1 Amphibole reaction rims as a record of pre-eruptive magmatic heating: An
2 experimental approach

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13

14 **Abstract**

15

16 Magmatic minerals record the pre-eruptive timescales of magma ascent and
17 mixing in crustal reservoirs and conduits. Investigations of the mineral records of
18 magmatic processes are fundamental to our understanding of what controls eruption style,
19 as ascent rates and magma mixing processes are well known to control and/or trigger
20 potentially hazardous explosive eruptions. Thus, amphibole reaction rims are often used
21 to infer pre-eruptive magma dynamics, and in particular to estimate magma ascent rates.
22 However, while several experimental studies have investigated amphibole destabilization
23 during decompression, only two investigated thermal destabilization relevant to magma

24 mixing processes. This study examines amphibole decomposition experimentally through
25 isobaric heating of magnesio-hornblende phenocrysts within a natural high-silica andesite
26 glass. The experiments first equilibrated for 24 hours at 870°C and 140 MPa at H₂O-
27 saturated conditions and $f\text{O}_2 \sim \text{Re-ReO}$ prior to rapid heating to 880, 900, or 920°C and
28 hold times of 3–48 hours. At 920°C, rim thicknesses increased from 17 μm after 3 h, to
29 55 μm after 12 h, and became pseudomorphs after longer durations. At 900°C, rim
30 thicknesses increased from 7 μm after 3 h, to 80 μm after 24 h, to pseudomorphs after
31 longer durations. At 880°C, rim thicknesses increased from 7 μm after 3 h, to 18 μm after
32 36 h, to pseudomorphs after 48 h. Reaction rim microlites vary from 5–16 μm in size,
33 with no systematic relationship between crystal size and the duration or magnitude of
34 heating. Time-averaged rim microlite growth rates decrease steadily with increasing
35 experimental duration (from $3.97 \times 10^{-7} \text{ mm s}^{-1}$ to 3.1 to $3.5 \times 10^{-8} \text{ mm s}^{-1}$). Time-averaged
36 microlite nucleation rates also decrease with increasing experimental duration (from
37 $1.2 \times 10^3 \text{ mm}^{-3} \text{ s}^{-1}$ to $5.3 \text{ mm}^{-3} \text{ s}^{-1}$). There is no systematic relationship between time-
38 averaged growth or nucleation rates and the magnitude of the heating step. Ortho- and
39 clinopyroxene together constitute 57–90 modal % mineralogy in each reaction rim. At
40 constant temperature, clinopyroxene abundances decrease with increasing experimental
41 duration, from 72 modal % (3 h at 900°C) to 0 % (48 h at 880°C, and 36 h at 900 and
42 920°C). Fe-Ti oxides increase from 6–12 modal % (after 3–6 h) to 26–34 modal % (after
43 36–48 h). Plagioclase occurs in relatively minor amounts (<1–11 modal %), with
44 anorthite contents that increase from An₅₆ to An₈₈ from 3 to 36 hours of heating. Distal
45 glass compositions (>500 μm from reacted amphibole) are consistent with inter-microlite
46 rim glasses (71.3–77.7 wt.% SiO₂) within a given experiment and there is a weakly

positive correlation between increasing run duration and inter-microlite melt SiO₂ (68.9–78.5 wt.%). Our results indicate that experimental heating-induced amphibole reaction rims have thicknesses, textures, and mineralogies consistent with many of the natural reaction rims seen at arc-andesite volcanoes. They are also texturally consistent with experimental decompression reaction rims. On this basis it may be challenging to distinguish between decompression and heating mechanisms in nature.

Keywords: Amphibole, Reaction Rim, Heating, Andesite

1. Introduction

The style and explosivity of volcanic eruptions are controlled by the mass eruption rate. In turn, mass eruption rate is controlled by the magmatic ascent rate and the physical and chemical properties of the magma (e.g., density, viscosity, crystallinity, and composition; Rutherford, 2008). Thus, understanding pre-eruptive processes that can influence magmatic ascent rates and eruption triggering is important for research into active and potentially hazardous volcanic eruptions. Magmatic ascent and eruption triggering processes are likely influenced by the pre-eruptive processes occurring within the shallow magma storage region, such as: magma mixing and mingling, heating, and/or changes in gas pressure. Phenocryst phases, including hydrous amphibole, residing in the subvolcanic plumbing system are well-known to be sensitive recorders of pre-eruptive magmatic processes.

Amphibole reaction rims are often used to unravel complex magma ascent and mixing processes. For example, researchers use ascent-driven dehydration and decomposition of amphibole to calibrate models for assessing magma ascent timescales

in intermediate arc magmas (Browne and Gardner, 2006; Rutherford and Devine, 2003; Rutherford and Hill, 1993). However, other factors also trigger amphibole breakdown (e.g., oxidation, fluxing of the melt with a CO₂ rich fluid, or heating; Rutherford and Hill, 1993). The role of heating is particularly important because many arc magmas display disequilibrium textures that record the heating of one magma by another during pre-eruptive mixing (e.g., Clyne, 1999; Devine et al., 2003; Eichelberger, 1975; Feeley and Sharp, 1996; Murphy et al., 2000; Ruprecht and Bachmann, 2010; Tepley et al., 2000; Venezky and Rutherford, 1999). This process may lead to the breakdown of amphibole as temperatures exceed its typical thermal stability boundary of ~880–900°C (Browne and Gardner, 2006; Henton De Angelis, 2013).

Many studies have used experimentally derived models of amphibole decomposition during controlled decompression to ascertain magma ascent rates from natural samples (e.g., Coombs et al., 2013; Devine et al., 1998; McCanta et al., 2007; Nicholis and Rutherford, 2004; Scott et al., 2012; Wolfe and Eichelberger, 1997; Plechov, 2008; Rutherford and Hill, 1993). In contrast, amphibole breakdown as a result of heating has only been systematically studied in a small number of experiments (Browne, 2005; Rutherford and Devine, 2003). Thus, there is no comparable tool to use for estimating timescales of amphibole decomposition triggered by heating. Furthermore, this lack of experimental data on heating induced amphibole breakdown makes the identification of reaction rims formed by heating in natural rocks problematic.

1.1. Natural Amphibole Reaction Rim Classifications

Natural amphibole reaction rims display a broad range of textures and mineralogies (Fig. 1; Browne, 2005; Browne and Gardner, 2006; Buckley et al., 2006; Coombs et al., 2013; Daag et al., 1996; Devine et al., 1998; Garcia and Jacobson, 1979; Humphreys et al., 2009; McCanta et al., 2007; Murphy et al., 2000; Plechov et al., 2008; Rutherford and Devine, 2003; Rutherford and Hill, 1993; Scott et al., 2012; Tepley et al., 2013). In addition to polycrystalline reaction rims, other studies have described amphibole mantled by or replaced by pseudomorphs of augite, formed as a single continuous crystal around the host amphibole (e.g., Holocene deposits of El Chichón; Andrews et al., 2008). Garcia and Jacobson (1979) describe two reaction rim types: ‘black’ and ‘gabbroic’. In ‘black’ type reaction rims the amphibole is replaced by ‘very fine-grained’ Fe-Ti oxide and pyroxene microlites. They conclude that ‘black’ rims result from dehydrogenation and oxidation during magma extrusion. This type of amphibole replacement is easily identified and commonly observed around phenocryst edges and along interior cracks and cleavage planes (Rutherford and Hill, 1993).

