Petrologic indicators of preeruption magma dynamics

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ABSTRACT

New phase-equilibria experiments on dacite from the June 1991 eruption of Mount Pinatubo allow calibration of a geobarometer for matrix glass at pressures of 160—220 MPa. Comparison with natural glass compositions suggests equilibration at lower $f_{\text{H}_2\text{O}}$ than is inferred from Al-in-hornblende geobarometry. The disparity between geobarometric techniques may be explained by a decrease in $f_{\text{H}_2\text{O}}$ and consequent crystallization several weeks before eruption—a time period too short for hornblende reequilibration. Reduced $f_{\text{H}_2\text{O}}$ could have resulted from processes associated with basalt magma injection, including (1) late-stage magma ascent (under H$_2$O-saturated conditions) or (2) influx of other volatiles (CO$_2$, SO$_2$) into the dacite magma system.

keywords: dacites, Pinatubo, geobarometry, phase equilibria, volatiles

INTRODUCTION

Physical, petrologic, and atmospheric observations of the 1991 Pinatubo eruption are unmatched in variety and scientific impact by those of any other large explosive volcanic eruption (e.g., McCormick et al., 1995; Robock, 2002). Studies of this event integrate
geophysical and geochemical techniques for quantifying the preeruptive static state, including magma-reservoir geometry and depth in the crust, as well as the dynamics of volcanic eruption (Newhall and Punongbayan, 1996). One of the most fruitful developments in volcano petrology of the last decade is the application of the principles of phase equilibria to precisely determine magma residence conditions prior to explosive eruptions. Quantitative understanding of all subsequent eruptive processes rely on accurate assessment of these “initial conditions” (Snyder, 2000).

Two independent petrologic studies determined preeruptive magma storage at 220±50 MPa (Rutherford and Devine, 1996; Scaillet and Evans, 1999). However, in attempting to investigate magma ascent and degassing processes, we discovered that this assessment of the equilibration pressure is incomplete. By virtue of their fast equilibration rates, glass compositions record partial equilibration at a lower partial pressure of H$_2$O ($P_{H2O}$) at least three weeks before the magma’s appearance at the surface. Differences in the rates of mineral-melt reactions may be similarly exploited at other volcanic systems to set limits on the timing and extent of preeruptive magma degassing.

**PROCESS PETROLOGY AT PINATUBO**

Various petrologic tools have been used to determine the temperature, oxygen fugacity ($f_{O_2}$), pressure (i.e., depth), and volatile concentrations of the climactic Pinatubo dacite prior to eruption. Temperature calculated with an iron-titanium oxide geothermometer yields equilibration temperatures of 780 ± 30 °C (Evans and Scaillet, 1997; Scaillet and Evans, 1999). This value probably represents the magmatic temperature soon before eruption because the equilibration rates of in-contact oxides are on the order of a week (Venezky and Rutherford,
The phase assemblage of the dacite helps estimate other intensive parameters. Rutherford and Devine (1996) showed that the natural assemblage is stable from 750 to 800 °C for a relatively wide range of pressure (110 – 370 MPa) at volatile saturation with an H₂O-rich fluid. Subsequent fine tuning of storage pressure was based on three petrologic techniques. (1) An empirical hornblende geobarometer relating pressure to hornblende composition (Schmidt, 1992) yields a magma equilibration pressure of 220 ± 50 MPa (Rutherford and Devine, 1996). In essence, the total Al content in hornblende increases with increasing pressure by a Tschermak exchange (Mg₁Al⁻¹Si₁Aliv) when hornblende is in equilibrium with plagioclase, K-feldspar, quartz, biotite, titanite, melt, an H₂O-rich fluid, and either magnetite or ilmenite. It is particularly important that aSiO²melt = 1 in order to buffer Aliv in hornblende, and this condition is satisfied for the Pinatubo dacite (Pallister et al., 1996). (2) Minimum pressure estimates were found by calculating the saturation pressure for the dissolved volatile composition preserved in glass inclusions (Gerlach et al., 1996; Pallister et al., 1996). Quartz-hosted glass inclusions contain 6.4 – 7.0 wt.% dissolved H₂O (Gerlach et al., 1996; Rutherford and Devine, 1996), giving a minimum saturation pressure of 206 MPa (Moore et al., 1998). All available evidence points toward saturation of the magma with an H₂O-rich fluid (Wallace and Gerlach, 1994). (3) The isothermal dacite liquid line of descent is tracked as a function of pressure to its intersection with the natural glass composition. Previous studies used this method to rule out pressures higher than 220 MPa for Pinatubo (Rutherford and Devine, 1996; Scaillet and Evans, 1999). However, experiments were not run at lower pressures, and the natural glass composition was never closely matched. Here we present the results of new experiments at lower pressures (Table 1) that bracket the natural glass compositions.
EXPERIMENTAL AND ANALYTICAL METHODS

