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EVOLUTION OF VOLATILE CONTENT OF THE PARENT MAGMA OF THE 1875 ERUPTION OF ASKJA VOLCANO, ICELAND

A Thesis Presented

by

HEATHER A. CLARK

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2012

Geosciences

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EVOLUTION OF VOLATILE CONTENT OF THE PARENT MAGMA OF THE 1875 ERUPTION OF ASKJA VOLCANO, ICELAND

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HEATHER A. CLARK

Approved as to style and content by:

Sheila J. Seaman, Chair

Christopher D. Condit, Member

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DEDICATION

This work is dedicated to my grandfather, Malcolm Sears Clark, a farmer in the hills of western Massachusetts all his life. Through his quiet example, he instilled in all of his children and grandchildren a deep and abiding love and respect for the land we live on. I was and continue to be inspired in my work every day by his endless curiosity about how the landscape came to be, what's inside every rock, and the simple enjoyment of a walk in the woods.

I wish I could hand this to him. This is for you grampa, I miss you like crazy.

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ABSTRACT

EVOLUTION OF VOLATILE CONTENT OF THE PARENT MAGMA OF THE 1875 ERUPTION OF ASKJA VOLCANO, ICELAND

MAY 2012

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The Askja central volcano is located in the northeastern rift zone in central Iceland. The bulk of the eruption of Askja on March 28-29 1875 consisted of a plinian eruption that lasted 6-7 hours, produced approximately 0.2 km³ of ash and rhyolitic pumice, and created a surge and partially welded ash/pumice fall deposit that crops out on the northeastern shore of the modern caldera lake (Sparks et al. 1981). This series of deposits was described by Sigurdsson & Sparks (1981) and divided into layers A through E corresponding to distinctive phases of the eruption. This study is an evaluation of the volatile budget of the magma during the eruption and focuses on water concentration in glass fragments and shards, glass adjacent to crystals, and melt inclusions (MIs) hosted in those crystals. Sparks et al. (1981) estimated that the gas exit velocity at the vent was 380 m/s during the plinian phase, and estimated the water concentration at 2.8 wt%. Measurements of water concentration in glass shards and fragments of basaltic and rhyolitic composition from layers C through E range from 0.15 to 0.5 wt%, with distinctive variations within layers, a steep drop in water concentration in layer D, and increase in water concentration in layer E. Plagioclase and pyroxene crystals from layers C through E contain glassy rhyolitic MIs with water concentrations ranging from 0.1 to 1.8 weight percent, some of which are significantly higher than the matrix glass. In one sample, crystals host rhyolitic MIs with water concentrations approximately 3 times higher than surrounding rhyolitic glass. Magma underwent

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significant degassing on its way to the surface. In several cases, rhyolitic glass adjacent to crystals hosting MIs has the highest water concentration, from 0.4 to 2.18 wt%. This characteristic, and the initial phreatoplinian eruptive style, both suggest interaction of magma with meteoric water prior to and during the eruption. Intimate mixtures of basaltic glasses of differing compositions within individual samples and basaltic glass fragments surrounded by rhyolitic glass support the conclusion of Sigurdsson and Sparks (1981) that magma batches mingled and possibly mixed prior to and during the eruption.

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CHAPTER 1

INTRODUCTION

The Askja volcano in the central highlands of Iceland (figure 2) erupted catastrophically on March 28 and 29, 1875 producing a caldera 4.5 km in diameter (11 km² in area). The caldera is now filled with the deepest lake in Iceland, Lake Öskjuvatn, which is 224 m deep in the center (Sigurdsson and Sparks, 1981). The eruption began with a phreatoplinian phase that produced stratified base surge (diffuse density current) deposits, and then after a brief relatively quiescent phase, quickly changed to a plinian-style eruption that lasted approximately 8 hours and produced the bulk of the ejecta, partially welded ash and pumice fall deposits that crop out on the northeastern shore of the modern lake (figure 4) (Sparks et al., 1981). These deposits consist of varying proportions of volcanic ash, rhyolitic pumice, scoria, glass fragments and crystals.

In this study, variations in volatile concentrations in melt inclusions, and the volatile-related magmatic processes that controlled the eruptive style(s) of the 1875 Askja eruption are documented, and an attempt is made to constrain the degassing history of the magma. Changes in eruptive style can be due to volatile concentration differences in one or more interacting magmas prior to eruption, or to the interaction of magma with external water sources as suggested by Carey, et al. (2009a, 2009b). Glass fragments in pumice and glassy melt inclusions in crystals record magma volatile contents at the moment of their entrapment. By measuring H₂O and CO₂ concentrations in glasses and melt inclusions from each of the layers in the base surge and pumice fall deposits using Fourier Transform Infrared (FTIR) spectroscopy, the volatile budget of the magma (or magmas) and the degassing path(s) of the magma(s) throughout the eruption can be documented. An intact stratigraphic sequence provides an opportunity to correlate volatile content and composition of the layers to time and phases of the

eruption, and to correlate the volatile concentration of glasses in the 1875 ash deposits with the compositional gradient in the magma chamber. Finally, this study provides an overview of the partitioning of volatile species between crystals, melt, and vapor in the stage preceding eruption.

CHAPTER 2

BACKGROUND

Geologic setting

Iceland (figure 1) is part of the North Atlantic Thulean igneous province, which includes most of the North Atlantic, Iceland and Greenland. Iceland sits directly atop the mid-Atlantic rift where the Eurasian and North American plates are diverging, and also above a large mantle plume (Wolfe et al., 1997; Trønnes, 2002; Larsen and Eiriksson, 2008). Iceland has been volcanically active for 20-25 my, and the oldest rocks above sea level have been K/Ar dated to ~14 my (Thordarson and Larsen, 2007). Iceland provides examples of virtually all volcano types and eruptive styles known on Earth, and volcanic activity over the last 1,100 years has produced approximately 87 km³ (dense rock equivalent) of material, of which ~79% is basaltic, ~16% intermediate and ~5% silicic (Thordarson and Larsen, 2007). The areas of active volcanism cover nearly one third of Iceland, and many are located in the modern rift zones which run generally from the southwest curving up through the center to the northeast (figure 3). The most active volcanic centers are on the Eastern Volcanic Zone (EVZ) producing ~82% of the volume of erupted material in the last 1,100 years, and the axial zone (Reykjanes, Western and Northern Volcanic Zones) has produced ~16% of the volume (Thordarson and Larsen, 2007). Much of the off-rift volcanism in Iceland is basaltic while the volcanic centers on the rift zones are generally bimodal. The bulk of the known silicic eruptions in Iceland were produced from Hekla, Torfajokull and Dyngjufjöll/Askja, all located in rift zones (Sigvaldason, 2002; Thordarson and Larsen, 2007; Larsen and Eiriksson, 2008).

The Askja volcano in the northeast central highlands of Iceland is part of the Dyngjufjöll central volcanic complex and associated fissure system and is located in the Northern Volcanic Zone, which is in the central/northeast part of the modern active rift

zone(figure 3). The Dyngjufjöll complex extends from the north edge of the Vatnajokull glacier in the south ~100km to the north, and is associated with Grimsvötn to the south and Sveinagiá to the north through lateral diking and interconnection of the fissure system (Nordvulk, 2006). The oldest exposed rocks in this area are upper Pleistocene (0.8 my), and this area has been active for >200,000 y (Thordarson and Larsen, 2007). The bulk of the rocks in the area are basaltic and therefore difficult to date precisely. A rhyolitic ash fall layer (the Dyngiufiöll tephra) that is present on high ground near Askia and is found on top of glacial deposits in coastal northeast Iceland has been found in the GRIP Central Greenland ice core (Gronvold et al., 1995). The Dyngjufjöll tephra layer is located in between two other known ash layers that have been ¹⁴C dated at 8.9 ky and 10.6 ky respectively (Sigvaldason, 2002), constraining the age of the Dyngjufjöll tephra to between those ages. The Dyngjufjöll tephra layer is not found in the area between the coastal deposits and Askja, indicating that the deposit fell on top of thinning glaciers in those areas, and that the area around Dyngjufjöll was ice free at that time. Consequently Sæmundsson (1991) surmised that the older Askja caldera was formed by the eruption that produced the Dyngjufjöll tephra and that eruption occurred around the end of the last glaciation, ~10 kya. Postglacial activity in the Dyngjufjöll complex has

produced a large amount of basaltic lavas and formed many shields in the surrounding area, including Kollóttadyngja, Flatadyngja, Litlandyngja and Svartadyngja to the north and Trölladyngja in the south. Together with Dyngjufjöll, these comprise the Ódádahraun lava desert (figure 5). ('Dyngja' in this context means 'shield'.) Volcanic activity was higher by a factor of 30 between 8 kya to 2.9 kya than it was from 2.9 kya to present, accounted for by pressure-induced changes in mantle melting due to deglaciation, and ice in central Iceland reached a maximum thickness of ~2000 m during the peak of glaciation (Nordvulk, 2006).

Besides the eruption that produced the Dyngjufjöll tephra at ~10 ky, the only eruption to produce a significant amount of silicic material from Askja was the eruption which took place on March 28 and 29, 1875 (Sigurdsson and Sparks, 1981). Regional rifting in 1874 and 1875 caused the activation of the Askia central volcano and its associated fissure swarm, resulting in a fissure eruption at Sveinagjá (approximately 50 km to the north of Askja), which produced 0.3km³ of basaltic lava and initiated caldera collapse in the area that is now Öskjuvatn (Sigurdsson and Sparks, 1978; Sigurdsson and Sparks, 1981). Five weeks later, on March 28, 1875, subsequent injection of basaltic magma into a stratified magma chamber beneath Askja (Sigurdsson and Sparks, 1981) triggered an eruption which lasted for approximately 17 hours and shifted several times from wet to dry eruptive conditions (Carey et al., 2009a). The eruption commenced with a dry subplinian phase, then shifted to a wetter phreatoplinian phase, and then shifted again to the main, drier, plinian phase which lasted approximately 8 hours and produced the bulk of the ejecta (Carey et al., 2009b). From the explosive eruption on March 28 and 29, 1875 to the present, there have been several subsequent basaltic eruptions on ring fractures and other fissures near the two calderas, but there has not been another large eruption akin to the one in 1875 (Nordvulk, 2006).