In ‘gabbroic’ reaction rims the amphibole is replaced by ‘fine–medium’ orthopyroxene, clinopyroxene, plagioclase, and Fe-Ti oxide microlites. Garcia and Jacobson (1979) concluded that these reaction rims form as a result of dehydration. Rutherford and Hill (1993) further recognized that this rim type forms only when the amphibole directly contacts the host melt. In subsequent studies on Soufrière Hills Volcano, Montserrat (e.g., Devine et al., 1998; Humphreys, 2009; Rutherford and Devine, 2003) a third rim type was identified: ‘thick’, coarse-grained clinopyroxene-rich reaction rims thought to be the result of heating.

While there are some exceptions, decompression-induced reaction rims are generally described as thin ($<60\ \mu\text{m}$), fine-grained ($5\text{--}30\ \mu\text{m}$ microlite size), and containing predominantly orthopyroxene, clinopyroxene, plagioclase, and Fe-Ti oxides (Fig. 1; Browne and Gardner, 2006; Rutherford and Hill, 1993). Experimental studies recreating amphibole reaction rim formation due to decompression indicate that those textural observations are generally accurate (Browne and Gardner, 2006; Rutherford and Devine, 2003; Rutherford and Hill, 1993); however, the reaction rims produced contain predominantly orthopyroxene with little or no clinopyroxene present (Browne and Gardner, 2006; Henton De Angelis, 2013).

Heating-induced reaction rims are generally classified as thick ($>\sim 60\ \mu\text{m}$), coarse-grained ($30\text{ to }>200\ \mu\text{m}$), clinopyroxene-rich, and plagioclase poor (e.g., Rutherford and Devine, 2003). Again, there are exceptions: rims as thin as $25\text{--}30\ \mu\text{m}$ (Plechov, 2008) and with grain sizes of $<30\ \mu\text{m}$ have also been attributed to heating (Humphreys, personal communication; Plechov, 2008). Rutherford and Devine (2003) report the experimental reproduction of heating reaction rims that match the natural coarse clinopyroxene-rich counterparts both texturally and mineralogically (following 12–36 hours of heating to $10\text{--}65^\circ\text{C}$ above amphibole stability). Browne (2005) experimentally reproduced heating reaction rims of $<1\text{--}136\ \mu\text{m}$ after 2.5 to >100 hours of heating to temperatures $10\text{--}50^\circ\text{C}$ above amphibole stability. However, these two studies included just a small number of experiments.

In this study we experimentally investigate rates of amphibole reaction rim formation when triggered by isobaric heating. We quantify the resulting reaction rims in terms of their thicknesses, textures, mineralogy, and the relative crystallographic orientation of

host amphiboles and reaction rim crystals (hereafter referred to as ‘microlites’). Finally, we apply our results to natural systems and compare the observations with those focused on decompression-induced reaction rims.

2. Experimental and Analytical Techniques

2.1. Starting Material

Heating experiments were conducted using finely ground fused glass, derived from a high-silica andesite (62.52 wt. % SiO₂) pumice with rhyolitic matrix glass (75.9 wt.% SiO₂; Table 1) from the 2006 eruption of Augustine Volcano, Alaska. Phase equilibria experiments on the starting material show that amphiboles are stable at >120 MPa and $\leq 870^{\circ}\text{C}$ (Fig. S1; Henton De Angelis, 2013).

The pumice was first hand crushed using an agate mortar and pestle. The glassy experimental starting material was produced by completely melting 15 g of the finely ground pumice in a platinum crucible, in air, at 1400°C for 30 minutes. The material was then re-ground to a fine powder and the process was repeated. Electron microprobe analyses of the twice-melted glass verified that there was no appreciable Fe loss to the platinum crucible (Henton De Angelis, 2013).

To ensure that experiments contained amphibole large enough to identify with ease, the starting material was seeded with amphibole phenocrysts, separated from their host using heavy liquids and then picked by hand. The relatively small size of amphiboles from the Augustine starting material precluded their use so seeds were taken from 2008 samples from Soufrière Hills Volcano, Montserrat. The naturally occurring magnesio-hornblendes in the starting material and those in the Montserrat samples are

compositionally very similar (Henton De Angelis, 2013; Table 1). For each experiment, ~0.05 g of glass powder was seeded with ~20 unreacted hornblende phenocrysts (~100–500 μm diameter) of uniform magnesio-hornblende composition, equivalent to ~10 wt.% amphibole seed crystals.

2.1.1. Influence of Starting Material

The initial experimental melt was more mafic than most of the natural andesite-dacite lithologies that we compare with. However, during the initial 24-hours equilibration (870°C/140 MPa), rapid groundmass crystallization produced melts with 71.29–77.71 wt.% SiO_2 (Table 1). Thus, the experimental reaction rims formed in rhyolitic melts comparable to the original Augustine groundmass and other studies of natural amphibole reaction rim formation (e.g., Buckley et al., 2006).

2.2. Experimental Methods

Seeded powders were placed within 4 mm Au capsules, with enough water to maintain vapor saturation, with separate $\text{Ag}_{70}\text{Pd}_{30}$ capsules holding the buffering compounds. Capsule ends were welded closed using a Puk 3 precision arc welder. As appropriate for Augustine Volcano, experiments were run at H_2O vapor saturated conditions and $f\text{O}_2 \sim \text{Re-ReO}$ ($\sim \text{NNO}+2$; Henton De Angelis, 2013; Webster et al., 2010), employing 3 mm $\text{Ag}_{70}\text{Pd}_{30}$ buffer capsules loaded with Re and ReO powders in a 1:1 molar ratio.

The experimental capsules were loaded into TZM and MHC alloy pressure vessels and externally heated using DelTech DT-30 furnaces. To help maintain $f\text{O}_2$ and

mitigate loss of hydrogen through the capsule, ~2.5 bars CH₄ was added to the Ar pressurizing gas. Each experimental run (Table 2) was held within the amphibole stability field (at 870°C/140 MPa) for 24 hours to thermally equilibrate. Following equilibration, single step isobaric heating involved increasing the furnace temperature to achieve 880°C (heating rate = ~7 °C/minute), 900°C (heating rate = ~4.5 °C/minute), or 920°C (heating rate = ~3.5 °C/minute) internally in the vessel, calibrated using an internal thermocouple. Experiments were held at the final temperature for 3–48 hours before rapid quenching following the method of Sisson and Grove (1993).

2.3. Analytical Methods

2.3.1. Backscatter Electron and X-ray Mapping

Backscatter electron images and X-ray maps were collected using a JEOL JSM-6510 Scanning Electron Microscope, equipped with an IXRF Iridium Ultra EDS, at the U.S. Geological Survey, Anchorage. Images were acquired with a 20 keV accelerating voltage, and a 10 mm working distance. Reaction rim images were measured using the National Institute of Health (NIH) ImageJ software package. For each reacted amphibole, mean rim thickness was calculated from 7–20 individual measurements, traversing the outer edge of the amphibole phenocryst to the edge of the reaction rim at regular spatial intervals around the phenocryst. Amphibole phenocrysts were not oriented crystallographically during the measurements. For each reaction rim, 15–212 individual microlites were cataloged according to: mineral phase, size (length of longest axis), and position within the reaction rim (distance outward from the unreacted amphibole core and inward from the surrounding glass). The proportions of mineral phases within reaction

206 rims were calculated from tallies and are presented as percentages of each crystal type
207 within the total crystal population. The number of microlites measured depended on the
208 size of the host amphibole and on the thickness of the reaction rim. For small host
209 phenocrysts, or for very thin reaction rims, all microlites visible in the cross section were
210 measured. For reaction rims with large numbers of microlites, regions of interest (ROIs)
211 were established at 5–10 locations within the reaction rim, with the size of ROIs
212 dependent on the magnification of the image and on the total reaction rim thickness..
213 ROIs extended from the edge of the host amphibole to the reaction rim-glass boundary,
214 and all microlites within each ROI were analyzed. ROIs were used to record data on
215 crystal (microlite) number densities (CNDs) and crystal (microlite) area fractions (Φ).
216 Data were then used to calculate microlite growth rates (G) and microlite nucleation rates
217 (I) following the method of Brugger and Hammer (2010).

