Magmatic storage conditions, decomposition rate, and incipient caldera collapse of the 1902 eruption of Santa Maria Volcano, Guatemala

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1. Introduction

Caldera formation is attributed to the under-pressurization that results from the evacuation of large volumes of magma from a chamber in the crust at a rate faster than the crust can elastically or fluidly respond (Druitt and Sparks, 1984). When the host rock can no longer withstand that under-pressure, the roof is drawn into the emptying chamber. The formation of calderas is generally thought to be dependent on the volume of erupted magma with some dependency on the depth of magma storage. In general, explosive eruptions that disperse more than 4–5 km$^3$ of magma (dense rock equivalent, DRE) often form calderas, and all else being equal, eruption from a shallow chamber is more likely to form a caldera than eruption from a deep chamber (e.g. Roche and Druitt, 2001; Lavallee et al., 2006). The onset of caldera collapse is often signaled in deposits by layers with increased lithic content, and collapse occurs during eruption, not after (e.g. Suzuki-Kamata et al., 1993; Browne and Gardner, 2004; Andrews et al., 2007). Caldera formation often results in the modification of conduit dimensions, the opening of new conduits, and in changes in eruptive behavior (e.g., Browne and Gardner, 2004; Andrews and Gardner, 2010). Analysis of natural samples and experimental petrology can help describe magmatic conditions prior to and during caldera formation.

The 1902 eruption of Santa Maria Volcano, Guatemala, provides an excellent case for detailed examination of the processes governing caldera formation as the eruptive volume is 8.5 km$^3$ (DRE), however, no obvious caldera is topographically observed. The eruption is not unique in lacking a caldera, indeed, the 1600 Huaynaputina (Peru) eruption of ~11 km$^3$ (Adams et al., 2001; Lavallee et al., 2006; de Silva et al., 2008) also did not form a caldera. The absence of topographic evidence of calderas at Santa Maria Volcano and Huaynaputina suggests that some controls on caldera formation remain undefined.

This paper presents pre-eruptive storage conditions, ascent rates, and conduit dimensions for the 1902 Santa Maria eruption obtained using phase equilibrium experiments, volatile contents from melt inclusions, and Al-thermobarometry. Those results, comparison with previous decompression experiments, and CONFLOW conduit modeling provide
a comprehensive evaluation of the Santa Maria volcanic system and investigation of controls on caldera formation. Together, this work indicates that the 1902 eruption ended when subsidence into the emptying magma reservoir blocked the eruption conduit(s); eruption was thus terminated by incipient caldera collapse.

2. Background

Previous workers, including Rose (1972), and Williams and Self (1983) provide detailed eruption chronologies and also describe the physical volcanology of the eruption. Briefly, eruptive activity began on 24 October 1902 with a series of earthquakes, and a steam column was observed on the mountain’s southern flank in the early afternoon. By ~1700 h, ash and pumice fall began in nearby communities, and by 2000 h, the eruption column height was estimated to be ~10 km. The eruption intensity increased such that by ~0100 h on 25 October a Plinian eruption column was established above the vent and detonations were heard as far as 850 km away. The Plinian phase of eruption ended after a duration of 18–20 h, and the maximum column height was estimated to be 27–29 km. Phreatomagmatic activity began on 26 October and continued into 1903. During the events of 24–25 October, the SW flank of the Santa Maria cone was largely removed. Investigators that traveled to Santa Maria in December 1902 described a series of six vents in the crater floor oriented in a line from W to E, with the largest approximately 30 m in diameter (Rose, 1972 and references therein).

The 1902 Plinian fall deposit comprises a single unit with little to no internal structure other than a gradual upward coarsening, reflecting an increase in eruption intensity (Williams and Self, 1983). No pyroclastic flows were observed during the course of the eruption, nor were pyroclastic flow deposits observed in the extensive works of Rose (1972) and Williams and Self (1983); this suggests that the eruption column never collapsed but rather remained in the wholly buoyant regime. The boundary between the Plinian pumice fall deposits and the overlying (phreatomagmatic) ash is marked by 4–5 cm of lithic-rich ash containing white dacite pumice; Williams and Self (1983) interpret this layer as representing a period of vent clearing. Isopach maps indicate a tephra volume of ~20 km$^3$, equivalent to ~8.5 km$^3$ of dacite magma (DRE) (Rose, 1972; Williams and Self, 1983). Isopleth maps of the largest pumice and lithic clasts and the plume rise equation of Wilson et al. (1978) suggest a peak eruption mass flux of ~3.3 × 10$^8$ kg/s and a column height of 35 km (Williams and Self, 1983); using those same data, Carey and Sparks (1986) estimate a column height of 34 km corresponding to a mass flux of 2–3 × 10$^8$ kg/s.

Notable eruptive activity resumed in June 1922 with the beginning of lava dome eruptions in the southwest portion of the 1902 crater. Essentially continuous activity since that time has constructed the Santiaguito lava dome complex comprising four domes, El Brujo, El Monje, La Mitad, and Caliente, in order of decreasing age, emplaced from W to E (Fig. 1). The earliest erupted dome lavas are compositionally identical to the 1902 dacite (Scott et al., 2013). As the eruption has progressed, the erupting magma composition has changed such that andesitic magma erupted in 2013. Recent work by Scott et al. (2012, 2013) describes the petrology and magmatic plumbing system of the Santiaguito dome complex, and links that system to the 1902 dacite. They suggest that the magma erupted from 1922 through at least 2012 is part of a continuous magma series related by differentiation and fractional crystallization. Based upon amphibole geothermobarometry, they reason that this magma originated from depths of 12–29 km (corresponding to pressures of 300–600 MPa) and temperatures of 900–1000 °C. Work by Singer et al. (2014) describes a compositionally and thermally zoned system with 1020 °C basaltic andesite and 870 °C dacite stored at pressures >180 MPa. Their analyses suggest that plagioclase crystals were exchanged between the two magmas and that much of the crystallization history recorded by those crystals occurred during decompression.