Two natural dacite samples were used as starting materials for isothermal (780 °C) phase-equilibrium experiments: (1) Pin 1-10, white pumice from a climactic air-fall deposit characterized in a previous experimental study (Rutherford and Devine, 1996), and (2) PC00, provided by R. Hoblitt of the U.S. Geological Survey (sample 3-18-92, Hoblitt et al., 1996), a dense juvenile dacite clast deposited by a pyroclastic density current a few hours prior to the climactic phase. Dacite erupted during pre-climactic explosive events was included to determine whether pre-eruptive storage conditions differed from those of the climactic dacite sample. Pin 1-10 and PC00 are both microlite-free and differ in vesicle texture and residual matrix-glass H2O contents (Hammer et al., 1999).

Isothermal, vapor-saturated experiments were run in cold-seal pressure vessels following well-established techniques (Rutherford and Devine, 1996; Hammer and Rutherford, 2002); the Re-ReO2 solid buffer assemblage was used (Pownceby and O'Neill, 1994). Temperature was maintained at 780°C ± 3 °C and pressure was precise to within ±5% relative. Glasses were analyzed with the Cameca Camebax electron microprobe at Brown University using a defocused beam operating at 10 nA and 15 keV. Alkali loss from the sample during analysis was mitigated by methods described by Devine et al. (1995).

RESULTS

Matrix-glass compositions for experiments using preclimactic and climactic Pinatubo dacite material follow identical trends on element variation diagrams (Fig. 1). This is an expected consequence of having the same bulk composition and a confirmation that differences in the
initial dissolved volatile content, vesicle texture, and (possibly) degree of glass polymerization are not important for the experimental conditions used.

The negative correlation of SiO$_2$ and Al$_2$O$_3$ contents (Fig. 1) of experimental matrix glasses suggests that the liquid line of descent is controlled by crystallization of feldspar. Linear mass-balance calculations indicate progressive crystallization of plagioclase (Ab$_{~60}$) and minor quartz with decreasing $P_{H2O}$. Maximum observed crystallization of 10 wt.% additional plagioclase occurred in the 150 MPa experiment (Table 1). Notably, the compositions of hornblendes in these runs are unchanged relative to the starting material and do not record exposure to $P_{H2O}$ below 220 MPa.

The anhydrous matrix-glass compositions are well characterized by the simple granite system; >90 wt.% of the glass can be apportioned to the haplogranite components albite (Ab), orthoclase (Or), and quartz (Qtz). The projection of experimental and natural Pinatubo liquid norms onto the H$_2$O-saturated haplogranite ternary (Fig. 2A; method of Cashman and Blundy, 2000) illustrates the path of the residual liquid with respect to experimentally-determined isobaric cotectics (Tuttle and Bowen, 1958). A geobarometer linearly relating $P_{H2O}$ [in MPa] to the projected Ab component, Ab’, over a limited range in pressure is: $P_{H2O} = 11.0 \times Ab’ - 383 \quad (R^2=0.995; \text{Fig. 2C})$. The glass geobarometer yields $P_{H2O}$ values of 144, 149, and 164 MPa for three independent measurements of natural dacite matrix glass composition.

