Experimental Studies of Melting and Crystallization Processes in Planetary Interiors

by

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Submitted in partial fulfillment of the requirements for the degree of
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Abstract

Melting and crystallization processes on the Earth and Moon are explored in this thesis, and the topics of melt generation, transport, and crystallization are discussed in three distinct geologic environments: the Moon's mantle, the Greenland ice sheet, and the Earth's crust. Experiments have been conducted to determine the conditions of origin for two high-titanium magmas from the Moon. The lunar experiments (Chapter 2) were designed to explore the effects of variable oxygen fugacity (f_{O_2}) on the high pressure and high temperature crystallization of olivine and orthopyroxene in high-Ti magmas. The results of these experiments showed that the source regions for the high-Ti lunar magmas are distributed both laterally and vertically within the lunar mantle, and that it is critical to estimate the pre-eruptive oxygen fugacity in order to determine true depth of origin for these magmas within the lunar mantle. Chapter 3 models the behavior of water flow through the Greenland ice sheet driven by hydrofracture of water through ice. The results show that melt water in the ablation zone of Greenland has almost immediate access to the base of the ice sheet in areas with up to two kilometers of ice. Chapter 4 is an experimental study of two hydrous high-silica mantle melts from the Mt. Shasta, CA region. Crystallization is simulated at H_2O saturated conditions at all crustal depths, and a new geobarometer-hygrometer based on amphibole magnesium number is calibrated. In Chapter 5 I use the new barometer to study a suite of mafic enclaves from the Mt. Shasta region, and apply it to amphiboles in these enclaves. Evidence for pre-eruptive H_2O contents of up to 14 wt% is presented, and bulk chemical analyses of the inclusions are used to show that extensive magma mixing has occurred at all crustal depths up to 35 km beneath Mt. Shasta.

Thesis Supervisor: Timothy L. Grove
Title: Professor of Geology, MIT

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My mother has told me a story my whole life, long before I joined the MIT/WHOI Joint Program, that when I was 2 years old and still just learning to talk, my parents asked me the question “Mike, where will you go to school?” and my heavily coached answer was always “M.I.T.”

It is a funny story, and obviously I missed a career opportunity as a prophet, but what it constantly reminds me of is the lifelong dedication and selfless support I have received from my family; they have taught me to strive for lofty goals and allowed me to follow my dreams and the wandering path I have taken to the geology career I love. Thanks Mom and Dad for everything, especially the example you have set for me about making better, the lives of the people who care about me the most! And to my brother and sister, thanks for always being there for each other. I love you guys, and I could have never written this thesis without you.

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Chapter 1

Introduction

Melting and crystallization are the processes that control chemical differentiation in the interiors of the terrestrial planets of our solar system. Indeed volcanism, magma transport, mantle convection, and chemical zoning on a global to microscopic scale, are all dependent on the process of melt generation and crystallization. This thesis takes a mainly experimental approach to study these processes in natural liquids in three different environments: the lunar mantle, the Greenland ice sheet, and the crustal environment of a terrestrial subduction zone.

The conditions of mantle melting, melt storage, and crystallization would be rather easy to determine if we could travel into and sample the deep crust, mantle, and cores of the terrestrial planets, but until we manufacture ‘unobtainium’ drill ships we cannot. Studying the molten materials that come from deep within a planet and erupt onto the surface is then the best option. The hard part is taking what we find on the surface and extrapolating in time, temperature, and pressure backwards along lava’s convoluted path to eruption, and is the focus of this thesis.

Chapter 2 concerns the generation of high titanium magmas in the lunar mantle. Lavas erupted on the Moon are called ‘basalts’ but are actually quite different than the compositionally monotonous basalts generated by mantle melting in mid-ocean ridge spreading centers on Earth. This chemical diversity among the lunar extrusive rock suite is a result of the lunar mantle being much more heterogeneous than the Earth’s mantle. The uniqueness of the high titanium lavas from the moon sparked

a wave of interest in the 1970's through 1990's to determine the depth of origin for such magmas within the Moon [Green et al., 1975, Delano, 1980, Wagner and Grove, 1997]. However these early studies neglected to take into account the fact that these magmas contain large amount of elements with variable oxidation state.

New experiments have been conducted in a piston cylinder apparatus using two different capsule materials in order to buffer the oxygen fugacities of our samples at two different levels. For the first time, the oxidation state of such experiments was both fixed and measured, and the range in the experiments is relevant to the reduced nature of the Moon.

Our results show that the oxidation state of titanium has a large effect on the equilibrium of non-Ti bearing minerals (olivine and orthopyroxene) and thus on the depth of origin inferred for these melts within the lunar mantle. These unexpected data lead to a new understanding of the stratigraphy of the lunar mantle and the depth of the source regions for this unique type of magma.

This chapter has been accepted for publication in *Geochimica et Cosmochimica Acta*.

Chapter 3 explores the fate of surface melt water from the ablation zone of the Greenland ice sheet. I have studied the transport of this seasonal water source through the ice by gravitationally driven hydro-fractures. The chapter is model based rather than experimental, but both the input parameters as well as the predictions from the model are grounded in field observations.

In the early 2000's a seasonal acceleration of ice flow was observed during the summer melting months in West Greenland [Zwally et al., 2002], and I have explored the possibility that melt water from large seasonal supraglacial lakes could provide the lubricant for this seasonal acceleration. It had long been speculated that seasonal and diurnal surface processes of an ice cap were decoupled from processes that occurred at the base of an ice sheet because the time scale for heat conduction is thousands of years for 1 km thick ice, and the fact that there is 1 km of subfreezing ice between surface melt water and the base of thick ice sheets. My model results show that the advection of water can be quite rapid through the ice sheet, and the majority of melt

water stored in supraglacial lakes can be drained to the bed in a matter of hours via hydro-fracture processes.

While this study might seem a bit of a departure from magma genesis and transportation, in fact it is not. This chapter employs a linear elastic dislocation based fracture mechanics model to study the propagation of fluid filled fractures down into the ice. This method was adapted for use in the water-ice system here, but similar ones had been developed in the Earth science community to study the fluid (magma) filled cracks (dikes) within the Earth's crust, which are critical in eruption and transport of magma within the crust [Bruce and Huppert, 1990, Lister and Kerr, 1991]. In addition this chapter exemplifies the diverse role that melting and crystallization processes have on the terrestrial planets, and we must remember that on some planets (e.g., Europa, Enceladus, etc.), water *is* the magma leading to volcanism and planetary heat dissipation.

The contents of this chapter have been published in *Geophysical Research Letters*:

Krawczynski, M.J., M.D. Behn, S.B. Das, and I. Joughin (2009), Constraints on the lake volume required for hydro-fracture through ice sheets, *Geophys. Res. Lett.*, 36, L10501, doi: 10.1029/2008GL036765.

Chapter 4 returns to the realm of high temperature igneous processes and presents experiments defining the crystallization sequence of a mantle derived H₂O saturated primitive andesite along its entire ascent through the crustal column. H₂O bearing magmas are derived from the mantle in subduction zones due to the dehydration of the down going lithospheric plate underneath magmatic arcs. Because arc related magmas are believed to play a role in the chemical differentiation of the mantle and the construction of continental crust on Earth, it is critical to understand the fate of these melts as they are emplaced in the crust and crystallized.

The experiments were also designed to look at the stability of the hydrous mineral amphibole in these arc magmas. The compositions of the experimental amphiboles are used to develop a new geobarometer-hygrometer based on amphibole magnesium numbers. The idea is to take advantage of the long known fact that the slope of the stability curve of amphibole in pressure and temperature space is opposite to that of

the liquidus for water saturated magma. We have now calibrated this dependence, and show that there is evidence recorded in the amphiboles of Mt. Shasta CA that these magmas once contained up to 14 wt% H₂O during crystallization. This is more than twice the amount of H₂O previously thought to be the norm for subduction zones [Wallace, 2005].

Chapter 5 is a petrographic and geochemical study of a fascinating suite of samples collected primarily during three field seasons at Mt. Shasta CA under the guidance of Prof. Tim Grove and the essential assistance of many of my colleagues in the experimental labs at MIT and WHOI. The rocks are mafic magmatic inclusions which preserve evidence of their primitive parental melts while being erupted in lavas from the main conduit system of the volcano. Using textural as well as bulk sample chemical analyses we show that over 80% of the 82 inclusions found represent H₂O bearing liquids that record early and deep crustal fractional crystallization and magma mixing.

These rocks served partially to inspire the experiments of Chapter 4, as we wanted to learn where in the crust these magmas were being mixed, and how much H₂O was necessary to produce the mineral assemblages we found. The amphibole geobarometer-hygrometer developed in Chapter 4 has been applied to the amphibole bearing rocks of this collection. The results show that the mafic inclusions record a very similar story to the amphibole antecrysts in Mt. Shasta lavas, and both data sets suggest that magma mixing and crystallization is happening throughout the crust underneath Mt. Shasta, and is not being processed in a long-lived large magma chamber at a fixed depth.

While not the original goal of my research when each of these projects was begun, this dissertation has been assembled with an intentional intellectual arc. It starts with magma genesis, then looks at the transport of buoyant fluids through fractures, and finally discusses the crystallization, mixing, cooling, and eruption of magma. While each of these chapters focuses on detailed research that is applied in very different geologic settings, the common theme has been to study melting and crystallization, a fundamental process which is a result of the dynamic interiors of terrestrial planets.

Chapter 2

Experimental Investigation of Lunar High-Ti Ultramafic Liquids

2.1 Introduction

The lunar high-titanium ultramafic glasses are among the most unusual volcanic rocks found in the solar system. These ultramafic glasses span a range of TiO_2 values from 9 to 16 wt% TiO_2 (Fig 2-1, Delano [1986]). The ultramafic glasses are believed to be the products of high-degree remelting of Ti-rich cumulates that are a product of extreme chemical differentiation of a global magma ocean that solidified early in lunar history [Snyder et al., 1992, Warren, 1985, Solomon and Longhi, 1977]. Experimental studies of these glasses, together with the high-Ti mare basalt suite, are a prerequisite for understanding the nature of their melting processes, source materials, and depth of origin in the lunar mantle. Experimental studies are also important to further explore the effects that high-Ti contents have on silicate melt structure. As demonstrated originally by Longhi et al. [1978], high-Ti melts have a significant influence on Fe–Mg partitioning between olivine and melt.

This paper presents new experimental data on the high-pressure, high-temperature phase relations of two high-Ti ultramafic glasses, the Apollo 15 red (A15R, 13.8 wt% TiO_2) and the Apollo 17 orange (A17O, 9 wt% TiO_2) glasses, over a range of moon-relevant oxygen fugacities (f_{O_2}). We find that variation in f_{O_2} has significant effects

on the high pressure phase equilibria. Assuming that these magmas come from a polyminerale source region in the lunar mantle, we use our experimental results to infer the pressure and temperature of melt generation based on co-saturation of olivine and orthopyroxene as liquidus phases, which is referred to as the multiple saturation point (MSP).

Previous experimental studies on high-Ti magmas have been carried out on a variety of compositions. Dickinson and Hess [1985] and Gaetani et al. [2008] used analogue liquids to determine the saturation of rutile in a range of silicate liquids. Xirouchakis et al. [2001] and Longhi et al. [1978] explored the effect of TiO_2 on major element partitioning in olivine-liquid equilibrium. Longhi et al. [1972] performed high-pressure experiments on Apollo 17 mare basalts and Green et al. [1975], Delano [1980], Wagner and Grove [1997] carried out studies on the Apollo 17 orange, Apollo 15 red, and Apollo 14 black glasses respectively. However, all of the previous studies were conducted in different labs and with different experimental procedures that may impose different oxygen fugacities on the experimental sample. In this study we will endeavor to reconcile the differences between these prior studies.

2.2 Experiments and Analytical Methods

2.2.1 Starting materials

The compositions of the A15R and A17O glasses were created by mixing high purity reagent grade oxides and silicates, MgO , CaSiO_3 , Fe_2O_3 , Cr_2O_3 , Al_2O_3 , MnO , Na_2SiO_3 , SiO_2 . Fe-metal sponge and Fe_2O_3 were added in proportion to obtain an overall stoichiometry of FeO . The oxides were mixed under ethanol in an automatic agate mortar for 3 hrs. Fe-metal sponge was then added to the mixture and ground for an additional 1 hour. The ground starting material was then conditioned at 1-atm pressure in a Deltech furnace for 24 hours at f_{O_2} conditions close to IW at 1000°C under a flow of CO_2 and H_2 gas. The conditioned powder was then reground dry in an agate mortar by hand. The composition of the starting material has been verified by

analyzing the products of liquid-only high pressure experiments, and closely matches the compositions of Delano [1986] (Table 2.1).

2.2.2 Experimental Techniques

Experiments were performed in the Massachusetts Institute of Technology experimental petrology laboratory in a 0.5" piston cylinder apparatus [Boyd and England, 1960]. The ground, conditioned starting material was packed into either graphite or spec-pure Fe capsules and dried at 120°C for between 24 hrs–4 weeks prior to running an experiment. Experiments on the A15R composition in graphite capsules were placed into an outer Pt tube that was welded shut. To eliminate Fe loss to the outer Pt capsule, we switched to graphite-only capsules for experiments on the A17O composition. The piston cylinder pressure cell assembly and experimental procedure is the same as that described in Wagner and Grove [1997]. Piston cylinder experiments on the A15R and A17O compositions were performed from 0.8 to 3.3 GPa and 1320 – 1570°C. Experimental durations varied from 4.5 to 46 hours. Experimental conditions are reported in Tables 2.2 and 2.3. The durations used in this study are significantly longer than previous studies on these two lunar compositions [Green et al., 1975, Delano, 1980], and the extended times ensured as close an approach to equilibrium as possible. Figure 2-2c and 2-2d show typical experiment results for graphite and Fe capsule experiments.

In order to obtain glass that did not form quench crystals during cooling of the experiment we used a pressure-quenching technique where the piston load was released at the same moment the power was shut off to the experiment [Putirka et al., 1996]. Thus the experiment is slightly superheated while the liquid is cooling below the glass transition temperature. The Cr-Ti rich garnets that crystallized during the experiments do not remain stable during pressure-quenching. The breakdown of garnet produced a glass with a garnet-like composition and sub-micron sized Cr-rich spinel that likely exsolved from the garnet. These garnet-like patches show Raman spectral characteristics of amorphous material with three broad and weak peaks at 580, 670, and 750 cm^{-1} . The composition of the garnets were reconstituted

by using broad beam (10-20 μm) electron microprobe analyses on the amorphous regions overlapping with the small Cr-spinel inclusions. Compositions of garnets from an experiment that was not pressure-quenched, and thus survived the quenching, were similar to the broad beam analyses of exsolved and decomposed garnets.

2.2.3 Analytical Methods

Experimental run products were analyzed by electron microprobe on the JEOL 733 Superprobe at MIT. Beam conditions were 15 kV accelerating voltage and a 10 nA current. All glass analyses were done with a 10 μm diameter beam, and all mineral phases were analyzed with a focused 1- 2 μm beam (with the exception of decomposed garnets). The CITZAF correction procedure of Armstrong [1995], using the atomic number correction from Duncomb and Reed, the absorption corrections with Heinrich's tabulation of mass-absorption coefficients, and the fluorescence corrections from Reed, was used to reduce the data and obtain quantitative analyses. A materials balance calculation was used to estimate phase proportions and to determine whether FeO had been gained or lost from the experimental charge through reaction with the sample capsule. These results are reported in Tables 2.2 and 2.3. Composition of all of the phases is reported in Tables 2.4 and 2.5. Errors reported are the 1- σ standard deviation of the arithmetic mean of replicate analyses on each phase.

2.3 Experimental Results

2.3.1 High Pressure Phase Relations

The phase diagrams for the A15R and A17O compositions are shown in Figures 2-3 and 2-4. The results for each capsule material are plotted separately, because the phase relations depend on the type of capsule material used in the piston cylinder experiment. The most striking difference between the graphite and Fe capsule experiments is the change in stability of olivine and pyroxene on the liquidus.

Apollo 15 red glass

In graphite capsules the A15R composition has a titanium-rich chromium spinel on the liquidus at all pressures, but this phase is never more than 1-2% of any experiment and usually <1%. Olivine is the next phase to appear at pressures <1.2 GPa, and opx is the next phase to appear after the Ti-rich chromite at pressures >1.3 GPa. The A15R glass is saturated with both olivine and opx at its liquidus at 1.3 GPa and $\sim 1350^{\circ}\text{C}$. When spec-pure Fe capsules are used the phase relations change significantly. Cr-Ti-rich spinel is no longer the liquidus phase. The olivine stability field expands and olivine is stable at pressures at least up to 2.3 GPa. Although we have no experiments with only olivine or opx, we infer that olivine is the liquidus phase below 2.2 GPa and opx is the liquidus phase at higher pressures based on the phase abundance changes (Table 2.2) and a similar topology of our phase relations to those of Delano [1980]. At 2.2 GPa and 1450°C both olivine and opx co-saturate on the liquidus, an increase of 0.9 GPa over the graphite capsules. Garnet is stable near the liquidus, and is a Cr-Ti rich garnet (Table 2.4).

Apollo 17 orange glass

In Figure 2-4 the influence of capsule material on phase equilibria is shown for the A17O starting material. In graphite capsules, the A17O composition is saturated on its liquidus with olivine and opx at 2.5 GPa and $\sim 1530^{\circ}\text{C}$. At lower pressure, olivine is the liquidus phase and at higher pressure we infer opx as the liquidus phase. For Fe capsules the olivine stability field expands and olivine is the liquidus phase at pressures up to 3.1 GPa. At 3.1 GPa and $\sim 1560^{\circ}\text{C}$ the liquid has olivine and opx stable at the liquidus. This is the stable liquidus assemblage to at least 3.3 GPa. Clinopyroxene (sub-calcic augite) and garnet are also stable near the liquidus at pressures >3.1 GPa. The difference in MSPs between graphite and Fe capsules for the A17O glass is 0.6 GPa, smaller than the 0.9 GPa of the A15R glass.

2.3.2 Comparison to Previous Experimental Studies

The phase relations of the A15R glass were determined by Delano [1980], and those of the A17O glass were determined by Green et al. [1975]. In both of these experimental studies experimental durations were short (5–120 mins) compared to the experimental durations used in this study. In addition, the experiments of Green et al. [1975] were run in a ‘mild steel’ capsule, an Fe-C alloy that will produce a smelting reaction, reducing FeO in the melt to Fe-metal, significantly changing the bulk composition of the silicate portion of the starting material. Our experiments were carried out in graphite and spec-pure Fe capsules. These capsule materials remain relatively inert with respect to the bulk composition of the silicate portion of the sample and also control the f_{O_2} of our system (see section 2.3.4).

Experiments on the A15R glass in spec-pure Fe capsules are generally similar to those by Delano [1980], who also used spec-pure Fe capsules. Our experiments produce an olivine-opx multiple saturation point at 2.2 GPa. At similar P and T conditions our boundaries for olivine and opx stability are slightly different than those of Delano [1980], however the inferred point of coexistence of opx and olivine on the liquidus in our experiments is within 0.2 GPa of Delano (~ 2.4 GPa). The main difference between our Fe capsule results and those of Delano is the presence of garnet near the liquidus.