3. Experimental and analytical methods

Pumice samples from the 1902 eruption were selected from the National Rock and Ore Collection at the Smithsonian Institution National Museum of Natural History (NMNH). Those samples were collected by Melson and Vogeli in 1973 from a ~2 m section exposed along the road to the top of the trail to the summit. The largest of the pumice, sample 113100-11 4/8 collected 4–34 cm above the base of the section, was split into separate pieces for bulk analysis, thin sectioning, and phase equilibria experiments.

3.1. Phase equilibria experiments

Starting material for phase equilibria experiments was obtained by lightly crushing the dacite pumice to a ~50 μm powder. Experiments were prepared by sealing aliquots of powdered pumice in Ag$\text{Pd}_{30}$ tubing, ranging in size from 2 to 5 mm O.D., with sufficient deionized H$_2$O such that all experiments were water saturated ($P_{\text{H}_2\text{O}} = P_{\text{total}}$). Experiments were conducted at NMNH in externally heated Waspalloy pressure vessels with Ni filler rods, where H$_2$O was the pressurizing medium. Geschwind and Rutherford (1992, 1995) have shown that the Ni filler rods and Waspalloy pressure vessels have an intrinsic oxygen fugacity of approximately one log unit (±0.5) above the Ni–NiO (NNO) buffer curve. All experiments were quenched with compressed air for...
approximately 30 s and then immersed in water; a test using a pressure-head that allows a thermocouple to fit in the “hot-spot” verified that this method quenches experiments to <500 °C within ~30 s of being pulled from the furnaces. After quenching, experimental capsules that contained excess water were considered successful. Experimental samples were mounted in 10 mm diameter epoxy rounds and polished for reflected light and electron microscopy. Four pairs of reversal experiments were run to verify phase stabilities. For the conditions of interest, aliquots of one sample previously run at a higher pressure and/or temperature and one sample from a lower pressure and/or temperature were reloaded and sealed in separate Ag25Pd75 tubes with sufficient deionized H2O to ensure saturation and run at the new conditions. The presence of the same phase assemblages and compositions within the two charges indicates phase stability and compositional equilibrium.

3.2. Compositional analyses

Bulk geochemical analyses were conducted at Franklin and Marshall College using X-ray fluorescence. Pumice 113100-11 4/8 was analyzed by powder X-ray diffraction at NMNH. Aliquots of the same powder used for bulk compositional analysis were mounted on glass fibers and analyzed using two D/Max Rapid microdiffractometers with imaging plate detectors, one with a Mo X-ray source and one with a Cu source. Images were collected for 5 and 10 min on the same two aliquots on both instruments. The diffraction data were analyzed using Rigaku and Jade software packages. Preferred orientation effects were minimized by using a randomly prepared sample mount, and by integration of the full Debye–Scherrer diffraction rings. Diffraction patterns were compared against experimental and calculated reference patterns in the International Centre for Diffraction Data powder diffraction database to identify the mineral phases present.

Mineral and glass compositions were analyzed at NMNH using the Department of Mineral Sciences Nova NanoSEM analytical scanning electron microscope and JEOL-8900 electron probe microanalyzer (EPMA). In general, stable phases assemblages were identified using the SEM and compositions were obtained using the EPMA. All EPMA analyses were collected using a 15 keV, 10 nA beam scanned over a 6 × 5 μm region. Analyses were processed using Probe for EPMA software. Sodium migration in glasses was monitored and corrected using the volatile correction routine within the Probe for EPMA software. Rhyolite glasses VG568, RLS-132, and MLV-36 were used to monitor drift during glass analyses. The SEM was used to analyze the compositions of plagioclase crystals too small for EPMA analysis (<15 μm); those analyses were collected using the Nova NanoSEM standardless EDS routine.

3.3. FTIR analyses

Plagioclase crystals from a lightly crushed fragment of pumice 113100-11 4/8 were selected for melt inclusion analysis. Those crystals were mounted in epoxy wafers and then polished on one side such that inclusions were intersected or near the exposed crystal surface. The polished sides of the wafers were then attached to metal pucks with superglue and the rough sides of the wafers were ground and polished using a lapping fixture such that the final crystal wafers were 30–200 μm thick with singly- and doubly-exposed melt inclusions. The doubly-polished crystals were released from the pucks by soaking in warm acetone.

Melt inclusion compositions were measured with Fourier transform infrared spectroscopy (FTIR); exposed inclusions were also analyzed with electron microprobe. FTIR analyses were conducted with a ThermoElectron Nicolet Continuum FTIR within the NMNH Department of Mineral Sciences. All analyses were conducted using transmission of white light through a salt window. The analysis aperture was oriented and sized to fit each inclusion; 128 to 512 scans were collected for each inclusion, depending on inclusion size, with a wavenumber resolution of 4 cm⁻¹. The resulting spectra were analyzed at 3550 cm⁻¹ for total H2O; CO2 was detected in no inclusions. Measured peak-to-background IR absorbances were converted to water concentrations following the methods of Stolper (1982), Newman et al. (1986), and Zhang et al. (1997). Absorptivity of 76 L mol⁻¹ cm⁻¹ was used for the total H2O 3550 cm⁻¹ absorption band.

Measurement of inclusion thickness presents the greatest source of uncertainty in quantitative FTIR measurement (e.g. Stolper, 1982; Newman et al., 1986; Nichols and Wysoczanski, 2007; Befus et al., 2012). Inclusion thicknesses were measured by first determining total crystal thickness with a micrometer, and then applying that measurement to calibrate the gradients on the fine focusing wheel of a petrographic microscope. In this manner, the thicknesses of inclusions that were not doubly intersected could be determined. Nichols and Wysoczanski (2007) have shown that such inclusions can still be used for FTIR analysis as there is no significant interference between the IR absorbance bands of H2O, CO2, and the host crystals (in this case, plagioclase). Befus et al. (2012) have shown that the thicknesses of unexposed inclusions can be measured optically, although the path length is often variably underestimated; despite that concern, they find that the average water contents of the same group of inclusions is statistically the same regardless of whether those inclusions are analyzed when unexposed, singly-exposed, or doubly-exposed. Replicate thickness measurements on Santa Maria inclusions and comparison with micrometer measurements in this study indicate uncertainties of <2 μm for inclusion thicknesses.

