev, 2000]

\[ \tau_i = b_{in} \tau_{in} + \frac{1}{J^2}. \]

where \( b_{in} \approx 1, V \) is the volume of the system and \( J \) is the actual nucleation rate. For small values of \( \tau_i \), as is the case here,

\[ \tau_i \approx \frac{1}{J^2}. \]

[31] As discussed in section 2, a subset of experiments had induction times that were greater than the duration of the experiment and did not nucleate bubbles (Table 1).

3.3. Nonclassical Theory for Thermodynamically Consistent Work of Nucleus Formation

[32] The classical nucleation work, \( W_{cl} \), is in principle valid for all possible values of thermodynamic parameters of the metastable phase, that is density fluctuations and nucleus size. The value of \( \sigma \), however, is usually only measurable for macroscopic conditions, where its value is expected to be larger than the surface tension associated with a critical cluster [Kashchiev, 2003, 2004], for which the interface is thought to be diffuse instead of sharp. To overcome this limitation, Kashchiev [2003, 2004] derived a higher-order approximation of the nucleation work, \( W_{nc} \), that permits the use of the macroscopic value of \( \sigma \), but is, nevertheless, valid across the whole range of nucleus sizes.

\[ W_{nc} = \frac{16 \pi \sigma^3}{3(p_b - p)^2}. \]

where \( \Delta p^* \) is a reference pressure, conventionally taken as the difference between \( p_b \) and the pressure at the spinodal, assuming it exists. This formulation is thermodynamically consistent in the sense that the classical value of \( W_{nc} \) is recovered at \( \xi \to 0 \), whereas the nucleation energy vanishes at \( \xi \to 1 \). The corresponding value of \( \sigma_{nc} \) is given by

\[ \sigma_{nc} = \sigma_{\infty} (1 - \xi^2)^{1/3}. \]

4. Modeling Approach

[33] Kashchiev’s formulation for the stationary nonclassical nucleation rate is

\[ J_{nc} = Ae^{-W_{nc}/k_B T}. \]

[34] It is based on the ratio of the nonclassical nucleation work to the classical value and is given by the approximation

\[ \frac{W_{nc}}{W_{cl}} = 1 - \xi^2. \]

[35] Here, \( W_{nc} \) is defined as

\[ W_{nc} = \frac{16 \pi \sigma_{nc}^3}{3(p_b - p)^2} \]

and \( \xi \) is defined as the normalized supersaturation pressure

\[ \xi = \frac{p_b - p}{\Delta p^*} = \frac{\Delta p_{ns}}{\Delta p^*}. \]

During each experiment, the hydrated melt was decompressed at an almost constant temperature, \( T \), from the initial pressure, \( p_{\text{initial}} \) at time \( t = 0 \), to the final pressure, \( p = p_{\text{final}} \) at time \( t = \tau_{\text{dec}} \). During the time interval \( 0 \leq t \leq \tau_{\text{dec}} \), the supersaturation pressure, \( \Delta p_{ns} \), steadily increased, unless the characteristic time scale of water diffusion into growing bubbles [e.g., Lensky et al., 2004; Gonnermann and Manga, 2007] became shorter than the characteristic decompression time before \( t = \tau_{\text{dec}} \) was reached. After decompression, the sample was held at \( p = p_{\text{final}} \) for a duration of \( \tau_{\text{final}} - \tau_{\text{dec}} \), at which time the sample was abruptly quenched. For all experiments \( 3 \leq \tau_{\text{dec}} \leq 35 \) s and \( \tau_{\text{final}} \) was either 30, 60, or 120 s (Table 1).
We model bubble nucleation over the entire time interval $0 \leq t \leq \tau_{\text{final}}$. In some experiments, and model simulations thereof, the nucleation work, $W_{\text{nc}}$, was too high and nucleation rates too low for any bubbles to nucleate within the sample over the duration of the experiment, that is $\tau_{\text{final}} < \tau_f$ and $N_m = 0$. For most experiments, however, nucleation rates were sufficiently high for bubbles to begin to nucleate after some time and to continue nucleating until the end of the experiment, or until volatile diffusion begins to deplete the melt of H$_2$O supersaturation and nucleation ceases.

Once a bubble has nucleated, H$_2$O diffuses from the melt into the bubble. Hence, the concentration of H$_2$O in the melt will no longer be uniform throughout the melt volume (Figure 4). Consequently, both bubble nucleation and growth need to be modeled in order to estimate the degree of volatile supersaturation throughout the melt volume, which in turn affects the rate of bubble nucleation. We will first summarize the methodology for bubble growth modeling in section 4.1 and subsequently discuss the approach to modeling of bubble nucleation in section 4.2.