The results on the A15R glass in graphite differ from those of Delano [1980] in several respects. The liquidus phase is an oxide and not olivine or opx. Another difference is that the MSP of olivine-opx is much lower in pressure (1.3 GPa). Ilmenite joins the crystallization sequence at lower temperatures, well below the liquidus, and after a Cr-Ti spinel saturates, which is consistent with what Delano [1980] observed. A high calcium clinopyroxene joins the crystallizing assemblage of opx+spnl+ilmenite and the liquids in equilibrium with this assemblage may be analogous to low degree melts of late stage magma ocean cumulates.

The MSP of the Apollo 17 orange glass occurs at the highest pressure of the three studied, and ranges from 2.5 GPa in graphite capsules to 3.1 GPa for the Fe metal

capsules. Like the A15R glass, there is garnet near the liquidus at high pressure in the Fe capsule runs. In the highest pressure and temperature experiments attempted here a sub-calcic augite is a near-liquidus pyroxene phase. The lower calcium content of the clinopyroxene is a function of the higher liquidus temperatures at these high pressures [Lindsley and Dixon, 1976]. This type of pyroxene is also seen in some of experiments on other low-Ti lunar glasses [Elkins-Tanton et al., 2003].

The phase relations reported here are quite different from those reported by Green et al. [1975], who determined a MSP of 2.0 GPa. This value is lower than our graphite capsule result, and possibly represents the slow nucleation of olivine and/or possible Fe-loss through reduction of Fe^{2+} by a smelting reaction facilitated by the carbon in the mild steel capsules used by Green et al. [1975]. Reduction of the FeO component of the melt leads to SiO_2 enrichment, and stabilizes opx to lower pressures by decreasing the overall $\frac{\text{MgO}+\text{FeO}}{\text{SiO}_2}$ of the melt. However, Green et al. [1975] do not report compositions of minerals or melts, so it is not possible to definitively determine the reasons for the difference observed here.

2.3.3 Approach to Equilibrium

To demonstrate that the experimental durations were sufficient to reach equilibrium, we used the common approach of calculating mineral-liquid Fe-Mg exchange coefficients ($K_D^{\text{Fe-Mg}}$, Tables 2.2, 2.3). We find that the $K_D^{\text{Fe-Mg}}$ value is not constant, but varies systematically with pressure, temperature, and f_{O_2} and is consistent with previous long-duration experimental studies of high-Ti liquids [Wagner and Grove, 1997, Xirouchakis et al., 2001].

In addition to the checks on the equilibrium partitioning of Fe-Mg, the phase compositions were used in a multiple linear regression analysis to determine Fe loss/gain. The Fe loss/gain was less than $\pm 6\%$ for 85% of the experiments reported here. For low crystallinity, near-liquidus experiments, the least squares analysis captures the mineral modes accurately. The multiple linear regression technique is not as successful for highly crystalline experiments as evidenced by large negative coefficients for some of the minerals (Tables 2.2 and 2.3). The negative coefficients occur because

the inversion technique is unable to distinguish between solutions to the system of equations with positive coefficients and unrealistic negative ones. This occurs when multiple solutions are equally good (or bad) fits to the data [Press et al., 1986]. However, even in experiments where the linear regression method fails, the K_D^{Fe-Mg} values for the silicates and oxides are similar to the low crystallinity ones.

2.3.4 Control of f_{O_2}

A series of experiments was devised to estimate the variations in f_{O_2} imposed by graphite and Fe capsules by adding a small f_{O_2} sensor to the capsule+starting material. These f_{O_2} sensor experiments were run in both graphite and Fe capsules and used metal-alloy equilibria to determine the oxygen fugacity imposed by each capsule type. Several investigators have inferred the f_{O_2} imposed by graphite sample containers in piston cylinder experiments [Ulmer and Luth, 1991, Holloway et al., 1992, Yasuda and Fujii, 1993, Medard et al., 2008]. The results of Medard et al. [2008] suggest that the graphite capsule assembly utilized in this study imposes an upper limit of $\Delta IW+2$ (where $\Delta IW \pm x$ is the value of f_{O_2} relative to the IW buffer in $\log_{10}$ units at the given temperature), however starting materials that were more reduced than this could maintain their lower f_{O_2} .

The f_{O_2} in the graphite capsule experiments was measured independently by the equilibrium between coexisting Cr-rich spinel, olivine, opx, and melt as well as by an experiment with a small bead of FePt metal. The FePt alloy was placed in a graphite capsule and allowed to equilibrate with the IW-conditioned melt and graphite capsule assembly at 1.7 GPa and 1420°C. The composition of this re-equilibrated alloy and the method of Grove [1981] were used to determine a f_{O_2} of $\Delta IW+1.5$ (Table 2.4, Figure 2-2a). For an experiment that was saturated with olivine, opx, and spinel at 1.1 GPa and 1320°C (C318) the f_{O_2} was determined using the oxybarometer of Ballhaus et al. [1991b,a]. The oxygen fugacity obtained was $\Delta IW+1.25$. These methods agreed to within 0.25 log units. Both methods yield f_{O_2} values higher than the IW conditioning of the starting material but are within the expected f_{O_2} range determined for graphite capsules [Medard et al., 2008, Ulmer and Luth, 1991, Holloway

et al., 1992, Yasuda and Fujii, 1993].

Little experimental work has been done to obtain a quantitative estimate of the f_{O_2} imposed by Fe capsules used in piston cylinder experiments. The presence of metallic Fe in equilibrium with the experimental melt, and the less than unity activity of FeO in the melt will control the f_{O_2} of the experiment to be below the IW buffer but the absolute value needs to be determined. In order to measure the f_{O_2} imposed by this assembly we devised an f_{O_2} sensor experiment using FeCr alloys to record f_{O_2} . We placed a layer of Cr_2O_3 (eskolaite) powder at the bottom of a spec-pure Fe-metal capsule and inserted an Fe foil cup that contained the A15R starting material. The assembly was then run at 1.3 GPa and 1420°C. The Fe foil disaggregated during the experiment into discrete FeCr alloy blebs (Figure 2-2b). The composition of these blebs was analyzed using the electron microprobe by running line transects across the diameter of the bleb. If a constant Cr content was observed, the bleb was assumed to have reached equilibrium, and this value of X_{Cr}^{FeCr} (0.0309) was used in the following calculation. The equilibrium constant is defined by the equation:

$$\ln K = \frac{(a_{Cr}^{FeCr})^2 (f_{O_2})^{\frac{3}{2}}}{a_{Cr_2O_3}^{esk}} \quad (2.1)$$

Where a_m^n is the activity of the m component in phase n and f_{O_2} is the oxygen fugacity. The non-ideality in the FeCr binary system can be represented with a Margules-parameter expansion:

$$RT \ln(\gamma_{Cr}^{FeCr}) = [W_{CrFe} + 2W_{CrFe} - W_{FeCr} X_{Cr}^{FeCr}] (X_{Fe}^{FeCr})^2 \quad (2.2)$$

Where γ_{Cr}^{FeCr} is the activity coefficient of Cr-metal in the FeCr alloy, and X_m^n is the mole fraction of component m in phase n . Using the values of W_{CrFe} and W_{FeCr} from Kessel et al. [2003], and the presence of pure Cr_2O_3 eskolaite to set the activity at 1, equation (2.1) can be solved for oxygen fugacity. For our experiment this was calculated to be $\Delta IW-2.1$. Thus the Fe-metal capsule does not preserve the f_{O_2} conditioning of the starting material, and the two capsules types produce a greater

than three log-unit spread of oxygen fugacity. The f_{O_2} of the orange glass falls between these values at $\Delta IW-0.6$ [Sato, 1979, Weitz et al., 1997, Nicholis and Rutherford, 2009] and thus is bracketed by these experiments.

2.4 Discussion

2.4.1 Effects of variable f_{O_2} on phase equilibria

The phase relations of these high-Ti lunar compositions are extremely sensitive to changes in the oxidation state imposed by the graphite and Fe metal capsule materials (Figs 2-3 and 2-4). The reason for this sensitivity is the high abundance of multiple valence elements Ti, Fe, and Cr. We have measured the f_{O_2} of our experiments in order to quantitatively constrain the effect variable f_{O_2} has on the phase equilibria, and ultimately the inferred origin of such high-Ti magmas.

The oxidation state of the high-Ti source region has been studied for the A17O glass, and estimates vary between $\Delta IW+1$ to $\Delta IW-2$ with the best estimate of $\Delta IW-0.6$ [Sato, 1979, Weitz et al., 1997, Nicholis and Rutherford, 2009]. This f_{O_2} falls in the range of our experimental end members of $\Delta IW+1.3$ and $\Delta IW-2.1$. Linear interpolation of the MSP between our two end members gives our best estimate for the depth of origin for the A17O glass (Fig 2-5). The A15R and A14B glasses have no independent estimates for the f_{O_2} of their source regions, but most lunar materials fall into a relatively narrow range of f_{O_2} between $\Delta IW-2$ to $\Delta IW=0$ [Sato et al., 1973, Haggerty, 1978].

Both the A17O and A15R starting materials have similar FeO and Cr_2O_3 contents, but have different TiO_2 contents. This allows us to examine the effect of variable TiO_2 , oxidation state, and speciation on the pressure of olivine-opx MSPs. The more oxidized experiments show lower pressure MSPs, in both the A17O and A15R glasses. The difference in the MSP for the A15R glass is 50% greater than that observed for the A17O glass over the same range in f_{O_2} , suggesting that the higher TiO_2 content ($\sim 40\%$ greater) of the A15R enhances the effects of f_{O_2} on the MSP. Thus we suggest

that the black glass of Apollo 14, which has more TiO_2 than the A15R glass, would show an even greater difference in MSP between graphite and Fe metal capsules (Fig 2-5).

We suggest that the f_{O_2} control on olivine-opx equilibria is caused by a shift in the $\text{TiO}_2\text{:Ti}_2\text{O}_3$ ratio of the experiment because this is the only major element that would change valence state at these reducing conditions, as almost all of the Fe is divalent over this range [Kress and Carmichael, 1991]. The partition coefficients for TiO_2^* (* indicates all of the element is calculated as a single valence) as measured by electron microprobe (Table 2.4 and 2.5; $D_{\text{Ti}}^{\text{olv-melt}}=0.017\pm0.002$ for A15R and $D_{\text{Ti}}^{\text{olv-melt}}=0.014\pm0.004$ for A17O) are similar to previous studies at low Ti concentration that used a high-Fe low silica basalt starting material [Colson et al., 1988]. This similarity suggests that Ti incorporation in silicates is not changing the phase equilibria. This leads us to infer that Ti^{3+} and Ti^{4+} are somehow influencing the melt structure and thus *indirectly* the liquidus phase stability. A possible mechanism for this change is by coordination of Ti and Fe in the melt. To link this melt speciation with the stability of olivine we must explain 1) the observed variations in Fe-Mg exchange coefficients (Fig 2-6) and 2) the change in the pressure of MSPs with f_{O_2} (Fig 2-5).

Variations in mineral-melt Fe-Mg exchange

The $K_D^{\text{Fe-Mg}}$ in most systems for olivine is extremely homogeneous at about 0.3–0.33 [Roeder and Emslie, 1970, Longhi et al., 1978, Toplis, 2005]. In experiments on lunar low-Ti ultramafic glasses (Fig 2-6) $K_D^{\text{Fe-Mg}}$ values are higher, but constant at 0.34–0.35. In our high-Ti experiments $K_D^{\text{Fe-Mg}}$ values range from 0.23 to 0.34. This range in $K_D^{\text{Fe-Mg}}$ is consistent with other studies of high-Ti compositions [Longhi et al., 1978, Delano, 1980, Xirouchakis et al., 2001, Wagner and Grove, 1997, Canil and Bellis, 2008]. The $K_D^{\text{Fe-Mg}}$ values are a function of TiO_2 content, pressure and/or temperature, as well as f_{O_2} . It is not possible to separate the effects of pressure and temperature in our experiments because the high pressure experiments with olivine and liquid are also the high temperature experiments. The pressure/temperature

effect was observed by Delano [1980] who found that, by using Fe-capsules, with increasing pressure the K_D^{Fe-Mg} becomes more ‘normal’ approaching the 0.34 value.

The change in the Fe-Mg exchange coefficient value provides insight into the silicate melt speciation. A low value of K_D^{Fe-Mg} (i.e. 0.23) signifies that the olivine is Fe-poor compared to normal values of 0.34. Complexing Ti with Fe may lower the amount of olivine-compatible FeO in the melt because Ti is an incompatible element in olivine. Jones [1988] first tried to explore the implications of Fe-Ti coupling in lowering the K_D^{Fe-Mg} , and suggested that a melt component similar to ferropseudobrookite ($FeTi_2O_5$) was present. Jones [1988] assumed that the activity of FeO in the melt was proportional to $X_{Fe}^{melt} - X_{Ti}^{melt}/2$ and then checked to see if the actual K_D^{Fe-Mg} ’s varied systematically with this adjusted activity. We expanded the approach of Jones [1988] to determine the best fit stoichiometry of the Fe-Ti melt complex by calculating the moles of Fe that must be subtracted from the melt to achieve a reference $K_{D,ref}^{Fe-Mg}$ and compared this to the total moles of TiO_2 in the melt. We have done these calculations using the following equation:

$$\Delta FeO = X_{FeO}^{melt} - \left(\frac{X_{FeO}^{olv}}{X_{MgO}^{olv}} \cdot \frac{X_{MgO}^{melt}}{K_{D,ref}^{Fe-Mg}} \right) \quad (2.3)$$

where the reference $K_{D,ref}^{Fe-Mg}$ in this case is 0.34, and X_m^n is the mole fraction of component m in phase n . The experiments on lunar compositions have FeO contents that range from 18-25 wt%, and are fit by a melt complex with a 5:2 ratio of Ti:Fe, slightly more Ti-rich than a ferropseudobrookite component (Fig 2-7a). However, the study of Xirouchakis et al. [2001] used an experimental composition with a lower amount of FeO (8.5-10 wt%), and their data is best fit by a line that matches a 7:1 ratio of Ti:Fe. There is a sharp shift in the behavior of Ti in the melt at about 7 mol% TiO_2 , and below this value all the data sets on high-Ti liquids show no evidence for coupling of Fe with Ti within error. This behavior is fit by the assumption that the Ti melt component at low Ti contents is pure TiO_2 (Fig 2-7a).

In order to account for the broad range of FeO contents in experimental studies, we have defined the $\% \Delta FeO$ as the ratio of the molar quantity ΔFeO to the total X_{FeO}

of a melt. In Figure 2-7b we show that all of the data sets (including the low FeO Xirouchakis et al. [2001] data) follow the same general trend. This would suggest that there is not a specific atomic proportion of the Fe-Ti complex. $\% \Delta \text{FeO}$ is in effect a partition coefficient for FeO between two different melt sites, one that is associated with Ti, and one that is not. We favor an interpretation where the FeO partitions itself between a Ti-rich melt site that cannot exchange with olivine and a Ti-poor melt site that does. Fe in the Ti-poor site is the Fe available for incorporation in the olivine. The partition coefficient, $\% \Delta \text{FeO}$, is a function of TiO_2 at mole percentages exceeding 7% and continues to increase with increasing TiO_2 (Fig 2-7b).

$K_D^{\text{Fe-Mg}}$ is a function of P-T and f_{O_2} as well as TiO_2 content and suggests the stability of the Fe-Ti melt complex decreases with increasing temperature/pressure and is stabilized by the presence of Ti^{3+} . At graphite capsule f_{O_2} conditions the P-T dependence is pronounced. There is probably only a small amount of Ti_2O_3 in the melt, and the Fe must be coordinating with only Ti^{4+} in the melt in order to cause the $K_D^{\text{Fe-Mg}}$ effects seen in graphite capsules. At the reducing conditions of the Fe-capsule runs there is more Ti^{3+} , but less than required to account for the 25–30% of the total $\% \Delta \text{FeO}$ on a mole for mole basis, and therefore not enough to account for the large shift in $K_D^{\text{Fe-Mg}}$ at lower f_{O_2} (e.g. the flat slope of Fe-capsule experiments in Fig 2-6). However, the small amounts of Ti^{3+} in the melt might significantly stabilize a Fe-Ti melt component to higher temperatures. Similar behavior of Ti^{3+} has been observed in stabilizing the solid solutions of Fe-Ti oxides like armalcolite [Kesson and Lindsley, 1975].

The $K_D^{\text{Fe-Mg}}$'s show a variation with f_{O_2} and show a negative correlation with bulk Ti content, and thus we infer that the high-Ti contents were responsible for this. There are several others who have noted the negative correlation of olivine $K_D^{\text{Fe-Mg}}$ with increasing TiO_2^* in the melt. [Longhi et al., 1978, Delano, 1980, Jones, 1988, Xirouchakis et al., 2001]. However other authors have suggested that it is not the increased Ti content that affects the $K_D^{\text{Fe-Mg}}$, but actually the low silica contents that necessarily accompany the increased Ti [Longhi et al., 1978, Toplis, 2005]. Our new results show the $K_D^{\text{Fe-Mg}}$ is strongly influenced by lowering the f_{O_2} (Fig 2-6),

as olivines in Fe-capsule runs show distinctly lower K_D^{Fe-Mg} than graphite capsule runs at the same pressure and temperature. This result provides support for Ti^{3+} in the melt as a component that is influencing the K_D^{Fe-Mg} in these high-Ti–low-silica liquids, because Si will be only tetravalent under both f_{O_2} conditions. Thus we can rule out silica activity as the sole control on the low K_D^{Fe-Mg} [Toplis, 2005].

The Ti^{3+} effect on MSP's

We have shown that the Fe-Mg systematics of olivine-melt is accounted for by the complexing of Fe^{2+} – Ti^{3+} – Ti^{4+} in the melt, and that the lowering of the K_D^{Fe-Mg} is related to Ti, not only silica activity. The role of Ti^{3+} can also account for the shifts in olivine-opx equilibria. A possible substitution mechanism for incorporating Ti^{3+} into an Fe-Ti melt component is by reduction of Ti^{4+} already in the complex, and therefore ejecting an Fe from the complex by charge balance. This substitution is similar to a Ti-Tschermak substitution as follows:

Here ‘cplx’ refers to the Fe-Ti complex in the melt that olivine cannot interact with, while Fe_{melt}^{2+} is then available to be incorporated into olivine.

We have adapted the projection scheme from Longhi et al. [1974] for displaying the bulk rock compositions of high-Ti basalts as a projection through an Fe-Ti oxide phase onto the plag+cpx-quartz–olivine plane (Fig 2-8). This projection allows us to examine the position of Ti-absent silicate phase boundaries for compositions of widely varying Ti content. By projecting through an Fe-Ti melt component with different Ti:Fe ratios, the silicate portion of the composition shifts to more/less olivine normative compositions (Fig 2-8). Compositions with higher TiO_2^* contents have the largest change in ‘normative olivine’ because they are closer to the Fe-Ti apex of the compositional tetrahedron (Fig 2-8). Using this projection scheme, we see the MSPs of the high-Ti compositions studied in graphite capsule experiments form a trend in this projection space; where deeper MSPs are more olivine normative compositions

(Fig 2-9).

Assuming that the Fe-Ti projection component is related to the actual Fe-Ti component of the melt, then according to equation (2.4) we must project through a composition closer to TiO_2 on the FeO- TiO_2 join for reduced systems. Projecting through a more Ti-rich melt complex indeed shifts the melt compositions to more olivine normative compositions, despite the overall bulk composition being the same. This is consistent with olivine being stable at higher pressures at low f_{O_2} , i.e. the melt is behaving more olivine normative under reducing conditions.