4. Results

4.1. Composition and texture of the 1902 dacite

The primary products of the Santa Maria 1902 eruption are white, dacite pumice containing minor mafic enclaves (<1 vol.%). Bulk chemical analysis of the pumice (including the enclaves) and the matrix glass are reported in Table 1.

Table 1 Compositions of 1902 Santa Maria whole rock and matrix glass. Whole rock XRF analysis was conducted at Franklin and Marshall College; whole rock analysis includes minor (<1 vol.%) mafic enclaves within the dacite host. Electron microprobe analyses were conducted at Smithsonian Institution National Museum of Natural History using the Department of Mineral Sciences JEOL 8900 electron probe microanalyzer. Analyses were conducted with a 15 keV, 10 nA beam rastered over a 6 × 5 μm region. Count times of 10–30 s on peak and 5–15 s off-peak were utilized. All microprobe analyses were conducted using Probe for EPMA software; glass analyses were collected using that program’s self-volatile calibration. Kakauan hornblende, Kakauan anorthoclase, Bytownite, rhyolite glass VG-568, basalt glass A-99,fluor-apatite, microcline, ilmenite, pyrite, and scapolite were used as analytical standards. Rhyolite glasses VG-568, RLS-132, and MLV-136 were used to monitor drift during glass analyses. Matrix glass compositions are normalized to 100 wt.% and values in parentheses indicate 1 standard deviation.

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>FeO</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>P₂O₅</th>
<th>LOI</th>
<th>Total</th>
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<tr>
<td>Bulk (XRF)</td>
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<td>16.60</td>
<td>1.24</td>
<td>2.30</td>
<td>0.16</td>
<td>1.15</td>
<td>3.63</td>
<td>4.99</td>
<td>1.88</td>
<td>0.19</td>
<td>1.36</td>
<td>100.07</td>
</tr>
<tr>
<td>SiO₂</td>
<td>TiO₂</td>
<td>Al₂O₃</td>
<td>FeO</td>
<td>MnO</td>
<td>MgO</td>
<td>CaO</td>
<td>Na₂O</td>
<td>K₂O</td>
<td>P₂O₅</td>
<td>LOI</td>
<td>Total</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Matrix glass</td>
<td>73.0 (.55)</td>
<td>0.23 (.05)</td>
<td>14.9 (.26)</td>
<td>1.97 (.38)</td>
<td>0.12 (.07)</td>
<td>0.44 (.06)</td>
<td>1.89 (.12)</td>
<td>4.91 (.61)</td>
<td>2.43 (.06)</td>
<td>0.13 (.05)</td>
<td>0.03 (.03)</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>
The pumice are highly vesicular (>75 vol.% estimated from thin section); vesicles range in size from 20 to 500 μm, with most vesicles ~100 μm across. Vesicle walls are nearly always <10 μm thick. SEM images show that the rhyodacite matrix glass contains sparse microlites that occur as either clusters of crystals along the margins of large amphiboles or as isolated crystals within vesicle walls. Microlites are generally <5 μm, highly elongate (aspect ratios >4:1), and often have poorly developed swallow-tail ends. Analysis of back-scattered electron SEM images following the methods described in Andrews and Gardner (2010) shows that microlite volumetric number densities are <10^2 mm^{-3}.

4.2. Phenocryst assemblage

The natural phenocryst assemblage observed with petrographic and electron microscopy comprises plagioclase, orthopyroxene, amphibole, titanomagnetite, and apatite. X-ray diffraction analysis confirms the presence of those phases. Williams and Self (1983) also describe the occurrence of biotite in the samples, but that phase was observed neither petrographically nor in X-ray diffraction analyses of samples used in this study. Overall crystallinity of the vesicle-free pumice is 23–28 vol.%, with plagioclase making up the majority of the phenocrysts, and orthopyroxene as the second most abundant phase. Amphibole, titanomagnetite and apatite occur in low abundances (<1%).

Plagioclase composes ~15–20 vol.% of the vesicle-free pumice (Fig. 2). Phenocrysts are typically euhedral, prismatic and 70–100 μm in length, although occasional plagioclase >200 μm in length are present. Representative compositions are shown in Table 2. Rim compositions range from An40 to An45. Crystals are typically zoned, and may be grouped into three main populations: those with compositional ranges between An20 and An45, those between An40 and An60, and those with An90 cores and monotonic or step-like decreases to ~An40–An45 rims. Rare crystals show albite twinning. Crystals often contain sieved or obviously resorbed zones. Glass inclusions are present in many plagioclase phenocrysts, and are particularly abundant in restricted zones.

Orthopyroxene occurs in the dacite as euhedral phenocrysts ~50 μm in length (Fig. 2). The prisms compose <5 vol.% of the vesicle free pumice. The phenocrysts are not compositionally zoned and have uniform compositions of En68–70Fs28–30Wo01–02 (Table 3). Orthopyroxene crystals often contain abundant apatite and less common Fe–Ti oxide inclusions; those mineral grains are generally euhedral and <30 μm.

Amphibole crystals compose <1 vol.% of the vesicle free pumice (Fig. 2). Based upon texture, two populations of crystals are present. Larger amphiboles are typically 50–100 μm in length, although...
occasional crystals are present up to 200 μm, and show green to yellow or pale brown pleochroism. Those crystals often have resorbed margins and prominent embayments (Fig. 2). Smaller amphibole microphenocrysts occur as euhedral prisms, typically ~20–200 μm in their longest dimension, and show no evidence of disequilibrium. Electron probe analysis shows that although the compositions can be classified as tschermakitic-paragasites, magnesiohornblendes, and low-Ca amphiboles following the method of Ridolfi et al. (2010), the compositions form a continuum (Table 4). Tschermakitic-paragasites and low-Ca amphiboles are the most common analyzed compositions. Most of the larger crystals contain tschermakitic-paragisite cores and either magnesiohornblende or low-Ca amphibole rims. The smallest amphibole microphenocrysts are generally low-Ca amphibole. Glass inclusions ~<20 μm are occasionally present in the amphibole phenocrysts.