Previous work: the Askja Volcanic Complex

This study focuses on an approximately 2.5 m-thick section of pumice fall and base surge (diffuse density current) deposits that crop out on the northeastern shore of Lake Öskjuvatn (figure 9). Abundant work has been done to characterize the petrology, stratigraphy, field relations (Self and Sparks, 1978; Sigurdsson and Sparks, 1978; Sigurdsson and Sparks, 1981; Sparks et al., 1981; MacDonald et al., 1987), eruptive style, shifts between wet and dry phases and possible vent locations (Carey et al.,

2009a, 2009b) of this eruption. However no previous workers are known to have directly measured water and carbon dioxide concentration of these materials. Water concentration was previously estimated to be between 1.5 and 3.0 wt% based on methods used by Sigurdsson & Sparks (1981), and described in the petrology section below.

Self & Sparks (1978) coined the term *phreatoplinian* to refer to a type of eruption and subsequently a type of pyroclastic deposit formed by the interaction of silicic magma and water. These eruptions share many characteristics with both phreatomagmatic (fragmentation, explosive eruptions due to interaction of water and silicic magma, structures such as base surges or thin beds near the source) and plinian style (sustained high eruption column, silicic, large volumes of ash and pumice produced) style eruptions, yet the deposits resulting from phreatoplinian eruptions contain a "finer and more complex grain size distribution" (Self and Sparks, 1978, p. 196) than plinian deposits. This is the result of two separate mechanisms of fragmentation, the first caused by exsolution of volatiles and vesiculation, and the second by the silicic magma coming into contact with water.

Sigurdsson & Sparks (1981) presented a detailed catalog of the occurrence and the petrology of the ejecta from the March 28 and 29, 1875 eruption of Askja. They stated that the eruption was triggered by the ascent of tholeiitic basaltic magma from depth during regional crustal rifting into a density-stratified magma chamber comprised of a rhyolitic upper part, an intermediate icelandite composition middle layer, and a ferrobasaltic bottom. The influx of new basaltic magma into the chamber caused convective mixing and hybridization in the already zoned magma, resulting in the plinian eruption. Over 17 hours, the eruption produced 0.2 km³ (dense rock equivalent) of ejecta that was predominately silicic at the outset, and graded to somewhat more mafic

near the end of the eruption. Sigurdsson & Sparks (1981) and Sparks et al. (1981) presented a stratigraphic column (figure 9, modified by Carey, 2009a, and this study) that characterizes deposits resulting from the eruption. Of the layers shown, C-E are the subject of this study. Layers C-D formed during the March 28/29, 1875 eruption, and layer E was produced by a later phreatomagmatic eruption taking place in April, 1875. Over 94% of the composition of layers C-D is white rhyolitic crystal-poor pumice and ash, 5% is pale to dark grey pumice composed of intimate mixtures of ~60% rhyolitic and ~40% basaltic glass, and less than 1% of the total ejecta is comprised of lithic clasts (obsidian fragments; rhyolitic, basaltic and mixed composition glass fragments; partially fused leucrocratic xenoliths; rounded crystal inclusions in while pumice clasts; and a variety of crystalline and altered basalt and palagonite tuff fragments) (Sigurdsson and Sparks, 1981; Sparks et al., 1981).

The following description of the petrology of the layers is derived from Sigurdsson & Sparks(1981). Layer C1 is a poorly-stratified and -sorted, fine-grained, highly-fragmented ash fall deposit containing < 0.5% crystals, of which plagioclase and clinopyroxene comprise 2-3% and .2-2% of the mode, respectively. Magnetite and other opaque minerals comprise 0.1-0.6% of the mode, and small amounts of quartz, originating as trondhjemite xenoliths, are also present. Basaltic glass fragments are found throughout as discrete shards and also enclosed by rhyolitic glass, as are leucrocratic xenoliths of trondhjemite (plagioclase, pyroxenes, quartz and accessory minerals such as apatite or illmenite) and icelandite (plagioclase, pyroxene, and opaque minerals). Rare olivine and orthopyroxene crystals are also present.

Layer C2 is a reversely-graded pumice and ash fall deposit, also highly fragmented, showing similar distribution of crystal phases and leucocratic xenolith inclusions. The icelandite inclusions found in layer C2 are highly vesicular, crystal rich,

and glassy, clearly showing evidence of partial melting and resorption. Basaltic glass fragments in layer C2 are frequently enclosed by light brown or clear rhyolitic glass. Layer D (subdivided into D1-D4 in this study) is a coarse plinian pumice fall deposit and partially welded tuff in places, comprised of grey, brown, and black pumice.

In the D layers, crystals make up ~39% of the mode, compared to <3% of the mode in the C layers (Sigurdsson and Sparks, 1981). Overall the D layers are still quite crystal-poor. A similar suite of phases as the C layers is present: plagioclase, clinopyroxene and opaque minerals, and inclusions of icelandite and trondhjemite. One distinctive feature of the D layers is that they contain pumice clasts consisting of "pale to dark grey pumice composed of exceedingly intimate mixtures of pale brown rhyolitic and dark brown basaltic glass" (Sigurdsson & Sparks, 1981, p. 47). These clasts comprise up to 10% of the deposit in places. These mixed pumices exist on both hand-sample scale (figure 26) and micro scale, indicating varying degrees of magma mingling in the system.

Layer E is comprised entirely of lithic clasts and obsidian fragments.

Another notable feature of layers C-E is the presence of magnetite, such that when the pumice clasts are crushed, there is enough magnetite to cause the resulting powder to entirely stick to a magnet.

The petrologic model proposed by Sigurdsson & Sparks (1981) suggests a complex model of fusion, hybridization and fractional crystallization to account for the generation of the rhyolitic magma, based on the observed compositional range of the eruptive products. They make two major points about the petrology: first, that the rhyolite shows extensive intimate physical mixing and varying degrees of chemical contamination with a range of basaltic magmas, and second that the rhyolitic ejecta are associated throughout the deposits with a suite of leucocratic granitic or trondhjemitic

xenoliths in various states of fusion, indicating that the xenoliths played an important role in the petrogenesis of the rhyolite. Weinberg (personal communication, 2012) was unable to document the complete mixing of end members. Sigurdsson and Sparks (1981) considered the principle volatile species present in the Askja rhyolite to be H_2O_1 , and they estimate the saturated water concentration of the magma to be from >1.5 wt% to 3.0 wt% using four main methods. The first is based on mineral geothermometry. In order to correlate calculated olivine and plagioclase temperatures of formation, $\mathsf{P}_{\mathsf{H}_2\mathsf{O}}$ of 500-1000 bars is required. Second, a P_{H_2O} of <1000 bars is indicated by the position of plagioclase-bearing rhyolitic glass in the salic tetrahedron, while the glasses formed by partial melting of xenoliths plot nearer to 500 bars, suggesting a saturated water concentration of ~3.0 wt%. Third, based on calculations of Wilson (1976) on the dispersal of large pumice bombs, the gas exit velocity at the vent during the plinian phase (layer D) was estimated to be 380 m/s (+/- 20 m/s), and to have remained relatively constant during the eruption. The water concentration was calculated at 2.8 wt% based on estimates using theoretical relationships between temperature, gas pressure, water content and gas velocity. Finally, they conclude that since the Sveinagjá basalt (erupted a few months previous to the March 1875 Askja eruption) was only able to reach an altitude of 600 feet above sea level, that also must represent the maximum hydrostatic level of the reservoir beneath Askja. The Askja rhyolite ascended to 1100m above sea level. To account for this, a saturated water content of greater than 1.5 wt% was necessary (due to exsolution of volatiles at depths >500m).

MacDonald et al. (1987) presented major and trace element data and Sr, Nd, and O isotope data from a range of eruptive products from the March 28 and 29, 1875 eruption. They stated that major and trace element data and Nd and Sr isotopic data largely confirm previous findings that fractional crystallization was the dominant process

responsible for the generation of the ferrobasalt-icelandite-rhyolite succession. However, enrichment in Rb, Th, and U, depletion in Cs, and low values of ⁸¹⁸O/⁸¹⁶O in the rhyolites cannot be explained by only fractional crystallization. They proposed that silicic magmas were contaminated by diffusion from partially melted granitic wall rocks, which are now incorporated as silicic xenoliths. Some of the xenoliths show extensive hydrothermal alteration, and this, combined with low ⁸¹⁸O/⁸¹⁶O ratios in the rhyolites, leads them to conclude that there was extensive interaction with meteoric water prior to and/or during the eruption. They note that most rhyolitic lavas in Iceland have comparable ⁸¹⁸O/⁸¹⁶O ratios to Icelandic basalts, but only rhyolitic pumice is known to be depleted in¹⁸O, indicating that the silicic tops of magma chambers in Iceland are probably interacting with and/or ingesting meteoric water and this may be the cause for the high volatile contents and explosive eruptions sometimes involved with Icelandic rhyolitic magmas. They also note that this is the first record of a combined fractional crystallization and selective contamination process in an Icelandic silicic complex.

Carey et al. (2009a) examined the products of four distinct phases of differing intensity and eruptive style during the March 28 and 29 eruption of Askja. They noted several shifts in eruptive style from drier to wetter conditions during the 17-hour long event, and also two pauses in eruptive activity, which they attribute to changes in external conditions accompanying changes in vent position, vent geometry, and the movement of the vent(s) into or out of external water sources rather than changes in mass flux. They state that all the major vents that were active during each phase of the eruption were located in what is now Lake Öskjuvatn. Drier subplinian deposits (layer B) contain fragments of basalt and hyaloclastite, indicating that the vent was located at the eastern side of the modern lake, near the contact between the older hyaloclastite walls of the Askja caldera and the later basalts infilling the caldera. Carey, et al. (2009a) state

that the vent that produced the wetter phreatoplinian deposits (C1 layer) is hard to specifically locate, but the similarly wet nature of the C2 layers suggests that the C1 layer erupted from a geographically similar location as C2, and flow direction in the C2 deposits indicates that the vent was in the north-central region of the present lake, within the Askja marginal fault zone, and that descriptions of a pre-eruptive geographical depression coincide with this observation. They go on to say that the lowest sub-unit of the plinian deposits (D layer) contains the most lithic clasts, which indicates the opening of a new vent. They point out that there are sharp unconformities and slump planes between the C2 layer and the D layer, which coincide with a pause in eruptive activity, and indicate the presence of strong ground shaking which would accompany the new vent opening. They state that the vent for the plinian phase of the eruption (D layers) was probably in the basalt-covered western area of the Askja caldera, southwest of the other two vents, and also in an area that is now under Lake Öskjuvatn. Carey, et al. (2009a) also observed that there were two separate vents on peripheral extensions of two structural weaknesses in the caldera, producing minor weak eruptive activity synchronous with the production of the plinian D layers. One was located along the southern extent of the caldera fault and the other at the northwest extent of the northwest/southeast trending fault. These vents produced layers D2 and D4 of the plinian deposits while the main vent for the plinian phase of the eruption produced layers D1, D3, and D5.