Our experiments show that under reducing conditions the MSPs move to deeper depths. A composition with the most Ti-rich liquid (i.e. the A15R glass) would have the largest change in ‘normative olivine’ because it is closest to the Fe-Ti apex of the tetrahedron, consistent with our experimental data (Fig 2-5). By shifting the projected Fe-Ti melt component towards the TiO_2 apex and reprojecting through this component, the compositions become more olivine normative, and their shift is proportional to the increase in the multiple saturation pressure for the orange and red glasses. This lends strength to the inference of the Fe-Ti behavior in the melt.

2.4.2 Significance for the petrogenesis of High-Ti liquids

The determination of the pressure of origin for these high-Ti lavas is critical for understanding the distribution of dense ilmenite rich cumulates within the Moon. Melting of these cumulates produces high density liquids. The high densities of these liquids have led many to investigate their compressibility [Delano, 1990, Circone and Agee, 1996, Sakamaki et al., 2010, van Kan Parker et al., 2011] and to speculate on their eruptability [Elkins Tanton et al., 2002, Hess, 1991]. With our experimental determination of the depth of origin we can evaluate these models.

We have calculated the compressibility curves for the A17O liquid following the methods of Delano [1990] and Lange and Carmichael [1987] using the zero pressure liquidus temperature of the orange glass and a $K'_T=6$, (Fig 2-10). Over the entire range we explored, and at our inferred pressure of origin at 2.8 GPa, the orange glass is buoyant with respect to a model differentiated lunar mantle composition [Hess and

Parmentier, 1995]. This is in agreement with the recent experimental study of the compressibility of the orange glass [van Kan Parker et al., 2011]. Unfortunately, there is no estimate for the source region f_{O_2} of the A15R glass, however the range explored in our experiments is inclusive of the f_{O_2} estimates that have been inferred for lunar materials (BVSP). The range in possible MSP's for the A15R glass is from 1.3 to 2.2 GPa, and it is notable that these pressures are at least 0.6 GPa lower (~ 120 km shallower) than the MSP of the A17O glass. The calculated densities of the A15R glass suggests that like the A17O glass it is buoyant over the entire range of f_{O_2} explored here (Fig 2-10).

The density and compressibility of the A14B glass has been theoretically [Delano, 1990] and experimentally [Circone and Agee, 1996, Sakamaki et al., 2010] determined to be buoyant with respect to a residual mantle at the depth of its graphite capsule MSP. However when considering the effect that f_{O_2} has on the MSP of the black glass, the highly compressible A14B glass is *only* buoyant at the high end of the f_{O_2} range. We thus suggest that its source region is more oxidizing than the orange glass source region. Linear interpolation between the $\Delta IW+1.3$ MSP at 1.5 GPa, and the point where it crosses the differentiated mantle density line of Hess and Parmentier [1995] places a constraint on the black glass source region of f_{O_2} at $> \Delta IW+0.6$ in order for it to be buoyant with respect to an olivine+opx mantle (Fig 2-10).

It is clear that the oxygen fugacity of the source region must be taken into account in determining the depth of origin for any high-Ti magma. Using this new and internally consistent data set it is apparent that the MSP's for high-Ti glasses span a range of pressures from 1.3 GPa up to 2.8 GPa. These values correspond to a depth interval of 250-540 km in the moon. The distribution of the source material for these glasses is thus spread over a large portion of the lunar mantle. This is evidence that both overturn and convective mixing of magma ocean cumulates was inefficient. It is possible that the lunar mantle is quite heterogeneous on a horizontal basis, as well as a vertical basis [Ringwood and Kesson, 1976, Hess and Parmentier, 1995, Elkins Tanton et al., 2002].

2.5 Figure captions

Figure 2-1: Compositional variations between the ultramafic picritic glass suites and the high-Ti basalts of Apollo 11 and 17.

Figure 2-2: A) Reflected light photomicrograph of a graphite capsule f_{O_2} sensor experiment. The experiment was ground away until a good exposure of the FePt bead was obtained. B) Reflected light photomicrograph of the Fe capsule f_{O_2} sensor experiment. The small disaggregated beads of FeCr were analyzed for their Cr content to determine the f_{O_2} . Notice the Cr_2O_3 starting material equilibrated with the melt to produce a Cr-rich spinel. C) Mg X-ray intensity map of experiment D190. Visible are the phases: melt, olivine, cpx, and opx. The black areas are the Fe-capsule (no Mg). D) Electron backscatter image of experiment C318. This experiment contains melt, olivine, opx, and spinel.

Figure 2-3: Phase diagrams of the composition A15R for experiments performed in Fe-metal and graphite capsules. Note the difference in olivine-opx multiple saturation for the different capsule types but similar compositions.

Figure 2-4: Phase diagrams of the composition A17O for experiments performed in Fe-metal and graphite capsules. Note the difference in olivine-opx multiple saturation for the different capsule types is smaller than for the A15R composition.

Figure 2-5: A) A simplified diagram showing the phase relations in the A15R for both the graphite (high f_{O_2}) and Fe capsule experiments (low f_{O_2}). The red circles represent the olivine-opx MSPs, and the star is a best estimate of the source region P-T for the A15R, based on interpolation to an f_{O_2} of $\Delta IW-0.6$. B) Same as A but for the orange glass. C) Summary of the MSP data for lunar ultramafic glasses. Open symbols are for experiments in Fe capsules and filled are for graphite.

Figure 2-6: The olivine–melt Fe–Mg exchange coefficient for each experiment is plotted versus the experimental temperature. Green glasses from Elkins-Tanton et al. [2003] and Red and Orange glasses are from Tables 2.4 and 2.5. Diamonds are graphite capsule experiments and squares are Fe-metal experiments. The lines shown are the best fit linear regressions to the high-Ti graphite and high-Ti Fe capsule experiments.

Figure 2-7: A) ΔFeO as a function of mole percent TiO_2^* , 0 corresponds to a $K_{D,ref}^{Fe-Mg}=0.34$. There is a break in slope corresponding to a possible shift in Ti-coordination in the melt. B) Similar to the plot in (A) but comparing the $\%\Delta\text{FeO}$ instead of the absolute amount of moles of FeO. The partitioning of FeO between a high-Ti and low-Ti melt component is a function of the mole percent TiO_2^* .

Figure 2-8: Adapted projection scheme of Longhi et al. [1974]. By projecting through different Fe-Ti melt components we can see the apparent effect on the composition. Lowering f_{O_2} would move the Fe-Ti melt component toward the TiO_2 end-member by introducing more Ti^{3+} . Three schematic liquid compositions are shown with varying amounts of $\text{FeO}+\text{MgO}+\text{TiO}_2$.

Figure 2-9: Enlarged portion of the Plag+Cpx-Olivine-Quartz psuedo-ternary diagram. Filled symbols are compositions that have had their MSP's experimentally determined in graphite capsules. There is a trend that more olivine normative compositions have higher MSP's. Filled symbols are projected through ilmenite (ilm, FeTiO_3) and open circles are projected through ferropsuedobrookite (fsb, FeTi_2O_5). The fsb projection is more 'reducing' assuming that Ti^{3+} is substituting into the Fe-Ti melt component by equation (2.4) and therefore appropriate for shifts in the phase boundaries for experiments in Fe-capsules.

Figure 2-10: Calculated liquid density-depth curves. We use the molar volumes from Lange and Carmichael [1987] to produce the zero pressure estimates of density of the liquid, and the method of Delano [1990] to calculate the high pressure densities assuming an intermediate value of 6 for K'. The density of the lunar mantle after cumulate overturn is shown from Hess and Parmentier [1995]. The ranges of MSP for the high-Ti glasses are shown as thick bars. The high pressure end of the range of black glass MSP is extrapolated to $\Delta\text{IW}-2.1$.

Table 2.1: Synthetic starting materials and natural compositions¹

Composition	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	Total
Natural A15R	35.6	13.8	7.15	0.77	21.9	0.25	12.1	7.89	0.49	0.12	100.07
Synthetic A15R	35.8	13.5	7.11	0.74	22.0	0.24	12.5	7.74	0.31	-	99.94
Natural A17O	38.5	9.12	5.79	0.69	22.9	-	14.9	7.40	0.38	-	99.68
Synthetic A17O	38.9	8.78	5.81	0.67	22.3	0.27	15.7	7.37	0.26	-	99.95

¹Natural compositions are from Delano [1986] and synthetic materials are an average of the glass compositions from experiments that were super-liquidus (C333, C346, C315 for A15O; D195, C397, and C409 for A17O)

Table 2.2: Run conditions and products for A15R starting material

Run	Capsule	T °C	GPa	Time (hrs)	Phases(calculated mode) [†]	Olv K _D [‡]	Opx K _D	Cpx K _D	Ilm K _D	Gt/Sp K _D	% FeO loss/gain
C321	Fe	1410	2	6.8	olv(2) + opx(4) + liq(93)	0.270	0.252				1.3
C322	Fe	1440	2.3	16.2	olv(1) + opx(6) + liq(93)	0.274	0.246				0.8
C323	Fe	1410	2.3	24.2	olv(3) + opx(3) + cpx(16) + gnt(3) + liq(75)	0.240	0.239			0.396	2.1
C324	Fe	1380	1.7	24	olv(3) + opx(7) + liq(89)	0.262	0.252				3.8
C326	Fe	1410	1.7	18.2	olv(6) + opx(3) + liq(90)	0.261	0.241				2.3
C329	Fe	1440	2	18	olv(1) + opx(3) + liq(96)	0.264	0.250				2.6
C333	Fe	1470	2	7.0	liq						9.0
C346	Fe	1440	1.7	19.3	liq						-0.8
B1058	Fe	1420	1.3	91.8	sp + esk + FeCr + liq						
C361	C	1420	1.7	24	olv + sp + PtFe + liq	0.258					
B1025	C + Pt	1350	0.8	4.6	olv + sp + liq	0.235	0.274				-0.1
B1027	C + Pt	1320	0.8	4.7	olv(19) + opx(-14) + sp(?) + liq(94)						-1.7
C309	C + Pt	1350	1.95	14	opx(27) + cpx(-22) + sp(1) + ilm(-7) + liq(100)		0.278	0.315	1.87	1.42	-2.1
C310	C + Pt	1320	1.7	21.5	opx(28) + cpx(-20) + sp(<1) + ilm(-6) + liq(98)		0.269	0.297	1.73	1.18	-11.3
C311	C + Pt	1380	2	19.8	opx(6) + sp(2) + liq(93)		0.310			1.54	-8.1
C312	C + Pt	1350	1.7	19.4	opx(7) + sp(2) + liq(93)		0.314			1.63	-7.5
C313	C + Pt	1410	2	15.5	opx(-3) + sp(1) + liq(103)		0.333			1.38	-10.5
C314	C + Pt	1380	1.7	15.1	opx(1) + sp(4) + liq(96)		0.276			1.37	-7.6
C315	C + Pt	1440	2	7.9	liq						-5.5
C316	C + Pt	1400	1.7	8.3	sp(2) + liq(98)					1.30	-5.6
C317	C + Pt	1350	1.4	21.4	opx(4) + sp(3) + liq(94)		0.250			1.37	-5.4
C318	C + Pt	1320	1.1	22.6	olv(10) + opx(-6) + sp(3) + liq(94)	0.263	0.256				-2.9
C319	C + Pt	1380	1.4	9.7	sp + liq	0.271				1.41	-0.4
C320	C + Pt	1350	1.1	7	olv(1) + sp(3) + liq(97)	0.249	0.227		1.35	1.34	
C332	C + Pt	1320	1.4	46.3	olv(4) + opx(13) + sp(2) + ilm(1) + liq(81)						
C338	C + Pt	1365	1.25	24	sp + liq						

[†] negative modes indicate a failure of the linear regression analysis. [‡] K_D is the Fe-Mg mineral-melt exchange coefficient. (?) no Sp observed in this experiment, but the mass balance has a Cr deficit and the position on the phase diagram suggests there should be a small amount of it. Abbreviations: olv=olivine, opx=orthopyroxene, cpx=clinopyroxene, sp=spinel, gt=garnet, ilm=ilmenite, esk=eskolaite, liq=quenched melt.

Table 2.3: Run conditions and products for A170 starting material

Run #	Capsule	T °C	GPa	Time (hrs)	Phases	Olv K _D	Opx K _D	Cpx K _D	Gt/Sp K _D	% FeO loss/gain
D176	Fe	1550	3.1	18.1	olv(10) + opx(-11) + liq(103)	0.282	0.300			-7.5
D187	Fe	1510	3.32	45.3	olv(9) + cpx(26) + gnt(11) + liq(55)	0.249		0.259	0.478	-2.3
D190	Fe	1550	3.15	23.1	olv(7) + opx(2) + cpx(7) + liq(84)	0.271	0.269	0.297		-2.2
C408	Fe	1535	2.85	19.8	olv(8) + liq(90)	0.283				21.4
D195	Fe	1570	3.15	10.5	liq(100)					-5.2
D198	Fe	1550	3.3	6.5	olv(5) + opx(18) + cpx(-13) + liq(90)	0.282	0.278	0.295		-1.9
D199	Fe	1570	3.31	7.4	olv(4) + opx(-2) + liq(98)	0.294	0.268			-1.4
B1050	C	1390	1.3	17.1	olv(8) + liq(91)	0.276				-1.5
C363	C	1380	1.5	6.7	olv(12) + opx(10) + sp(1) + liq(77)	0.278	0.239		1.35	0.5
C364	C	1360	1.3	13.4	olv(15) + opx(6) + sp(1) + liq(79)	0.281	0.243		1.41	0
C365	C	1340	1.3	8.8	olv(16) + opx(6) + sp(1) + liq(78)	0.292	0.247		1.48	0.4
C366	C	1420	1.7	15.8	olv + sp + liq	0.301				
C367	C	1405	1.5	22.5	olv(7) + sp(2) + liq(92)	0.348			1.61	-6.1
C368	C	1410	1.3	21.7	olv(10) + sp(1) + liq(89)	0.293			1.49	-1.6
C370	C	1420	1.6	12.6	olv(12) + opx(-4) + sp(<1) + liq(92)	0.296	0.263		1.41	0.1
C371	C	1430	1.9	26.2	olv(9) + opx(3) + liq(88)	0.289	0.253			0.2
C373	C	1440	2.15	9.1	olv(8) + opx(14) + sp(<1) + liq(77)	0.256	0.225		1.09	0.9
C376	C	1460	2.15	19.7	olv(5) + opx(8) + liq(86)	0.289	0.249			0.6
C380	C	1470	1.9	21.9	olv(2) + liq(98)	0.332				-4.4
C381	C	1480	2.1	19.7	olv(4) + liq(96)	0.324				-4.6
C382	C	1450	1.9	24.9	olv(9) + liq(91)	0.302				-2.3
C388	C	1490	2.3	23	olv(7) + opx(-1) + liq(94)	0.280	0.252			-0.2
C389	C	1510	2.3	20.7	olv(4) + liq(96)	0.298				-3.7
C395	C	1540	2.5	8	olv(2) + opx(-1) + liq(100)	0.317	0.284			-1.9
C396	C	1520	2.5	26.8	olv(6) + opx(-12) + liq(107)	0.354	0.313			-2.5
C397	C	1560	2.5	8.7	liq(100)					0.6
C409	C	1555	2.7	14.3	liq(100)					-4.5

See Table 2.2 for explanations of abbreviations.

Table 2.4: EMP analyses of A15R experiments in oxide weight percents

Run	Phase	n*	SiO ₂ *	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	Total									
C321	glass	29	35.1	0.23	14.41	0.23	7.43	0.13	0.73	0.04	22.7	0.3	0.25	0.03	10.75	0.22	8.36	0.18	0.35	0.06	100.10
	olv	12	37.7	0.34	0.23	0.01	0.12	0.01	0.40	0.01	22.3	0.4	0.18	0.02	39.05	0.59	0.26	0.01	-	-	100.19
C322	opx	10	52.3	0.75	1.57	0.22	4.05	0.72	0.81	0.08	13.9	0.3	0.19	0.02	25.99	0.60	1.95	0.07	0.05	0.01	100.78
	glass	28	34.8	0.69	14.55	0.46	7.50	0.21	0.73	0.06	22.9	0.6	0.25	0.04	10.96	0.25	8.50	0.22	0.31	0.09	100.49
C323	olv	4	38.1	0.28	0.24	0.04	0.11	0.01	0.41	0.01	22.2	0.3	0.23	0.04	38.79	0.30	0.27	0.04	0.02	0.02	100.38
	opx	4	52.2	0.06	1.65	0.06	4.24	0.14	0.88	0.02	13.5	0.2	0.16	0.03	26.20	0.29	2.01	0.08	0.06	0.03	100.92
C324	glass	43	32.0	0.33	17.57	0.59	7.42	0.10	0.65	0.05	24.3	0.6	0.27	0.04	9.07	0.15	8.27	0.18	0.46	0.09	100.04
	olv	12	37.6	0.22	0.28	0.04	0.18	0.16	0.33	0.02	24.0	0.4	0.23	0.01	37.30	0.27	0.31	0.06	-	-	100.17
C326	opx	6	50.9	0.64	1.78	0.21	5.05	0.61	0.86	0.09	15.3	0.4	0.18	0.02	23.84	0.45	2.24	0.11	0.04	0.03	100.18
	cpx	17	50.0	0.46	2.11	0.25	5.10	0.53	0.91	0.06	13.8	0.5	0.21	0.04	19.06	0.55	8.84	0.65	0.29	0.03	100.24
C329	gnt	15	38.9	0.19	3.02	0.19	20.17	0.25	2.55	0.12	15.3	0.3	0.32	0.02	14.39	0.29	6.26	0.19	0.00	0.01	100.90
	glass	11	34.5	0.57	13.82	0.82	7.73	0.27	0.71	0.08	23.4	0.6	0.31	0.02	9.57	0.29	8.85	0.29	0.42	0.08	99.34
C333	olv	8	38.2	0.36	0.20	0.06	0.12	0.11	0.38	0.04	23.7	1.9	0.21	0.04	37.13	0.98	0.30	0.07	-	-	100.22
	opx	7	50.9	0.83	1.71	0.24	4.38	0.68	1.02	0.10	15.5	0.7	0.20	0.04	25.13	0.29	2.12	0.31	0.02	0.03	100.99
C346	glass	27	35.5	1.99	14.46	0.77	7.79	0.76	0.64	0.40	22.9	1.4	0.26	0.12	9.75	1.37	8.69	0.65	0.34	0.19	100.38
	olv	10	38.1	0.59	0.25	0.06	0.11	0.03	0.38	0.06	23.4	0.7	0.20	0.05	38.14	0.82	0.29	0.05	-	-	100.92
B1058	opx	5	51.4	0.73	1.69	0.26	4.18	0.43	0.88	0.09	14.6	0.4	0.17	0.02	25.67	0.78	2.02	0.36	0.05	0.02	100.62
	glass	15	35.6	0.51	13.57	0.64	7.23	0.37	0.72	0.10	22.9	0.7	0.30	0.05	11.25	0.40	8.13	0.25	0.36	0.13	100.11
C333	olv	5	38.8	0.74	0.23	0.04	0.13	0.04	0.38	0.03	21.3	0.8	0.19	0.03	39.57	0.40	0.27	0.04	-	-	100.87
	opx	5	52.0	0.44	1.55	0.35	3.82	0.94	0.74	0.12	13.7	0.3	0.15	0.03	26.93	0.44	1.93	0.18	0.06	0.04	100.97
C346	glass	20	35.3	0.65	13.06	0.66	7.08	0.22	0.73	0.07	24.0	0.9	0.26	0.14	12.11	0.34	7.79	0.36	0.32	0.10	100.70
	glass	15	36.0	0.33	13.53	0.20	7.10	0.08	0.70	0.03	21.7	0.2	0.23	0.02	12.16	0.09	7.77	0.08	0.37	0.05	99.56
B1058	glass	12	39.8	0.28	12.76	0.21	6.39	0.07	3.41	0.21	16.7	0.4	0.27	0.02	10.80	0.12	8.57	0.18	0.37	0.05	99.12
	sp	17	0.1	0.03	7.30	1.24	4.73	1.55	57.41	3.54	21.6	0.4	0.30	0.02	8.97	0.63	0.02	0.01	-	-	100.46
FeCr		19	-	-	-	-	3.16	0.60	99.0	0.9	-	-	-	-	-	-	-	-	-	-	102.15