Titanomagnetite phenocrysts occur as 100–200 μm euhedral cubes and compose <1 vol.% of the vesicle-free pumice. Apatite phenocrysts compose ~<1 vol.% of the dacite pumice. Those crystals are euhedral, hexagonal prisms, generally 40–100 μm in length, and frequently contain glass inclusions (Fig. 2).

4.3. Glass inclusions

Glass inclusions are present in many plagioclase phenocrysts. Two populations of inclusions are typically present: small (~<30 μm) euhedral or slightly rounded, equant inclusions that often contain a single vapor bubble, and larger, irreguarly shaped inclusions that often contain multiple vapor bubbles. This paper focuses on the smaller inclusions as they do not show obvious communication with crystal exteriors.

Plagioclase-hosted glass inclusions show a broad range in dissolved H2O concentrations, from <1 to 8.8 wt.%, with most inclusions containing <5 wt.% (Fig. 3; Table 6). CO2 was detected in no inclusions. Electron probe analyses of a subset of those inclusions indicate that the glasses are rhyolitic (Table 5) but of variable composition. Specifically, SiO2 ranges from 71.4 to 78.3 wt.%, Al2O3 from 14.4 to 17.2 wt.%, and FeO from 0.6 to 2.3 wt.% (Fig. 3).

4.4. Experimental results

Experimental results and phase stabilities are summarized in Figs. 4 and 5. Plagioclase is stable below 925 °C at 100 MPa, below 850 °C at 200 MPa, and below 825 °C at 250 MPa. Amphibole is stable at pressures above 100 MPa for temperatures ~<850 °C, and at temperatures below 850–875 °C for pressures >150 MPa. Orthopyroxene is stable below 925 °C at 100 MPa, below 850 °C at 175 MPa; as temperature decreases and pressure increases, however, orthopyroxene is not stable, such that there is a narrow range of P-T conditions where both amphibole and orthopyroxene are stable. The position of the orthopyroxene-out curve is ~40 °C higher than the orthopyroxene-out cummingtontine-in curve of Geschwind and Rutherford (1992); no cummingtonte was found in the experiments in this study. Titanomagnetite is stable below 800 °C at 250 MPa and below 925 °C for pressures of 100 MPa. Apatite was stable in all experiments except for the run at 925 °C and 100 MPa. No experiments contained biotite.

Plagioclase compositions vary systematically with temperature, pressure and dissolved melt H2O content (Fig. 4; Table 6). The most anorthitic plagioclase, An40, occur at 125 MPa and 875 °C and 100 MPa and 900 °C, An40 plagioclase occur at conditions between 800 °C at 225 MPa and ~860 °C at 100 MPa, and An30 plagioclase occur between 800 °C at 150 MPa and 830 °C at 100 MPa. The most albitic plagioclase, An92, occur in experiments run at 775 °C at 150 MPa and 800 °C at 100 MPa. Amphibole compositions show complicated variation with pressure and temperature. Many experiments contain tschermakitic-paragasites, magnesiohornblendes, and low-calcium amphiboles (Supplementary Material 1). The compositional similarities between the tschermakitic-paragasites and the resorbed phenocrysts in the natural pumice suggest that some amphiboles in the experiments are likely antecrystic fragments and not newly grown crystals.

Table 2

Representative electron microprobe analyses of two plagioclase crystals in the 1902 Santa Maria dacite. "Crystal 1" is an oscillatory-zoned crystal with An50 rim and "Crystal 2" is a crystal with ~An50 core and An55 rim. Analyses were conducted with a 15 keV, 10 nA beam rastered over a 6 × 5 μm region. An, Ab, and Or indicate mole percents anorthite, albite, and orthoclase, respectively. Count times of 10 s on-peak and 5 s off-peak were utilized. All microprobe analyses were conducted using Probe for EPMA software. Kakani anorthoclase, Bytownite, rhyolite glass VC-568, basalt glass A-99, and microcline, were used as analytical standards. Microprobe uncertainties are reported in Table 1. Bytownite and anorthoclase were used to monitor drift.

<table>
<thead>
<tr>
<th>Plagioclase</th>
<th>SiO2</th>
<th>TiO2</th>
<th>Al2O3</th>
<th>FeO</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
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<tr>
<td>Crystal &quot;1&quot;</td>
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<td>26.59</td>
<td>0.60</td>
<td>0.00</td>
<td>0.00</td>
<td>8.73</td>
<td>6.53</td>
<td>0.25</td>
<td>100.52</td>
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<td>0.57</td>
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<tr>
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<td>0.00</td>
<td>0.00</td>
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<td>6.03</td>
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<td>98.25</td>
<td>0.44</td>
<td>0.55</td>
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<td>0.00</td>
<td>8.44</td>
<td>6.42</td>
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<td>95.61</td>
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<td>6.54</td>
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<td>6.24</td>
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<td>100.19</td>
<td>0.43</td>
<td>0.55</td>
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<td>0.00</td>
<td>0.04</td>
<td>9.53</td>
<td>5.86</td>
<td>0.15</td>
<td>99.18</td>
<td>0.47</td>
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<td>0.05</td>
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<td>0.00</td>
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<td>4.14</td>
<td>0.09</td>
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<td>0.62</td>
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<td>1.14</td>
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<td>0.03</td>
<td>0.03</td>
<td>17.87</td>
<td>1.61</td>
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<td>32.03</td>
<td>0.94</td>
<td>0.00</td>
<td>0.00</td>
<td>14.70</td>
<td>2.62</td>
<td>0.04</td>
<td>98.86</td>
<td>0.75</td>
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<td>Crystal &quot;2&quot;</td>
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<td>0.04</td>
<td>12.49</td>
<td>4.52</td>
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<td>0.00</td>
<td>9.51</td>
<td>6.20</td>
<td>0.18</td>
<td>99.15</td>
<td>0.45</td>
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Table 4
Representative amphibole microprobe analyses with pressure–temperature conditions as estimated using the Ridolfi et al. (2010) method. Amphibole type is indicated as low-Ca amphibole (low-Ca), magnesiohornblende (Mg-Hbl), or tschermakitic-paragasite (Tsch-Prg). All microprobe analyses were conducted using Probe for EPMA software. Kakanui hornblende, Kakanui anorthoclase, basalt glass A-99, fluor-apatite, microcline, ilmenite, pyrite, and scapolite were used as analytical standards. Microprobe uncertainties are reported in Table 1. Kakanui hornblende was used as a secondary standard and drift monitor. Uncertainties in pressure and temperature are 30 MPa and ~2 °C.