219 2.3.2. *Electron Microprobe Analyses*

220 Major oxide compositions of experimental glasses, amphibole phenocrysts, and
221 reaction rim microlites were collected using a JEOL 8900 Superprobe at the U.S.
222 Geological Survey, Menlo Park. Data on SiO₂, TiO₂, Al₂O₃, FeO, MnO, and MgO were
223 collected for all phases, while CaO, Na₂O, K₂O, Cr₂O₃, V₂O₃, F, and Cl data collection
224 was phase dependent (Table S1). All mineral analyses were conducted using a focused
225 (1–3 μ m diameter) beam with a 15 keV accelerating voltage. Beam currents of 10 nA, 15
226 nA, and 20 nA were utilized for plagioclase, pyroxene and amphibole, and Fe-Ti oxide
227 data collection, respectively. Glass analyses were conducted using a defocused beam (5–
228 10 μ m diameter), 5 nA beam with a 15 keV accelerating voltage. Count times of 20

seconds peak and 10 seconds background were utilized, with the exception of Na, for which count times of 10 second peak and 5 seconds background were used. All standards (see supplementary electronic data depository for details) were held to a standard deviation of <0.50%.

Given their small size, microlite compositional data were collected from single points on multiple individual crystals per rim. Reported uncertainties represent one standard deviation about the mean. Microlites were chosen to ensure the greatest possible spatial distribution. Amphibole data represent a combination of single spot analyses and transects across phenocrysts, which are compositionally unzoned. Distal glass and groundmass phase data were measured at distances of >500 μm from reacted amphiboles.

Major oxides were used for mass balance of experimental reaction rims following the methods of Buckley et al. (2006) and Wright and Doherty (1970). For the purpose of mass balance calculations, mean major oxide compositions were normalized to 100%. Glass data were not included as an input phase. Instead, the role of melt in the reaction is represented by the calculated residuals. To some extent, residuals represent uncertainties in analytical data and calculation methods; however, in general a positive residual indicates an excess of that oxide in the host amphibole phenocryst, resulting in a net release into the adjacent melt. In contrast, a negative residual indicates that the bulk amphibole composition did not contain enough of the oxide in question and, as such, the reaction required an input from the adjacent melt.

2.3.3. Electron Backscatter Diffraction Analyses

Crystal orientations were collected using electron backscatter diffraction (EBSD). Analyses were performed using a CamScan X500 Crystal Probe SEM with a field emission gun at the University of Liverpool. Beam conditions of 20 keV accelerating voltage and a current of 45–50 nA were utilized. Data were processed using the CHANNEL 5 software package from Oxford Instruments Ltd. Data were collected for a total of 14 experimental heating induced reaction rims (Table 2) and 7 natural reaction rims identified in the 2006 Augustine Volcano deposits (06AUMLC259e Grain 2; 06AUKB002c grains 1 and 5; 06AUMRT37e grains 1 and 7; 06AUMC008bp1 Grain 4; 06AUJFL001b Grain 1; De Angelis et al., 2013).

3. Results

3.1. Reaction Rim Textures

3.1.1. Thickness and Microlite Size

The polycrystalline reaction rims change systematically in both mineralogy and texture with increasing experiment duration and temperature (Fig. 2; Table 2). At 920°C, reaction rim thicknesses increase from $17 \pm 5 \mu\text{m}$ after 3 h to $55 \pm 6 \mu\text{m}$ after 12 h (Fig. 3A). Beyond 12 h of heating, all amphiboles held at 920°C completely reacted to form pseudomorphs. Reaction rims formed at 900°C increase in thickness from $7 \pm 1 \mu\text{m}$ after 3 h to $80 \pm 19 \mu\text{m}$ after 24 h. All amphiboles held at 900°C for >24 h formed pseudomorphs (Fig. 2E–F), except for one large phenocryst, which formed a very thick rim ($203 \pm 63 \mu\text{m}$) after 48 h of heating. Rim growth was slowest at 880°C, with thicknesses increasing linearly from $7 \pm 2 \mu\text{m}$ after 3 h to $18 \pm 12 \mu\text{m}$ after 36 h (Fig. 3). Beyond 36 h the reaction rate accelerated and by 48 h at 880°C all amphiboles formed

pseudomorphs, which have an appearance similar to those formed after 48 hours at 900°C (Fig. 2F).

Mean rim microlite sizes, calculated for each experimental duration and temperature, vary from 5–16 μm (mean = $10 \pm 5 \mu\text{m}$; Fig. 3D). However, when viewed on a phase-by-phase basis, some orthopyroxene microlites reach $\sim 25 \mu\text{m}$, while Fe-Ti oxides rarely exceed 10 μm (Fig. S2). There is no systematic relationship between the sizes of individual microlites and the duration or magnitude of heating (Fig. 3D; Fig. S2A–D).

3.1.2. Microlite Growth and Nucleation Rates

Time-averaged microlite growth rates calculated both as all-phase means for each temperature and run duration (Fig. 3B), as well as for each individual phase (Fig. S2E–G), decrease steadily with increasing experimental duration. After 3 hours, growth rates range between $9.3 \times 10^{-7} \text{ mm s}^{-1}$ (clinopyroxene at 900°C) and $5.7 \times 10^{-7} \text{ mm s}^{-1}$ (Fe-Ti oxides at 880°C). By 48 hours, growth rates fall to $8.7 \times 10^{-8} \text{ mm s}^{-1}$ (clinopyroxene at 900°C). Time-averaged microlite nucleation rates also decrease with increasing experimental duration, although the trend is less well defined (Fig. 3C). At hold times as low as 3 hours, nucleation rates are as high as $1.2 \times 10^3 \text{ mm}^{-3} \text{ s}^{-1}$ (recorded at 880°C). The lowest measured nucleation rate ($5.3 \text{ mm}^{-3} \text{ s}^{-1}$) was recorded after 36 hours at 900°C. There is no systematic relationship between growth or nucleation rates as a function of heating magnitude.

3.1.3. Microlite Number Density and Area Fraction

Reaction rim CNDs vary widely, ranging from 88400 mm^{-2} ($\pm 9700 \text{ mm}^{-2}$) after 6 hours of heating at 900°C , to 8500 mm^{-2} ($\pm 4300 \text{ mm}^{-2}$) after 24 hours of heating at 900°C (Fig. 3E). However, variations are weakly systematic showing decreasing CND with increasing time, but no clear relationship exists between CND and heating magnitude. In contrast, microlite area fractions do not vary widely (Fig. 3F), ranging from 0.58 ± 0.06 (12 hours at 900°C) to 0.74 ± 0.04 (3 hours at 920°C). Observed variations are not systematically related to either heating magnitude or duration.