Table 2.4 – Continued

Run	Phase	n	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	Total						
C361	glass	19	35.9	0.35	7.14	0.07	0.05	21.9	0.4	0.24	0.02	12.25	0.49	7.90	0.19	0.37	0.07	100.57
	PtFe	16	-	-	-	Pt:	83.77	0.34	18.3	0.3	-	-	-	-	-	-	-	102.03
B1025	glass	20	36.4	0.40	13.90	0.12	0.03	21.6	0.3	0.26	0.02	11.31	0.12	8.13	0.12	0.29	0.14	99.72
	olv	3	38.8	0.13	0.23	0.00	0.01	20.2	0.5	0.21	0.02	41.07	0.24	0.24	0.02	-	-	101.07
B1027	sp																	
	glass	15	37.5	0.31	14.73	0.05	0.06	20.9	0.1	0.27	0.03	8.33	0.47	9.18	0.22	0.40	0.02	99.71
	olv	10	38.2	0.29	0.28	0.01	0.02	22.5	0.6	0.21	0.03	38.20	0.42	0.25	0.02	-	-	99.89
	opx	10	50.9	0.41	1.89	0.12	0.03	15.4	0.3	0.27	0.02	22.48	0.14	4.01	0.18	0.02	0.06	99.48
C309	glass	15	32.3	0.45	17.47	0.39	0.05	22.0	0.6	0.27	0.02	10.06	0.34	9.60	0.33	0.32	0.09	100.03
	opx	10	51.2	0.79	1.13	0.81	0.12	15.0	0.2	0.21	0.02	24.63	0.38	2.32	0.04	0.11	0.05	100.30
	cpx	10	49.6	0.66	1.76	0.39	0.08	12.6	0.6	0.22	0.02	18.35	0.83	10.66	1.15	0.30	0.04	100.48
	ilm	7	0.1	0.02	51.51	0.04	0.09	32.4	0.5	0.22	0.03	7.93	0.07	0.29	0.03	-	-	99.32
C310	sp	8	0.2	0.01	11.52	0.55	0.57	32.3	0.2	0.21	0.03	10.46	0.13	0.12	0.05	-	-	99.75
	glass	15	32.6	0.31	15.88	0.15	0.03	24.1	0.7	0.28	0.03	8.99	0.64	9.26	0.55	0.47	0.14	100.30
	opx	10	49.3	0.32	1.41	0.47	0.03	16.7	0.3	0.23	0.02	23.17	0.32	2.34	0.11	0.03	0.03	100.25
	cpx	15	48.6	0.52	1.91	0.53	0.05	13.8	0.5	0.22	0.02	17.31	0.72	10.41	0.92	0.18	0.03	99.76
	ilm	6	0.2	0.08	53.17	0.08	0.13	34.3	0.2	0.24	0.02	7.38	0.31	0.29	0.05	-	-	100.05
	sp	7	0.3	0.01	10.85	0.49	0.16	32.5	0.2	0.21	0.02	10.22	0.14	0.11	0.03	-	-	100.13
C311	glass	15	34.5	0.31	16.32	0.40	0.05	19.2	0.3	0.29	0.03	12.07	0.54	8.69	0.40	0.33	0.11	99.57
	opx	10	52.1	0.55	1.03	0.37	0.08	13.0	0.3	0.21	0.02	26.40	0.47	1.84	0.13	0.09	0.04	100.22
C312	sp	4	0.3	0.02	7.54	0.23	0.66	26.4	0.2	0.19	0.02	10.78	0.59	0.06	0.02	-	-	99.66
	glass	15	34.2	0.67	16.15	0.13	0.04	20.0	0.5	0.28	0.02	12.25	0.35	8.37	0.31	0.16	0.11	99.41
	opx	11	51.2	0.45	1.23	0.07	0.06	13.4	0.2	0.18	0.02	26.27	0.55	1.97	0.19	0.05	0.02	99.58
	sp	4	0.2	0.02	10.33	0.97	0.64	28.8	0.1	0.25	0.03	10.82	0.71	0.07	0.01	-	-	99.07
C313	glass	15	36.8	0.28	14.73	0.18	0.07	19.1	0.7	0.23	0.04	13.84	0.92	7.77	0.50	0.24	0.05	100.87
	opx	1	52.4	1.02	4.12	1.32	12.8	0.18	27.87	1.66	0.03	27.87						101.41

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Table 2.4 – Continued

Run	Phase	n	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	Total									
C314	sp	1	0.3	7.29	13.49	38.33	24.8	0.25	13.07	0.16	0.07	97.69									
	glass	3	36.6	0.19	14.80	0.19	7.55	0.06	0.55	0.04	18.9	0.3	0.23	0.04	11.33	0.06	8.41	0.05	0.51	0.03	98.80
	opx	12	52.6	0.80	1.12	0.12	3.66	0.56	1.11	0.10	12.6	0.3	0.20	0.02	27.38	1.04	1.66	0.17	0.04	0.02	100.30
C315	sp	6	0.2	0.02	9.29	0.29	15.66	0.86	35.44	0.45	26.9	0.2	0.23	0.03	11.75	0.61	0.11	0.03	-	-	99.50
	glass	15	36.3	0.27	13.92	0.31	7.15	0.09	0.79	0.08	20.3	0.6	0.24	0.03	13.26	0.70	7.67	0.34	0.23	0.06	99.90
C316	glass	5	36.3	0.12	13.68	0.16	7.17	0.03	0.58	0.04	20.3	0.4	0.24	0.02	12.24	0.11	7.86	0.09	0.38	0.07	98.70
C317	sp	6	0.2	0.02	8.59	0.14	15.80	0.21	37.88	0.43	25.5	0.2	0.25	0.02	11.88	0.38	0.17	0.01	-	-	100.20
	glass	8	35.6	0.36	14.69	0.24	7.48	0.04	0.41	0.02	20.3	0.1	0.25	0.04	11.06	0.05	8.49	0.04	0.40	0.12	98.70
	opx	16	52.2	0.37	1.19	0.08	3.31	0.15	1.06	0.04	12.7	0.2	0.20	0.03	27.60	0.58	1.57	0.11	0.02	0.02	99.80
C318	sp	5	0.2	0.02	10.72	0.07	14.79	0.16	33.26	0.21	28.1	0.4	0.20	0.04	11.74	0.33	0.12	0.05	-	-	99.10
	glass	3	36.2	0.12	15.10	0.57	8.11	0.22	0.28	0.08	19.6	0.2	0.28	0.02	10.42	0.46	8.79	0.27	0.42	0.05	99.27
	olv	4	38.6	0.33	0.26	0.07	0.07	0.01	0.21	0.02	20.1	0.4	0.24	0.04	40.50	0.27	0.25	0.01	-	-	100.26
C320	opx	5	52.7	0.20	1.43	0.08	3.50	0.16	1.03	0.04	13.1	0.3	0.20	0.03	27.16	0.40	1.59	0.11	0.04	0.02	100.73
	sp	4	0.2	0.01	12.55	0.31	12.52	0.20	31.09	0.22	30.1	0.2	0.26	0.01	11.72	0.12	0.13	0.05	-	-	98.63
	glass	18	37.0	0.27	13.42	0.30	7.06	0.08	0.49	0.04	20.9	0.2	0.25	0.03	11.48	0.15	7.73	0.15	0.54	0.09	98.86
C332	olv	12	38.9	0.27	0.19	0.04	0.09	0.02	0.30	0.05	19.8	0.4	0.19	0.03	39.94	0.28	0.22	0.01	-	-	99.63
	sp	7	0.1	0.02	11.78	0.20	12.47	0.14	36.35	0.45	27.7	0.3	0.23	0.02	10.78	0.47	0.10	0.03	-	-	99.52
	glass	46	33.7	0.44	15.95	0.22	7.88	0.08	0.25	0.03	22.2	0.2	0.27	0.03	8.79	0.12	9.49	0.15	0.45	0.08	98.94
	olv	12	38.1	0.40	0.36	0.41	0.11	0.05	0.17	0.03	23.8	0.4	0.24	0.03	36.93	0.37	0.28	0.02	-	-	99.99
	opx	12	51.4	0.61	1.33	0.12	4.22	0.47	0.85	0.10	14.7	0.2	0.20	0.02	25.63	0.60	2.19	0.09	0.06	0.02	100.65
	ilm	10	0.1	0.02	53.96	0.41	1.30	0.03	3.44	0.12	31.7	0.5	0.23	0.02	9.26	0.30	0.12	0.03	-	-	100.12
	sp	4	0.2	0.03	15.44	0.10	15.88	0.39	22.60	0.12	35.0	0.1	0.23	0.02	10.33	0.33	0.14	0.05	-	-	99.76

* n=number of probe analyses. ★ columns directly following the oxide wt% are 1- σ errors from replicate analyses.

Table 2.5: EMP analyses of Al7O experiments in oxide weight percents

Run	Phase	n	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	Total										
D176	glass	15	39.3	0.18	10.39	0.17	6.48	0.05	0.61	0.05	20.2	0.3	0.28	0.03	14.15	0.20	8.38	0.13	0.32	0.10	100.11	
	olv	10	39.2	0.14	0.17	0.02	0.10	0.01	0.30	0.02	17.3	0.3	0.19	0.02	42.97	0.30	0.27	0.02	-	-	100.46	
D187	opx	10	54.1	0.31	0.89	0.08	2.75	0.27	0.51	0.03	12.1	0.2	0.19	0.03	28.28	0.30	2.08	0.03	0.09	0.05	101.01	
	glass	15	32.1	0.25	16.75	0.28	5.47	0.07	0.53	0.04	26.9	0.4	0.30	0.02	10.02	0.14	7.65	0.16	0.33	0.07	100.08	
D190	olv	9	37.5	0.30	0.25	0.03	0.17	0.15	0.27	0.02	24.4	0.6	0.24	0.03	36.62	0.35	0.34	0.04	-	-	99.89	
	cpx	15	51.5	0.30	1.38	0.07	3.52	0.18	0.53	0.03	14.0	0.4	0.24	0.02	20.09	0.51	8.75	0.76	0.22	0.05	100.20	
	gnt	11	38.8	1.15	3.52	0.58	19.28	0.69	1.78	0.59	15.9	0.6	0.35	0.02	12.43	0.98	7.21	0.58	0.09	0.04	99.37	
	glass	15	36.7	0.19	11.52	0.17	6.75	0.09	0.66	0.03	23.4	0.3	0.26	0.04	12.04	0.16	8.41	0.12	0.38	0.08	100.23	
C408	olv	10	38.4	0.19	0.17	0.02	0.13	0.01	0.32	0.01	20.9	0.3	0.26	0.02	39.53	0.17	0.32	0.01	-	-	100.00	
	opx	7	53.1	0.51	0.89	0.11	3.16	0.39	0.60	0.05	13.9	0.3	0.21	0.01	26.53	0.26	2.39	0.10	0.11	0.03	100.90	
	cpx	14	52.5	0.20	1.05	0.07	3.46	0.17	0.63	0.02	13.4	0.4	0.25	0.03	23.21	0.49	6.20	0.42	0.20	0.04	100.89	
	glass	14	36.1	0.18	8.36	0.12	5.42	0.09	0.56	0.02	29.1	0.2	0.25	0.02	13.57	0.17	6.96	0.14	0.27	0.11	100.69	
D195	olv	5	37.9	0.43	0.12	0.03	0.11	0.02	0.28	0.03	23.2	0.6	0.21	0.02	38.28	0.51	0.32	0.02	-	-	100.45	
	glass	15	39.3	0.17	8.85	0.15	5.84	0.05	0.61	0.03	21.7	0.2	0.31	0.02	15.47	0.16	7.28	0.14	0.22	0.09	99.55	
	D198	glass	28	37.4	0.33	10.74	0.33	6.64	0.12	0.64	0.05	23.0	0.40	0.30	0.02	12.66	0.19	8.65	0.15	0.25	0.07	100.24
		olv	12	38.0	0.26	0.23	0.02	0.13	0.01	0.34	0.02	20.8	0.2	0.21	0.03	40.61	0.32	0.33	0.01	-	-	100.63
D199	opx	12	53.4	0.48	0.71	0.14	2.97	0.48	0.35	0.04	13.5	0.4	0.14	0.02	26.74	0.36	2.31	0.15	0.07	0.03	100.13	
	cpx	15	53.0	0.47	0.98	0.08	3.14	0.21	0.54	0.02	13.0	0.7	0.21	0.03	24.24	0.73	5.57	0.94	0.13	0.03	100.86	
	glass	13	39.0	0.16	9.57	0.19	6.11	0.10	0.67	0.03	22.6	0.3	0.29	0.03	14.34	0.17	8.14	0.05	0.19	0.03	100.89	
	olv	8	38.9	0.45	0.21	0.02	0.15	0.03	0.33	0.03	19.2	0.4	0.19	0.02	41.47	0.38	0.29	0.02	-	-	100.77	
B1050	opx	12	54.4	0.47	0.70	0.11	2.65	0.43	0.29	0.03	12.0	0.2	0.14	0.02	28.37	0.42	1.99	0.05	0.06	0.02	100.61	
	glass	5	38.8	0.31	9.65	0.40	6.29	0.23	0.66	0.08	22.7	0.5	0.25	0.03	12.43	0.25	7.86	0.26	0.27	0.14	98.86	
C363	olv	5	38.4	0.28	0.11	0.06	0.07	0.01	0.29	0.03	20.5	0.7	0.23	0.04	40.60	0.58	0.24	0.04	-	-	100.44	
	glass	27	37.1	0.38	11.27	0.23	7.11	0.10	0.42	0.04	23.8	0.3	0.28	0.03	9.89	0.31	9.25	0.12	0.42	0.07	99.54	
	olv	12	37.3	0.29	0.20	0.05	0.08	0.01	0.20	0.02	24.5	0.2	0.27	0.03	36.69	0.41	0.34	0.02	-	-	99.57	

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Table 2.5 – Continued

Run	Phase	n	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	Total								
C364	opx	14	52.8	0.76	0.12	2.88	0.69	1.01	0.18	14.8	0.2	0.22	0.02	25.70	0.41	2.20	0.13	0.01	0.02	100.59
	sp	4	0.2	0.02	10.55	0.12	14.70	0.31	31.46	0.39	31.1	0.5	0.27	0.04	9.55	0.33	0.10	0.04	-	97.92
	glass	14	37.8	0.44	11.20	0.68	7.39	0.17	0.34	0.07	23.1	0.5	0.26	0.06	10.02	0.29	9.00	0.22	0.39	99.47
	olv	13	37.6	0.56	0.13	0.04	0.08	0.03	0.23	0.05	24.0	0.7	0.22	0.03	37.01	0.83	0.27	0.03	-	99.62
C365	opx	10	52.8	0.57	0.90	0.08	2.67	0.46	0.92	0.13	14.5	0.3	0.19	0.02	25.82	0.47	1.92	0.11	0.01	99.75
	sp	2	0.5	0.36	9.85	0.05	12.74	0.28	34.2	0.11	31.9	0.1	0.34	0.02	9.79	0.62	0.12	0.02	-	99.51
	glass	11	37.7	0.44	11.20	0.44	7.29	0.16	0.32	0.04	23.0	0.3	0.25	0.02	9.81	0.55	9.04	0.21	0.39	99.08
	olv	11	37.9	0.32	0.21	0.05	0.09	0.01	0.22	0.04	24.5	0.4	0.21	0.02	35.73	0.49	0.32	0.02	-	99.19
C366	opx	12	52.3	0.46	1.03	0.06	3.08	0.32	0.98	0.09	14.7	0.2	0.17	0.02	25.34	0.30	2.01	0.14	0.01	99.58
	sp	3	0.3	0.16	11.09	0.18	13.02	0.13	31.3	0.16	33.0	0.2	0.27	0.02	9.51	0.06	0.21	0.03	-	98.77
	glass	13	38.9	0.22	9.68	0.21	6.73	0.07	0.60	0.05	22.5	0.2	0.24	0.03	11.91	0.12	7.93	0.12	0.58	99.05
	olv	11	38.1	0.26	0.15	0.02	0.09	0.01	0.35	0.02	21.8	0.1	0.18	0.03	38.37	0.25	0.26	0.01	0.01	99.33
C367	sp																			
	glass	18	40.3	0.85	9.47	0.53	6.85	0.13	0.66	0.15	21.4	1.2	0.26	0.03	13.42	0.59	8.11	0.33	0.29	100.79
	olv	11	38.1	0.27	0.10	0.03	0.08	0.01	0.30	0.02	21.5	0.3	0.17	0.03	38.66	0.24	0.24	0.01	-	99.13
	sp	8	0.2	0.06	7.63	0.35	11.95	0.61	40.51	0.77	27.3	0.9	0.29	0.06	10.64	0.77	0.08	0.04	-	98.85
C368	glass	13	39.0	0.24	9.65	0.19	6.70	0.05	0.56	0.05	22.5	0.3	0.25	0.03	12.12	0.23	7.88	0.17	0.36	99.05
	olv	10	38.4	0.34	0.10	0.01	0.07	0.01	0.30	0.01	21.1	0.2	0.18	0.02	38.93	0.49	0.23	0.01	-	99.32
	sp	7	0.2	0.01	7.79	0.05	11.86	0.30	41.44	0.24	27.2	0.3	0.27	0.02	9.85	0.17	0.11	0.02	-	99.06
	glass	2	38.7	0.39	9.70	0.05	6.43	0.04	0.72	0.10	22.4	0.3	0.25	0.03	12.11	0.08	8.02	0.12	0.34	98.65
C370	olv	4	38.5	0.53	0.11	0.02	0.07	0.01	0.28	0.01	21.5	0.6	0.19	0.03	39.36	0.21	0.24	0.02	-	100.29
	opx	4	53.4	0.43	0.79	0.03	2.65	0.25	1.16	0.04	13.4	0.3	0.15	0.02	27.49	0.29	1.69	0.14	0.00	100.73
	sp	4	0.2	0.03	7.63	0.14	12.63	0.42	39.95	0.69	27.8	0.4	0.24	0.02	10.65	0.24	0.04	0.03	-	99.19
	glass	16	38.0	0.29	10.01	0.20	6.70	0.07	0.70	0.05	23.3	0.2	0.28	0.03	11.95	0.21	8.42	0.13	0.45	99.80
C371	olv	15	38.0	0.33	0.11	0.03	0.08	0.01	0.32	0.02	22.1	0.3	0.21	0.02	39.26	0.36	0.26	0.01	-	100.30
	opx	14	53.4	0.58	0.76	0.10	2.64	0.41	1.13	0.14	13.4	0.2	0.20	0.03	27.23	0.56	1.83	0.05	0.06	100.60