<table>
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<tr>
<th>Amphibole</th>
<th>SiO$_2$</th>
<th>TiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>FeO</th>
<th>MnO</th>
<th>MgO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>Cl</th>
<th>Total</th>
<th>P (MPa)</th>
<th>T (°C)</th>
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<td>9.54</td>
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<td>0.42</td>
<td>98.99</td>
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<tr>
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<td>0.27</td>
<td>100.05</td>
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<td>11.08</td>
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<tr>
<td>Mg-Hbl</td>
<td>44.17</td>
<td>1.40</td>
<td>12.70</td>
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<td>0.29</td>
<td>96.21</td>
<td>495</td>
<td>961</td>
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</table>

Fig. 3.A) Melt inclusions show a broad range of dissolved water concentrations, with nearly all inclusions containing ~15 wt.% H$_2$O. B) Microprobe analyses of a subset of inclusions show systematic variation in glass compositions, suggesting post entrapment crystallization. Plotted compositions are anhydrous, with K$_2$O plotted with gray diamonds and CaO plotted with white squares. Matrix glass compositions are indicated with the larger symbols plotted at 73.0 wt.% SiO$_2$.

5. Discussion

5.1. Pre-eruptive storage conditions

5.1.1. Experimental petrology

Comparison of the natural pumice and glass inclusions with experimental phase stabilities and compositions constrains the pre-eruptive storage conditions. The phase assemblage of the Santa Maria dacite (plagioclase + orthopyroxene + titanomagnetite + amphibole + apatite) is stable at 110–140 MPa at temperatures ~850 °C and between ~850 °C and ~875 °C for pressures between 140 and 175 MPa (Fig. 4).
Consideration of plagioclase composition further constrains the likely storage conditions to between the An40 and An45 plagioclase compositional contours. Together those observations suggest that prior to eruption the magma was stored at approximately 140–150 MPa and 840–850 °C.

Experimental and natural glass compositions also suggest pre-eruptive storage at approximately 150–160 MPa and 840–860 °C. At those conditions, the concentrations of SiO2, Al2O3, CaO, MgO, K2O, and FeO within the experimental glasses are compositionally similar to the natural matrix glass (within 1 standard deviation as measured in the natural samples). At higher pressures, the Al2O3 composition of the natural glass indicates lower storage temperatures than the other oxide components, whereas at lower pressures, amphibole is not stable.

### 5.1.2. Glass inclusions in plagioclase

Glass inclusions provide independent evidence of entrapment pressure and thus storage depth. The inclusions span a broad range of water contents (~1 to 8.8 wt.%) but have a much narrower range of SiO2 concentrations (~71 to 78 wt.%) (Fig. 3). Anhydrous composition of the matrix glass is 73.0 wt.% SiO2, and 2.4 wt.% K2O; using those compositions as a starting point, most of the compositional array can be explained by up to 30% crystallization. As the magma contains amphibole as a stable phase, a minimum of ~4 wt.% water was initially dissolved in the magma (e.g. Browne and Gardner, 2006), and thus the inclusions most likely contained at least that much water at the time of entrapment. As water is incompatible in the host crystals, post-entrapment crystallization will increase water content relative to the initial composition; instead, most inclusions contain <5 wt.% H2O, suggesting that most of the range in water concentrations is the result of leaking during decompression and eruption. The most likely pre-eruptive dissolved water concentration was 4.5–5 wt.%. Application of the Moore et al. (1998) solubility model to the experimental glass compositions and 4.5–5 wt.% H2O constrains pre-eruptive conditions to 140–170 MPa (Fig. 4).

### 5.1.3. Plagioclase hygrometry

The Santa Maria experimental dataset provides an opportunity to test the recent extension of the plagioclase liquid hygrometer of Lange et al. (2006) to rhyolites in the recalibrated hygrometer of Waters and Lange (submitted for publication). Fig. 5 presents a comparison between the dissolved H2O concentration predicted by the Waters and Lange hygrometer and the concentration as predicted by the Moore et al. (1998) solubility model for each experiment that contains both plagioclase and glass. The two sets of calculations agree to within ~0.5 wt.%, with the Moore et al. model typically predicting lower dissolved H2O. If the maximum measured An content is used in hygrometer calculations for each experiment, the difference between the solubility model and hygrometer decreases only slightly. Notably, although the hygrometer requires that a pressure be assumed, it is not particularly sensitive to that pressure (changing the assumed pressure from 0.1 to 250 MPa only produces a ~0.2 wt.% change in calculated melt water concentration) (Lange et al., 2009). Application of that hygrometer to the 1902 matrix glass and plagioclase compositions recovers the observed range in water concentrations (4.5–5.0 wt.%) for temperatures between 825 and 865 °C for plagioclase with compositions ranging from An40–An45.