This study aims to fill a gap in the data on Askja, notably by directly measuring volatiles in the system. To our knowledge, no previous work has been done on direct measurement of volatiles. Only estimates have been made based on various conditions (Sigurdsson and Sparks, 1981). In light of work by Carey et al. (2009a; 2009b) investigating changing vent locations and their migration in and out of possible external

sources of water as a control on eruption dynamics, it is relevant to attempt to quantify the pre-eruptive volatile content of the magma(s). It could be possible to distinguish differing availability of volatiles in magma source areas, and to constrain degassing paths and conditions in the magma chamber prior to the eruption.

Volatiles in Magmas

Melt inclusions (figure 12) are small samples of silicate melt that are trapped in phenocrysts at magmatic temperatures and pressures, thus recording the composition of the melt at the moment of their entrapment and preserving the amount of dissolved volatiles present in the melt (Cashman, 2004; Lowenstern, 2003). The crystal acts as a container and maintains those conditions (providing it is not cracked or otherwise compromised) as the system continues to evolve. By measuring the dissolved volatile content of the melt inclusions, the pressure of vapor-melt equilibration at the time of entrapment can be estimated (Lowenstern, 2003). By combining measurements of compositions of melt inclusions and their host crystals, dissolved volatile contents and host magma compositions, it is possible to document the processes that control eruptive style of volcanoes (Metrich and Wallace, 2008) and reconstruct possible degassing paths (Blundy and Cashman, 2008).

A computer program called VolatileCalc, developed by Newman and Lowenstern (2002), calculates vapor-melt equilibria for basalt- H_2O-CO_2 or rhyolite- H_2O-CO_2 systems based on a thermodynamic solubility model for hydrous silicate melts (Silver and Stolper, 1985), and applied to rhyolite by Silver (1988). Results agree well with the model of Moore et al. (2008) for the rhyolite- H_2O-CO_2 system (Newman and Lowenstern, 2002). The following information is summarized from Newman and Lowenstern (2002), and corresponding equations can be found therein.

VolatileCalc can be used to calculate saturation pressure (minimum pressure of formation of melt inclusions), isobar and isopleth plots, vapor fugacities, solubility vs. pressure calculations, and degassing paths. A melt is modeled as an ideal mixture of OH⁻ groups, water molecules, and O atoms, and equilibrium constants are used to determine the partitioning of water into either OH groups or H₂O molecules. Then solubility of water is linked to the fugacity of water in the vapor (Newman and Lowenstern, 2002, equation 1). Using measured values of dissolved H₂O and CO₂ in samples, the program calculates the molar concentration of water and carbon dioxide by assigning the appropriate amount (mol fraction) of H₂O vs. OH⁻ and the mol fraction of CO₂ that should be dissolved in the melt based on existing experimental solubility model data. Using the calculated molar concentration of H₂O and CO₂ and a measured or estimated temperature of formation, vapor composition is determined. It is assumed that volatile solubility of gases in the melt follows Henry's Rule, such that dilution of H₂O in the vapor phase linearly decreases its concentration in the melt. Pressure is iterated until a set of conditions are found wherein the partial pressures of H_2O and CO_2 in the vapor phase equal unity. Saturation pressure of a melt inclusion is the pressure at which a melt of known dissolved H_2O and CO_2 would be saturated with a vapor phase, and provides the minimum pressure (therefore depth) of formation of the melt inclusion at a given temperature. Degassing paths can be calculated using VolatileCalc (Newman and Lowenstern, 2002). Degassing paths are constructed using a series of volatile compositions of both melt and vapor that a magma would follow during depressurization, and can be calculated for either open or closed system conditions. The user inputs the measured dissolved H_2O and CO_2 concentrations in the melt, the T in °C (measured or estimated), and specifies how many points to generate along the degassing path. The program calculates wt% H₂O and CO₂ dissolved in the melt, H₂O speciation, vapor

composition, and pressure at all points along the path. For a closed system (where gases are not able to escape), the melt and vapor compositions are re-calculated at each step of magma depressurization until they are in equilibrium with the total vapor exsolved from all previous steps. The user specifies the initial presence of exsolved vapor in equilibrium with the melt composition (this value can be obtained from the saturation pressure calculation). The open system calculation is done similarly, except for each step of magma depressurization, the melt and vapor compositions are recalculated until they are in equilibrium with the vapor exsolved at that step. It is assumed that all the previously exsolved gases have escaped from the system.

In order to determine what sort of degassing path is followed by a magma or magmas being studied, a set of measurements of dissolved H₂O and CO₂ concentrations of melt inclusions is analyzed. Fluid saturation pressure is calculated for all melt inclusions to determine which were formed deepest within the system, and those are assumed to be the least degassed. This value is then used to calculate the initial vapor present in the system, which in turn is used to construct and plot open and closed system degassing paths (Newman and Lowenstern, 2002). The data set of measured dissolved H₂O and CO₂ concentrations in all melt inclusions is then plotted on the chart with the calculated degassing paths for the system. Combining as many melt inclusion measurements as possible can help to determine if the type of degassing process was open system or closed system (Moore, 2008). In experimental models, degassing paths are clearly delineated, but in natural systems it is unlikely that one clear degassing path will emerge. A more realistic expectation is that the data will describe either development of the system under changing conditions (e.g. initially closed system, then evolving to open system) or mixing of melt inclusions from different sources (Blundy and Cashman, 2008; Kent, 2008), revealing an even more complex history.

Whether a magmatic system evolves under open or closed system conditions exerts a major control on eruptive dynamics (Blundy and Cashman, 2008). Closed system degassing (magma ascends with gas phase entrained) is typically associated with large, violently explosive eruptions (Metrich and Wallace, 2008). When the magma reaches the surface, exsolved gases have not escaped, leading to rapid depressurization, exsolution, vesiculation and fragmentation. Usually plinian or similar style eruptions result. Open system degassing, which allows exsolved volatiles to escape, is more typically associated with calmer, less explosive, more effusive eruptions (Blundy and Cashman, 2008).

CHAPTER 3

METHODS

Sample preparation

FTIR analyses were done using the Brucker Vertex 70 Fourier transform infrared (FTIR) spectrometer and Hyperion 3000 microscope housed in the Department of Geosciences at the University of Massachusetts, Amherst. Samples were prepared by sorting through material obtained by very carefully crushing pumice chunks to release the small crystals and glass shards within them and then separating out plagioclase, guartz, and pyroxene crystals, and shards of glass. Crystals and glass grains were mounted in Petropoxy molds approximately 1" in diameter and then polished using a succession of silicon carbide grits from 400 grit to 5 μ m. Diamond paste of 1 μ m, 0.3 μ m, and 0.1µm were used in the final stages of polishing. The grains were exposed before affixing the section to a glass slide using Crystalbond (a mounting adhesive that begins to melt at the relatively low temperature of 71°C and is soluble in acetone). The sections were then cut off, ground down, and once again polished to a mirror-like finish using the same protocol described above. Sections were polished to thicknesses ranging from 50-200 microns. Each section was then gently heated to approximately 80°C on a hotplate, until the Crystalbond melted enough to remove the section. The sections were then carefully washed in acetone several times until there was no remaining Crystalbond restive, and allowed to dry thoroughly before analysis was performed. Exact $(+/-1 \mu m)$ thickness of samples was determined by measurement with a Starrett #733 digital micrometer. For FTIR analysis, the sections were placed between two glass slides into which a 1 cm-diameter central hole had been drilled.

Spectroscopic measurements

FTIR analysis was done in transmitted light mode to obtain individual spectra (figure 11) for points within samples and maps (figures 32-38) of larger areas of material to determine the amount of volatiles (H_2O , OH, CO_2 and $CO_3^{(2)}$ in crystals, glasses and glassy melt inclusions. See figure 39 (tables) for exact number of spectra collected from each material in each layer. Spectra were collected in the Fourier Transform Infrared Spectroscopy Laboratory in the Department of Geosciences at the University of Massachusetts using a conventional silicon carbide globar source. A Bruker Vertex 70 spectrometer was used with a Hyperion 3000 microscope. The instrument at the University of Massachusetts has a KBr beamsplitter and a MCT-B detector in the microscope, and a 64×64 focal plane array (FPA) of detectors that was used to rapidly generate water- and carbon dioxide-concentration maps of larger areas of sample. Each detector has a spatial resolution of 2.6 µm, producing a 166×166 µm image. In addition, the FPA detector can build images in a two-dimensional array of steps, resulting in rapid collection of much larger images.

Spectra were collected on discrete points on glass shards, glassy melt inclusions and plagioclase and pyroxene crystals that host melt inclusions. Spot sizes were approximately 25×25µm. Spectra were typically collected using 64 scans, and a polynomial flexicurve baseline correction was applied prior to calculation of peak heights and areas.

Major element analyses

Major element analyses (point analyses and some major element maps) were obtained using the Cameca SX 50 electron microprobe in the Department of Geosciences at the University of Massachusetts under the supervision of Dr. Michael J.