4.1. Modeling Bubble Growth

We assume that the size of the critical bubble nucleus can be derived from the Laplace relation, which describes the mechanical equilibrium condition for a bubble

$$p_s - p = \frac{2\sigma_{\infty}}{R}, \quad (18)$$

where $p_s$ is the pressure inside the bubble and $R$ its radius. The critical bubble radius, $R_c$, that satisfies equation (18) is given by [e.g., Proussevitch et al., 1993]

$$R_c = \frac{2\sigma_{\infty}}{\Delta p_s}. \quad (19)$$

Typically, $R_c$ is of the order of 1–10 nm and if $R < R_c$, the bubble will shrink and disappear. Because the value of $\sigma_{\infty}$ is not known a priori, we use $\sigma_{\infty}$ instead of $\sigma_{nc}$ in equation (19). The difference between the two values is at most a factor of two and, as already discussed in Gonnermann and Houghton [2012], small variations in surface tension do not sufficiently affect the diffusive bubble growth calculations.

Bubble growth is a consequence of the volume expansion of the already exsolved H$_2$O vapor and the diffusion of H$_2$O from the melt into existing bubbles. The latter typically accounts for about 99.90–99.99% of the final bubble volume, with final bubble radii typically of the order of $10^{-5}–10^{-4}$ m. The mass flux of H$_2$O into each bubble is determined by the concentration gradient in the melt at the melt-vapor interface, that is at radius $r = R$. It is calculated as

$$q = D \left( \frac{\partial c}{\partial r} \right)_{r=R}. \quad (20)$$

The diffusivity of H$_2$O within rhyolite melt, $D$, is based on the formulation of Ni and Zhang [2008]. The value of $q$ is calculated from a diffusion model for bubble growth [e.g., Amon and Denson, 1984; Arefmanesh and Advani, 1991; Proussevitch et al., 1993], wherein bubbles are assumed to be spatially distributed, such that each bubble can be approximated as a sphere.
surrounded by a spherical melt shell of thickness \( S-R \) (Figure 4). Because of the spherical symmetry inherent in this approximation, volatile diffusion simplifies to

\[
\frac{\partial c}{\partial t} + v_r \frac{\partial c}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right),
\]

where \( v_r = dR/dt \) is the radial velocity of melt at \( r = S \). Equation (21) is solved using an implicit finite difference scheme, employing a Lagrangian frame of reference, a nonuniform grid [Arefmanesh and Advani, 1991; Proussevitch et al., 1993] and a Neumann boundary condition at \( r = S \), given by

\[
\left( \frac{\partial c}{\partial r} \right)_{r=S} = 0.
\]

[44] Mass conservation of \( \text{H}_2\text{O} \) requires that

\[
\frac{d}{dt} \left( \rho_m R^3 \right) = 4R^2 \rho_m q,
\]

where \( \rho_m \) is the melt density and the density of the exsolved gas phase, denoted as \( \rho_g \), depends on \( p_g \) via an equation of state. Here, we use the modified Redlich-Kwong equation of state of Kerrick and Jacobs [1981].

[45] Bubble growth is resisted by viscous and capillary stresses, which are balanced by the pressure difference between the gas mixture inside the bubble and the surrounding melt

\[
p_g(t) - p(t) = \frac{2\sigma_\infty}{R} + 4\eta_c \frac{1}{R} \frac{dR}{dt}.
\]

[46] The effective viscosity, \( \eta_e \), accounts for the radially variable, \( \text{H}_2\text{O} \)-dependent Newtonian viscosity of the melt [Lensky et al., 2001; Hui and Zhang, 2007].

[47] Bubble growth for a representative bubble, nucleated at time \( t_i \), is calculated for the time interval \( (t_i \leq t \leq t_{\text{final}}) \). At each bubble-growth time step the coupled equations (21), (23), and (24) are solved iteratively until convergence of \( p_g \), similar to the methodology described in Proussevitch et al. [1993]. This results in the required data arrays \( c_{i,j} \) and \( v_{i,j} \), which are subsequently used during the calculation of bubble nucleation, in order to estimate the degree of supersaturation throughout the modeled melt volume.

Figure 5. The value of \( \sigma_\infty \) used to calculate \( W_d \) (equation (7)). The value of \( \sigma_\infty \) is based on a fit of measured surface tension values of haplogranitic melt at 1000°C, adjusted to the corresponding temperatures of 825°C, 850°C, and 875°C [Bagdassarov et al., 2000], using \( d\sigma/dT = 7.5 \times 10^{-2}\text{Nm}^{-1} \text{C}^{-1} \) [Bagdassarov et al., 2000]. Solid squares are the measured values of Bagdassarov et al. [2000] adjusted to 850°C, all other symbols are the same as in Figure 1.