### 5.1.4. Amphibole geothermobarometry

Scott et al. (2012) apply the Ridolfi et al. (2010) thermo-oxybarometer to amphiboles from the Santa Maria 1902 dacite and Santiago volcano lava domes and describe amphibole crystallization conditions of 300–600 MPa, 900–1000 °C and oxygen fugacities of NNO + 0.4 to NNO + 1.2. Application of that same technique to natural amphibole phenocrysts and microphenocrysts in this study suggests a similarly broad range in conditions: 160–500 MPa, 840–980 °C, and oxygen fugacity of NNO + 1.5 ± 0.2 (Fig. 6). The lower end of that range overlaps the pre-eruptive storage conditions indicated by experimental phase equilibria, melt inclusions, and plagioclase hygrometry. If only the magnesiohornblende microphenocrysts are considered, then the Ridolfi et al. method returns a much more restricted range in conditions: 180 ± 50 MPa and 852 ± 20 °C. Although the Ridolfi et al. method calculates total pressure, rather than Ptotal as indicated by melt inclusions, phase equilibria, and plagioclase hygrometry, it is unlikely that this difference in calculation accounts for the discrepancies between storage conditions as no CO2 was detected in any of the glass inclusions. Notably, the Ridolfi et al. method does not return pressure–temperature–fO2 estimates for amphiboles with Al2O3 > 0.21; ~40% of the amphibole analyses are low-Ca amphiboles with Al2O3 > 0.21.

Application of the Ridolfi et al. thermo-oxybarometer to amphiboles in phase equilibria experiments can test the accuracy and precision of the technique and possibly explain the calculated range in storage conditions suggested by natural amphibole compositions (Fig. 6). Conditions indicated by most of the tschermakitic-paragases do not vary systematically with the experimental run conditions but do broadly overlap with the natural amphiboles. In contrast, the compositions of the experimentally grown magnesiohornblendes and a subset of the tschermakitic-paragases suggest crystallization conditions closer to the host experiments. But those calculated conditions are still hotter and usually higher pressure than measured run conditions: often > 50 °C and >50 MPa. The discrepancies between calculated and experimental conditions are generally greater than the uncertainties in the Ridolfi et al. thermo-oxybarometer (e.g. 30–50 MPa and ~20 °C). These results suggest that the Ridolfi et al. (2010) geothermobarometer must be used with caution as it returns systematically high estimates of pressure and temperature and cannot be applied to significant fractions of amphibole compositions.
Comparison of the experimental results and analyses of natural amphiboles suggests that most of the tschermakitic-paragasites present in the experiments are not newly grown, but rather fragments of amphiboles in the experimental pumices. Similarly, those crystals in the natural dacite do not record crystallization conditions of the dacite magma, but rather the experiments are not newly grown, but rather fragments of amphiboles in the starting material (those crystals are effectively antecrysts). Similarly, those crystals in the natural dacite do not display well-developed reaction rims, and euhedral amphibole microphenocrysts are present in the pumice, thus the magma likely did not exit amphibole stability until the temperature conditions that occurred prior to shallow level storage. Disparate origins of the magnesiohornblende and tschermakitic-paragasites are consistent with the work of Singer et al. (2014) who suggest exchange of crystals between the dacite and other magmas during mingling, mixing, and ascent. Further, the broad range in amphibole inclusion compositions (and their implied pressures and temperatures of crystallization) suggests that during ascent from relatively high pressure (up to 500 MPa) to shallow storage, nucleation and growth of new amphibole microphenocrysts were kinetically favored over reequilibration of pre-existing amphiboles. Although some of the larger amphiboles show evidence for resorption, the phenocrysts do not display well-developed reaction rims, and euhedral amphibole microphenocrysts are present in the pumice, thus the magma likely did not exit amphibole stability until the final, syn-eruptive decompression. The eruptive decompression rate was fast enough to prevent development of reaction rims (Rutherford and Hill, 1993; Rutherford and Devine, 2003; Browne and Gardner, 2006).

5.2. Decompression rate

The matrix glass of the dacite pumice is nearly free of microlites (<10^4 mm^-3), indicating that decompression of the magma immediately prior to eruption was too fast for homogeneous nucleation and growth of microlites. Similarly, the presence of euhedral amphibole microphenocrysts indicates decompression timescales faster than that of amphibole breakdown (Rutherford and Hill, 1993; Rutherford and Devine, 2003; Browne and Gardner, 2006). Previous workers have used microlite nucleation and growth in decompression experiments to constrain decompression rates of rhyodacite and rhyolite magmas (e.g. Hammer and Rutherford, 2002; Castro and Dingwell, 2009; Andrews and Gardner, 2010). Those studies show that microlite sizes and number densities are controlled by decompression rate. Recent work by Waters et al. (submitted for publication) suggests that the initial viscosity of the decompressing magma and the rate of change in partial viscosity of the decompressing magma are important parameters for microlite nucleation and growth; attention to those parameters can allow decompression rates experimentally determined for one magma to be applied to a different magma provided that the compositions are reasonably similar.

Assuming decompression began at 150 MPa and 850 °C, then the Santa Maria pre-eruptive melt viscosity was 10^4 Pa s as calculated using the method of Giordano et al. (2008). Andrews and Gardner (2010) used multi-step decompression experiments to examine a rhyodacite decompressed from 150 to 20 MPa at 890 °C in 5 MPa increments and found that ~10^4 mm^-3 new microlites occurred in samples decompressed slower than 0.01 MPa/s but faster than 0.005 MPa/s. As the initial viscosity of the Ksudach KS1 rhyodacite magma, 10^3 Pa s,
is lower than that of the 1902 Santa Maria dacite, the dacite could likely have decompressed somewhat more slowly than 0.01 MPa/s and still grown <10^3 mm m -3 microlites. Castro and Dingwell (2009) decompressed aliquots of the 2008 Chaiten rhyolite from 150 MPa and 825 °C, using 5 MPa steps; their experiments decompressed at ~0.005 MPa/s grew microlites whereas those decompressed at ~0.01 MPa/s did not. The melt viscosities of those experiments, 10^4.7 Pa s, are slightly higher than for the 1902 dacite, thus the Santa Maria dacite could have decompressed faster than ~0.005 MPa/s, but more slowly than ~0.01 MPa/s, and nucleated and grown ~10^6 mm m -3 microlites. Together, the Castro and Dingwell (2009) and Andrews and Gardner (2010) studies constrain the likely average decompression rate to between 0.005 and 0.01 MPa/s, corresponding to ascent rates of ~0.2 to ~0.4 m/s (assuming a lithostatic pressure gradient of 0.025 MPa/m) or ~4 to ~8 h for a single parcel of magma to move from the storage reservoir to the vent. Those rates are minima as they represent the decompression of H2O, and if the magmatic fluid was a H2O-CO2 mixture, then the total rate would be faster. Although the minimum decompression rates are fast, they are comparable to the decompression rates of other large, explosive silicic eruptions such as the 2008 Chaiten (Castro and Dingwell, 2009) and ~240 C.E. Ksudach KS1 (Andrews and Gardner, 2010) eruptions.