Jercinovic and Dr. Julien Allaz. The Cameca SX 50 is equipped with five wavelengthdispersive spectrometers for quantitative analysis. Instrument control and implementation of quantitative analyses were done using the Cameca SX 50 operating system running in the Solaris environment on a Sun Sparc-20 computer. Corrections for differential matrix effects were done on-line using the PAP procedure(Pouchou and Pichoir, 1984). After FTIR analyses were done, the FTIR sections were re-mounted to glass slides and carbon coated for electron microprobe analysis with the SX-50. The spots for microprobe analysis were chosen to be as close as possible to the same spots on which FTIR analyses were collected. Glass analyses were done with a defocused beam (~20 µm diameter), comparable in analytical area to the beam used for FTIR analyses, and at 15 kV.

FTIR spectroscopy of glasses

Determination of water concentration

The following form of the Beer–Lambert Law was used for calculating water concentration in glass (Stolper, 1982):

 $c = (18:02*Absorbance)/(t*D*\epsilon)$

where c is the weight fraction of water, 18.02 is the molecular weight of water, absorbance is the height of the absorption peak, t is thickness in cm, and D is density in g/liter, and ε is linear absorption coefficient, in l/mol cm. The 3550 cm⁻¹ (2.8 µm) band results from the fundamental O–H stretching vibrations of both molecular H₂O and SiOH and AIOH structural groups and the overtone of H–O–H bending (Stolper, 1982; Ihinger et al., 1994). It is commonly used to determine total water concentration (Dixon et al., 1988; Dixon and Clague, 2001; Saito, 2001; King et al., 2002; Wysoczanski and Tani, 2006). In this study, we have used the height of this band, which commonly extends from approximately 2900 cm⁻¹ to 3700 cm⁻¹, to calculate water concentration in glass (Stolper, 1982; Dixon et al., 1988; Ohlhorst et al., 2001; Mandeville et al., 2002). For isotropic materials such as glasses (quenched melts), OH⁻ and H₂O complexes should have no crystallographic preferred orientation and hence any optical direction should have the same value for A. Thus, the water concentration of a glass can be measured with a single FTIR spectrum. Several workers (Stolper, 1982; Newman et al., 1986; Zhang et al., 1997; Ohlhorst et al., 2001; Mandeville et al., 2002) have established molar absorption coefficients for both near-IR (5200 cm⁻¹ and 4500 cm⁻¹) bands and mid-IR (3200–3500 cm⁻¹) bands in a wide range of glass compositions. A systematic error of ±10% is taken into account (Dixon et al., 1988; King et al., 2002) for all FTIR measurements of dissolved water in glasses.

Determination of carbon dioxide concentration

To determine the carbon dioxide concentration in glasses we use the same form of the Beer-Lambert law as we do for water, with the following modifications.

 $c = (44.01 \text{ Absorbance}) / (t^*D^*\varepsilon)$

where c is the weight fraction of carbon dioxide, 44.01 is the molecular weight of carbon dioxide, absorbance is the height of the absorption peak, t is thickness in cm, and D is density in g/liter, and ε is linear absorption coefficient, in l/mol cm. We measured the height of the 2350 cm/⁻¹ band, which results from the asymmetric stretching of molecular CO₂ (Fine and Stolper, 1986). Whereas the absorption coefficient for water in glasses is minimally affected by changes in glass composition, in the case of carbon dioxide the absorption coefficient varies considerably more. Absorption coefficients for CO₂ have also been found to vary when CO₂ concentrations become very high (Fine and Stolper, 1986). This is not relevant to the present study

since the CO₂ concentration in these samples is quite low. In this study, absorption coefficients of 1066 for rhyolitic glass (Blank, 1993) and 796 for basaltic glass (Morizet et al., 2002) were used. Systematic error of $\pm 10\%$ for measurements of CO₂ in basaltic glasses (Fine and Stolper, 1986), $\pm 16\%$ in andesitic glasses (King et al., 2002), and $\pm 21\%$ in rhyolitic glasses (Fogel and Rutherford, 1989) were used.

CHAPTER 4

RESULTS

Water concentration

Water and carbon dioxide concentrations were measured in discrete glass fragments, melt inclusions hosted in predominately plagioclase (and to a lesser extent pyroxene) crystals, and glass adjacent to the crystals hosting the melt inclusions. In samples from layers C-E of this deposit, nearly all of the spectra collected show water occurring as OH⁻ (rather than molecular water). This is seen as the broad asymmetrical peak occurring at 3500 cm⁻¹, which represents the fundamental stretching of OH⁻ groups, as well as the overtone of O-H-O bending. The absence of a peak at 1630cm⁻¹, which would indicate the presence of molecular water, shows that the total water represented by the 3500 cm⁻¹ peak is present as OH⁻. In silicic melts where the water concentration is less than 2 wt%, water preferentially occurs as OH⁻ groups, and above 2 wt%, the amount of molecular water increases as the OH⁻ groups become saturated in the melt (Philpotts and Ague, 2008).

Water concentration in melt inclusions

Glassy rhyolitic melt inclusions of sufficient size (at least 25 µm) contained within plagioclase and pyroxene crystals were analyzed to determine water content. Melt inclusions that were not fractured or otherwise compromised (necking out into matrix glass or occurring at the edges of crystals in contact with matrix glass) were chosen to best reflect the dissolved volatile contents of the magma prior to eruption. Melt inclusions that were analyzed were exposed on both the top and bottom of the section, to ensure that the IR beam passed through only the sample, and not the mounting medium.

Water concentration in melt inclusions was found to vary throughout the layers of the deposit, and there are wide variations even within samples. The lowest measured water concentration in a melt inclusion, 0.02 ± 0.002 wt%, and the highest, $1.86 \pm$.19wt%, are both found in (different) plagioclase-hosted melt inclusions from layer D1, part of the deposit resulting from the 8-hour sustained plinian style part of the eruption.

Measurements from melt inclusions hosted by plagioclase crystals from each layer were averaged (generally 20-30 points per layer, see figure 39 for number of analyses, and appendix for complete data tables) to more easily see the overall trend of changing water content. Layer C2A did not yield any crystals hosting usable melt inclusions so it is not included in the dataset. When averaged, the changes in water concentration throughout the layers can be seen to form a sawtooth pattern (figure 15). The average water concentration starts out at 0.6 ± 0.06 wt% at the bottom of the deposit (layer C1, formed by the initial phreatoplinian phase of the eruption), rises to 0.8 ± 0.08 wt% in layer C2B, then declines to below 0.4 ± 0.04 wt% in layer C2E, rises again to 0.8 ± 0.08 wt% in layer C2G (the transitional layer between the somewhat quiescent phase following the initial phreatoplinian phase and the beginning of the sustained plinian phase). In layer D3 we see a local low average point of 0.2 ± 0.02 wt%, after which the water concentration recovers to 0.36 ± 0.04 wt% in layer D4, and then falls to the lowest measured average in plagioclase hosted melt inclusions of 0.1 ± 0.01 wt% in layer E.

These shifts in water concentration are also seen in a reduced dataset of analyses of melt inclusions hosted by pyroxene crystals. Melt inclusions are scarce in pyroxene crystals, so few data points exist (34 total points in pyroxene hosted MIs vs. 201 in plagioclase hosted MIs). The layers not included in figure 16 did not yield any measureable melt inclusions in pyroxene crystals. In this data, the sawtooth pattern is

again visible (figure 16). Initially the averaged water concentration value is 0.18 ± 0.02 wt% in layer C2C, a jump to 0.55 ± 0.06 wt% in layer C2D (the beginning of the somewhat quiescent phase of the eruption) and then a consistent decline throughout the layers representing the plinian phase to the lowest measured average of 0.1 ± 0.01 wt% in layer D3.

Water concentration in glass fragments

 H_2O was measured in discrete glass fragments and obsidian shards that were separated from pumice clasts that were sampled from all layers of the deposit. Overall, there is less variation within samples than there was in the melt inclusion samples (see figure 39 for number of points averaged from all layers and standard deviations). The water concentration of the glass fragments is considerably lower overall than the melt inclusion water concentration, glass fragments containing approximately half the average values of the melt inclusions. The measured values in glass fragments range from average lows of 0.03 ± 0.003 wt% in layers C2F and D3, and a high average value of 1.52 ± 0.15 wt% in layer D4. The 1.52 ± 0.15 wt% value is somewhat anomalous as it occurs in a fragment of clear rhyolitic glass, and the majority of the glasses sampled are basaltic in composition and contain less dissolved water. The high values measured are generally $0.3-0.4 \pm 0.03-0.04$ wt% in all layers, and represent water in basaltic glass. The E layer is the most internally consistent, with the majority of measurements near 0.25 ± 0.03 wt%.

When averaged, the water concentration of the glass fragments also shows a variation throughout the layers of the deposit much like the melt inclusion data. Water concentration data for the glass fragments also form a sawtooth pattern (figure 17). At the bottom of the deposit in layer C1, the average water concentration starts out at 0.33±

0.03wt%, then falls to 0.28 ± 0.03 wt% in layer C2A, rises again to 0.37 ± 0.04 wt% in layer C2B, declines to 0.25 ± 0.03 wt% in layer C2F. The water concentration jumps to the highest average value of 0.38 ± 0.04 wt% in layer C2G and then declines to the lowest measured average of 0.18 ± 0.02 wt% in layer D3, recovers to 0.28 ± 0.03 wt% in layer D4, and then falls to 0.24 ± 0.02 wt% in layer E, the top of the deposit.