**RECONCILING PETROLOGIC BAROMETERS**

The equilibration pressure indicated by experimentally calibrated Pinatubo glass geobarometry (155 ± 5 MPa) is somewhat less than the previously reported 220 ± 50 MPa based on Al-in-hornblende geobarometry. One explanation for the disparity is that the mineral and
glass geobarometers refer to different time periods prior to eruption. That is, $P_{\text{H}_2\text{O}}$ may have decreased from 220 to 155 MPa after growth of hornblende phenocrysts and prior to eruption. The mass-balance calculations show that changing melt composition with decreasing $P_{\text{H}_2\text{O}}$ is mainly due to feldspar crystallization. The rate of hornblende equilibration in response to a decrease in dissolved H$_2$O content is much slower than the rate of feldspar crystallization because the former requires coupled exchange of network-forming cations between the amphibole, melt, and other minerals. The latter is usually limited by comparatively rapid diffusion of mineral-forming components in the melt (Kirkpatrick, 1981). It is also important to note that the glass compositions indicate either equilibration at an ambient pressure of ~155 MPa or simply arrested approach to equilibrium at an even lower $P_{\text{H}_2\text{O}}$. Either way, the differential response rates for these local equilibria may provide additional information about the timing of perturbations in intensive parameters.

Feldspar crystallization rates and the timescales of melt equilibration following decompression from 220 MPa have been determined for this system (Hammer and Rutherford, 2002). In the case of a -70 MPa perturbation (corresponding to an effective undercooling of ~35 °C), crystallization begins immediately by growth of existing crystals. Those experiments show that the glass composition closely approaches the equilibrium composition within 500 h. This result suggests that a similar decrease in $P_{\text{H}_2\text{O}}$ in the natural dacite reservoir would be recorded by the glass compositions within three weeks of the perturbation.

**PREERUPTIVE MAGMATIC PROCESSES AT PINATUBO**

Key geophysical observations leading up to the explosive eruptions of Pinatubo (White, 1996) include the unprecedented record of deep long-period (DLP) seismicity generated 28-40
km below the summit. Two episodes of intense deep energy release that occurred on 26 – 28 May and 31 May – June 8 are correlated with near-surface LP seismicity, tremor, and increased steam emissions and/or explosions. Later DLP earthquakes immediately preceded inflation of the summit and the emergence of a hybrid andesite lava dome bearing inclusions of olivine basalt derived from the deep crust. The DLP earthquakes are interpreted to result from a choked (supersonic) flow of fluids associated with injection of basalt into the base of the dacite magma reservoir (Chouet, 1996; White, 1996). The eruption in 1991 is widely attributed to this basalt injection (Pallister et al., 1992; Pallister et al., 1996; Kress, 1997; Snyder, 2000). The injection occurred ~400 h prior to the onset of explosive activity and 480 h prior to the climactic Plinian event. Thus, the timing of basalt entering the dacite reservoir prior to eruption is comparable to the time required for melt to equilibrate to a reduction in $P_{\text{H}_2\text{O}}$ of 70 MPa by feldspar crystallization (~500 h). Can the introduction of basalt into the dacite reservoir have caused the change in the $P_{\text{H}_2\text{O}}$ reflected in the dacite matrix glass?