3.2. Reaction Rim Chemistry

3.2.1. Mineralogy

Reaction rim mineralogy was assessed using two methods: 1) population modes based on the analysis of composite X-ray maps, and; 2) mass balance, based on microprobe-derived major oxide compositions. We encountered difficulties with the mass balance method that resulted in a limited data set. Mass balance requires compositional data for both the host amphibole and all reaction rim microlite phases present. The small size of individual microlites ($<20 \text{ }\mu\text{m}$ to $<5 \text{ }\mu\text{m}$) made major oxide data collection difficult. In addition, calculated mass balance results for reaction rims containing only 2–3 phases were highly suspect and clearly at odds with other observations, such as when mass balance results predicted 0% of a phase that was clearly visible in X-ray maps. Thus, we only use mass balance results for reaction rims where identification and microprobe data exist for at least 4 phases. The acceptable mass balance results are broadly consistent with the modal mineralogy (Table 3). On this basis, the reaction rim

mineralogy results discussed hereafter rely largely on the modal data derived from composite X-ray maps.

Our experimental reaction rims contain varying proportions of ortho- and clinopyroxene, plagioclase, Fe-Ti oxides, and in some cases shards of amphibole (Fig. 4). Ortho- and clinopyroxene are the primary phases, constituting a combined 57–90 modal % of each reaction rim (Fig. 4). At constant temperature, clinopyroxene abundances decrease with increasing experimental duration, from a maximum of 72 modal % (3 h at 900°C) to 0 modal % (48 h at 880°C, and 36 h at 900 and 920°C). There is a corresponding increase in orthopyroxene from ~10 modal % after 3 h (at 900°C) to >65 modal % after 36–48 hours. Fe-Ti oxides represent 6–12 modal % of reaction rim microlites in the 3–6 h experiments, increasing to 26–34 modal % after 36–48 h. Plagioclase occurs in relatively minor amounts (<1–11 modal %) at all experimental conditions. Fragments of amphibole, disconnected from the host phenocryst, are observed in short duration (3 h) experiments at 880 and 900°C.

3.2.2. Phase Compositions

Interstitial reaction rim glass compositions range from 68.9–78.5 wt.% SiO₂ (Table S1; Fig. 5A). There is a positive correlation between heating time and silica content, with longer duration experiments resulting in more silicic glasses. Distal glasses, which range from 71.3–77.7 wt.% SiO₂, are similar to inter-microlite reaction rim glasses within a given experiment.

The anorthite (An) content of reaction rim plagioclase microlites increases from An₅₆ at 3 hours to a peak of An₈₈ at 36 hours (at 900°C; Fig. 5B). These compositions

progressively cross over the equilibrium An values (880°C/ 140 MPa = ~An60; 900°C/ 140 MPa = ~An65; 920°C/ 140 MPa = ~An70) estimated from phase equilibria experiments (Fig. S1; Henton De Angelis, 2013). Distal groundmass plagioclase compositions follow a similar trend. At 900°C, groundmass plagioclase microlite contents vary from An58 (3 h) to An83 (48 h; Fig. 5B). There is no clear relationship between An values and heating temperature.

Plotting the rim pyroxene compositions on the pyroxene quadrilateral (Fig. 5C) reveals that all crystals cluster in the augite compositional field. There is little systematic compositional variation with experimental duration, although the clinopyroxene in the shortest duration experiments (3 hours) tend to be enriched in ferrosillite (e.g., Fe) and depleted in the wollastonite (e.g., Ca). In the distal groundmass, clinopyroxene from the 900°C/3-hour experiment is the most Fe enriched and Ca depleted. In contrast, distal clinopyroxene from the 900°C/12-hour experiment is consistent with the majority of reaction rim crystals. Orthopyroxene compositions from both reaction rims and distal matrix crystals trend away from the pigeonite field, towards Mg-rich enstatite with increasing experimental duration.

3.3. Relative Crystal Orientation: EBSD

Visually, most of the reaction rims considered in this study appear to contain randomly oriented microlites. However, a small number show an apparent alignment of microlites by habit (Fig. 6A). EBSD data reveal that of 7 natural reaction rims analyzed, only 4 show a clear topotactic relationship between the host amphibole and all or most of the pyroxene microlites. For the other 3 natural reaction rims, most pyroxene microlites

are randomly oriented with respect to the host amphibole (Figure 6B). In contrast, crystal orientation maps (Fig. 6C) and pole figures (Fig. 6D) for the 14 experimental heating-induced reaction rims analyzed indicate a strong topotactic relationship between the host amphibole and the reaction rim pyroxenes.

4. Discussion

4.1. Reaction Rim Textures

The results of this study demonstrate the complexities involved in interpreting the genesis of amphibole reaction rims. For example, experimental reaction rim growth rates for heating induced breakdown (2×10^{-7} to 3×10^{-9} cm/s) are generally higher than those seen in decompression-based experiments (e.g., 2×10^{-9} to 9×10^{-10} cm/s; Browne and Gardner, 2006). This is unsurprising because while decompression destabilizes amphibole, it also leads to increased melt viscosity and a slowing of reaction kinetics due to dewatering of the melt. In contrast, heating both destabilizes amphibole and also reduces melt viscosity, favoring faster reaction kinetics. However, the timescales of breakdown in natural systems are largely unknown and growth rates cannot be accurately estimated. Experiments provide insights into natural systems only if parameters like reaction rim widths can be easily measured in both. Unfortunately when using these simple datasets ambiguities remain between the results of different processes (e.g., heating vs. decompression).

We also observed an increase in the reaction rate with time (Fig. 3A), corresponding to a fall in the growth rates of individual crystals (Fig. 3B; Fig. S2E–H). The fall in crystal growth rates does not correspond with an increase in crystal sizes (Fig.

3D; Fig S2A–D), thus ruling out a volume effect. Instead, the falling growth rate may be related to the reduction in the host amphibole surface area. At the same time, the rate of overall rim thickening increases with time, most notably between 36 and 48 hours in the 880°C series (Fig. 3A), where all amphibole suddenly form pseudomorphs. Amphibole phenocryst sizes in this experiment were consistent with those in the other experiments, thus ruling out the possibility that pseudomorphs formed due to small grain size. Instead, the results indicate that pseudomorph formation must sometimes occur in a catastrophic manner; perhaps when a threshold regarding the balance between the reaction products and the host amphibole is crossed. Unravelling the nature of this threshold, and more broadly the complexities of multi-phase crystallization kinetics in reaction rim formation environments, provides a potentially rich avenue for future investigation.

Reaction rims interpreted to have been caused by heating tend to be thicker than those interpreted as created by decompression (typically <60 μm). However, more than 50% of our heating experiments contain reaction rims with a mean thickness of <40 μm (Fig. 3A). Greater than 70% of the heating-induced reaction rims produced in this study overlap with the range of thicknesses produced in decompression experiments (2–60 μm ; Fig. 1; Browne and Gardner, 2006; Rutherford and Devine, 2003; Rutherford and Hill, 1993). Furthermore, many reaction rims described from natural samples have thicknesses within the ranges created by both the prior decompression experiments and our new heating experiments (Fig. 1A). The overlap between the experimental decompression and heating rim thicknesses calls into question the use of thickness alone to distinguish between decompression and heating in nature. Rims with 10–60 μm thicknesses are the most ambiguous according to our results.

With microlites that rarely exceed 20 μm ($\sim 2\text{--}20\ \mu\text{m}$; or $10 \pm 5\ \mu\text{m}$; Fig 3B), the heating-induced rims produced in this study can also be classified as ‘fine grained’ and thus texturally similar to those described as resulting from decompression (Fig. 1B). Furthermore, as with reaction rim thicknesses, the microlite sizes observed in natural samples often overlap with those produced in both heating and decompression experiments (Fig. 1B).