While the composition of the glassy melt inclusions is uniformly rhyolitic, the composition of the glass fragments varies widely, resulting in the average water concentration values containing measurements from predominately basaltic glasses but also some rhyolitic glasses and significantly fewer glasses of dacitic composition. Water concentration of rhyolitic glass spans the range of water concentration of the entire data set, although the highest water concentration measured was hosted by rhyolitic glass. This is true also for the glasses of other compositions throughout the deposit. Sigurdsson & Sparks (1981) identified two distinct populations of basaltic glasses present in these layers based on MgO content. One population is significantly more primitive, having MgO contents >5.5 wt% (type I), and represents more than 75% of the basaltic glasses. The other more evolved population represents less than 25% of the basaltic glasses and is characterized by MgO contents of between 5.5 wt% and 4.5 wt% (type II). When these populations were separated in our samples, slight but noticeable variations between them were noted (figures 19 and 20). The more primitive type I basaltic glasses have the same or higher water concentrations than the more evolved type II basaltic glasses found in the same sample layer. Type I basaltic glasses occur in all layers with the exception of C2C, whereas type II basaltic glasses were only found in layers C2B, C2C, C2F, D3 and D4.In type I glasses, average water concentration ranges from a high value of 0.37 ± 0.04 wt% to a low value of 0.23 ± 0.02 wt%, and in type II glasses, the range is from 0.32 ± 0.03 wt% to 0.05 ± 0.005 wt%.
Water concentration in glass adjacent to crystals

Water concentration in glass adjacent to crystals hosting melt inclusions ("edge glass") was measured. Figure 18 shows that water concentrations in the edge glasses are the highest of all those measured, up to 2.18 ± 0.22 wt%, the highest value in any sample. Initial microprobe data indicates that the edge glasses are rhyolitic, and are even more silica rich than the melt inclusions hosted in the crystals on which the glass adheres. In layer C2C, there is a melt inclusion with a SiO₂ content of 71.9 wt% hosted in a plagioclase crystal, and the glass adjacent to that crystal has a SiO₂ content of 73.9 wt%. In layer C2A, a clear rhyolitic glass shard (average 73.9 wt% SiO₂) encases a pyroxene crystal which in turn hosts a rhyolitic melt inclusion, and the clear rhyolitic glass has a water concentration of 1.5 ± 0.15 wt%, comparable to the high water wt% averages seen in other edge glass. There are distinctive fluctuations in water C1, rising to a high value of 1.79 ± 0.18 wt% in layer C2G and then falling to the low average value of 0.12 ± 0.01 wt% in layer D4 and finally ending at 0.42 ± 0.04 wt% in layer E.

Carbon dioxide

Nearly all the carbon dioxide detected in samples was measured as the peak occurring at 2350 cm⁻¹, which represents the asymmetric stretching vibration of ¹²C-O bonds (Stolper and Fine, 1987). This peak represents dissolved CO₂ in samples, as opposed to $CO_3^{2^-}$. After a background scan was performed and the atmospheric CO₂ was removed from the spectrum, the peak at 2350 cm⁻¹ could still be observed in some samples, indicating the presence of dissolved CO₂.

Measuring dissolved carbon dioxide in these samples proved to be somewhat problematic. CO_2 concentrations in these samples are low, therefore variations in local CO_2 concentration due to the respiration of the analyst necessitate frequent repetition of background analyses. Measurement of CO_2 concentration immediately after measurement of backgrounds produced the most successful analyses, but in some samples with low CO_2 concentrations, negative CO_2 bands indicate that atmospheric CO_2 concentration varies too much to be accurately measured. Analyses shown in figures 21 and 22 may under represent actual CO_2 concentrations.

Carbon dioxide in glass fragments

CO₂ values were measured in discrete glass fragments and obsidian shards. Values were averaged for each layer of the deposit (figure 21).The data produced a trend similar to the sawtooth pattern observed in the water concentration data. A correlation can be drawn from the carbon dioxide data to the water data. At least three intervals of change in CO₂ concentration occur during the eruption, roughly corresponding to similar changes in water concentration at similar phases of the eruption. The overall quantity of CO₂ is small, in the range of 0-125 ppm throughout the layers. Average CO₂ concentration in layer C1 is 20 ±2.0 ppm, falling to 14 ±1.4 ppm in layer C2C, rising slightly to 16 ± 1.6 ppm in C2D. In layer C2E the average CO₂ concentration rises to 52 ±5.2 ppm and then declines steadily to the measured low average value of 8± 0.8 ppm in layer D1, then jumps to the high measured average value of 125 ± 12.5 ppm in layer D2. After that the average CO₂ concentration declines steadily again to 49 ± 4.9 ppm in layer E.

Carbon dioxide in melt inclusions

 CO_2 was also detected in melt inclusions, although in notably smaller amounts than both water in the same melt inclusions and CO_2 in discrete glass fragments (figure 22). In all layers, with the exception of C1, there is less CO_2 in glasses than in melt inclusions from the same layers. CO_2 in melt inclusions produces a somewhat reduced sawtooth pattern when plotted by layer, showing two main intervals of changing CO_2 concentration in melt inclusions. CO_2 concentration starts out at 17 ± 3.57 ppm in layer C1 and falls to the lowest value of 5 ± 1.05 ppm in layer C2C before jumping up to the high value of 25 ± 5.25 ppm in layer D3, and then declining again to 19 ± 3.99 ppm in layer D4. There were no melt inclusions with measured CO_2 in layer E. The most noticeable point about the CO_2 data is that both the glass fragments and the melt inclusions contain higher amounts of CO_2 in the D layers, the later erupted part of the deposit that represents the deeper part of the magma chamber.

Degassing paths

Saturation pressures

Saturation pressures (minimum pressure of formation) of melt inclusions were calculated using VolatileCalc (Newman and Lowenstern, 2002). Melt inclusions having measurements for both H_2O and CO_2 were used, and 1000 °C was used as the temperature of formation (after Sigurdsson and Sparks, 1981). They estimated that the rhyolite evolved at 990-1010 °C. Calculated saturation pressures for all melt inclusions having measured amounts of both H_2O and CO_2 range from 370 to 13 bars. The melt inclusion that produced the saturation pressure of 370 bars was considered to be the earliest formed melt inclusion in the dataset and was therefore chosen to represent the

initial dissolved volatile concentration and pressure from which to calculate the degassing paths.

Degassing paths

Degassing paths were calculated using VolatileCalc (Newman and Lowenstern, 2002). Figure 23 shows calculated degassing paths based on an initial dissolved H₂O and CO₂ concentration of 1.38 wt% and 94 ppm respectively, and a corresponding saturation pressure (minimum pressure of formation of the melt inclusion) of 370 bars. Theoretical degassing paths for open system, closed system with 1% initial exsolved vapor, and closed system with 1.5% initial exsolved vapor are plotted for comparison. A closed system with 0% initial exsolved vapor is virtually identical to the open system degassing path. Melt inclusion dissolved volatile measurements are plotted on the same chart. It is evident that no distinct degassing path can be distinguished with this dataset.

Major element composition: microprobe analysis

The primary purpose for acquiring microprobe analysis of glass fragments, melt inclusions and glass adjacent to crystals was to distinguish between basaltic, dacitic and rhyolitic compositions. Absorption coefficients used for calculating volatile concentrations in glasses from FTIR measurements using the Beer-Lambert law are dependent on compositional variations, so knowing the major element composition of samples allows us to employ the correct absorption coefficient for each respective sample. In addition, glass compositions are essential for evaluating the compositional zoning of the magma chamber, and the type of magma that was expelled during each phase of the eruption. Major element compositions were also used to distinguish between type I and type II basaltic glasses (Sigurdsson and Sparks, 1981) based on their MgO content.

Microprobe analysis of glasses

Major element analysis with the microprobe shows that there are basaltic glass fragments present in all layers of this deposit, as well as rhyolitic glass fragments in most layers, and some intermediate dacitic composition glasses in a few locations (see data appendix for complete major element analyses). In addition to discrete fragments of all compositions of glass, there also exist several examples of intimate mechanical mixtures of glasses of differing compositions. Most mechanically mixed glasses are of two different basaltic compositions, with the exception being a few examples of clear and light brown rhyolitic glass physically mixed or showing flow-banding, and one example of rhyolitic glass physically mixed with glass of an intermediate dacitic composition. Sigurdsson and Sparks (1981) documented several examples of basaltic glass inclusions surrounded by flow-banded rhyolitic glass, and glasses of a hybrid dacitic composition occurring in early lava flows.

Analysis of MgO content and to some extent FeO and SiO₂ contents allow us to distinguish between the two distinct populations of basaltic glasses previously mentioned (Sigurdsson and Sparks, 1981). The two basaltic glasses are referred to as type I (MgO>5.5 wt%) and type II (MgO between 5.5 and 4.5 wt%). There is no microprobe data for layers C2D and D1 due to sample breakage. All glass fragments in layers C1, C2B, C2C, C2E, C2F, D2 and E were basaltic, ranging from 45.0 to 53.1 wt % SiO₂. Type I basaltic glass with MgO contents ranging from 5.5 to 7.0 wt % was found in all of these layers with the exception of C2C, whereas type II basaltic glass with MgO content ranging from 4.5 to 5.5 wt% was found in only layers C2B, C2C, C2F, D3 and D4. Rhyolitic glass fragments with SiO₂ content ranging from 70.0 to 74.5 wt % were found in layers C2C, D3, and D4, and some glasses of intermediate dacitic composition (64.4 to 69.7 wt % SiO₂) were found in layers D3 and D4.

Layers D3 and D4 show the most variety in glass compositions. Layer D3 contains discrete fragments of type I and type II basaltic glass, dacitic glass, and rhyolitic glass as well as several examples of intimately physically mixed glasses of two basaltic compositions. Grain D3G-F is a xenolith clot of plagioclase and pyroxene crystals embedded in rhyolitic glass, surrounded by an intimate mixture of basaltic (avg. 49.4 wt% SiO₂) and rhyolitic (avg. 70.7 wt % SiO₂) glasses. Grain D3G-K is an example of mingled dacitic and rhyolitic glasses (68.5 to 71.7 wt % SiO₂).

Layer D4 also contains the whole suite of glass compositions, type I and type II basaltic glasses, and similar mingled composition glasses as layer D3. A line traverse across rhyolitic glass grain D4G-G shows an average composition of 73.9 wt % SiO₂ (average of 38 points), and a similar line traverse across basaltic glass grain D4G-F yields an average composition of 50.2 wt % SiO₂ (average of 52 points), and reveals that it is a mixture of type I and type II basaltic glasses, with some points lying on either side of the 5.5 wt % MgO value that defines the two populations.

Microprobe analysis of melt inclusions and glass adjacent to crystals

Initial microprobe analysis indicates that the glassy melt inclusions hosted in plagioclase and pyroxene crystals are rhyolitic in composition, with SiO₂ content ranging from 71.0 to 76.0 wt %. This is consistent with previous work done on these melt inclusions (Sparks & Sigurdsson, 1977; Sigurdsson & Sparks, 1981), which states that the melt inclusions are light brown rhyolitic glass.