Basalt injection may have initiated either of two physical processes that lowered $P_{\text{H}_2\text{O}}$ in the dacite and caused feldspar to crystallize. One is ascent of H$_2$O-saturated dacite from a depth corresponding to 220 MPa to a level corresponding to 155 MPa. Assuming overburden density of 2500 kg m$^{-3}$ (Pallister et al., 1996; Rutherford and Devine, 1996), this pressure change corresponds to rise of the reservoir “crown” from 9 to 6.3 km below the surface (Fig. 3A). The shallower level is still well within the magma-reservoir volume inferred from the volcano’s post-eruption three-dimensional seismic velocity structure (Mori et al., 1996), yet corresponds to a region previously interpreted to contain uneruptable material (Rutherford and Devine, 1996) on the basis of the estimated equilibration pressures.
Alternatively, an influx of other volatiles could have lowered $P_{H_2O}$ ($f_{H_2O}$) without magma ascent, and stimulated crystallization. In this case, the match to natural glass compositions by experimental glasses formed at 155 MPa where $X_{H_2O}^{fl} = 1$ would occur at higher $P_{total}$ and lower $X_{H_2O}^{fl}$. For example, consider the erupted volume of dacite magma (5 km$^3$) coexisting with an $H_2O$-rich fluid phase of nominal volume at $P_{total} = 220$ MPa. The addition of 6 mol% CO$_2$ ($X_{H_2O}^{fl} = 0.94$) to the vapor phase lowers $f_{H_2O}$ to 155 MPa (calculations using solubility model of Moore et al., 1998). The amount of $H_2O$ released into the vapor by the rhyolite melt encountering such an influx of CO$_2$ is small ($2 \times 10^{10}$ kg; ~0.035 km$^3$) because the solubility of $H_2O$ in the melt is little reduced by in-mixing of CO$_2$. However, the effect of 10 wt% crystallization upon lowered $f_{H_2O}$ is significant, because $H_2O$ concentrated in the remaining melt far exceeds its solubility. More than double the amount of $H_2O$ released initially would be added to the vapor because of crystallization. Furthermore, additional CO$_2$ is required to maintain $X_{H_2O}^{fl} = 0.94$. If basalt containing 200 ppm CO$_2$ before mixing (Johnson et al., 1994) liberates all dissolved CO$_2$ to the vapor phase, the minimum volume of basalt involved in mixing is 1.4 km$^3$ (Fig. 3B). Each additional weight percent crystallized would require 0.1 km$^3$ more basalt to compensate.

As yet there are no independent estimates of the volume of basalt injected to the dacite reservoir for comparison. This idea could be tested by analyzing glass inclusions at the rims of feldspar phenocrysts for CO$_2$ (or S). However, no such inclusions have been found, and decompression experiments demonstrate that crystals growing under these conditions are unlikely to trap surrounding melt as inclusions (Hammer and Rutherford, 2002).

The volatile flux model is theoretically consistent with massive sulfur release into the vapor phase proposed by Kress (1997). In this case, magmatic $f_{H_2O}$ would be reduced by a combination of SO$_2$ and CO$_2$ entering the vapor phase, and moving into the dacite. Magmatic
sulfides in quenched basalt (Pallister et al., 1996) suggest that the basalt was reduced and sulfur-rich, as required by this model. The physical significance of the volatile-flux model for reducing $f_{H_2O}$ is that the total volume of the system (basalt + dacite + vapor) is increased by $\geq 30\%$. A basalt injection of the minimum magnitude considered would substantially pressurize the dacite reservoir if the additional volume could not be accommodated by deformation of the country rock.

**IMPLICATIONS**

A consequence of variable mineral-melt reaction rates is that local disequilibrium preserves information about the timing of changes in intensive parameters prior to eruption. Growth of feldspar crystals is sufficiently rapid that changing melt composition indicates decreasing $f_{H_2O}$ over time scales not accessible to mineral-melt exchange reactions. Likewise, changes in intensive parameters over minutes to hours are probably inaccessible to glass geobarometry. The results of this study suggest that matrix-glass compositions of stratigraphically controlled tephra fall units could be used as chronological $f_{H_2O}$ probes of magma reservoirs.

**ACKNOWLEDGMENTS**

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**REFERENCES CITED**


FIGURE CAPTIONS

Figure 1. Compositional trends of experimental and natural matrix glasses. Indicated pressures <300 MPa are interpolated isograds. R&D = (Rutherford and Devine, 1996). Error bars are 1σ from multiple analyses of a given sample.

Figure 2. Averaged normative glass compositions projected onto ternary haplogranite system. A: Cotectics for pure haplogranite system for varying $P_{H_2O}$ (Tuttle and Bowen, 1958) shown for comparison. Symbols are as defined in Fig. 1; compositions of reversed experiments (compositionally indistinguishable within 1σ) are averaged for clarity. B: Detail of shaded area in (A). Error symbol represents typical 1σ variation in weight percent CaO analyses (5%
relative) propagated through norm calculation and projection scheme. C: Ab' contents of natural matrix glasses are indicated with arrows, with corresponding $P_{H_2O}$ in parentheses.