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Table 2.5 – Continued

Run	Phase	n	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	Total									
C373	glass	19	36.2	0.36	11.07	0.19	6.88	0.10	0.63	0.05	24.8	0.5	0.30	0.04	10.28	0.61	9.12	0.17	0.40	0.10	99.67
	olv	13	37.4	0.20	0.16	0.03	0.10	0.02	0.28	0.02	23.8	0.3	0.22	0.02	38.57	0.38	0.34	0.02	-	-	100.80
	opx	12	52.6	0.35	0.89	0.03	3.52	0.11	1.18	0.05	14.2	0.2	0.21	0.02	26.25	0.20	2.19	0.15	0.05	0.02	101.10
	sp	7	0.3	0.02	8.64	0.11	17.51	0.61	33.29	0.37	28.4	0.5	0.20	0.05	10.77	0.35	0.13	0.05	-	-	99.24
C376	glass	10	36.9	0.33	9.91	0.25	6.59	0.07	0.63	0.04	23.9	0.5	0.28	0.03	12.10	0.18	8.42	0.10	0.56	0.06	99.32
	olv	16	37.9	0.14	0.12	0.02	0.10	0.01	0.31	0.01	22.2	0.5	0.23	0.03	38.97	0.45	0.28	0.01	-	-	100.08
C380	opx	14	53.2	0.43	0.71	0.04	2.80	0.23	1.03	0.06	13.4	0.3	0.20	0.02	27.28	0.27	1.84	0.04	0.03	0.02	100.49
	glass	43	39.3	0.59	9.47	0.24	6.23	0.10	0.74	0.11	22.1	0.88	0.27	0.03	14.54	0.65	7.80	0.25	0.18	0.06	100.61
C381	olv	10	38.9	0.25	0.09	0.02	0.10	0.02	0.31	0.01	20.1	0.2	0.20	0.04	39.88	0.20	0.24	0.01	-	-	99.87
	glass	16	39.0	0.44	9.67	0.22	6.33	0.10	0.71	0.07	22.0	0.66	0.29	0.02	13.91	0.37	8.18	0.26	0.24	0.07	100.28
C382	olv	10	38.3	0.17	0.10	0.03	0.09	0.01	0.34	0.02	20.3	0.2	0.20	0.02	39.81	0.25	0.26	0.02	-	-	99.45
	glass	11	38.7	0.25	9.68	0.24	6.48	0.04	0.64	0.05	22.3	0.3	0.30	0.03	12.47	0.44	8.05	0.11	0.50	0.15	99.16
C388	olv	10	38.2	0.30	0.11	0.02	0.09	0.01	0.35	0.01	21.3	0.2	0.20	0.03	39.39	0.37	0.25	0.01	-	-	99.94
	glass	16	38.4	0.22	9.63	0.19	6.18	0.10	0.68	0.03	22.9	0.3	0.31	0.03	13.20	0.18	7.93	0.16	0.42	0.07	99.75
C389	olv	4	39.2	0.16	0.13	0.02	0.07	0.01	0.34	0.01	19.8	0.5	0.22	0.02	40.76	0.23	0.27	0.01	-	-	100.87
	opx	5	54.3	0.60	0.61	0.12	2.27	0.52	0.85	0.14	12.3	0.1	0.17	0.02	28.15	0.37	1.75	0.03	0.14	0.05	100.55
C389	glass	13	39.0	0.50	8.97	0.14	6.18	0.07	0.71	0.05	22.1	0.5	0.27	0.03	13.69	0.36	8.12	0.15	0.40	0.14	99.38
	olv	14	38.3	0.23	0.10	0.03	0.09	0.01	0.31	0.01	19.8	0.3	0.18	0.03	41.17	0.28	0.26	0.02	-	-	100.18
C395	glass	12	38.7	0.60	9.47	0.25	6.21	0.13	0.73	0.08	22.5	0.9	0.28	0.04	14.80	0.45	8.14	0.33	0.13	0.08	100.99
	olv	15	38.4	0.28	0.10	0.03	0.09	0.01	0.29	0.02	19.9	0.3	0.18	0.02	41.18	0.42	0.26	0.01	-	-	100.32
C396	opx	11	53.8	0.40	0.61	0.07	2.52	0.29	0.87	0.09	12.3	0.3	0.16	0.04	28.51	0.47	1.74	0.04	0.03	0.02	100.55
	glass	19	39.9	1.10	8.79	0.61	6.51	0.16	0.81	0.09	21.2	1.3	0.29	0.03	15.19	0.80	7.77	0.26	0.29	0.09	100.83
C397	olv	12	38.3	0.50	0.11	0.02	0.11	0.02	0.30	0.01	20.1	0.2	0.21	0.02	40.56	0.59	0.26	0.01	-	-	99.96
	opx	10	54.4	0.49	0.63	0.06	2.73	0.26	0.88	0.08	12.3	0.2	0.18	0.03	28.10	0.38	1.67	0.16	0.03	0.01	100.92
C397	glass	16	38.5	0.18	8.55	0.17	5.71	0.05	0.68	0.04	23.1	0.2	0.25	0.03	15.41	0.16	7.40	0.13	0.23	0.07	99.86
	glass	17	38.8	0.80	8.95	0.32	5.89	0.14	0.72	0.08	22.0	1.0	0.25	0.02	16.12	1.11	7.43	0.37	0.34	0.43	100.65

Figure 2-1: Compositional variations between the ultramafic glass suites and the high-Ti basalts of Apollo 11 and 17

Figure 2-2: Images of experimental results

Figure 2-3: Phase diagrams for the A15R

Figure 2-4: Phase diagrams for the A170

Figure 2-5: Summary of multiply saturated ultramafic liquids

Figure 2-7: Ti effect on Fe-Mg partitioning in olivine

Figure 2-8: Projection scheme for high-Ti liquids

Figure 2-9: Projection of high-Ti liquids onto plag-cpx-oliv-quartz plane

Figure 2-10: Density crossovers in the lunar mantle

Chapter 3

Constraints on lake volume required for hydro-fracture through thick ice sheets

3.1 Introduction

During the summer much of the ablation zone of the Greenland Ice Sheet is covered with supraglacial melt water lakes. These lakes are controlled by bedrock topography and thus form in the same position from year to year, filling gradually during the melt season from June-August before in some cases draining rapidly in the late summer [Box and Ski, 2007]. This type of drainage has also been seen in smaller cold-temperate glaciers [Boon and Sharp, 2003]. Das et al. [2008] observed a 3-fold increase in the background flow rate of the Greenland Ice Sheet coinciding with the rapid (~ 2 hr) drainage of a large (2.7 km average diameter) supraglacial lake near Jakobshavn Isbrae in the summer of 2006. This drainage event was also characterized by rapid ice sheet uplift and elevated seismicity providing strong evidence that in this location surface melt water reached the base of the ice sheet by a hydro-fracture process. It remains unclear, however, whether hydro-fracture occurs beneath only the largest lakes and what fraction of the water contained in supraglacial lakes is

transported to the base of the ice sheet. Thus, constraints on dynamic advection of water from the surface to the bed and the subsequent impact on ice flow will be critical for climatologists to incorporate into models of the future behavior of ice sheets and accompanying changes in global sea level [Intergovernmental Panel on Climate Change, 2007].

The goal of this study is to determine the extent to which supraglacial lakes supply water to the base of thick, cold ice sheets via the propagation of water-filled cracks. The problem of crevasse propagation was originally outlined in a series of classic papers by Weertman [1971a,b, 1973, 1996] in which he showed that due to the density contrast between ice and water, a water-filled crack will always continue to propagate until it reaches the base of an ice sheet. If a crack remains water-filled during its evolution, which is likely the case for cracks formed under supraglacial lakes, the propagation depth is limited only by the volume of water available to fill the crack (Figure 3-1). Thus, determination of crack opening widths is of utmost importance in determining whether a supraglacial lake contains a sufficient volume of water to keep the crack water-filled until it reaches the bed. Here we adopt the Weertman dislocation-based fracture mechanics model for the crevassing of ice, and quantify the evolution of the crack shape. By doing so, we constrain the volume of water necessary to keep fractures water-filled and thus hydraulically drive them to depths corresponding to the thickness of the Greenland Ice Sheet under the ablation region. Because supraglacial lakes have finite volumes, calculating the crack opening geometry is a key improvement over previous studies that simply assumed an *a priori* crack width (e.g., Alley et al. [2005], van der Veen [2007]).

3.2 Model for water-filled fracture geometry

3.2.1 Numerical approach

We model water-filled crack propagation in a 2-D ice sheet with an elastic half-space model geometry (Figure 3-1, inset). For an edge crack to propagate in a solid medium,

the stress intensity at the crack tip must exceed the fracture toughness of the material. The maximum depth of propagation will depend on the deviatoric (longitudinal) stress, the hydrostatic pressure of the ice, the amount of water filling the crack, and the finite thickness of the ice sheet. Using the propagation depth determined above, we calculate the opening displacement as the integral of the dislocation density over the length of the crack, which is proportional to the depth of crack penetration [Weertman, 1971a, 1996].

The first question we address when discussing supraglacial lake drainage is whether there are favorable conditions for deep crack formation. We use the stress intensity factor at the crack tip to determine whether critical crack propagation will occur for a given set of parameters, and calculate the equilibrium crack depth if there is propagation. The stress intensity factor, K_{tot} , at the tip of the crack is a linear combination of the individual stress intensities for the longitudinal stress (T), hydrostatic pressure of overlying ice (I , overburden), and the pressure of water filling the crack (W):

$$K_{tot} = K_T + K_I + K_W \quad (3.1)$$

where the terms on the right hand side of the equation are expressed as:

$$K_{T,I,W} = \sigma_{T,I,W} \sqrt{\pi z} F\left(\frac{z}{H}\right) \quad (3.2)$$

thus K_{tot} is a function of the deviatoric (longitudinal) stress σ_T (assumed to be independent of z), the ice overburden pressure $\sigma_I = -\rho_i g z$, as well as the added stress of the water filling a crack $\sigma_W = \rho_w g [z - d_w]$. Here, z is the crack depth, ρ is density, d_w is the depth to the top of the water in the crack, and F is a polynomial function added to account for the finite thickness of the ice sheet, H [Kenneally, PhD thesis, 2003]. When K_{tot} is greater than the fracture toughness of ice, the crack will propagate. For simplicity we use a single value for the fracture toughness of ice, 0.1 MPa [Hooke, 2005], which strictly speaking is a function of temperature. However, we feel this is a reasonable approximation, as the fracture toughness within the bulk of the ice sheet will not greatly vary.

Because of the dependence of Equation (3.2) on z , critical crack propagation requires an initial (small) crack to be present in order for K_{tot} to exceed the fracture toughness. We have calculated the depth an initial crack must reach before it starts to critically propagate for the water-filled condition as a function of the differential stress which varies widely in the ice sheet from tensile to compressive. We find this initial depth is typically <1 m, but even under cases of neutral differential stress, or slight compression, initial cracks of only 4-7 m are necessary (Figure 3-2). This initial flaw length is frequently observed in many regions of the Greenland ice sheet in the form of dry crevasses. These dry crevasses may be created far from supraglacial lakes in areas of overall tension, and later serve as the initial cracks needed for water-filled critical propagation once advected by ice sheet flow into the lake basin.

The depth of a crack can then be determined as a function of the fracture toughness, water content, and the longitudinal stress. This crack length is unbounded in the case of water-filled cracks because K_W and K_I are of opposite signs, and K_W is always greater than K_I (Figure 3-3). The depth of the crack tip (z) is then used to calculate the opening geometry of an edge crack, D , after Weertman (1996):

$$\begin{aligned}
D(y) = & \frac{2\alpha\sigma}{\mu} \sqrt{z^2 - y^2} + \frac{2\alpha\rho_i g}{\pi\mu} \sqrt{z^2 - d_w^2} \sqrt{z^2 - y^2} \\
& - 2\alpha\rho_i g \frac{y^2}{2\pi\mu} \ln \left(\frac{z + \sqrt{z^2 - y^2}}{z - \sqrt{z^2 - y^2}} \right) + 2\alpha\rho_w g \frac{y^2 - d_w^2}{2\pi\mu} \ln \left| \frac{\sqrt{z^2 - d_w^2} + \sqrt{z^2 - y^2}}{\sqrt{z^2 - d_w^2} - \sqrt{z^2 - y^2}} \right| \\
& - 2\alpha\rho_w g \frac{d_w y}{\pi\mu} \ln \left| \frac{d_w \sqrt{z^2 - y^2} + y \sqrt{z^2 - d_w^2}}{d_w \sqrt{z^2 - y^2} - y \sqrt{z^2 - d_w^2}} \right| + 2\alpha\rho_w g \frac{d_w^2}{\pi\mu} \ln \left| \frac{\sqrt{z^2 - y^2} + \sqrt{z^2 - d_w^2}}{\sqrt{z^2 - y^2} - \sqrt{z^2 - d_w^2}} \right|
\end{aligned} \tag{3.3}$$

where stress, σ , is expressed as:

$$\sigma = \sigma_T - \frac{2\rho_i g z}{\pi} - \rho_w g d_w + \frac{2\rho_w g d_w}{\pi} \arcsin \left(\frac{d_w}{z} \right) + \frac{2\rho_w g}{\pi} \sqrt{z^2 - d_w^2} \tag{3.4}$$

The derivation of these equations is outlined in Weertman (1973) and Weertman (1996). $D(y)$ is the displacement of one side of the crack with respect to the center line as a function of the depth, y . α is $(1-\nu)$, where ν is Poisson's ratio and a value

of 0.3 is used for ice. The depth to the top of the water in the crack as measured from the surface (d_w) can be varied, and $d_w=0$ for water filled cracks. The shear modulus for ice (μ) has been found to vary based on loading rates, grain size, and temperature, all of which are not constrained by our model. We use 3 different values across the known range for the shear moduli (3.9, 1.5, and 0.32 GPa) to determine the sensitivity in our model to this variable [Vaughan, 1995] (Fig 3-1, 3-4). The density of water (ρ_w) and ice (ρ_i) are 1000 and 920 kg/m³, respectively. g is the gravitational constant, 9.78 m/s². We ignore uncompacted snow or firn at the surface of the ice sheet as it is likely a negligible component for the lake bottom environment in the Greenland ablation zone. Two example calculations are shown in Figure 3-5, one for the dry case ($z = d_w$) and one for a completely water filled case ($d_w = 0$).

Using this approach we investigate the influences of longitudinal stress, ice sheet thickness, and the amount of water filling the crack on the predicted crack geometry. The cross-sectional area of a crack can then be determined by numerically integrating Equation 3.3, the opening geometry over the depth of the crack, and extended in the third dimension to obtain a volume. We note that the cracks described here form on time scales (hours) short enough to ignore the viscous flow of ice, and are thus modeled as a purely elastic phenomenon.

3.2.2 Calculating lake drainage times

Because the general shape of a water-filled crack does not vary significantly with depth, we approximated it as a channel with parallel sides in the calculations of lake drainage time. The mean opening of the crack is used for this calculation, and is determined by dividing twice the integral of D from 0 to z by z . Water flow through the crack systems is calculated to be turbulent, with a Reynolds number on the order of $\sim 10^6$. Using the average crack opening, we then estimate the flux of water through the ice sheet assuming turbulent flow for end member cases of channel and pipe flow [White, 1974] (Fig 3-6). Pipe flow is used to simulate a moulin, which is a possible drainage mechanism for supraglacial lakes. The moulin drainage (pipe flow) represents a volume per time calculation, while the calculation for a crack drainage

(channel flow) is a 2-D flux. The channel flow always produces higher fluxes, due to the pipe having greater frictional forces. The turbulent flux through the pipe is calculated using the method of White (1974). We include the case for pipe flow because the initial planar crack is not infinite in its horizontal extent, and likely localizes to one or more discrete moulins with time during and following lake drainage [Das et al., 2008], similar to the evolution in vent geometry observed for volcanic fissure eruptions [Bruce and Huppert, 1990].

Using the flux, the drainage time can be calculated for any lake of a known volume. We calculate drainage time for a lake with a conduit established by hydro-fracture as a function of lake size and conduit geometry (Figure 3-7). Because the most easily observable characteristic of supraglacial lakes is their surface area and not their volume, we relate the mean lake surface diameter to its volume assuming a simple conical lake geometry and a diameter:depth ratio of 100:1. This approximation is consistent with surface slopes and depth-to-diameter relationships observed in 2 lakes south of Jakobshavn Isbrae [Das et al., 2008] and yields depths up to tens of meters for lakes with diameters >1 km, consistent with lake depths reported by previous studies in Greenland [Box and Ski, 2007, Sneed and Hamilton, 2007, Echelmeyer et al., 1991, McMillan et al., 2007].

We used daily MODIS images collected throughout the 2006 melt season to determine the maximum summer lake surface area extent of 1300 lakes across our study area. Lake boundaries were determined by thresholding the ratio of the blue to the other visible channels. Lake locations were tracked through time and transient features were discarded (e.g. single-day false detections caused by clouds). Daily lake extent was then tabulated for each lake throughout each summer allowing us to determine the maximum lake surface area.

3.2.3 Field observations supporting our model

Field observations of crevasse opening widths at depth are difficult to make because most crevasses visible on the surface have been modified by melt-back, calving, plastic flow of ice, and/or ‘healed’ by water refreezing within the crack. Although it is im-

possible to measure the shape and depth of crevasses at significant depth in the field, observations that have been made do support the validity of the Weertman model for opening geometry, as well as our calculations of the crack volume and our conclusions about modeling lake drainage through channel flow [M.D. Behn, pers comm]. Areas of the ice sheet that had previously been submerged beneath a supraglacial lake display a distinctive ‘egg-carton’ like appearance on the surface, due to the melting processes that occur at the lake bottom. Many crevasses that are now frozen closed (healed) running across the ice sheet through areas displaying these egg-carton textures have been observed (Fig 3-8), indicating that they were once at the bottom of a lake. It is easy to see these crevasses because the ice filling them has a distinctly bluer color than surrounding lake bottom material. It is common for these crevasses to be longer than 1 km in their horizontal dimension, and they maintain a constant opening width across their entire length. Healed crevasses also typically have one or more sets of thin lines of bubbles indicating that they re-froze from the outside in (Fig 3-8).

Ice canyons, which are erosional features formed from surface meltwater flow, can be tens of meters deep, and provide 3-D observations of these healed crevasses (Figure 3-9). In these cases we see that the dilation of the crevasses remains remarkably constant in the vertical as well as horizontal dimension, consistent with a model in which the crack was water filled during its formation (Figure 3-5). The ‘healing’ process for these crevasses is ideal to study them, because it prevents the crevasse from being distorted by viscous flow and deformation processes, and ‘fossilizes’ the shape the crevasse has when it initially forms (i.e. parallel sides, constant opening width, etc.).

In our model we only consider the simplest case of an isolated crack; however since a water-filled crevasse can propagate without longitudinal tension, reduction of longitudinal stress by the blocking effect of neighboring crevasses is not as important for water-filled cracks as it is for dry ones [Nye, 1955].

3.3 Model results

For a dry crack, the increase in overburden stress with depth will eventually cause the stress intensity at the crack tip to decrease below the fracture toughness and prevent further propagation of the crack (Figure 3-3). When considering longitudinal stresses within the range observed in nature (0-0.5 MPa) dry cracks will only reach depths of order 10 m, consistent with field observations. However as has been shown by previous studies (e.g., Weertman [1971a], Alley et al. [2005], van der Veen [2007]), if a crack remains water-filled, the density of the water will offset the overburden stress and allow for continued propagation.