Glasses adjacent to crystals hosting melt inclusions were also analyzed for major element concentrations. These glasses were found to be rhyolitic as well, and in fact in several cases have a higher SiO₂ content than the melt inclusions within the same crystal onto which the glass was adhered. In grain C2G-G from layer C2G, edge glass

has an SiO₂ content of 73.9 wt %, whereas the melt inclusion within the crystal has an SiO₂ content of 71.8 wt %.

Glass color, texture, and composition

There is an impressive variety of different textures, colors and compositions of volcanic glass found throughout this deposit. Volcanic glass captures the state of the magma at the moment of quenching, so it preserves a series of dynamic snapshots of the processes operating during an eruption. It captures aspects of eruption dynamics, volatile contents, bubble morphology, geochemical composition of the magma, color, and flow features to name a few. Relative presence of different colors, textures, compositions and mixtures thereof in layers of the deposit records information about the interaction of different parts of the system, and glasses of mingled composition give us compelling evidence for two or more magma batches mingling and mixing, prior to and during the eruption.

Figure 24 is a summary of the different colors of glass found throughout the deposit, as well as some textural characteristics. There is a general trend in the basaltic glasses from dark brown through lighter brown, amber, olive and finally green from the more silicic bottom of the deposit (top of the magma chamber) to the more mafic top of the deposit (nearer the bottom of the magma chamber). It must be emphasized that nearly all types of glass are found throughout the deposit, clearly indicating extensive mechanical mixing of erupted products.

Three main types of rhyolitic glass are distinguishable on the basis of color and morphology. White or grey pumice and ash comprises 94% of the ejecta from this eruption. Volatiles in the pumice and ash were not directly measured in this study. The morphology and texture of the material prohibited sample preparation for FTIR analysis

due to its extreme fragmentation and large amount of vesicles. The vesicles filled with epoxy when the samples were mounted, and the excess epoxy interfered with the FTIR signal, rendering analysis of these deposits impossible.

Two types of rhyolitic glass, clear glass shards and light brown rhyolitic glass, were analyzed. Both are found throughout the C and D layers. (Rhyolitic glass is not found in layer E.) Clear rhyolitic glass fragments are present, as well as pale brown and slightly darker brown rhyolitic glass that encloses crystals and other basaltic and rhyolitic glass fragments. The pale brown melt inclusions found within plagioclase and pyroxene crystals are also comprised of rhyolitic glass.

Basaltic glass ranges in color from dark brown through light brown, amber, olive and finally green. Basaltic glass from layer C1 is entirely dark brown, entirely amber in layer C2C, and entirely green in layer E, but all other layers contain two or more colors. Layers C2D, D2, D3, and D4 contain all of the different colors of basaltic glass. Different colors of basaltic glass do not vary in any significant way with respect to composition. Green glass from layer E has an average SiO₂ content of 49.6 wt%, amber glass from layer C2C is 48.6 wt% SiO₂, and dark brown glass from layer C1 is 48.9 wt% SiO₂. Type I and type II basaltic glasses (distinguished by MgO content) are slightly different colors of medium to dark brown. Sigurdsson and Sparks (1981) stated that there is no correlation between composition of glass and pumice to position in the stratigraphic sequence, and likewise no correlation of color of pumice to composition, rather that the variety of colors of pumice were due to temperature of emplacement. It is possible that this is true also of basaltic glasses.

Textures of glass and pumice vary widely throughout the deposit. The C layers are comprised almost entirely of totally fragmented rhyolitic glass, present as ash and filamentous light grey pumice, which is clear in thin section. Figure 25 is a fragment of

clear rhyolitic glass that is not totally fragmented, it contains many small vesicles and some flattened bubbles, but is overall minimally vesicular. The plain light image in figure 32 shows a similar fragment of minimally vesicular clear rhyolitic glass, this time encasing a pyroxene crystal. A third type of rhyolitic glass found throughout the deposits is light brown, non-vesicular glass present as melt inclusions in plagioclase and pyroxene crystals, and adhered to the edges of those crystals.

Basaltic glass is generally present as discrete shards of brown, amber or green glass with abundant round vesicles. In addition to the discrete shards that are one color, basaltic glass is also found in varying states of mingling and disorder. Layers D3 and D4 contain the greatest variety of glass textures. Figure 27 shows a highly vesicular basaltic glass shard from layer D3. Also from layer D3, figure 28 is a layered, flowbanded fragment of two different colors of basaltic glass, light brown and darker brown. Microprobe analysis reveals that the two different colors in this fragment are the type I and type II basaltic glasses of Sigurdsson and Sparks (1981), and are possibly two different magmas interacting. This fragment also has many flattened vesicles, and this, in addition to the flow-banding, are good indicators of active movement within the system. Figure 29 is a highly disordered fragment of basaltic glass from layer D3 that contains flattened and misshapen vesicles, disrupted layering, and inclusions of a dark brown or black glass. Some structures resemble fiamme. The glass fragment in figure 30 (from layer D4) is comprised of intimately mingled swirled layers of type I and type II basaltic glass with several large vesicles. The basaltic glass encases a large inclusion of considerably more water-rich clear glass. The green glass from layer E (figure 31) has abundant flattened and sheared vesicles. The presence of such varying materials with varying textures, compositions and volatile concentrations is clear evidence that magma batches mingled prior to and during the eruption.

CHAPTER 5

DISCUSSION

Changes in volatile concentrations throughout the eruption

Distinctive fluctuations in both water and carbon dioxide concentration occur throughout the layers of this deposit, and this is probably due to several factors. The three observable pulses and subsequent smooth decreases in water concentration (and to a lesser degree carbon dioxide) could represent another level of internal stratification within the layers of the already compositionally and density stratified magma chamber. Sigurdsson & Sparks (1981) suggested that prior to the regional rifting that took place in 1874-75, the magma chamber beneath Askja had developed into a stably stratified system consisting of ferrobasalt, icelandite and rhyolite, and that the rhyolite was itself stratified, with silica content increasing upwards. We could hypothesize that the other layers also could have been internally stratified, compositionally and also in regards to volatile concentration. Water is more soluble in rhyolitic magmas than in more mafic ones, whereas carbon dioxide is more soluble in silica undersaturated melts (Philpotts and Ague, 2008), and the solubility of carbon dioxide is largely pressure dependent, such that carbon dioxide requires higher pressures than water to remain dissolved in the melt (Papale, 1997). Thus the pulses in water concentration to high values could indicate the top layers of the internally stratified layers within the magma chamber, with the water concentration decreasing until the top of the next layer is reached, with another smooth decrease to the next layer. Overall there is slightly more water in the rhyolitic melt inclusions than in the basaltic glass fragments and this is probably because water is more soluble in higher silica melts. Similarly, there is slightly more carbon dioxide in basaltic glass fragments than in rhyolitic melt inclusions, again consistent with the solubility of carbon dioxide being higher in basaltic magmas. Also consistent with

this idea is the observed jump in carbon dioxide in the D layers in both glass fragments and melt inclusions, indicating that there was more carbon dioxide in the lower parts of the magma chamber where the pressure was greater and the composition was more mafic. The lack of carbon dioxide in measureable amounts in the material from the C layers could indicate that carbon dioxide degassed quickly as pressure was released, so that the carbon dioxide in the top of the magma chamber was largely degassed before the eruption commenced, resulting in little or no carbon dioxide remaining in the rhyolitic pumice and glasses. The basaltic glasses and crystals in the D layers resided for longer in the higher pressure bottom of the magma chamber. The convection, mixing of layers, and exsolution of volatiles due to temperature increase and pressure decrease that was caused by the intruding basalt and that initially triggered the eruption occurred relatively quickly (on a scale of weeks before the eruption, according to Sigurdsson & Sparks (1981)), thus transporting the basaltic materials to the surface and quenching them as glass fragments before they had a chance to completely degas. The basaltic glasses from the D layers are highly vesicular, indicating that this magma underwent degassing. Despite the fact that the carbon dioxide concentrations from the D layers are noticeably higher than those from the C layers, a significant amount of degassing of carbon dioxide had already occurred and therefore carbon dioxide was probably initially more abundant than indicated by present values.

The fact that the D layers contain more CO_2 than the C layers is consistent both with the greater solubility of CO_2 at higher pressures and lower Si content (Philpotts & Ague, 2008), and the likelihood that much of the CO_2 in the system would have degassed before reaching the top of the magma chamber (the C layers of the deposit) due to both lower pressure and higher Si content. The overall greater amount of CO_2 in basaltic glass fragments relative to melt inclusions, especially in the D layers of the

deposit, may also be related to CO_2 solubility being lower in melts with higher Si content, and the possibility that the crystals hosting the MIs formed nearer the upper part of the magma chamber where both the pressure was lower and the Si content of the melt was higher, whereas the glass fragments represent samples of the melt from a deeper source, a higher pressure, and significantly lower Si content, which were transported quickly to the surface during the eruption.

Averages of the water and carbon dioxide concentrations in each sample layer are based on several measurements, even within the same sample (see figure 39 for total number of analyses, averages, and standard deviation). One factor that can account for the wide variety of measurements of both water and carbon dioxide in glass fragments is displacement of the original stratification of the magma chamber by the vigorous convection that was caused by the intruding basalt just prior to the eruption. Convection caused mixing of layers, transporting the different components of the system away from their original layers and resulting in materials erupted together and deposited near each other that actually originated from locations with differing availability of volatiles or compositions. When measured, these materials contribute widely differing volatile concentrations to the average values. Similarly, melt inclusions continue to be trapped in crystals throughout the evolution of the magma chamber, and they sample the melt at differing points along its path through compositional, temperature/pressure path, and volatile concentration evolution. It is possible that due to convection and other preeruptive processes, melt inclusions that formed at various times during the evolution of this system are all present in the same layers of the deposit. The wide variation of water content may be due to the differing origin of the crystals hosting the melt inclusions and the differing availability of volatiles in those locations.

Finally, mapping of water concentrations in discrete glass fragments and single melt inclusions illustrates the heterogeneity of water concentration in glass on the micron scale. This is likely to reflect heterogeneity of volatile concentrations in the melt prior to quenching. This heterogeneity is yet another explanation for the range of water and carbon dioxide concentrations measured within single layers.