However, some naturally occurring reaction rims are significantly more coarsely grained than any produced experimentally, with some containing microlites $>200\ \mu\text{m}$ in size, (Fig. 1B). The growth of very coarse rim microlites, observed in some natural samples ($>200\ \mu\text{m}$; Fig. 1B), probably require conditions only found in natural volcanic systems, where reaction timescales can be much longer and the magnitude of heating or decompression may be relatively small, triggering very slow nucleation and growth rates that allow microlites to coarsen through growth or coalescence. Such conditions could conceivably be achieved in various pre-eruptive environments. When heating is involved, such conditions are most likely where amphiboles are heated to just a few degrees ($<10^\circ\text{C}$) above their stability curve for a sustained period of time, perhaps during periods of replenishment by hotter magma thermally buffered across the magma storage region. With regard to decompression, Murphy et al. (2000) surmise that such thick and coarse rims could be the result of long periods of residence in the conduit (years to decades) at depths shallower than amphibole stability. These amphiboles, held in an increasingly cool, crystalline, and viscous melt would be subject to very sluggish reaction kinetics. However, recreating such timescales in a laboratory setting is very difficult both economically and practically.

We conclude that heating timescales up to 40 hours result in rims that agree both in thickness and microlite size with decompression experiment results and natural reaction rims interpreted to be the result of decompression. Therefore, on the basis of thickness and microlite size alone, heating and decompression induced reaction rims can be indistinguishable, especially in the 1–60 μm thickness range.

4.2. Controls on Phase Abundance and Composition

The relative proportions of clino- and orthopyroxene in amphibole reaction rims are of particular interest because while some natural reaction rims have abundant orthopyroxene microlites (Fig. 4; Browne and Gardner, 2006; De Angelis, 2013), others, from similar arc calc-alkaline volcanic systems, are clinopyroxene dominated (e.g., Buckley et al., 2006). Our experimental heating-induced reaction rims almost always contain both orthopyroxene (11.0–81.7 modal %) and clinopyroxene (5.5–71.6 modal %). The only single-pyroxene rims identified are orthopyroxene-only rims and pseudomorphs observed in the longest experiments (36 h at 900–920°C and 48 h at all temperatures).

An interesting feature of our experimental heating rims is that the abundance of clinopyroxene drops significantly with experimental duration (Fig. 4). In addition, we observe a zonation in clinopyroxene abundance across some pseudomorphs (e.g., HSAS 15), where clinopyroxene is concentrated at the center, while the outside edges are composed entirely of orthopyroxene. Clinopyroxene microlite sizes do not systematically increase with decreasing modal % (Fig. 4; Fig. S2), thus ruling out Ostwald ripening. Solid-state cation diffusion rates in pyroxenes are slow, and so it is unlikely that

clinopyroxene is transforming into orthopyroxene as a solid-state reaction on the short experimental timescales (e.g., Brady and McCallister, 1983). It is possible that the changing abundances of the two pyroxenes relate to a dissolution and re-precipitation reaction linked with changing melt compositions near the reacting amphiboles.

The decreasing abundance of clinopyroxene appears to extend to the distal groundmass in longer duration experiments. Thus, any reaction causing the reduction of clinopyroxene in the rims also extended to the external experimental melt. This reduction is not observed in the equilibrium phase diagram for this system (Fig. S1; Henton De Angelis, 2013), suggesting a process unique to this disequilibrium environment.

Coincident with the reduction in clinopyroxene, we observe significant increases in plagioclase anorthite content to a level considerably higher than those in equilibrium experiments (Fig. S1; Fig. 5B). With increasing experimental duration, the amphibole seed crystals progressively breakdown and release MgO, FeO, and CaO into the melt. The addition of FeO and MgO to the melt appears to stabilize orthopyroxene, as might be expected. Contrary to our expectations, increasing CaO in the melt does not translate into stabilization of clinopyroxene, but rather leads to increasing An content in the plagioclase. Therefore, the changing melt composition appears to trigger dissolution of Ca-rich, clinopyroxene in favor of increased crystallization of Mg and Fe-rich orthopyroxene and Ca-rich anorthitic plagioclase. Therefore, the whole experimental system responds to the change in melt composition as the amphibole seed crystals disintegrate. This is likely because we seeded the experiments with up to ~10 wt.% amphibole crystals, which we felt was necessary, despite clearly altering the phase relationships of the system, because any fewer seed crystals meant we could not find the

seeds when we polished the quenched experiments. Therefore, because our experiments represent a somewhat artificial environment, we are not certain whether this observation extends to reaction rims observed in natural volcanic rocks.

In contrast to clinopyroxene, the abundance of reaction rim Fe-Ti oxides increases systematically with time (from 6–12 modal % after 3–6 h to 26–34 modal % after 36–48 h; Fig. 4). There are two likely explanations for this observation: 1) the experimental charges oxidized with increasing run time, despite the use of a buffer assemblages, and/or; 2) Fe-Ti oxide microlites become easier to identify with time. With regards to the former, a lack of Fe-Ti oxide touching pairs within experiments makes the assessment of changing fO_2 challenging. Non-touching pairs provide unreasonable T and fO_2 values; however, the general pattern may indicate a weak relationship between increasing experimental time and increasing fO_2 . This would be consistent with observations of other experimental studies (e.g., Shea and Hammer, 2013). With regards to the latter, Fe-Ti oxides are usually significantly smaller than the other phases (Fig. S2) and are often challenging to measure. After just a few hours of rim growth, Fe-Ti oxides may be too small ($\ll 1 \mu\text{m}$) to identify with ease and as such may be underestimated. In longer duration experiments oxides are larger ($> 2\text{--}3 \mu\text{m}$) and easier to measure; however, they remain small in size relative to other phases. This may over inflate their importance because the modal data is based on a tally of identified crystals and the method assigns the same weighting to a single small microlite as to a single large microlite. Therefore, where oxides look to be in equal abundance with pyroxene, in terms of reaction rim volume they may represent a smaller share.

Prior studies conclude that the composition of the host amphibole controls the mineralogy of a reaction rim (e.g., Tepley et al., 2013). However, in our experimental study, despite host amphiboles of relatively uniform composition (Table 1), reaction rims contain widely varying abundances of difference phases (Fig. 4). For example, the three reactions rims formed in the 900°C/ 24 h experiment range in clinopyroxene abundance from 0–10 modal %. Therefore, while host amphibole composition must have an impact on mineralogy, we exclude it as a principal controlling factor for the experimental heating reaction rims of this study.

4.3. Applying Experimental Data to Natural Systems

Laboratory experiments cannot completely capture the complexity of nature, particularly when each volcanic system has unique characteristics with regard to magma compositions and plumbing system conditions. For example, it is fairly common for andesitic arc volcanic systems to contain diverse populations of amphiboles with highly variable compositions and reaction rim textures (e.g., Redoubt and Augustine; Coombs et al., 2013; De Angelis et al., 2013). Amphibole textural variability observed even at the thin section scale reflects compositional diversity from multiple magma batches and extensive fine-scale magma mixing and mingling that can operate during single eruptions. The heterogeneous populations of amphibole reaction rims may also indicate multiple different processes at different spatial and temporal conditions. For example, prior studies have reported amphibole reaction rims that show evidence for overprinting of different processes, such as decompression during ascent followed by oxidation in the shallow conduit (Genereau and Clarke, 2010; McCanta et al., 2007). Furthermore, all

amphiboles experience decompression prior to eruption and depending on the speed of magma ascent, heating-induced reaction rims formed in the magma storage region could be overprinted by subsequent amphibole breakdown during decompression. Experimental calibrations of amphibole heating rim development are thus most useful for cases where magma mixing and ascent processes are constrained and potentially separable based on independent lines of petrological evidence.