Our calculations show that typical opening widths vary between hundreds of microns for short cracks (<10 m; consistent with Kenneally and Hughes [2006]), up to 1–2 meters for either very deep cracks (>1500 m) or high longitudinal tensile stress gradients. In contrast to dry cracks which have ‘V’ shaped cross-sections, water-filled cracks are ‘U’ shaped with little variation in opening width for most of their depth (Fig 3-5). Intriguingly, we find that for any fixed volume of water, water-filled cracks are predicted to propagate the deepest in regions with less tension (or even slight *compression*) because thinner cracks require less water to remain filled. Because supraglacial melt-water lakes often form in compressive stress regimes due to the concave topography of the lake basin, this surface geometry would facilitate the propagation of deep cracks that can fully drain a lake.

Channel flow along a crack with a surface length equal to the lake diameter (as observed in the field) produces drainage times of 2-5 hours for lake diameters of 0.1–3 km (Figure 3-7). This is consistent with the supraglacial drainage time observed by Das et al. [2008] near Jakobshavn Isbrae. As discussed by Alley et al. [2005], the refreezing time of a 10 cm crevasse (the minimum width required to propagate through a 1 km thick ice sheet) in -20°C isothermal ice is 3–10 times slower than the predicted drainage times (Figure 3-7), implying that it is unlikely a water-filled crack will ‘heal’ before lake drainage is complete.

Drainage times calculated for a single moulin assuming pipe flow are significantly

longer than for channel flow along a crack. For example, a moulin with a 1 m diameter would take >100 hr to drain a 2 km diameter lake, while a ~ 0.5 m crack would drain the same lake in about 1.2 hrs. Moreover, to drain a 2 km lake through a moulin in 2 hours, similar to the time-scale of lake drainage observed by Das et al. [2008], would require a ~ 7.5 m diameter pipe. Our field observations suggest that the majority of rapid drainage events occur through long cracks with localization of meltwater flow into discrete moulins occurring only late in the drainage event after flow rates slow [Das et al., 2008].

It should also be noted that Fountain et al. [2005] have shown that in some small temperate alpine glaciers the hydrological system can be dominated by fractures that convey water at slow speed englacially, rather than through a direct surface-to-bed connection. While our model results can not entirely rule out this possibility, the ice sheet conditions encountered beneath most supraglacial lakes (sub-freezing englacial temperatures and high overburden stress) are substantially different than those found in the thin, temperate glaciers, and would argue against the formation and persistence of englacial conduits. Surface observations during a lake drainage event also suggest a direct surface-to-bed connection [Das et al., 2008].

3.4 Implications for supraglacial lake drainage

As discussed above, the opening geometry of a crack is controlled by the depth of propagation, while the propagation depth is limited by the available volume of water. Because the crack must remain nearly completely water-filled to reach the base of thick ice sheets (Figure 3-3), we use the crack volume to constrain the minimum water volume that must be contained in a supraglacial lake in order for it to be capable of driving a hydro-fracture to the base of the ice sheet. To apply our model results to natural settings, we calculate the minimum lake size required to drive water-filled cracks to the base of an ice sheet of given thickness (Figure 3-4). If a crack is positioned underneath a supraglacial lake and is to remain water-filled throughout its propagation, then the cross sectional area of the lake must be at least equal to the

cross-sectional area of the crack. There is a simple geometric relationship between the area of the crack and the minimum mean lake diameter necessary to keep the crack water-filled assuming our conical geometer and 100:1 diameter to depth ratio:

$$\text{lake diameter} \geq \sqrt{400A} \quad (3.5)$$

Where A is the cross-sectional area of a crack, which can be calculated by integrating Equation (3.3) over the entire length of the crack and multiplying it by two, to account for both sides of the crack. Using the above equation a minimum lake size can be estimated for a given ice sheet thickness (Figure 3-4).

The total flux of water from supraglacial lakes to the ice sheet bed in a specific area can then be determined by summing the volume of all lakes larger than this minimum size, as discussed above. There are more sophisticated methods for measuring supraglacial lake volume, and there is a growing database available for seasonal lake volumes [Sneed and Hamilton, 2007, Box and Ski, 2007, Das et al., 2008], which can be incorporated into future modeling studies to improve accuracy.

For this study we analyzed the maximum extent of supraglacial lakes that formed along a 500 km North-South stretch of the West Greenland Ice Sheet centered near Jakobshaven Isbrae between June-August 2006 (Figure 3-10a). The ice thickness in this region is ~ 1 km and we assume zero longitudinal stress. Under these conditions a water-filled crack will have a cross-sectional area of $\sim 750 \text{ m}^2$, implying that lakes with mean surface diameters of $> 250\text{-}800$ m (depending on the shear modulus used, Fig 3-4) will deliver water to the bed. Lakes as small as 250 m can be hard to detect remotely due to the coarse resolution of the MODIS data used in this study (see auxiliary material), so to account for the volume of water held in small lakes we fit an exponential function of the form $y = y_o \exp(bx)$ to the size-frequency distribution of supraglacial lakes observed in this region in 2006 (Figure 3-10b). By integrating this function from the minimum lake size calculated to deliver water to the bed (~ 500 m), to the maximum lake size observed (3.3 km) we can obtain a volume of water held in lakes that are big enough to drive cracks through the ice sheet. The total volume of

melt water held in lakes large enough to drain is 5.7 km^3 which represents $\sim 98\%$ of all the melt water held in supraglacial lakes in the study area. There is considerable uncertainty in this estimate because our model does not allow us to predict which lakes will drain in a given year. If a majority of the lakes drain, however, the annual flux of water to the ice sheet bed could even be larger than we calculate because once a lake has drained moulins typically remain open along the crack for the remainder of the melting season facilitating further drainage [Das et al., 2008]. Our estimates are consistent with other independent estimates of melt water drained from the surface in this area of the Greenland Ice Sheet [McMillan et al., 2007]

3.5 Conclusions

Our calculations show that lakes that are only $\sim 250\text{-}800 \text{ m}$ across and $2\text{-}5 \text{ m}$ deep contain a sufficient volume of water to drive a water-filled crack to the base of a 1 km -thick ice sheet. Lakes that are smaller may also be drained, however it requires fractures that are fed by multiple basins. This range in lake sizes represents the majority of supraglacial lakes in the ablation zone along the western margin of the Greenland Ice Sheet. Thus we propose that a large fraction of the melt water produced in the summer (on order of several cubic kilometers) could rapidly reach the base of the ice sheet via this mechanism.

Figure Captions

Figure 3-1: Mean opening width versus depth of a water-filled crack for varying longitudinal stresses. Mean openings are shown for 3 different shear moduli of ice (0.32 , 1.5 , and 3.9 GPa illustrated in darkening shades of grey). Each field is centered on the curve for a neutral stress regime, and shows the range of differential stresses from -0.1 MPa (compression) to 0.1 MPa (tension). Calculations assume a 100% water filled crack. Figure inset shows the variables and geometry considered for our model.

Figure 3-2: Crack length needed to support critical propagation as a function of the differential stress in the ice sheet. Cracks will propagate even in areas with overall compression as long as a long enough initial crack is provided, such as a dry crevasse.

Figure 3-3: Maximum propagation depth vs. water content. The lines represent longitudinal differential stress contours. For a given amount of water, a greater tensile stress will create a deeper crevasse. Note also that any crevasse that stays filled with water to at least $\sim 92\%$ will not have a maximum depth and will penetrate to the base of an ice sheet, as long as the far field stress is tensile or neutral.

Figure 3-4: Maximum propagation depth of a water-filled crack versus lake diameter. Stress and moduli contours are as in Figure 1. Thick black line shows ice thickness of 980 m in the western Greenland study area.

Figure 3-5: Calculation of opening geometries for 15 m crevasses, one dry and one water-filled. The overall tension is 0.1 MPa and the shear modulus is 1.5 GPa. The water-filled crevasse is much wider and keeps a more constant opening shape. Note the extreme horizontal exaggeration.

Figure 3-6: Mean flux of water through a channel or pipe versus the depth of the crevasse. As depth increases so does the width of the channel, and thus the flux as well. Flux through the channel is always greater than for a pipe, leading to faster drainage times. Curve labels are for longitudinal differential stress.

Figure 3-7: End member drainage times are calculated assuming pipe (moulin) and channel (crack) flow. Pipe flow curves are labeled with conduit diameter, and the channel flow curves are labeled by opening width (in meters). The time to refreeze a 10 cm crevasse is also shown (thick black line, Alley et al. 2005). All calculations assume zero differential stress. Star illustrates the drainage time of a 2.7 km diameter supraglacial lake observed by Das et al. [2008].

Figure 3-8: A healed crack in an area of ice that was once underneath a lake. This crack maintains an average width of 10 cm for over 100 m. In the middle of the healed crevasse is a line of bubbles, indicative of that the crevasse froze from the sides in. This crevasse is typical of many found in the field area. Photo courtesy of M.D. Behn.

Figure 3-9: An ice canyon allowing for a 3-D view of one of the healed crevasses. The canyon is ~ 20 m deep, and the crevasse shown by the arrows has a similar opening width at the top and bottom of the canyon. This 'U-shaped' geometry is consistent with the Weertman model for water filled cracks. Note the ~ 2 m scientists for scale. Photo courtesy of M.D. Behn.

Figure 3-10: (a) Satellite view of the supraglacial lakes on the West Greenland Ice Sheet near Jakobshaven Isbr during summer 2006. (b) Supraglacial lake size-frequency distribution binned in increments of 100 m diameter. The data are fit with an expression of the form $y = y_o \exp(bx)$, where $y_o = 707.2$ and $b = -2.03$. Filled circles show the data that were regressed, open circles show data for lakes that are too small to be reliably counted by the satellite resolution, or too large to be statistically meaningful. The shaded region shows the lakes that are too small to propagate a crack to the ice sheet bed. Based on this distribution, there are >1000 lakes that contain sufficient water to drive hydro-fractures to the ice bed.

Figure 3-1: Calculated crack depths and model parameters

Figure 3-2: Initial flaw required to exceed fracture toughness

Figure 3-3: Maximum crack depth as a function of water content

Figure 3-4: Lake size required for crack propagation

Figure 3-5: 2-D cross sections of calculated crack shapes

Figure 3-6: Water flux through a channel or pipe

Figure 3-7: Timescales to drain supraglacial lakes

Figure 3-8: Healed crevasse

Figure 3-9: Ice canyon showing deep cuts of crevasses

Figure 3-10: Distribution of supraglacial melt water lakes

Chapter 4

The fate of wet mantle melts: The role of H₂O and deep crust fractional crystallization

4.1 Introduction

This study examines the H₂O-saturated phase relations of two primitive arc magmas; a basaltic andesite (BA) and primitive magnesian andesite (PMA) from the Mt. Shasta region, CA. Each of these compositions represent examples of hydrous magmas in equilibrium with a mantle peridotite source at depth [Grove et al., 2003]. The H₂O saturated phase relations of the PMA have been determined over a range of crustal pressures (0.1-800 MPa) and oxygen fugacities from NNO to NNO+3. Previous studies have shown that the phase assemblages and compositions in hydrous systems, especially liquidus temperatures and appearance of amphibole, are highly dependent on water content [Holloway and Burnham, 1972, Anderson, 1980, Medard and Grove, 2008], f_{O_2} [Helz, 1973, 1976], and alkali content [Cawthorn and Ohara, 1976]. These studies agree that near liquidus crystallization of amphibole together with Ca-rich pyroxene (cpx) and olivine at 500-800 MPa can produce calc-alkaline liquids.

Previous experimental studies have focused on either tholeiitic basalts [Holloway and Burnham, 1972, Helz, 1973, Anderson, 1980], more evolved andesitic and dacitic magmas that compositionally match evolved eruptive products at large volcanic centers [Allen and Boettcher, 1983, Rutherford and Devine, 1988, Prouteau and Scaillet, 2003, Alonso-Perez et al., 2009], or primitive compositions with affinities to arcs but with experiments done over limited pressure ranges [Moore and Carmichael, 1998, Blatter and Carmichael, 1998, Pichavant and MacDonald, 2007]. These experimental studies along with studies of natural samples [Grove and Donnelly-Nolan, 1986, Romick et al., 1992, Davidson et al., 2007] have shown that amphibole crystallizes from a wide variety of liquids at crustal pressures and can be an important fractionating phase in arc systems. We extend these studies to the PMA and BA compositional systems and explore the effect of P_{H_2O} on amphibole composition. Amphibole composition is dependent on H_2O pressure because the pressure-temperature slope of the first appearance of amphibole in the crystallization sequence, over the pressure range explored here, is opposite in sign to the H_2O saturated liquidus. For a single bulk composition the molar ratio of $Mg/(Mg+Fe)$ with all Fe as Fe^{2+} (Mg#) of the first amphibole to crystallize changes dramatically over crustal relevant pressure ranges. We have calibrated this compositional variation for two lavas, report our results as a new amphibole Mg# geobarometer-hygrometer, and apply the barometer-hygrometer to amphibole antecrysts in lavas from Mt. Shasta, CA.

4.2 Experiments

4.2.1 Starting materials:

Experiments were conducted on two different bulk compositions. One is a primitive magnesian andesite, 85-41c, from the topographic saddle between the Whaleback and Deer Mountain, erupted as a cinder cone and associated lava flows, 18.5 km to the north-northeast of the Mt. Shasta summit [Baker et al., 1994]. This is the high-silica (57 wt% SiO_2), high-MgO (9 wt% MgO), high Mg# (0.75) end member of a suite

of primitive lavas from the Mt. Shasta region that have $Mg\#$'s >0.7 , and contains Fo_{94} olivine antecrysts [Baker et al., 1994, Grove et al., 2003, Ruscitto et al., 2010]. The second composition is a primitive basaltic andesite ($Mg\#=0.71$), 85-44, erupted from Cinder Cone, 11 km to the northwest of the Mt. Shasta summit [Baker et al., 1994, Grove et al., 2003, 2005]. This basaltic andesite is a low-silica (52 wt% SiO_2), high-MgO (10.5 wt% MgO) end member of the primitive lava suite that contains Fo_{90} equilibrium olivine. These lavas represent primitive inputs into the Mt. Shasta plumbing system and are both hydrous with pre-eruptive H_2O contents between 3 and 6 wt% H_2O [Anderson, 1974, Grove et al., 2003, Ruscitto et al., 2010].

Whole rock samples of these two compositions were ground in an Al_2O_3 shatter box and then reground under ethanol by hand in an agate mortar to create experimental starting materials. The ground powders were melted at $1700^\circ C$ in a Pt crucible in air for 2 hours, then quenched in the crucible by dropping it in water. The glass was extracted from the crucible and ground in an agate mortar. The ground glass was then remelted in air and quenched and crushed following the same procedures to ensure homogeneity. The compositions of the starting materials are reported in Table 4.1. Experiments were conducted on both the powdered rock and glass starting materials (Table 4.2).

4.2.2 Experimental Procedures:

Experiments at 200 and 800 MPa were carried out in the MIT experimental petrology lab in cold seal molybdenum-hafnium-carbide vessels and a 1/2" piston cylinder assembly respectively. The 500 MPa experiments were carried out at the Institut für Mineralogie, Hannover, Germany in internally heated pressure vessels. For H_2O saturated experiments, the presence of excess H_2O after the end of an experiment was used to assure the experiment remained H_2O saturated throughout the run.

For the 200 MPa and $915-1070^\circ C$ experiments the pressure medium was an argon-methane gas mixture in a ratio of 1000:11. Methane breaks down to $C+H_2$ at the conditions of the experiment, and the partial pressure of H_2 outside the capsule slows water loss and sample oxidation by hydrogen diffusion through the gold capsule. Ex-

periments were carried out in Au outer capsules and Au inner sample capsules (Table 4.2). A typical double capsule technique was used to control oxygen fugacity at the Nickel-Nickel Oxide (NNO) or Rhenium-Rhenium Oxide (RRO=NNO+2; Pownceby and O'Neill [1994]) buffer conditions with inner Pt capsules used to enclose the NNO buffer material and Au capsules for the RRO buffer material [Ulmer, 1971]. The outer capsule is welded at both ends, and inner capsules are welded at one end, but only crimped shut on the other to facilitate equilibration of the silicate charge through the fluid phase with the buffer assemblage. Experiments were quenched by inverting the pressure vessel and allowing the charge to drop to the water-cooled cold seal end of the pressure vessel.

In the 500 MPa and 945-1025°C experiments, pure argon gas, or an argon-H₂ mixture was the pressure medium. All of these experiments were conducted in Au capsules, some at H₂O saturated conditions and some with a mixed H₂O-CO₂ volatile component. Volatiles were added as free water and silver oxalate (Ag₂C₂O₄). Capsules for both the 200 and 500 MPa experiments were cooled with liquid N₂ and then welded shut and weighed pre and post welding to assure no water loss. Oxygen fugacity was controlled at NNO by adding small amounts of hydrogen gas to the vessel and the partial pressure of H₂ was measured directly using a hydrogen permeable Pt membrane. Experiments conducted at NNO+3 were done in pure Ar with no added H₂, utilizing an intrinsic f_{H_2} imposed by the H₂ permeable pressure vessel walls to buffer experiments at that level. The f_{O_2} of the oxidizing experiments was not specifically measured but the intrinsic internally heated pressure vessel f_{O_2} is known to vary between NNO+2.6 and NNO+3.5 [Schuessler et al., 2008] so we have assumed an average of NNO+3. A detailed experimental procedure for the Hannover internally heated pressure vessel laboratory is presented in Berndt et al. [2002]. Capsules of 85-41c rock powder and powdered glass starting material were run simultaneously on some experiments. Phase assemblages for these runs were identical for both starting materials, and the compositions were analyzed and compared (Table 4.3). In this way we were able to perform phase appearance reversals on 500 MPa experiments. Experiments were quenched using the rapid quench technique described in Berndt

et al. [2002], and quench rates are about 150 °C/s [Benne and Behrens, 2003].

Experiments at 800 MPa were carried out on the 1/2" piston cylinder apparatus at MIT [Boyd and England, 1960]. The capsule in this experimental design was an Au ‘trash-can’ [Ayers et al., 1992] in which an outer capsule is prepared with a small lip, and fitted with a lid that is cold welded by pressure. The lid seals when the piston load is applied to the capsule during pressurization before heating (Fig 4-1). The outer Au trash-can capsule is surrounded by an unfired-pyrophyllite ring. During compression the pyrophyllite ring deforms with the Au capsule and helps avoid any shear stresses from developing. Two smaller capsules are placed inside the trash can. Both inner capsules were welded at one end, and only crimped at the other. One is an Au capsule containing the sample, and the other is a Pt capsule containing the NNO solid state buffer. Starting material was the finely ground 85-41c rock powder. The experiments were carried out at H₂O-saturated conditions and free water was added to both the inner and outer Au capsule. The experiments were quenched by turning off the power. Experimental durations for all pressures were 7.4 to 26 hrs. Longer run times were not possible due to problems with Fe-loss to the Pt buffer capsule or H₂O loss from the trash can (Table 4.2).