Rhyolitic glass adjacent to crystals hosting melt inclusions has the highest water concentration of all samples. This glass is also the most silicic of all samples, averaging 73-74 wt% SiO₂. Sigurdsson & Sparks (1981) described hydrothermally altered xenolithic components found in the Askja ejecta and suggest that the top of the magma chamber was interacting with external water prior to the eruption of 1875. Macdonald et al. (1987) presented isotopic evidence for ingestion of meteoric water into the Askja rhyolite. They stated that the basalts from the Askja eruption of 1875 are similar to the basalts found in the rest of Iceland (slightly ¹⁸O-depleted) but the rhyolites are significantly more ¹⁸O-depleted than other Icelandic silicic rocks. They suggested that the ¹⁸O-depletion of the rhyolites is due to isotopic exchange with ¹⁸O-depleted meteoric waters in the rhyolitic top of the magma chamber. If meteoric water was being absorbed into the system, this could account for the high water concentration of the glass adjacent to crystals hosting melt inclusions. Isotopic data on these samples does not exist, so meteoric and magmatic water cannot be differentiated in these samples. The addition of water into the system could also have caused rates of crystallization to increase, thus partitioning more water into the melt as water was rejected by the crystallizing phases. It is possible that water-rich glass adjacent to crystals is recording this area of enriched water in the melt immediately outside of the crystallizing plagioclase and pyroxene phases. Baker et al. (2005) suggest a phenomenon called "volatile pile-up" occurs when crystallization rates outpace diffusion rates of volatiles through the melt, resulting in

volatile enrichment at the crystal/melt interface. This is consistent with our observations of areas of water rich glass adjacent to crystals.

It is also possible that glass adjacent to crystals hosting melt inclusions represents the quenched magma from the silicic top of the magma chamber, where the water concentration was highest in the whole system. The fact that the crystals with high-water content silicic glass adjacent to them are found throughout the deposits can be explained by the rapid convection and mixing of layers in the magma chamber immediately prior to and during the eruption. Crystals could have been transported up to the top level of the magma chamber from other parts of the system, and the glass adjacent to the crystals is the quenched magma from the silica- and water-rich top layer. It is not necessary that all crystals hosting melt inclusions and having water-rich silicic glass adjacent to them formed in the top layer of the magma chamber.

The two distinct basaltic glass populations (type I and type II basalts) that occur in the Askja deposits have differing water concentrations. The type I basalts (the more primitive composition) have a slightly higher water concentration than the more evolved type II basalts, which seems counterintuitive in that higher water concentration is commonly associated with more silicic melts (Philpotts& Ague, 2008). If composition alone controlled the solubility of water in these samples, the more evolved basaltic glasses should have the higher water concentrations. However it is generally accepted that this eruption was triggered by the injection of basaltic magma into a previously existing stratified magma chamber (Sigurdsson & Sparks, 1981). The basaltic glasses in this deposit may have were formed from different source magmas that mingled and mixed prior to and during this eruption. In this case, composition alone would not have controlled the amount of water dissolved in the magma. Rather a combination of factors controlled this parameter, the most important of which may be the availability of volatiles

at the source of each magma and throughout the system through which the magmas traveled on their way to the surface.

Changing eruption style and dynamics, if not volatile concentration directly, were strongly influenced by availability of water at the actual geographic location of the eruption, i.e. the vent. (Carey et al. 2009a; 2009b) suggested that changing vent locations intercepted existing water sources, resulting in what would have been a simple plinian eruption shifting into a multi-phase and multi-style eruption. The process initiated by the influx of new basalt (convection, heating of the magma chamber, pressure release initiating exsolution of volatiles and the beginning of fragmentation) could have become increasingly complex due to the interaction of magma with standing water at the vent. The interaction of the magma with external water is reflected not so much in the recorded water concentrations in melt inclusions or discrete glass fragments that may have come from deeper in the system, but rather in the extensive fragmentation of the silicic magma, and the large volumes of ash and pumice that were produced.

Figure 23 shows calculated degassing paths based on an initial saturation pressure of 370 bars, along with dissolved H_2O and CO_2 concentrations of melt inclusions. A minimum pressure of formation of 370 bars is consistent with the estimate of Sigurdsson and Sparks (1981) that the rhyolite evolved under <500 bars. It is clear that the data cannot specifically constrain the degassing path, and this may be due to several factors. It is possible that the magmatic system was not completely closed or open at all times throughout its history, but rather progressed from an initial closed system to a later open system, or vice versa. It is also possible that melt inclusions formed in different parts of the system where different conditions were predominant, or were formed at different times in the history of the system when conditions may have been different. Another possibility is that crystals hosting melt inclusions could have

originated from two or more distinct magmas, each having complex histories, which later interacted to produce the suite of melt inclusions present. Finally, the spread in the data could be due to inaccurate measurements of volatiles, or limited by the relatively small size of the dataset. It is generally accepted that melt inclusion studies are vastly improved with respect to accuracy by including as many measurements as possible (Blundy and Cashman, 2008; Moore, 2008). It is clear that this system did not evolve under one distinct set of conditions.

Heterogeneity of water in glasses

FTIR maps of water concentration (figures 34-37) show that water is not homogenously distributed in glasses. The sample from layer D4 (figure 37) is an example of two different compositions of basaltic glass (type I and type II basaltic glasses) swirled around an oval shaped glass inclusion of yet a third composition. The transmitted light image shows the bands of light brown and nearly clear glass, and the FTIR map shows that water distribution in the sample does not correspond to those boundaries. Figure 34 shows a basaltic glass fragment from layer C2C. In transmitted light, the glass looks relatively homogeneous, but the FTIR map of the same area reveals distinct zones of differing water concentration in the sample. This heterogeneity of water distribution relative to composition is evident in all glasses. While the distribution of water does not seem to rigidly follow compositional boundaries, it is known that water has increasing difficulty diffusing through melts with increasing silica content (reference). It is possible that the heterogeneous distribution of water in some of these samples is due to barriers to diffusion.

In some cases, the uneven water distribution in samples is due to migration of water along microfractures or other structural defects in the glass. Figure 32 shows a

fragment of rhyolitic glass from layer C2C encasing a pyroxene crystal which in turn hosts a rhyolitic melt inclusion. In the transmitted light image, small fractures can clearly be seen, and the high water concentration in those areas is evident on the FTIR map of the same area. It is interesting to note that there are also areas of higher water concentration in the rhyolitic glass that do not appear to be directly related to fractures, indicating that there is heterogeneity in water concentration that is not caused by structural flaws, or that the fractures annealed and can only be identified on the basis of high water concentration.

The heterogeneous distribution of water in glasses may be due to the formation of "pre-bubble zones". In magmas just prior to vesiculation, it is possible that areas of higher water concentration may be present in an area that will soon become an exsolved volatile bubble. Dissolved water could diffuse through the melt or otherwise gather in a pre-bubble zone in preparation for coming out of solution as a separate vapor phase (Seaman and Chapman, 2008). Figure 38 shows a crystal clot surrounded by basaltic glass from layer D4. There are areas of higher water concentration near the edges of the crystals. It is known that crystals provide sites for bubble nucleation (Cashman, 2004), and that crystallizing anhydrous phases preferentially segregate water into the melt (Castro et al., 2008; Seaman et al., 2009).

The combination of heightened water immediately outside the crystal and the processes already operating in the system that had initiated exsolution of volatiles and degassing in the system could have produced the pre-bubble zones that were recorded in this sample. Figure 33 also shows a crystal clot surrounded by glass with uneven water distribution where the water concentration is higher immediately adjacent to crystals.

Heterogeneity in glasses could indicate some sort of compositional immiscibility. Magmas of differing compositions, temperatures, and volatile contents take time to fully chemically equilibrate (Sigurdsson & Sparks, 1981). The magma mixing event that triggered this eruption took place relatively quickly, resulting in magmas that were (sometimes quite intimately) mingled, but not truly chemically and physically mixed (Sigurdsson and Sparks, 1981). Therefore it is possible that this non-equilibration of magmas could have influenced the distribution of water in the samples. Water concentrations may have responded to some factor for which evidence is not preserved or was not analyzed in this study, like chemical non-equilibrium, pressure related differences that didn't have time to equilibrate before being erupted, or differences in initial water concentration that didn't fully mix. Diffusion of cations is involved in hybridization, and different diffusion rates for water through magmas of different compositions would cause distribution of water vs. composition to be different at the time when the glasses were quenched. Diffusion rates of water through silicic melts increase with increasing water concentration and with increasing temperature in both basaltic and rhyolitic melts (Baker et al., 2005). Activation energies for lower water concentrations are higher, therefore higher temperature increases diffusion rates at the same water concentration. In a rhyolitic melt having 6 wt% H₂O at approximately 1000°C, the diffusion rate is 10⁻¹⁰ m²/sec, and in a rhyolitic melt with 2 wt% H₂O at the same temperature the diffusion rate is 10⁻¹¹ m²/sec. In a basaltic melt at the same temperature with only 0.2 wt% H₂O, the diffusion rate is 10^{-10} m²/sec (Baker et al., 2005).

It is also possible existing water in the system was influenced by ingested meteoric water just prior to eruption, and it similarly did not have time to fully mix or equilibrate.