However, despite the complexities discussed above, our results provide important constraints that can be used to help decipher the origins of different classes of amphibole reaction rims. Our results indicate that reaction rim thicknesses created by heating and decompression over laboratory timescales produce similar thicknesses (0–60 μm) and microlite sizes ($<20 \mu\text{m}$) and those two measures are not likely to uniquely distinguish between heating and decompression processes in natural samples. However, our results also indicate that reaction rim mineralogy is a promising tool to help researchers decipher processes operating on natural samples. Two prior studies to calibrate amphibole breakdown due to decompression document only orthopyroxene forming in the reaction rim products, with clinopyroxene absent, regardless of the duration of the experiment. The heating experiments from this study contain abundant clinopyroxene from the time the rim starts to form until the amphibole completely reacts to form pseudomorphs. Orthopyroxene becomes dominant only after pseudomorph formation is observed. Thus, our study predicts that short duration heating events in a volcanic system could produce rims rich in clinopyroxene, whereas decompression should produce rims containing orthopyroxene only (e.g., Browne and Gardner, 2006; Rutherford and Hill, 1993). In summary, our results indicate that reaction rims in volcanic samples that contain

clinopyroxene in more than trace amounts can be interpreted as heating-induced, regardless of the texture and thickness of the reaction rim. Reaction rims that contain only orthopyroxene could either be: a) the result of heating for >40 h, in which case the reaction rim is likely to be very thick, or the amphibole pseudomorphed, or b) the result of decompression.

We can apply our experimental results to the natural reaction rims of the 2006 Augustine Volcano eruption (De Angelis et al., 2013). Over 60% of the reacted amphiboles in the 2006 deposits are < 60 μm thick and all within that group have mean microlite sizes of 20 μm or less (De Angelis et al., 2013). Thus, to first order, those Augustine reaction rims are texturally consistent with a decompression origin, similar to the conclusions of prior studies from other volcanoes (Fig. 1). However, none of the Augustine amphibole reaction rims are consistent with the orthopyroxene-only mineralogy predicted by the decompression experimental studies (Browne and Gardner, 2006; De Angelis et al., 2013; Rutherford and Hill, 1993;). In fact, the mineralogies (Fig. 4) and textures (De Angelis et al., 2013) of the <60- μm -thick reaction rims are all consistent with the heating-induced experimental rims from this study. On this basis alone it would appear that heating is likely the dominant process in creating the natural Augustine reaction rims, perhaps even eclipsing all effects of decompression. This conclusion is quite reasonable for the Augustine system and the 2006 eruption in particular. The lithologies erupted in 2006 contain abundant petrological evidence for mafic replenishment resulting in a range in magmatic temperatures recorded in Fe-Ti oxide phases, and extensive mingling, mixing, and hybridization between multiple magma compositions (De Angelis et al., 2013; Larsen et al., 2010; Webster et al., 2010).

However, the EBSD results reveal an even greater complexity to the story (Fig. 6). Only 4 of the 7 natural Augustine reaction rims studied exhibit a topotactic host amphibole–reaction rim relationship, compared with 100% of the experimental heating induced reaction rims. This EBSD dataset is small and more work is needed to provide a more robust observation. However, the results indicate that a strong topotactic relationship may be unique to heating-induced rims; although, it is also possible the lack of topotaxy in natural reaction rims may relate to other processes that act to re-arrange reaction rim crystals (e.g., magma shearing). To test this requires applying the EBSD method to decompression-induced reaction rims from additional experiments, and to many more natural reaction rims, which is beyond the scope of this study. However, if topotaxy is a hallmark of the heating reaction, then >50% of the reaction rims from the 2006 eruption of Augustine Volcano can be attributed to heating.

Despite the results of past experimental studies, it is also possible that natural decompression-induced reaction rims could contain clinopyroxene in appreciable quantities. If this were the case, questions arise about why prior experimental studies produced rims that only contain orthopyroxene. One possibility, as highlighted by the results of this study, is that clinopyroxene produced in the early stages of the reaction may have been replaced by orthopyroxene before experiments were quenched. In experimental systems with lower melt viscosities (e.g., lower glass SiO₂), the replacement of clinopyroxene may occur over timescales even shorter than those observed here. In summary, our results point to a mineralogical and structural basis for discriminating heating versus decompression-induced reaction rims at Augustine Volcano, with caveats that more experimental work is needed to address the outstanding

questions raised above.

5. Conclusions

Our experimental study demonstrates that amphibole reaction rims can form quickly, over a 3–48 hour timescale, with heating to 10–50°C over their stability limit. The resulting reaction rims have thicknesses that range from 7–80 μm and grain sizes of $< 25 \mu\text{m}$. Pseudomorph formation is observed after 36, 24, and 12 hours at 880, 900, and 920°C, respectively. The reaction rim thicknesses and microlite sizes are consistent with prior experimental results focused on decompression (Browne and Gardner, 2006; Rutherford and Hill, 1993). However, the reaction rims mineralogies (plagioclase, Fe-Ti oxides, ortho and clinopyroxene) are in contrast to those decompression experiments (orthopyroxene, plagioclase, and Fe-Ti oxides). In our experiments, we observe an increase in the proportion of orthopyroxene with experimental duration. Furthermore, clinopyroxene levels decrease with time, so much so that after 36, 24, and 24 hours at 880, 900, and 920°C, respectively, clinopyroxene is apparently absent. Coincident with the changes in clinopyroxene, we observe increases in plagioclase An contents, both within reaction rims and in the distal groundmass. It remains unclear if these changes are a general feature of heating induced reactions rims, or simply reflective of the somewhat artificial experimental environment.

We conclude that the mineralogies in natural reaction rims may be a way to discriminate heating from decompression processes in natural volcanic systems. However, complexities remain that we do not yet fully understand. Nonetheless, the results of this study suggest that at Augustine Volcano, a significant proportion of the

reaction rims (50% or more) from the 2006 eruption show evidence for a heating-induced origin, based on the combination of clinopyroxene in the rim and the topotactic relationship revealed by electron backscatter diffraction (EBSD) data. This is not surprising given Augustine's complex and highly mingled, mixed, and hybridized andesite lithologies; however, it does highlight the fact that heating occurred within hours or days prior to eruptions, and perhaps served as a trigger for renewed activity. While these results provide estimates on amphibole breakdown rates at Augustine Volcano, systems exhibiting lower silica, higher water contents, and/or higher temperature melts (and thus lower viscosities) would likely see even more rapid reactions (with higher silica, lower water contents, and/or lower temperatures providing the opposite result).