4.2.3 Analytical Methods:

Experimental run products were analyzed by electron microprobe on the JEOL 733 Superprobe at MIT. Beam conditions were 15 kV accelerating voltage and a 10 nA current. All glass analyses were done with a 10 micron diameter beam to reduce Na-migration in the hydrous glass, and all mineral phases were analyzed with a focused 1-2 micron beam. The CITZAF correction procedure of Armstrong [1995], using the atomic number correction from Duncomb and Reed, the absorption corrections with Heinrich’s tabulation of mass-absorption coefficients, and the fluorescence corrections from Reed, was used to reduce the data and obtain quantitative analyses. A materials balance calculation was used to estimate phase proportions and to determine whether FeO had been gained or lost from the experimental charge through reaction with the sample capsule. These results are reported in Table 4.2. Compositions of all of the

phases are reported in Table 4.3. Errors reported are the 1- σ standard deviation of the arithmetic mean of replicate analyses on each phase.

4.3 Experimental Results

4.3.1 Phase diagram and phase appearances:

Run products for the experiments on the PMA starting material are summarized in Table 4.2, and the phase assemblages and analyses are presented in Table 4.3. At 0.1 MPa under anhydrous conditions, the phase appearance sequence has been previously determined by Grove et al. [2003]. Spinel and olivine are liquidus phases at $\sim 1260^\circ\text{C}$. Orthopyroxene (opx) appears at 1210°C , followed by plagioclase (plag) at 1200°C and then by clinopyroxene (cpx) at 1160°C . At 200 MPa and H_2O saturated conditions, both olivine and spinel are still the liquidus phases however the liquidus drops by about 100°C to 1175°C . Cpx joins the crystallizing phases at $\sim 1070^\circ\text{C}$, and opx crystallizes at 1030°C . Olivine has reacted out by 1000°C and plagioclase crystallizes at approximately the same temperature. Amphibole does not crystallize until 920°C , when there is less $<50\%$ liquid.

At 500 MPa the near-liquidus H_2O saturated crystallization sequence is not as well constrained because of the low melting point of Au. Spinel, olivine and cpx are still the high temperature phases, and the appearance of cpx occurs at a temperature $>1025^\circ\text{C}$. The appearance of opx is depressed by a further 40°C to 990°C , and plagioclase crystallization is depressed by $>60^\circ\text{C}$ relative to the 200 MPa appearance because of the increase in dissolved H_2O content at these elevated pressures. Amphibole however appears 40°C higher in the sequence compared to 200 MPa experiments (Fig 4-4). The appearance of amphibole is related to the olivine-out reaction (Fig 4-5) [Grove and Donnelly-Nolan, 1986, Sisson and Grove, 1993].

At 800 MPa orthopyroxene is present along with olivine and cpx in the highest temperature experiment at 1050°C , an increase of at least 60°C from the 500 MPa experiments representing a change in sign of the slope of the opx-in curve with the

minimum temperature in the curve at around 500 MPa. Also at 800 MPa amphibole appears between 1000°C and 1050°C, closer to the liquidus than amphibole appearance in lower pressure experiments by at least 50°C. Amphibole and olivine coexist in this experiment.

We were unable to determine water contents of the high pressure experimental liquids. Due to the strong pressure dependence on the solubility of H₂O in silicate melts [Hamilton et al., 1964, Moore and Carmichael, 1998], we expect that our highest pressure H₂O-saturated experimental liquids will contain >10 wt% H₂O. However, the liquids in experiments at 500 and 800 MPa quenched to vesiculated glasses and microprobe analyses of the hydrous glasses show a deficit from 100% totals of about 8-11 wt% (Table 4.3). We propose that this value represents the maximum quenchable H₂O content for this starting composition and experimental procedure, and the actual H₂O contents in the liquids are greater.

4.3.2 Approach to Equilibrium:

Experimental durations were designed to be as long as possible for each experimental technique, to allow the experiments to reach equilibrium. Practical limitations were the exhaustion of the buffer assemblage or loss of H₂O from the capsule by diffusion of H₂ through the outer capsule wall. For the 200 and 500 MPa experiments typical experimental durations were 24-72 hours and at 800 MPa experiments were run for between 7-26 hrs. A multiple linear regression mass balance calculation was used to obtain the phase proportions in each experiment and check for loss of Fe due to interaction with the capsule material (Table 4.2). In the 500 MPa experiments the large volume of the internally heated pressure vessel allowed us to run multiple experiments simultaneously using both a glass starting material and powdered rock starting material. The results of these experiments are reported in Tables 4.2 and 4.3, and the compositions of phases in these runs are very similar.

4.3.3 Effects of P, H₂O, f_{O_2} on mineral chemistry in the PMA:

Olivine

At 200 MPa there is a 90°C gap between the olivine and amphibole stability fields, with the most Fe-rich, low temperature olivine being Fo_{81.7}. At 500 MPa, forsterite contents in the experimental olivines range from 87.1 mol% at 1025°C to 84.6 mol% at 975°C. At most there is a 30°C gap between the amph and olivine stability fields at 500 MPa under H₂O saturated conditions. At 800 MPa the olivines range from Fo_{86.8} at 1050°C to Fo_{83.3} at 1000°C. At 800 MPa and 1000°C olivine coexists with amphibole that has a Mg# of 81.7. The Fo content and amph Mg# are calculated as the average of a pair of experiments that were run at the same conditions. Coexistence of olivine and amphibole is restricted to a narrow range of temperature, above 500 MPa pressure, and at high H₂O contents (Fig 4-5). The olivine is slightly more magnesian than the coexisting amphibole at 800 MPa with Mg#'s, 83.3 and 81.7 respectively.

Clinopyroxene

The temperature of the first appearance of cpx in the H₂O-saturated crystallization sequence is relatively constant from 200 to 800 MPa. At 500 MPa, and NNO f_{O_2} , the cpx ranges from Mg# 89.2 coexisting with Fo_{87.1} olivine at 1025°C to Mg# 82.7 coexisting with Mg# 79.9 amphibole at 945°C. The NNO+3 experiments at 950 and 975°C have cpx of 82.7 and 87.0 Mg# respectively. There appears to be no systematic variation in cpx aluminum content over the pressure and temperature range investigated.

Orthopyroxene

At 200 MPa the 85-41c experiments have orthopyroxene coexisting with cpx, amphibole, and plagioclase. The opx Mg# is 74.9 in our 915°C experiment at NNO, and 79.3 at 930°C and RRO. There is a minimum in temperature for the opx-in curve that occurs at around 500 MPa. The first opx to crystallize at 500 MPa is Mg# 87.0

at NNO, and 88.8 at NNO+3, at 975°C. At 800 MPa opx is present at 1000°C and has a lower Mg# at 85.3.

In the H₂O undersaturated experiments at 500 MPa and 1000°C opx+cpx are the stable Fe-Mg silicates, instead of olivine+cpx, as in the H₂O saturated experiments. The effect of water is to stabilize opx closer to the liquidus at these elevated pressures [Baker et al., 1994]. The opx in the H₂O undersaturated experiment has an Mg# of 85.7, lower than the first opx to crystallize in the H₂O saturated experiments.

Plagioclase

Plagioclase is only stable in 200 MPa experiments below 1025°C. At 915°C, NNO the plagioclase is An_{58.9} and at 930°C and NNO+3 the plag is An_{71.9}. At 1-atm pressure plagioclase is stable at 1200°C and is An_{62.1} [Grove et al., 2003].

Amphibole

At 200 MPa the first amphibole to crystallize has 9.9% Al₂O₃ while the first-appearing amphibole at 500 MPa contains 12.5% Al₂O₃. The first amphibole at 800 MPa has a higher Mg# than the lower pressure amphiboles but also contains lower Al₂O₃ (11.9 wt%). The 200 MPa amphiboles have the lowest Al₂O₃ because they were crystallized at the lowest pressure and co-precipitated with plagioclase, from liquids depleted in an Al-rich plag component. There is also no systematic variation of tetrahedrally coordinated Al (Al^{IV}) with octahedrally coordinated Al (Al^{VI}) observed in the first-appearing amphiboles. We compare our amphibole data to that of the literature in Fig. 4-3. Amphiboles that occur in high thermodynamic variance systems (i.e. the amphibole coexists with only a few other phases, but the system has many components) display no relationship between Al^{IV} and Al^{VI}. This is in contrast to amphiboles that coexist with many other phases (i.e. low variance systems [Hammarstrom and Zen, 1986, Johnson et al., 1989, Schmidt, 1992] where there are pressure sensitive relationships between these two crystal-chemical variables).

Experiments at higher oxygen fugacities crystallize a more magnesium-rich amphibole for a given pressure and temperature than those at NNO. This is due to

the fact that amphibole composition and the temperature of its first appearance are sensitive to the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in the melt. Our experiments were conducted at NNO for all pressures, RRO for 200 MPa experiments and NNO+3 at 500 MPa. The Mg# in amphibole increases by 3-4 units for coexistence with a melt of similar Mg# between the oxidized and reduced systems. The compositions of the amphiboles in our experiments are on the border between compositional regimes and are classified as a mix of pargasite, magnesio-hastingsite, magnesio-hornblende, and tschermakite [Leake et al., 1997]. So for simplicity we will simply use amphibole in this paper.

In the H_2O undersaturated experiments amphibole is stabilized to higher temperatures, however the amphibole in the H_2O undersaturated experiments has a lower Mg#, because the liquidus is at a higher temperature for the PMA under H_2O undersaturated conditions (experiments 41c-106, 117, and 118, Table 4.2).

Liquid

The liquid compositions vary from 57.8% SiO_2 in near liquidus experiments to 65.4% SiO_2 in the lowest temperature experiment at 200 MPa for the PMA composition, normalized anhydrous. The suppression of plagioclase crystallization in the higher pressure experiments allows the liquids to continue to increase in Al_2O_3 content down temperature, and for similar MgO contents the 500 and 800 MPa experiments have up to 19.3% Al_2O_3 vs. about 17.7 wt% for the 200 MPa experiments, which are saturated with plagioclase.

4.4 Discussion

4.4.1 Effects of P, H_2O on phase equilibria:

The phase appearance sequence, and crystallization temperatures for the PMA water saturated experiments changes in response to variations in pressure/ H_2O content. With increasing pressure, the amphibole-in curve increases in temperature and the liquidus decreases, and thus the difference in temperature between the first amphibole

and the liquidus monotonically decreases with increasing P_{H_2O} . Olivine is the liquidus phase at all pressures. At 200 MPa there is a 90°C gap between the disappearance of olivine and the appearance of amphibole, and a 220°C gap between amphibole first appearance and the liquidus. At 500 MPa the disappearance of olivine in the crystallization sequence coincides with the appearance of amphibole, and at 800 MPa olivine and amphibole coexist (Fig 4-5). The 500 MPa coexistence defines the low-pressure end of a narrow field of P-T space where both amphibole and olivine are coexisting, though this is a reaction relationship (Fig 4-7).

The appearance temperature of clinopyroxene drops between 0.1 and 200 MPa by about 100°C but remains relatively constant until at least 800 MPa. The temperature difference between the orthopyroxene-in curve and the liquidus increases between 0.1 and 500 MPa, this is the opposite sense to the behavior of amphibole. Between 500 and 800 MPa the temperature difference between opx appearance and the liquidus decreases, similar to the slope of the amphibole-in curve. The change in sign of the slope of the opx-in curve in P-T space is related to the competing effects of H_2O and pressure on the size of the olivine phase stability field. The position of the opx-in boundary also moves in composition space (Fig 4-7). At 0.1 MPa opx crystallizes before cpx, and at 200 and 500 MPa it first crystallizes after the first appearance of cpx. This crystallization sequence occurs because the effect of increasing P_{H_2O} is to expand the olivine primary phase volume [Kushiro, 1969]. The olivine-orthopyroxene reaction boundary moves to higher SiO_2 contents with increasing P_{H_2O} , and this change is most dramatic between 0.1 and 200 MPa. From 200 to 800 MPa the boundary does not shift. The effects of increasing H_2O in the melt (serving to expand the boundary) and increased pressure (causing the boundary to shrink) apparently cancel each other out (Fig 4-7). The crystallization sequence between opx and cpx at 800 MPa has not been determined.

Plagioclase saturation has only been found in experiments at 200 MPa, and there is a 170° drop in the appearance temperature compared to 1-atm crystallization experiments. The lowest experimental temperature at 500 MPa is 945°C, and the liquid contains 19.3 wt% Al_2O_3 , normalized anhydrous, and this liquid is not saturated

with plagioclase at $P_{H_2O}=P_{tot}$ conditions. At 200 MPa plagioclase first crystallized at 1000°C, from a liquid with 17.7 wt% Al_2O_3 . The drop in plagioclase appearance temperature from 1-atm to 500 MPa at H_2O saturated conditions is at least 265°C in the PMA composition.

4.4.2 High-Mg Andesite LLD's at 200–800 MPa

Because the near liquidus phase assemblages for H_2O saturated PMA are similar from 200-800 MPa (Olivine-Cpx-Opx), the major elements follow very similar liquid lines of descent (LLD) for the early part of the crystallization sequence at all pressures. Therefore, bulk-rock major element chemical trends developed in liquids crystallized at different pressures will be generally similar in hydrous primitive arc magmas (>5 wt% MgO) that crystallize over a large range of crustal depths. For primitive high-Mg andesites and basaltic andesites, polybaric magmatic fractionation and evolution that has been seen at magmatic arcs [Prouteau and Scaillet, 2003] has similar major element signatures as ponding and differentiation at a single depth in a fixed magma chamber [Sherrod et al., 2008, Barclay et al., 1998]. At lower MgO contents, and more evolved compositions, there are significant differences between experimental liquids produced by crystal fractionation at various crustal depths, particularly in their Al_2O_3 variations. It has been shown that the crystallization of plagioclase is highly dependent on H_2O content [Sisson and Grove, 1993, Panjasawatwong et al., 1995]. All of our experiments are done at high- H_2O contents and thus it is the H_2O pressure (i.e. the solubility of H_2O in silicate liquids) that controls the plagioclase appearance. The switch in the order of amphibole and plagioclase crystallization takes place at about 300 MPa. Because of the aluminum rich nature of plagioclase, crystal fractionation at shallow pressures (<300 MPa) will produce lower Al_2O_3 contents in residual liquids than higher pressure (>300 MPa) crystal fractionation at a given MgO content.

The liquid compositions for experiments are plotted in pseudo-ternary diagrams in Figure 4-7. In the PMA composition olivine+opx+cpx saturation occurs at the same part of composition space from 200 to 800 MPa indicating that H_2O pressure

does not change the compositional characteristics of the melt in equilibrium with these three phases. The olivine+opx+cpx saturation boundary is a reaction boundary down temperature and the liquids become enriched in the SiO_2 (Qtz) component with decreasing temperature. However, the appearance temperature of opx *does* vary with pressure, see Fig 4-5. At 200 MPa the appearance of amphibole and the disappearance of olivine in the crystallizing assemblage are widely separated, and amphibole appears at a distributary point where opx+cpx+amph+liquid are stable. At 500 and 800 MPa olivine stability terminates at a distributary reaction point where amphibole becomes stable on the down temperature side. The composition of the liquid at this reaction point varies systematically in the Olv-Cpx-Qtz projection, moving to less SiO_2 and less corundum normative compositions with increasing pressure. In the Olv-Qtz-Plag projection, the 200 MPa liquid composition at the distributary reaction point is very Qtz-rich. This is caused by the appearance of plagioclase before amphibole drives the liquid away from the Plag apex. Above 300 MPa the amphibole appears before plagioclase, and the distributary point appears at more Plag-rich compositions (Fig 4-7). In the Oliv-Cpx-Qtz projection the distributary point systematically moves to lower Qtz values with increasing $P_{\text{H}_2\text{O}}$.

4.4.3 Effect of pressure on crystallization under anhydrous and hydrous conditions

The focus of this paper is on H_2O -saturated experiments at variable pressure and oxygen fugacity, but it is worth contrasting this work with the phase appearance sequence that would be expected if these magmas crystallized under anhydrous conditions. At near surface conditions the crystallization sequence in the PMA and BA are very similar (Fig 4-8). The phase equilibria of BA 85-44 was investigated by Baker et al. [1994] at 1000 MPa and variable H_2O content. The most noticeable difference is the increase in liquidus temperature and the absence of olivine as a liquidus phase at high pressures and low $P_{\text{H}_2\text{O}}$. The PMA loses olivine as a liquidus phase by ~ 100 MPa and crystallizes opx followed closely by plagioclase. This crystallization sequence

would most likely remain the same at 500 and 800 MPa, anhydrous, and the liquidus temperature would continue to climb to values that would approach or exceed the liquidus of 85-44 under anhydrous conditions. When we compare the experimental results to natural settings like Mt. Shasta, the mineral assemblage observed bears no resemblance to the dry phase appearances. The presence of olivine and amphibole in primitive natural arc magmas is strong evidence for very high-pre-eruptive H₂O contents and saturated conditions. In addition the mineral assemblages in Mt. Shasta rocks record much lower temperatures for magmas in the crust. At 800-1000 MPa there is a 500 °C difference between hydrous amphibole bearing magmas and an anhydrous magma of the same bulk composition.

4.4.4 Empirical Amphibole barometry

Amphibole has long been targeted for use in mineral geobarometry because of its dramatic chemical variability, its common occurrence in igneous rocks (particularly in plutonic environments), and the absence of other mineral assemblages in the rock that can be used to estimate crystallization pressure. Pioneering studies on natural amphibole barometry by Hammarstrom and Zen [1986], calibrated by correlation with estimates of metamorphic pressure in the contact aureole of the pluton, and experimentally calibrated barometers of Johnson et al. [1989] and Schmidt [1992] have focused on evolved magmatic systems in the rhyolite to tonalite range. These barometers are all based on the aluminum content in the amphibole and they are applicable only to rocks with mineral assemblages creating low thermodynamic variance. Such barometers are not relevant for amphiboles that crystallize from less evolved (andesitic to basaltic) magmas where only one or two other minerals are present with melt. Here we calibrate an amphibole barometer-hygrometer based on the Mg# of primary igneous amphiboles that is applicable to crystals precipitated from primitive magnesian andesites and basaltic andesites.

Amphibole is increasingly thought to be a common crystallizing phase in arc magmas. Although amphibole is found in many arc magmas, it is not as abundant as pyroxene, plagioclase and olivine as a phenocryst phase in arc lavas. Its participation

in magmatic crystallization is thought to be 'cryptic' in a wide range of arc related magmas, because it becomes unstable at low pressure and low H_2O contents that occur when arc magmas ascend to shallow pressure magma chambers, become vapor-saturated, degas and dehydrate. The more limited temperature and water content range from which amphibole will crystallize contributes to the mineral being less common as an erupted phenocryst. Significant amphibole fractionation has been inferred to occur at arcs such as Panama [Hidalgo and Rooney, 2010], Chile [Kratzmann et al., 2009], and globally [Davidson et al., 2007]. Olivine-bearing, plagioclase-free amphibole cumulates have been identified in the Bonanza Jurassic arc in British Columbia [Larocque and Canil, 2010], and the Adamello batholith [Tiepolo et al., 2011]. High-Mg# amphiboles have also been found as xenocrysts/phenocrysts at arc volcanoes as well [Prouteau and Scaillet, 2003, Grove et al., 2005, Blatter and Carmichael, 1998]. Because of this prevalence of evidence for near-liquidus fractionation it is useful to extend our experimental results to determine the pressure and oxygen fugacity of crystallization of high-Mg# igneous amphibole phenocrysts and cumulates in natural systems.