Figure 3. A: Posteruption earthquake hypocenters (after Mori et al., 1996) and equilibration depths of magma from Al-in hornblende geobarometry (I) and glass geobarometry (II). Uncertainty in depth of II is smaller than the symbol. One hypothesis for reducing $f_{H_2O}$ in the dacite prior to eruption is ascent of erupted magma from I to II less than three weeks before eruption. B: Alternatively, evolved CO$_2$ from the basalt may have lowered $f_{H_2O}$ in the dacite and caused crystallization (illustration after Pallister et al., 1996). Model calculations indicate 1.4 km$^3$ basalt would produce the observed crystallization in the erupted volume of dacite (5 km$^3$); crystallization of half the ~90 km$^3$ reservoir would require 11 km$^3$ basalt.
<table>
<thead>
<tr>
<th>Natural dacite</th>
<th>Sample</th>
<th>Reference*</th>
<th>Amount crystallized† (%)</th>
<th>Σ(R²)</th>
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<td></td>
<td>13.7</td>
<td>0.200</td>
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<tr>
<td>MG</td>
<td>2</td>
<td></td>
<td>6.7</td>
<td>0.066</td>
</tr>
<tr>
<td>PC00</td>
<td>this study</td>
<td></td>
<td>10.1</td>
<td>0.101</td>
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**Experiments**

<table>
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<th>Run</th>
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<th>P, H₂O (MPa)</th>
<th>time (h)</th>
<th>Amount crystallized† (%)</th>
<th>Σ(R²)</th>
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<tr>
<td>P75a</td>
<td>P12</td>
<td>150</td>
<td>719</td>
<td>10.0</td>
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<td>Pin 1-10</td>
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<td>719</td>
<td>10.0</td>
<td>0.073</td>
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<tr>
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<td>PC00</td>
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<td>62</td>
<td>6.3</td>
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<tr>
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<td>718</td>
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</tr>
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<td>718</td>
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<td>170</td>
<td>718</td>
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<tr>
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<tr>
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Mass balance calculation determines the proportions of plagioclase, quartz, and liquid (matrix glass) required match the bulk composition given by 220 MPa glass (PC01). This calculation assumes that the matrix melt does not exchange mass with existing phenocrysts during crystallization (Hammer and Rutherford 2002). The sum of crystalline phases and goodness of fit are reported as “percent crystallized” and the sum of squares of the residuals Σ(R²), respectively.

P10 and P12 are crystal rich starting materials created by running Pin 1-10 under H₂O-saturated conditions at pressures 50-60 MPa lower than the experimental pressure. This higher-crystallinity material was run simultaneously with natural material as a reversed approach to chemical equilibrium (Edgar, 1973). Other starting materials are described in text.
Experimental matrix glasses

+ Pin 1-10 (62 h)

PC00 (718 h)

Pin 1-10 (144-600 h)

Rutherford and Devine (1996)

Natural matrix glasses

● Pallister et al. (1996)

★ Rutherford and Devine (1996)

▲ this study

$\text{SiO}_2$ (wt. %)

$\text{Al}_2\text{O}_3$ (wt. %)

390 MPa

390

300

220 MPa

150

200

180

170

160

150

73.0 74.0 75.0 76.0 77.0 78.0 79.0
\[ \text{Ab}' = 0.090\,(\text{PH}_2\text{O}) + 34.857 \]
\[ \text{PH}_2\text{O} = 11.0 - 383(\text{Ab}') \]
\[ R^2 = 0.995 \]
A

- Marked points indicate pressures at 155 ± 10 MPa and 220 ± 50 MPa,
- Arrows point to the boundary of magma storage zone.

B

- \(90 \text{ km}^3\) of \(\text{H}_2\text{O}-\text{saturated dacite porphyry pluton}\)
- \(11 \text{ km}^3\) and \(1.4 \text{ km}^3\) of mixed volatile phase
- Activity from 26 May to 8 June