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FIGURES

Figure 1. Textural characteristics of natural amphibole Ranges natural reaction rim (A) thickness (μm) and (B) microlite sizes (μm), as reported by previous studies. Data are classified by the inferred cause of reaction rim formation (decompression, heating, unassigned, and 'alternate'). Data on very thin oxidation or 'black type' (Garcia and Jacobson, 1979) reaction rims are not included. Diagonal crosshatched shading denotes data ranges for experimental reaction rims formed through decompression (Browne and Gardner, 2006; Rutherford and Devine, 2003; Rutherford and Hill, 1993). Grey shading denotes data ranges for experimental reaction rims formed through heating (Browne, 2005; this study). Arrows indicate datasets where the data range exceeds the axes of the figure. Volcano abbreviations: SHV = Soufrière Hills Volcano; MSH = Mount St Helens. Data sources: a = Rutherford and Hill, 1993; b = Browne and Gardner, 2006; c = Coombs et al., 2013; d = Devine et al., 1998; e =

789 Rutherford and Devine, 2003; f = Buckley et al., 2006; g = Daag et al., 1996; h =
790 McCanta et al., 2007; i = Scott et al., 2012; j = Plechov et al., 2008; k = Humphreys
791 (personal communication); l = De Angelis et al., 2013; m = Murphy et al., 2000.
792

Figure 2. X-ray maps of experimental heating-induced amphibole reaction rims

Composite X-ray maps of experimental heating-induced amphibole reaction rims formed at T = 900°C/ P = 140 MPa for: A) 3 h; B) 6 h; C) 12 h; D) 24 h; E) 36 h; and F) 48 h.

Exact shading varies, but in general: blue = glass; purple = plagioclase (plag); red = magnetite (mt); yellow = ilmenite (il); ‘olive’ green = amphibole (amph); green = orthopyroxene (opx); yellow/green = clinopyroxene (cpx).

Figure 3. Textural characteristics of experimental heating induced reaction rims

Textural characteristics of experimental heating induced reaction rims as a function of experimental duration (hours): A) Average thicknesses (μm); B) Time-averaged crystal (microlite) growth rates (s^{-1}); C) Time-averaged crystal (microlite) nucleation rates ($\text{mm}^{-3} \text{s}^{-1}$); D) Microlite sizes (μm); E) Crystal (microlite) number densities (mm^{-2}); F) Crystal (microlite) area fractions. In plot A, pseudomorph data is not included, excepting data for 880°C and 48 h. Linked by the dashed line in panel A, this data point is included to demonstrate the rapid increase in reaction rate. In plot A, crosses denote data points from experiments using Redoubt Volcano samples (Browne, 2005). Experiments by Browne (2005) were heated to 940°C at a pressure of 150 MPa. This represents ~40–50°C of heating above the maximum amphibole stability temperature at 150 MPa (Browne and Gardner, 2006). Error bars represent 1-sigma uncertainty and where not present indicate uncertainty smaller than the data point.

Figure 4. Mineralogy of natural and experimental amphibole reaction rims

Experimental and natural heating-induced amphibole reaction rim mineralogies (see Fig. S2 for mineral specific textural data) from heating experiments and natural samples. Data for experimental reaction rims and those from the 2006 eruption of Augustine Volcano (the eruption from which starting materials for this study were utilized) represent population modal percentages from X-ray map analysis. Natural reaction rim data for Soufrière Hills Volcano, Mount St Helens Volcano, Bezymianni Volcano, and El Misti Volcano represent mass balance calculations. Fe-Ti = iron-titanium oxides; Opx = orthopyroxene; Cpx = clinopyroxene; Plag = plagioclase; Amph = amphibole; Px* = pyroxene (Opx and Cpx data combined). Data sources: a = De Angelis et al., 2013; b = Rutherford and Hill, 1993; c = Buckley et al., 2006; d = Plechov et al., 2008; e = Tepley et al., 2013. ** = Mean values for multiple analyses.

Figure 5. Phase compositions in heating experiments

Compositional characterization of experimental heating induced reaction rims: A) Wt.% CaO as a function of Wt.% SiO₂ (data normalized to 100%) for starting material whole rock, starting material matrix glass, inter-microlite experimental reaction rim glass, and experimental matrix glass distal (>500 μm) to reacted amphibole. Data are classified by experimental duration (hours). Dashed boxes link reaction rim glasses with distal glass compositions from the same experiment. Numbers alongside data points or dashed boxes denote heating temperatures; B) Plagioclase anorthite number (An) as a function of experimental heating duration (hours). Data classified by experimental heating temperature (°C); C) Classification of pyroxene microlites in experimental reaction rims. Data classified by experimental duration (hours). Error bars represent 1-sigma uncertainty and where not present indicate uncertainty smaller than the data point.

Figure 6. Amphibole reaction rim microlite crystal orientations

Example images of amphibole reaction rim microlite crystal orientation: A) Composite X-ray map of an experimental amphibole pseudomorph formed after 36 hours of heating at $T = 920^{\circ}\text{C}$ / $P = 140$ MPa. Colors denote different mineral phases: orthopyroxene (opx) = light green, plagioclase (plag) = purple, magnetite (mt) = red, ilmenite (il) = yellow. Pseudomorph microlites are almost exclusively orthopyroxene and are aligned along the crystallographic C-axis of the parent amphibole; B) EBSD crystal orientation map of an amphibole with an experimentally induced reaction rim formed after 12 hours of heating at $T = 920^{\circ}\text{C}$ / $P = 140$ MPa. Colors denote crystal orientation, with like colors indicating like crystal orientation; (C) the reaction rim clinopyroxene and host amphibole $\{100\}$, $\{010\}$, and $\langle 001 \rangle$ pole figures, derived from (B), showing the crystallographic relationship between the host amphibole and the reaction rim microlites; (D) the reaction rim clinopyroxene and host amphibole $\{100\}$, $\{010\}$, and $\langle 001 \rangle$ pole figures for natural Augustine Volcano 2006 amphibole 06AUMRT037e (De Angelis et al., 2013).

TABLES

Table 1: Representative Starting Material Compositions

	HSA Whole Rock^a	HSA Amph^{b/c}	SHV Seed Amph^{d/e}	HSA Matrix Glass^{a/e}
SiO ₂	62.52	46.65 (0.52)	47.21 (0.10)	75.86 (0.64)
TiO ₂	0.56	1.57 (0.27)	1.39 (0.03)	0.44 (0.18)
Al ₂ O ₃	16.48	8.71 (0.36)	7.44 (0.07)	12.81 (0.36)
FeO (t)	5.39	11.93 (0.42)	14.23 (0.21)	2.08 (0.18)
MnO	0.13	0.48 (0.09)	0.56 (0.07)	0.08 (0.09)
MgO	3.43	15.31 (0.33)	13.99 (0.16)	0.41 (0.06)
CaO	6.58	10.64 (0.18)	10.76 (0.03)	2.09 (0.19)
Na ₂ O	3.78	1.74 (0.10)	1.20 (0.07)	3.65 (0.27)
K ₂ O	0.99	0.12 (0.03)	0.14 (0.02)	2.22 (0.20)
P ₂ O ₅	0.14	N/A	N/A	0.08 (0.04)
Cl	N/A	N/A	N/A	0.28 (0.06)
Total	100.34	97.15 (0.51)	96.91 (0.31)	99.49 (0.64)
n [*]	N/A	9	5	37

^a High silica andesite (HSA) sample 06AUMC004c. Data from Larsen et al. 2010

^b Example composition of HSA (06AUMC004c) amphibole.

^c Full dataset available in the Electronic Supplementary Material.

^d Example composition of Soufrière Hills Volcano amphibole (sample SH08).

^e Glass oxide data are normalized to 100, although original totals are reported.