CHAPTER 6

CONCLUSIONS

In this study the correlation between volatile concentrations and composition was tested with the goal of determining their effects on eruptive style. The well-observed and documented plinian eruption of Askja in 1875 provides a unique opportunity to examine the activity of volatiles and magma composition in an eruptive event. Distinctive fluctuations in water and carbon dioxide occur throughout the deposit. Three pulses and subsequent decreases in water (and to a lesser degree carbon dioxide) concentration could be due to internal compositional stratification within the magma chamber. High water concentrations may represent the Si- and water-rich tops of internally stratified layers. CO₂ is richer in basaltic glass and in the D layers of the deposit, which originated deeper in the magma chamber, at a higher pressure where CO₂ is more soluble. Lack of CO_2 in the C layers indicates near total degassing of the top layers of the magma chamber prior to the eruption. Higher CO₂ in D layers and basaltic glasses represents magma originating in the lower parts of the system and transported quickly to the surface by rapid convection immediately preceding the eruption, and quenched at the time of eruption, not having had time to degas. The widely differing H_2O and CO_2 measurements within layers could be due to displacement of the original internal stratification of the magma chamber by vigorous convection and subsequent mingling together of samples originating from different parts of the magma chamber. Rhyolitic glass adjacent to crystals hosting melt inclusions has the highest measured H_2O concentration and is the most silica rich of all samples. This glass may represent the silica- and water-rich top layer of the magma chamber. The crystals onto which the glass adheres could have formed in various parts of the system and been transported to the surface by convection, where the water-rich rhyolitic glass quenched on them just

prior to eruption. Alternatively, these crystals may have originated in a more silicic, more water-rich melt, and carried adhered melt into the Askja magma. Meteoric water was probably ingested into the top layer of the magma chamber, further enriching the top layers with water and possibly accelerating crystallization. Crystallizing anhydrous phases further enrich the melt with water, preferentially partitioning water into the melt as they crystallize. Areas of water-rich glass adjacent to crystals may be a record of this process occurring in the Askja melt. Heterogeneity of water in glass is likely to reflect heterogeneity of volatile concentrations in the melt prior to quenching. Water enriched areas in glass may represent pre-bubble zones, where volatiles gather just prior to exsolving. Type I and type II basaltic glasses have differing water concentrations, with the more primitive (type I) having the higher water concentration. This indicates that composition alone does not control volatile concentration, but rather a combination of factors, including composition and availability of volatiles at the source, influence final volatile concentration and distribution. Eruption dynamics were strongly influenced by availability of water at the vent location, which changed several times throughout the eruption (Carey et al. 2009a; 2009b). No distinct degassing path can be seen based on the data from this study, but it is clear that the system did not evolve as a single magmatic system under closed conditions. It is likely that two or more magmas interacted under changing conditions throughout the history of this event.











Figure 3. Principal elements of geology in Iceland, showing the North Volcanic Zone (NVZ), on which Askja is located. From Thordarson & Larsen, 2007.



Figure 4. Map of Askja caldera and modern Lake Öskjuvatn. Outcrop shown in red, study area in small box.



Figure 5. Map of Ódáðahraun lava desert near Askja.



Figure 6. View looking north from the edge of Lake Öskjuvatn (the modern caldera rim). The low black line at the base of the mountains is the ancient (~10 ka) caldera rim.



Figure 7. View of the small phreatomagmatic crater Viti in the foreground, and Lake Öskjuvatn in the background.



Figure 8. Study area, northeastern shore of Lake Öskjuvatn.



Strat. column adapted from Self and Sparks, 1978 and Sparks et al, 1981; revisions by Carey, et al. (2009)

TABLE 1								
Modal analyses of Askja 1875 products: (vesicle-free basis)								
	AS-16	AS-61	AS-162	AS-255	AS-28			
Colourless glass	97-0 per cent	84.0 per cent	96.0 per cent	97-3 per cent	59.8 per cent			
Pale-brown glass	0.5	8.0			er e per cent			
Basic glass	0-1	2.0						
Plagioclase	2.0	3.0	2.7	1.2	18.9			
Pyroxene	0.2	2.0	1.0	1.0	14.1			
Opaques	0-1	0.5	0.6	0.5	7.2			
AS-16: Obsidian AS-61: Dacitic hy AS-162: Obsidian AS-255: Obsidian AS-28: Pumice fro	lava. /brid glass from lay fragment from lay fragment from lay om plinian layer D.	er C ₁ . er E. er E.			-			

Figure 9	. Stratigraphic	column and	d photos	of the	outcrop.
	5 1				

Figure 10. Modal analysis of Askja ejecta. From Sigurdsson & Sparks, 1981.



Figure 11. Sample FTIR spectrum showing peaks for total water and carbon dioxide.



Figure 12. Plagioclase crystal hosting melt inclusions.



Fig. 1. Examples of output from VOLATILECALC. (a) Isobars represent locus of values for dissolved H_2O and CO_2 in rhyolitic melt in equilibrium with H_2O-CO_2 vapor at 800°C and selected pressures. (b) Similarly, isopleths represent locus of rhyolitic melt compositions in equilibrium with the given vapor compositions (20, 50 and 80 mol% H_2O shown here) at 800°C. Overlaid in gray are isobars from Fig. 1a. (c) Degassing trends are shown for 1200°C and demonstrate paths taken by basaltic (49 wt% SiO₂) melt with 4 wt% H_2O and 3000 pm CO₂ under open- and closed-system conditions. One path demonstrates closed-system trend where melt ascends with 2 wt% exsolved vapor present at initial pressure (relative to total system of melt plus vapor).

Figure 13. Examples of output from VolatileCalc. Isobar, isopleth and degassing path plots. From Newman and Lowenstern, 2002.



Figure 8. (a) Schematic illustration of open- and closed-system degassing. (b) CO_2 -H₂O solubility diagram illustrating schematic open- and closed-system degassing paths. (c) Calculated change in vesicle volume fraction with pressure under closed-system conditions for a range of initial volatile contents (labeled on curves in wt%). Highlighted are example open- and closed-system degassing paths for an initial H₂O content of 5 wt%.

Figure 14. Illustration of open and closed system degassing. From Cashman, 2004.



Figure 15. Water (wt%) in melt inclusions in plagioclase.



Figure 16. Water (wt%) in melt inclusions in pyroxene.



Figure 17. Water (wt%) in glass fragments and shards.



Figure 18. Water (wt%) in glass adjacent to crystals hosting melt inclusions.



Figure 19. Water (wt%) in type I basaltic glass.



Figure 20. Water (wt%) in type II basaltic glass.



Figure 21. Carbon dioxide (ppm) in glass fragments.



Figure 22. Carbon dioxide (ppm) in melt inclusions.



Figure 23. Calculated degassing paths (using VolatileCalc, Newman and Lowenstern, 2002) and melt inclusion H_2O and CO_2 concentrations.



Figure 24. Stratigraphic column with corresponding occurrence of different glass colors and textures. Stratigraphic column devised by Self & Sparks, 1978 and Sparks, et al. 1981, with adaptations by Carey, et al., 2009.


Figure 25. Clear rhyolitic glass from layer C1. Minimally vesicular, but with flattened bubbles.



Figure 26. Mixed pumices from the plinian phase.



Figure 27. Highly vesicular basaltic glass from layer D3.



Figure 28. Layered, flow-banded mingled basaltic glass with flattened bubbles from layer D3.



Figure 29. Highly disordered mingled basaltic glass from layer D3.



Figure 30. Swirled (possibly type I and type II) basaltic glasses from layer D4.



Figure 31. Light greenish-brown basaltic glass with sheared bubbles from layer E.







Figure 33. Transmitted light image (top) and FTIR map of water concentration of a crystal clot surrounded by glass from layer C2C.





Figure 34. Transmitted light image (top) and FTIR map of water concentration of a basaltic glass fragment from layer C2C.



Figure 35. Transmitted light image (top) and FTIR map of water concentration of a basaltic glass fragment from layer C2C.



Figure 36. Transmitted light image (top) and FTIR map of water concentration of a plagioclase crystal hosting a rhyolitic melt inclusion from layer C2E.



Figure 37. Transmitted light image (top) FTIR map of water concentration of a mixed type I and type II basaltic glass fragment hosting an inclusion of another type of glass with a much higher water concentration from layer D4.



Figure 38. Transmitted light image (top) FTIR map of water concentration of a crystal clot surrounded by basaltic glass and two volatile bubbles from layer D4.

		Water in glass, wt%			
Sample layer	Points averaged	Average	Standard deviation		
C1	20	.33	.06		
C2A	6	.28	.08		
C2B	24	.37	.05		
C2C	23	.28	.06		
C2D	24	.29	.07		
C2E	13	.27	.09		
C2F	29	.25	.10		
C2G	9	.38	.03		
D1	5	.35	.01		
D2	18	.29	.06		
D3	28	.18	.13		
D4	33	.28	.32		
E	30	.24	.04		

Figure 39. Total number of analyses, averages, and standard deviations.

	Water in melt inclusions (plagioclase hosted), wt%		
Sample layer	Points averaged	Average	Standard deviation
C1	5	.63	.24
C2A	0		
C2B	10	.85	.39
C2C	15	.56	.19
C2D	20	.61	.40
C2E	31	.38	.25
C2F	14	.56	.35
C2G	20	.83	.35
D1	40	.52	.39
D2	21	.44	.34
D3	14	.19	.18
D4	12	.36	.19
E	5	.13	.04

	Water in melt inclusions (pyroxene hosted), wt%		
Sample layer	Points	Average	Standard deviation
	averaged	-	
C1	2	.45	.06
C2A	0		
C2B	3	.34	.12
C2C	9	.21	.10
C2D	5	.58	.26
C2E	0		
C2F	0		
C2G	1	.54	
D1	8	.35	.30
D2	0		
D3	6	.14	.01
D4	0		
F	0		

	Water in edge glass, wt%		
Sample layer	Points averaged	Average	Standard deviation
C1	5	.82	.22
C2A	0		
C2B	0		
C2C	1	1.11	
C2D	1	1.79	
C2E	4	.69	.22
C2F	0		
C2G	1	1.60	
D1	4	1.10	.99
D2	1	1.39	
D3	0		
D4	1	.12	
Е	1	.42	

	Carbon dioxide in glass (ppm)		
Sample layer	Points	Average	Standard deviation
	averaged	-	
C1	8	20	15.18
C2A	0		
C2B	0		
C2C	11	14	18.15
C2D	6	16	9.94
C2E	4	52	22.07
C2F	24	23	18.52
C2G	3	16	7.72
D1	1	8	
D2	8	125	73.05
D3	9	71	68.44
D4	14	63	60.44
E	10	49	47.24

	Carbon dioxide in melt inclusions (ppm)		
Sample layer	Points	Average	Standard deviation
	averaged		
C1	9	26	17.05
C2A	0		
C2B	7	23	11.87
C2C	4	15	5.20
C2D	0		
C2E	6	28	22.03
C2F	0		
C2G	0		
D1	0		
D2	4	61	23.22
D3	10	28	26.45
D4	11	25	19.12
E	0		

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