4.2. Modeling Bubble Nucleation

[48] We calculate the number of bubbles that nucleate during the time interval \( t_i \leq t \leq t_i + \Delta t \) and within a given subvolume of melt, \( v_{i,k} \), as

\[
n_{i,k} = v_{i,k} J_{\text{nc}}(i,k) \Delta t.
\]

[49] Here \( t_i = i\Delta t \) and \( J_{\text{nc}}(i,k) \) is calculated from equation (13) for the average concentration of \( \text{H}_2\text{O} \) at time \( t_i + \Delta t/2 \) and within the subvolume of melt denoted by the subscript \( k = 1 \ldots m \). The value of \( J_{\text{nc}}(i,k) \) depends on the pressure \( p \) at time \( t_i + \Delta t/2 \), as well as on the average \( \text{H}_2\text{O} \) concentration at that time and within the given subvolume of melt \( v_{i,k} \). Here, the spatio-temporal distribution of \( \text{H}_2\text{O} \) concentration is, as already discussed in section 4.1, obtained from the diffusive bubble growth calculations. The total volume of bubbles at time \( t_i + \Delta t/2 \) within the entire melt volume is then calculated as

\[
N_m(t_i) = \sum_{j=1}^{i} \left( \sum_{k=1}^{m} n_{i,k} \right).
\]

[50] The value of \( \sigma_{\text{nc}}(t_i) \) required for the calculation of \( J_{\text{nc}} \) is calculated from equation (17), which is based on contact angle measurements of \( \sigma_\infty \) for haplogranitic melt by Bagdassarov et al. [2000], albeit extrapolated to the temperature of our experiments using \( d\sigma/dT = 7.5 \times 10^{-2}\text{Nm}^{-1} \text{C}^{-1} \) [Bagdassarov et al., 2000]. The resultant values of \( \sigma_\infty \) for both the contact angle measurements and our experiments are shown in Figure 5.
5. Results and Discussion

[51] We modeled homogeneous bubble nucleation in the experiments of section 2 by integrating equation (26), which requires the calculation of $J_{nc}$ and, hence, $\sigma_{nc}$. The latter is estimated from equation (17), wherein the value $\Delta p^*$ is not known a priori. For each experiment, we therefore repeated the entire analysis over a range of $\Delta p^*$, with the objective of finding a value for $\Delta p^*$, that minimizes the difference between observed and predicted bubble number densities. The match between observed and calculated values of $N_m$ is quantified as a misfit, $0 \leq \chi \leq 1$, which is defined as

$$\chi = |N_{m,pred} / N_{m,obs} - 1| \text{for} N_{m,pred} < N_{m,obs}$$  \hspace{1cm} (27a)  

$$\chi = |N_{m,obs} / N_{m,pred} - 1| \text{for} N_{m,pred} \geq N_{m,obs}$$  \hspace{1cm} (27b)

[52] For each experiment, the value of $\chi$, as a function of $\Delta p^*$, is shown in Figure 6. For all cases a unique and well-defined minimum identifies the value of $\Delta p^*$ at which $\chi \ll 0.01$ and $N_{m,pred} \approx N_{m,obs}$. For experiments where $N_{m,obs}$ is small, relatively modest changes in $\Delta p^*$ result in a large change in $N_{m,pred}$, relative to $N_{m,obs}$. Consequently, $\chi$ has a narrow minimum. In contrast, for larger values of $N_{m,obs}$ there is a broader minimum in $\chi$, because at a given change in $\Delta p^*$ the change in $N_{m,pred}$, relative to $N_{m,obs}$, is smaller.

[53] Two contrasting examples of combined bubble nucleation and growth modeling are shown in Figure 7. In the case of G-1112, nucleation rates and resulting bubble number densities were too low for water diffusion into existing bubbles to significantly affect the supersaturation of most of the sample. Consequently, most of the sample remained fully saturated (e.g., Figure 4) and bubbles nucleated until the sample was quenched after 60 s. In contrast, for G-1233 nucleation rates and resulting bubble number densities were high. Water diffused into existing bubbles from the entire melt volume within a short time after the onset of nucleation and, consequently, there was only a short burst of nucleation, albeit at high rates. These two examples illustrate the critical importance to accurately model diffusive bubble growth, in order to accurately calculate the change in bubble nucleation rate, $J$, throughout the experiment.