5.3. Eruption conduit dimensions

Decompression rate and mass flux can help to constrain conduit dimensions (e.g. Andrews and Gardner, 2010). The 1-dimensional numerical model CONFLOW (Mastin and Ghiorso, 2000; Mastin, 2002) provides a means of determining steady state decompression rate and mass flux for a given magma (with specified melt composition, phenocryst content, water content, and temperature) ascending a cylindrical conduit of length L with basal and top diameters of d_b and d_t. Using the measured matrix glass composition, 5.0 wt.% initially dissolved H2O, 25 vol.% crystals (assumed to be all plagioclase for the model), the measured matrix glass composition, 5.0 wt.% initially dissolved H2O, 25 vol.% crystals (assumed to be all plagioclase for the model), and nucleated and grown ~10^6 mm m -3 microlites. Together, the Castro and Dingwell (2009) and Andrews and Gardner (2010) studies constrain the likely average decompression rate to between 0.005 and 0.01 MPa/s, corresponding to ascent rates of ~0.2 to ~0.4 m/s (assuming a lithostatic pressure gradient of 0.025 MPa/m) or ~4 to ~8 h for a single parcel of magma to move from the storage reservoir to the vent. Those rates are minima as they represent the decompression of H2O, and if the magmatic fluid was a H2O-CO2 mixture, then the total rate would be faster. Although the minimum decompression rates are fast, they are comparable to the decompression rates of other large, explosive silicic eruptions such as the 2008 Chaiten (Castro and Dingwell, 2009) and ~240 C.E. Ksudach KS1 (Andrews and Gardner, 2010) eruptions.
Fig. 6. Pressure–temperature conditions calculated using the Ridolfi et al. (2010) amphibole geothermobarometer as applied to natural samples (A) and experiments (B). A) Amphibole microphenocrysts show a broad range in calculated pressures and temperatures, with magnesiohornblende (gray squares) crystals indicating pressures and temperatures similar to those suggested by melt inclusions, plagioclase compositions, and phase equilibria. B) Large disparities exist between experimental run conditions (black squares) and amphibole microphenocrysts showing a broad range in calculated pressures and temperatures, with magnesiohornblende (gray squares) crystals indicating pressures and temperatures similar to those suggested by melt inclusions, plagioclase compositions, and phase equilibria. Conditions indicated by circles. B) Large disparities exist between experimental run conditions (black squares) and amphibole microphenocrysts showing a broad range in calculated pressures and temperatures, with magnesiohornblende (gray squares) crystals indicating pressures and temperatures similar to those suggested by melt inclusions, plagioclase compositions, and phase equilibria. Conditions indicated by circles.

model results provide useful insights regarding the characteristic conduit length scales, but do not completely describe the actual conduit geometry. It should also be noted that CONFLOW assumes that the system remains at equilibrium during decompression and that the eruption rate may be underestimated by as much as a factor of two (Mangan et al., 2003).

Assuming a cylindrical conduit \( \left( d_c = d_t \right) \), the mass flux can be approximated when the conduit diameter is \( \sim 100 \) m. At that diameter, however, the average decomposition rate prior to modeled fragmentation is \( -2 \) orders of magnitude too high \( (\sim 0.5 \text{ MPa/s}) \). Modeled cylindrical conduits with diameters as small as 5 m all predict decomposition rates an order of magnitude (or more) too high, and mass fluxes up to three orders of magnitude too low. If the conduit is modeled with a conical geometry, as was done by Andrews and Gardner (2010) for the Ksudach rhyodacite, then a conduit with \( d_c = 100 \) m and \( d_t = 10 \) m predicts the appropriate decomposition rate, but the mass flux is \( -2 \) orders of magnitude too low \( (\sim 4 \times 10^6 \text{ kg/s}) \). If a tapering conduit with a constriction at a depth of 3 km is considered, then \( d_c = 50 \) m and \( d_t = 25 \) m predict the appropriate decomposition rate, but again a mass flux that is far too low \( (\sim 1 \times 10^6 \text{ kg/s}) \) in this scenario. It is at a depth of 3 km, and we assume that the conduit above this point is cylindrical and has no further effect on the conduit flow.

The CONFLOW model results suggest that it is unlikely that the 1902 Santa Maria conduit had a simple cylindrical or conical geometry. The tapering or conical conduits are the only geometries that predict the appropriate decomposition rates, but those geometries predict mass fluxes that are two orders of magnitude too low. One way to resolve that discrepancy is by considering a dike-like conduit. Using the 1D CONFLOW simulations as a guide, a dike-like geometry with a comparatively broad basal aperture tapering to a narrower top or constriction could account for both the decomposition rate and the mass flux. As a highly simplified starting point for discussion, linear extrapolation of the 1D CONFLOW results to an elongate geometry suggests that a dike of 5–7 km in length originating from a 6 km depth with a basal aperture of 50–100 m tapering to 25 m at a depth of 3 km (and maintaining that aperture to the surface) would produce the proper decomposition rate and mass flux. If, as is likely considering reduced drag from the conduit walls, a dike-like geometry increases the decomposition rate and the mass flux is not a simple linear product of the 1D CONFLOW results, then more realistic, albeit less specific, conduit geometries can be inferred, e.g. a kilometer long dike tapering from a basal aperture on the order of \( -50 \) m to a constriction on the order of \( -25 \) m at a depth of 3000 m. Fully modeling such geometries is, however, beyond the scope of this paper.