^{*} Data average of 'n' analyses with standard deviation in brackets

888 Table 2: Experiments and Mean Experimental Reaction Rim Measurements

Final Conditions ^a				Reaction R Measurements ^b						
T (°C)	P (MPa)	Time (Hr)	n	Width (μm)	Grain Size (μm)	CND (mm ⁻²) ^c	Φ ^d	I (mm ⁻³ s ⁻¹) ^e	G (mm s ⁻¹) ^f	
HSAS 31*	880	140	3	2	6.96 (2)	6.62 (4)	7.3 (1.4) x10 ⁴	0.72 (0.06)	1201 (647)	2.91 (0.11) x10 ⁻⁷
HSAS 24	880	140	12	2	8.56 (3)	10.90 (5)	2.8 x10 ⁴	0.62 (0.11)	62 (20)	1.09 (0.05) x10 ⁻⁷
HSAS 41	880	140	24	3	13.94 (4)	5.53 (3)	2.6 (1.1) x10 ⁴	0.71 (0.06)	56 (14)	6.11 (0.64) x10 ⁻⁸
HSAS 34	880	140	36	3	17.57 (5)	5.55 (4)	2.6 (0.9) x10 ⁴	0.65 (0.04)	43 (36)	4.89 (2.66) x10 ⁻⁸
HSAS 14	880	140	48	3	184.62 (49)**	15.44 (12)	1.7 (0.4) x10 ⁴	0.65 (0.05)	8 (3)	3.46 (0.44) x10 ⁻⁸
HSAS 3*	900	140	3	4	6.62 (2)	9.95 (6)	5.7 (2.9) x10 ⁴	0.62 (0.10)	575 (565)	3.97 (2.04) x10 ⁻⁷
HSAS 5	900	140	6	4	10.91 (4)	4.58 (2)	8.8 (2.5) x10 ⁴	0.68 (0.06)	904 (143)	1.28 (0.12) x10 ⁻⁷
HSAS 16*	900	140	12	2	20.77 (8)	12.76 (7)	1.3 (0.4) x10 ⁴	0.58 (0.06)	24 (10)	1.57 (0.25) x10 ⁻⁷
HSAS 17*	900	140	24	3	72.15 (19)+	15.31 (11)	8.0 (0.3) x10 ⁴	0.63 (0.04)	7 (5)	1.10 (0.40) x10 ⁻⁷
HSAS 11*	900	140	36	2	113.83 (17)**	18.27 (15)	1.2 (0.5) x10 ⁴	0.64 (0.05)	5 (3)	5.92 (1.75) x10 ⁻⁸
HSAS 6*	900	140	48	2	186.63 (37)	9.89 (7)	2.1 (0.6) x10 ⁴	0.68 (0.05)	14 (11)	3.41 (0.86) x10 ⁻⁸
HSAS 10	920	140	3	4	16.73 (7)	7.55 (4)	3.9 (1.0) x10 ⁴	0.61 (0.05)	510 (212)	3.71 (0.20) x10 ⁻⁷
HSAS 44	920	140	6	4	19.62 (8)	6.21 (3)	5.1 (1.1) x10 ⁴	0.69 (0.05)	409 (307)	1.92 (0.64) x10 ⁻⁷
HSAS 22*	920	140	12	3	54.37 (29)	16.16 (9)	1.8 (0.4) x10 ⁴	0.66 (0.05)	29 (17)	1.48 (0.38) x10 ⁻⁷
HSAS 15	920	140	24	3	124.92 (24)**	6.07 (3)	6.2 (1.4) x10 ⁴	0.74 (0.04)	137 (140)	4.60 (1.47) x10 ⁻⁸
HSAS 8*	920	140	36	3	119.36 (37)**	13.43 (8)	1.6 (0.5) x10 ⁴	0.63 (0.05)	10 (4)	4.89 (0.43) x10 ⁻⁸

890 ^a Final experimental conditions (excluding 24 hour equilibration at 870°C and 140 MPa)

891 ^b 'n' = number of amphibole reactions rims identified and measured. Mean and standard deviation of results are given in brackets.

892 ^c Crystal Number Density. Rounded to the nearest 1000 (k). Data collected through point counting of regions of interest (ROIs).

893 ^d Crystal Area Fraction

894 ^e Crystal Nucleation Rate. Rounded to the nearest whole number.

895 ^f Crystal Growth Rate

896 * Reaction rims from these experiments were used for EBSD analysis: HSAS 31 grains 1 and 2; HSAS 03 grains 1, 3, and 4; HSAS 16 grains 1 and 2; HSAS 17 grains 1 and 2; HSAS 11 Pseudo 1; HSAS 06 Grain 1; HSAS 22 grains 1 and 2; HSAS 08 Pseudo 1.

898 ** All amphibole are pseudomorphed, therefore mean width values are wholly controlled by the size of the initial host phenocryst.

899 + Some amphibole exhibit reaction rims, some are wholly pseudomorphed. Mean width excludes data from the pseudomorphed grains.

900 Table 3. Comparison of a Representative Mass Balance Calculation (from electron microprobe data) to Observed Modal Mineralogy

Run HSAS 16-1^a: *Amph* $\Rightarrow$ *Plag* + *Cpx* + *Opx* + *Mt* + *Il* ^{b, c}

	Mass Balance: Input ^d						Output		Mineralogy		
	Amph	Plag	Cpx	Opx	Mt	Il	Bulk R	Residuals		Mass Balance	Modal Data ^e
n.	12	5	6	4	4	1					
SiO ₂	49.34 (0.51)	54.40 (1.32)	51.10 (0.38)	52.73 (0.37)	0.50 (0.06)	0.05	49.45	-0.11			
Al ₂ O ₃	7.04 (0.15)	29.15 (1.20)	3.19 (0.30)	2.41 (1.10)	3.57 (0.22)	0.37	6.94	0.10	Plag	15.80	12.53
TiO ₂	1.47 (0.06)	0.00	0.76 (0.09)	0.31 (0.02)	6.73 (0.27)	41.71	1.49	-0.02	Cpx	44.46	40.85
FeO	14.66 (0.42)	0.67 (0.18)	9.97 (0.31)	20.80 (1.12)	85.56 (0.33)	52.80	14.67	-0.01	Opx	34.38	33.28
CaO	11.23 (0.18)	11.26 (1.02)	19.54 (0.37)	2.02 (0.57)	0.00	0.00	11.16	0.07	Mt	2.16	11.73
MgO	14.20 (0.16)	0.04 (0.03)	14.75 (0.36)	20.95 (1.34)	3.11 (0.09)	4.54	13.93	0.27	Il	2.15	1.61
MnO	0.52 (0.03)	0.02 (0.01)	0.40 (0.03)	0.65 (0.10)	0.52 (0.02)	0.53	0.43	0.09	Ox (t)	4.31	13.34
K ₂ O	0.19 (0.02)	0.13 (0.03)	0.03 (0.01)	0.02 (0.01)	0.00	0.00	0.04	0.15			
Na ₂ O	1.34 (0.07)	4.34 (0.54)	0.24 (0.03)	0.10 (0.12)	0.00	0.00	0.83	0.51			

901 ^a Experimental conditions (excluding 24 hour equilibration at 870°C and 140 MPa): 900°C for 12 hours.

902 ^b Following Buckley et al. (2006), glass data not included in mass balance calculations. Interaction with glass assumed to be represented
903 by calculated residuals.

904 ^c Amph = amphibole (hornblende); Plag = plagioclase; Cpx = clinopyroxene; Opx = orthopyroxene; Mt = magnetite; Il = ilmenite; Ox
905 (t) = total Fe-Ti oxides.

906 ^d Phases data in mass balance calculations were normalized to 100% (Buckley et al., 2006).

907 ^e Modal mineralogy corrected to mass fraction

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