[54] During modeling the value of $W_{cl}$ is calculated from equation (7), with $\sigma_{\infty}$ based on the work of Bagdassarov et al. [2000] and using the maximum value of $\Delta p$, attained during the experiment. The value of the nonclassical nucleation work, $W_{nc}$, is calculated from equation (14), at the time-dependent value of $\Delta p$, and the value of $\Delta p^*$ where $\chi$ has its minimum. The resultant values of $W_{nc}/W_{cl}$, as a function of $\xi = \Delta p/\Delta p^*$, are shown in Figure 8, which demonstrates that the nucleation work for homogeneous bubble nucleation in rhyolitic melt is significantly lower than would be predicted from CNT. Estimates of $W_{nc}/W_{cl}$ are based on the formulation of Kashchiev [2003, 2004] and represent the fractional reduction in nucleation work, resulting from the diffuse
interface between bubble nuclei and surrounding melt phase and ensuing dependence of surface tension on the degree of supersaturation, also observed in other types polymer melts [Guo et al., 2012]. Although it remains to be shown theoretically what precise functional form a nonclassical formulation for nucleation work in silicate melts should have, the approach is in principle valid for one component and multi-component liquids [Kashchiev, 2004].

Figure 9 shows that for all experiments in which bubbles nucleated, the dimensionless nucleation work, \( W_{nc}/k_BT \), depends on \( \Delta p_s \) and falls approximately along the empirical trend

\[
W_{nc}/k_BT = 67.5 - e^{(\Delta p_s/84.5\text{MPa})^2}. \tag{28}
\]

[56] We note that this trend is purely empirical and has no theoretical basis. It is, nevertheless, distinctly different from the trend predicted by classical nucleation theory. For \( \Delta p_s \) approximately <95 MPa the dimensionless nucleation work is almost constant, decreasing only slightly as supersaturation increases. This is a consequence of the dependence of \( W_{nc} \) on \( \sigma_{nc}^3/\Delta p_s^2 \) (equation 15) and the concurrent increase of \( \sigma_{nc} \) and \( \Delta p_s \), as shown in Figure 11. The resultant nucleation rates are almost constant, which is shown in Figure 12. In contrast, CNT would predict large increases in nucleation rate (Figure 9) under the same conditions [e.g., Mangan and Sisson, 2005]. The trend obtained from our experiments reverses, however, for \( \Delta p_s \) approximately >95 MPa, because \( \sigma_{nc} \) decreases with further increase in \( \Delta p_s \).
increase in nucleation rate with supersaturation is larger than would be predicted by CNT (Figure 9), presumably because of CNT’s assumption of a constant surface tension. One may speculate whether this rapid increase in nucleation rate, compared to CNT, might relax the high decompression rates required by CNT, in order to produce bubble number densities \( \geq 10^{14} \text{m}^{-3} \) [Toramaru, 2006].

[57] As shown in Figure 10, the empirical fit of equation (28) is able to predict bubble number densities, \( N_{m,\text{pred}} \), to within approximately one order of magnitude of the observed value, \( N_{m,\text{obs}} \), across six orders of magnitude. We also find that the value of \( \sigma_{\text{nc}} \) is always lower than \( \sigma_{\infty} \) (Figure 11). This dependence of \( \sigma_{\text{nc}} \) and, hence, \( W_{\text{nc}}/k_B T \) on the degree of supersaturation, \( \Delta p_s \), is consistent with the work of Kashchiev [2003, 2004]. Moreover, the maximum values of \( W_{\text{nc}}/k_B T \) at which nucleation is observed are similar to those obtained from other nucleation experiments [e.g., Kelton and Greer, 2010, and references therein].

6. Conclusions

[58] As a result of our integrated study of homogeneous bubble nucleation during decompression experiments of hydrous rhyolitic melt and numerical modeling based on nonclassical nucleation theory, we find that the surface tension between critical bubble nuclei and surrounding melt is smaller than the macroscopically measurable surface tension. This is consistent with a diffuse interface between the nucleating phase and the surrounding metastable liquid, resulting in a dependence of surface tension on the degree of supersaturation. Our results explain the discrepancy between surface tension estimates from bubble nucleation experiments and macroscopic surface tension measurements in silicate melts.

[59] We show that the dependence of nucleus surface tension on supersaturation can in principle be modeled, albeit with the caveat that the difference between the internal pressure of the bubble nucleus and the spinodal is not known a priori, thus introducing an additional parameter. Perhaps the best way forward will be to obtain an empirical formulation for the nucleation work, which is independent of this parameter. For the experiments analyzed herein such an empirical equation predicts homogeneous bubble nucleation rates for our experiments to within one order of magnitude of actual values. At low (high) degrees of...
supersaturation the nucleation work decreases more gradually (steeply) with increasing supersaturation than predicted by classical nucleation theory. How this departure from the classical theory affects predictions of bubble nucleation during explosive volcanic eruptions requires further work.

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