Two lines of evidence support a dike-like conduit and vent geometry at Santa Maria. First, the mass flux of the eruption, \( 2-3 \times 10^8 \text{ kg/s} \), was sufficiently high that the eruption column should have been in the collapsing or partially collapsing regime (e.g. Sparks, 1986), but no pyroclastic flows or their resulting deposits were observed. One way to resolve that discrepancy is for the eruption to occur from an elongate vent such that the eruption column has an enhanced surface area through which turbulent mixing and air entrainment can occur; eruption column collapse and pyroclastic flow generation occur at much higher mass fluxes from fissure or ring vents than from cylindrical vents (Legros et al., 2000). Second, aligned vents in the crater floor observed in December 1902 and the lava dome complex emplaced along a W–E trend both suggest a dike. The maximum vent size described in December 1902 was \( -30 \) m in diameter, and the distance from the summit of the western dome (Brujo) to the eastern dome (Caliente) is \( -1.75 \) km (Fig. 1); taken as a highly simplified map projection of the conduit, those dimensions are of the same order as the dike length inferred by the CONFLOW modeling.

5.4. Incipient caldera formation

Several parameters of the 1902 eruption are similar to those of caldera-forming events, suggesting that conditions of the Santa Maria system were necessary, although evidently not sufficient, for caldera formation. First, the eruption evacuated \( 8.5 \) km\(^3\) of magma from the crust (Williams and Self, 1983); this volume is comparable to or larger than other caldera-forming eruptions (e.g. Scott et al., 1996; Gardner and Tait, 2000; Andrews et al., 2007). Second, the pre-eruption storage depth of 6–7 km is similar to or shallower than other magmatic systems that have formed calderas (Rutherford and Devine, 1996; Roche and Druitt, 2001; Lavallee et al., 2006; Andrews and Gardner, 2010).

Although a well-developed caldera did not form during the 1902 eruption, two lines of evidence suggest that the onset of caldera formation collapsed the conduit thereby terminating the eruption and preventing full caldera collapse. First, the aligned vents observed in the crater floor following the eruption are likely the surface manifestation of a dike, and it can be expected that this dike could act as a caldera-bounding fault (or a pre-existing fault have acted as the conduit). The aligned vents and present Caliente dome complex occur along the southern margin of the crater beneath Santa Maria. That position is consistent with a fault that accommodated some of the slip required to form the 1902 crater. The southwest flank of Santa Maria...
collapsed during the eruption, leaving a >1000 m scarp. The domes, the scarp, and a steep ridge northwest of the domes circumscribe the (failed) caldera floor.

Second, lithic-rich layers are prominent in the upper part of the eruption deposits. The lithic-rich layers likely record a large pulse of conduit erosion generated by motion across the dike. As the caldera began to form, motion on the dike/fault closed the conduit and terminated the eruption. The volume of lithics is likely much smaller than for true caldera-forming eruptions (Browne and Gardner, 2004; Andrews et al., 2007), but this is expected as termination of the eruption at the onset of caldera collapse would result in ejection of fewer lithics (and lack of a true caldera). This hypothesis suggests that slip across the dike occurred with a normal sense of motion: collapse of the southern portion of the Santa Maria edifice was partly accommodated by slip across the northward dipping eruption conduit, but that motion sealed the conduit (Fig. 7). Eruption termination by collapse of the conduit system rather than exhaustion of the magma supply is further supported by the compositions of the earliest erupted Santiaguito dome lavas in 1922. Those lavas have essentially identical bulk compositions to the 1902 dacite (Scott et al., 2012), although their phenocryst assemblages and reaction rims on amphiboles show evidence for slow decompression (Scott et al., 2012). Eruption of the same magma after a hiatus indicates that the original magma reservoir was not exhausted, and that reestablishing a conduit through the structure that collapsed in 1902 required 20 years. The proposed incipient collapse is similar to the “cryptic caldera” at Huaynaputina proposed by Lavallee et al. (2006), with the important addition that this new hypothesis can explain both the termination of eruption and the lack of a southern well-developed caldera. Williams and Self (1983) interpreted the lithic-rich layers as recording clearing of the conduit in the newly formed crater, but there is no indication of an increase in eruptive mass flux that might accompany such a widening. Instead the eruption ceased shortly after deposition of the layers and no waning phase was observed nor represented in the deposits (Williams and Self, 1983). Absent another process, termination of the eruption immediately following conduit widening would require that the system exhausted all eruptible magma, but the first lavas erupted from the Santiaguito dome complex were compositionally indistinguishable from the 1902 dacite (Scott et al., 2013).

6. Conclusions

Phase equilibria experiments, glass inclusions, and plagioclase hygrometry indicate that the Santa Maria 1902 dacite was stored at 140–170 MPa and 840–850 °C prior to eruption. Those storage conditions are markedly cooler and shallower than previous estimates based upon amphibole geothermobarometry; this discrepancy results from amphiboles being present as antecrysts (recording earlier higher pressure, higher temperature conditions) and a systematic bias in the amphibole geothermobarometer toward hotter and deeper conditions. During eruption, the dacite magma decompressed at an average rate of ~0.005 to 0.01 MPa/s. Balancing that decompression rate with eruption mass fluxes suggests a dike-like conduit with basal aperture on the order of 50 m, narrowing to an aperture of ~25 m at a depth of 3000 m. The eruption of 8.5 km$^3$ dacite magma (DRE) resulted in incipient caldera collapse that was accommodated at least partly by motion across the conduit. That motion collapsed the conduit, abruptly terminating the Plinian eruption and arresting full caldera collapse.

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