Calibration of an Amphibole Mg# Geobarometer-hygrometer

The temperature difference between the liquidus and first appearance of amphibole in H_2O saturated experiments decreases with increasing pressure, as has been noted by several authors in the past [Holloway and Burnham, 1972, Helz, 1973, Cawthorn and Ohara, 1976, Anderson, 1980]. A direct result of this observation is that amphibole first crystallizes from higher Mg# liquids at higher P_{H_2O} . Thus the Fe/Mg ratio of the first amphibole to crystallize changes along the phase stability boundary in P-T space due to the change in Mg# of the liquid, which in turn is dependent on overall crystallinity and relative proportions of other Fe-Mg phases. The magnitude of this change depends on the bulk composition of the system, and amphibole Mg# is also a function of f_{O_2} . We use the H_2O saturated experiments on the PMA and BA compositions to calibrate the variation in Mg# in order to get a minimum pressure and f_{O_2} of crystallization of natural amphiboles.

A power law least squares fit was made using the experimental pressures, amphibole Mg#’s, for experiments on the PMA at NNO. The reason for choosing this mathematical formulation is that the Mg# of the first amphiboles to crystallize describes a non-linear convex-up trend that tends to flatten out in pressure-Mg# space with increasing pressure. Amphibole Mg# variation is responding to its change in its P-T stability, because the amphibole stability curve becomes sub parallel with the liquidus curve (Fig 4-5). Experiments done at the NNO buffer contain amphiboles with lower Mg# than those produced at NNO+3 or RRO for a given pressure (Fig 4-9), and thus an additional term is required in the fit. This term is simply assumed to be linear over the range of conditions investigated and is expressed as a function of ΔNNO in log units. The regression produces the following expression:

$$P_{H_2O}(\text{MPa}) = \left[\frac{Mg\#}{0.527} - 0.014 * \Delta NNO \right]^{15.12} \quad (4.1)$$

Only the composition of the first-appearing amphibole in a crystallization sequence at a given pressure is used in the calibration. This barometer is only to be used on amphiboles with Mg# 0.72 or greater. Below this value the curve fit is not meaningful. This fit curve is concave downward in amphibole Mg#-pressure space because there is a smaller change in the Mg# of the first amphibole to appear at high pressure and high H₂O contents. At higher pressures garnet may also become a stable crystallizing phase, which will affect the chemical composition and appearance of amphibole [Müntener et al., 2001, Alonso-Perez et al., 2009], and we do not recommend extrapolating this model beyond 950 MPa.

The increase in Mg# with pressure along the amphibole-in boundary curve is greater for the PMA than the BA (Fig 4-9). Since both of these sets of experiments were conducted H₂O saturated and over similar temperature ranges, it is likely that this difference is caused by the temperature difference between the amphibole-in curve and the liquidus in each composition. However the difference between the amphibole compositions in the PMA and BA parental melts is small below 500 MPa, and these two magma compositions are end member compositions in the spectrum of mantle

derived melts in the Mt. Shasta region [Baker et al., 1994], and likely globally [Gaetani and Grove, 2003], and thus bound the compositional variability of possible near-liquidus amphiboles. We are confident in including this spectrum of compositions in our regression at low pressures. At pressures above 500 MPa this barometer gives a *minimum* pressure only, assuming that primitive arc melts usually fall between the PMA and BA in composition space.

This barometer-hygrometer is convenient because it does not rely on the presence of many coexisting phases including uncommon accessory phases that fix the activities of various substitution components in the amphibole. It is important to note that the first amphibole to crystallize at a given pressure usually occurs in an assemblage that is in equilibrium with >50% melt by weight. Further crystallization at the same pressure would produce amphibole with lower Mg#. The same is true if the magma is H₂O-undersaturated, as this will increase the liquidus temperature of the magma, and thus the crystallization temperature of the first amphibole may be at a higher temperature, but will give a lower Mg# [Eggler, 1972]. Thus the geobarometer-hygrometer presented here should only be applied to the most Mg-rich amphiboles in a given sample suite, and even then only represents a minimum crystallization pressure.

Calibration of an empirical Al^{VI} amphibole barometer

Larocque and Canil [2010] proposed an empirical geobarometer based on the calculated Al^{VI} content of igneous amphiboles. Using the experimental data available in the literature they showed an approximately linear relationship between Al^{VI} and pressure (Fig 4-10). We have added our experimental amphiboles as well as those from several other studies [Müntener et al., 2001, Grove et al., 2005, Barclay and Carmichael, 2004, Pichavant and MacDonald, 2007, Blatter and Carmichael, 1998, 2001] with high Mg# andesite and basaltic andesite starting materials (Table 4.4), and show that a clear relationship between pressure and Al^{VI} remains, but there is significant variability in the aluminum content at any single pressure. Much of this variability likely results from the large compositional range in the experimental liquids

used in the calibration. On one hand, that compositional variability in experimental liquids is good because it matches what is in nature, but on the other it makes a simple barometer like this harder to implement because of the multitude of variables it introduces. Ridolfi et al. [2010] have a more complicated barometer based on amphibole compositions, but it excludes much of the literature data. Figure 4-10a shows the calculated vs. actual pressure for experimental amphiboles using the Larocque and Canil [2010] barometer, and the square root of the sum of the differences squared from the 1:1 line is 142 MPa. We have recalibrated this barometer using the same method of Larocque and Canil [2010] but with the added experiments, and obtain an updated equation:

$$P(\text{MPa}) = 1675 * Al^{VI} - 48 \quad (4.2)$$

Where Al^{VI} is the calculated octahedrally coordinated Al atoms in the amphibole based on normalization to 23 oxygens. Equation (4.2) reproduces pressures that are slightly different than the equation of Larocque and Canil [2010] and have better reproducibility for the data, but with similar poor absolute uncertainty on the pressure (± 142 MPa, Fig 4-10b). The scatter in these plots results from complicated amphibole compositional variability including non-pressure dependent Al^{VI} content and highly variable Ti contents.

We added a term to the linear regression to adjust the pressure based on aluminum content in the melt, and this improves the ability of the regression to recover experimental pressures (± 111 MPa 67% confidence interval, Fig 4-10c). However in some natural applications it is difficult to estimate the aluminum content of the melt, and so this barometer while better, is more difficult to implement. The fact that including a term for Al_2O_3 content of parental melts improves the fit highlights that some of the uncertainty in the use of a strictly empirical Al^{VI} barometer is related to non-pressure dependent, mineral/liquid partitioning of Al^{VI} content in amphibole.

Although neither the Mg# hygrometer or Al^{VI} barometer presented here are perfect, they are both independent and complement each other. The Mg# barometer should always be used with the most Mg-rich amphibole of a given rock suite to

estimate the pressure, however this is not guaranteed to be the most Mg-rich amphibole that was crystallized from a parental magma because of down temperature reaction removing primitive amphibole, metamorphic redistribution of Fe-Mg in plutonic rocks, or under sampling. Thus we would expect some underestimation of the pressure using this barometer. Conversely use of the Al^{VI} barometer on an amphibole with lower Mg# than the most Mg-rich amphibole possible for a particular bulk composition will over estimate the pressure, because of the increase in Al_2O_3 content in the melt from some excessive crystallization of phases in which Al_2O_3 is incompatible. Thus by averaging the Mg# barometer and the Al^{VI} barometer, and applying them to the same suite of rocks can help with the non-uniqueness of each barometer (± 94 MPa, Fig 4-10e).

In order to apply the Mg# barometer-hygrometer we stress that a rigorous petrologic approach needs to be implemented. The association of amphibole with olivine and/or pyroxene, and the relation of the amphibole to the crystallization of plagioclase need to be considered when applying this technique for pressure estimates. For instance if pressure estimates of >300 MPa from this barometer-hygrometer are obtained, there should be clear corroborating textural evidence for amphibole as an early crystallizing phase appearing after or co-precipitating with olivine, opx and/or cpx and before plagioclase appearance. In addition normal or oscillatory zoned amphiboles are common in igneous rocks, because the Mg# barometer-hygrometer only applies to the most Mg-rich amphiboles that crystallize at high temperatures and H_2O contents, only the most Mg-rich cores from a petrologically related suite of samples should be used to estimate pressure.

4.5 Example of near liquidus amphibole crystallization at Mt. Shasta, CA

High-Mg amphibole antecrysts are present in mixed andesites erupted from Mt. Shasta, CA. These crystals are typically overgrowths on magnesian olivine and cpx

[Grove et al., 2003], both of which are early crystallizing phases from a hydrous PMA or BA (Fig 4-5). The amphiboles reported in Grove et al. [2003] and Grove et al. [2005] (Fig. 4-11) range in their Mg# from .57 to .833 and in Al^{VI} content from 0.164 to 0.313. These amphiboles crystallized from liquids similar to the ones used in the experiments and the amphiboles from the 200, 500 and 800 MPa are plotted along with the amphiboles found in the Shasta lavas (Fig 4-11). It is clear that there is good evidence from amphibole composition that Mt. Shasta lavas were crystallizing at lower crustal depths and contained high H_2O contents. We can also estimate an oxygen fugacity for these Mt. Shasta eruptive products as an average of NNO+0.5 from measurements of coexisting oxides from 32 separate lava flows from the Mt. Shasta stratocone Grove et al. [2005]. Using equation (1) to estimate the P_{H_2O} gives a range from 276 to 948 MPa for amphiboles with Mg# 0.73 or greater (Table 4.5). This implies that these antecrysts came from magmas at or near the Moho underneath Mt. Shasta [Zucca et al., 1986].

4.5.1 Evidence from amphibole for high magmatic H_2O in primary magmas from subduction zones

We can use the composition of these amphiboles to estimate the water content of these magmas at the pressures determined from the Mg# of the amphiboles, and because of the very narrow temperature stability window for amphibole, we know that the temperature of crystallization must be between 915-1050°C. Hamilton et al. [1964] determined the H_2O contents of a Mt. Hood andesite composition equilibrated with a pure H_2O fluid from 100 to 500 MPa to be 4.5 and 10 wt% respectively. More recent measurements on a Mt. Unzen andesite composition equilibrated with a pure H_2O fluid determined the solubility of H_2O to be 5.5 and 10 wt% at 200 and 500 MPa [Botcharnikov et al., 2006]. These estimates agree well with those obtained from averaging 75% basalt and 25% rhyolite H_2O solubilities at 950°C using the VolatileCalc software of Newman and Lowenstern [2002]. A linear extrapolation of the averaged estimate from VolatileCalc to 950 MPa result in 14-15wt% H_2O . Therefore the magmas

being fed into the Mt. Shasta plumbing system are H₂O-rich magmas, and the phase equilibrium constraints require minimum H₂O contents significantly higher than the amounts preserved in melt inclusions in olivine phenocrysts [Anderson, 1974, Ruscitto et al., 2010, Sisson and Layne, 1993]. Even with the variations in pressure and water content introduced by variation in f_{O_2} , these igneous amphiboles with high Mg# require pre-eruptive H₂O contents that exceed 12 wt% and crystallization pressures that extend into the lower crust.

The experiments presented in this paper allow a new upper limit to be placed on magmatic H₂O contents in the Cascade arc. Using our experimental results to link amphibole composition to temperature of crystallization, and using extrapolated H₂O solubilities from VolatileCalc, the high-Mg# amphibole antecrysts of Mt. Shasta lavas record pre-eruptive temperatures of 1050°C at lower crustal depths with H₂O contents that are at 14 wt% (Fig 4-12). The trend defined by the Mt. Shasta amphibole antecrysts in Fig 4-12 is evidence preserved in Mt. Shasta lavas that fractional crystallization of primitive lavas occurs over a great depth range extending from the base of the crust to magmas that pond near the base of the Mt. Shasta edifice. The presence of multiple compositions of these amphiboles in single lava flows suggests magmas are mixed throughout the crustal column just prior to eruption. Grove et al. [2005] suggest that vapor-saturation of high-H₂O primitive magmas near the base of the crust is the trigger for mixing of lavas. These deep, high H₂O magmas are mingled with lower-pressure evolved liquids and degassed shallower products of fractional crystallization. Thus the erupted andesite collected products of vapor saturated crystallization over a range of depths.

Studies of basalts and basaltic andesites from the South Cascade region have revealed evidence for variable pre-eruptive water contents and temperatures that range from 8 to <1 wt% H₂O and 1000-1250° (Fig 4-12) using olivine-liquid and plagioclase-liquid equilibrium thermometer/hygrometers [Sisson and Grove, 1993]. These variations in water content are primary features of the melt generation processes that are taking place in subduction zones [Grove et al., 2002]. The high-T, low H₂O end of the spectrum represents ‘dry’ adiabatic decompression melting of mantle peridotite

that is convecting into the wedge corner. The low- T , high H_2O end of the spectrum is being generated by flux melting of the mantle wedge that occurs when H_2O is added at the slab-wedge interface, leading to reactive porous flow melting that is controlled by the inverted temperature gradient in the wedge.

The trend defined by polybaric H_2O saturated crystallization in the melt conduit beneath Mt. Shasta (diamonds in Fig 4-12) intersects the trend defined by the South Cascades high-alumina basalts and basaltic andesites (circles in Fig 4-12) at about 450 MPa, which is to be expected because the S. Cascades magmas become vapor saturated at this pressure. The two trends come from independent hygrometers. The Mt. Shasta trend defined by the amphibole antecrysts extends the range of magmatic H_2O contents in the South Cascades region to significantly higher values and pressures.

These high H_2O contents are not the first to be inferred from petrologic evidence. Indeed, Carmichael [2002] proposed that the lavas from the Mexican Volcanic Belt contained up to 16 wt% pre-eruptive H_2O . Carmichael [2002] also suggested that these lavas would become H_2O saturated at significant depth and remain water saturated as they ascend through the crust. They could initially contain higher H_2O contents than the phenocrysts that crystallized at shallower depths record. Ridolfi et al. [2010] infer lower crustal depths of crystallization for amphiboles at Mount St. Helens, Redoubt, El Reventador, and Soufriere Hills, which would require high H_2O contents to crystallize. Lavas that are erupted on the surface may experience complicated ascent (decompression) crystallization and mixing paths to their site of eruption [Blundy et al., 2006], and experiments like the ones presented here provide critical evidence for understanding the ultimate fate of H_2O -rich magmas between their source regions in the mantle and the erupted products we are privileged to study.

4.6 Figure Captions:

Figure 1: Cross-section of the experimental assembly used in the 800 MPa ‘trash-can’ experiments. The outer Au capsule contains an inner capsule of sample material, a

Pt buffer capsule, and enough free H_2O to ensure vapor saturation. There is a thin Au lid placed on the trash-can and when the assembly is subjected to a 800 MPa piston load while cold, this junction is pressure welded shut.

Figure 2: Backscattered electron images of experimental run products. A) Experiment 41c-117, 975°C, 500 MPa, NNO+3, and mixed volatile. Crystals are opx, cpx, amphibole, and magnetite set in a matrix of quenched and slightly vesiculated glass. B) Experiment B1160, 1000°C, 800 MPa, NNO, H_2O saturated. Visible crystals are olivine, amphibole, cpx, and over growths of equilibrium opx on unreacted pyroxene cores from the starting material, set in a matrix of vesiculated glass. C) Experiment 44-102, 1000°C, 500 MPa, NNO+3, H_2O saturated. Small grey crystals are amphibole, bright white crystals are magnetite, and the large crystal is a sector zoned cpx, set in a matrix of vesiculated glass.

Figure 3: Calculated Al site partitioning in experimental amphiboles crystallized from primitive arc magma starting materials from this study and the experimental literature. For these high thermodynamic variance systems there is no observable trend with tetrahedral coordinated Al vs. octahedral coordinated Al. Site assignments are calculated with the algorithm of Leake et al. [1997] on a 23 oxygen basis.

Figure 4: Crystallization sequence at various pressures for water saturated experiments on the PMA. Solid black dots are each one experiment at the particular P and T, and a horizontal line through each of these points will intersect with the phases that are present in the experiment. 1-atm and many 200 MPa experiments are from Grove et al. [2003]. Olivine is the liquidus phase at all pressures, followed by cpx at pressures above 1-atm. Notice the complete suppression of the crystallization of plagioclase at the temperature and H_2O contents investigated here. The appearance temperature of amphibole in the crystallization sequence rises with increasing pressure such that between 500-800 MPa we infer a coexistence with olivine and amphibole.

Figure 5: Phase diagram showing all water saturated experiments on the PMA composition. Phase appearance lines for experiments at NNO are thin black lines, olivines last appearances is demarcated by a long dashed line, and amphibole stability

in NNO+3 experiments are the short dashed lines. Mg# of Fe-Mg phases are also show in numbers next to each experiments, black for olivine, green for cpx, brown for opx, and bold italic for amphibole Mg#s. Notice that amphibole is stabilized to higher T at oxidizing conditions. Above 500 MPa there is a narrow zone of coexistence between olivine and amphibole, and is marked with a grey field.

Figure 6: Variation diagrams showing the compositions of experimental glasses, with the composition normalized anhydrous. It should be noted that crystallization over a wide range of pressure produces indistinguishable compositions in major elements, except for low values of MgO and high Al_2O_3 where the presence/absence of plagioclase greatly affects the Al_2O_3 content (see text for discussion).

Figure 7: Pseudo-ternary diagrams showing experimental liquid compositions recalculated into their respective mineral components in oxygen units following the method of Tormey et al. [1987]. Also shown are the compositions of the primitive lavas from the Mt. Shasta region and amphiboles from our experiments. Notice that the amphibole stability field is a distributary reaction point. A) Projection from the cpx apex into the Oliv-Plag-Qtz plane. Notice the large difference between the liquid compositions in equilibrium with amphibole between 200 and 500 MPa due to the switching of amphibole and plagioclase in the crystallization sequence. B) Projection through the plag apex into the Oliv-Cpx-Qtz plane. Notice that the opx-in point does not vary much with pressure due to the counteracting effects of increased pressure and increased water content.

Figure 8: Experimental crystallization sequences for the PMA water saturated compared to the BA experiments of Baker et al. [1994] on the BA at various H_2O contents. Note the very large temperature difference and different phase assemblages in the BA and PMA at high pressure and varying H_2O content. Both magmas have very similar phase assemblages and mineral appearance at 1-atm but are vastly different dry vs. H_2O saturated at high pressure. Numbers next to the columns represent the amount of H_2O in wt% dissolved in the liquid.

Figure 9: Variation of the Mg# of the first amphibole to crystallize from a primitive arc magma with pressure. Blue symbols are experimental amphiboles at NNO+3,

and black symbols are for experimental amphiboles at NNO. The range between amphibole Mg# between the PMA and BA starting materials is highlighted in the filled fields. Squares are experiments on the BA and circles are for the PMA. Experiments from Blatter and Carmichael [1998] (hexagons), and Moore and Carmichael [1998] (stars) are shown for comparison. For those experiments that have their f_{O_2} determined, it is provided in the figure. The Mg# of the first amphibole to crystallize from these magmas increases with increasing pressure and we have calibrated this change to be used as a geobarometer-hygrometer.

Figure 10: Empirical amphibole barometer reproducibility of experimental pressures. Shown in each plot is the calculated pressure vs. the experimental pressure, and a 1:1 line. On each figure the standard deviation from the 1:1 line is shown. Experiments are from the sources listed in Table 4.4. A) Al^{VI} barometer of Larocque and Canil [2010]. B) Adjusted barometer of Larocque and Canil [2010] including the calibration all of the experiments in Table 4.4. C) The same as (B) but with an added term that accounts for the Al_2O_3 content of the melt in equilibrium with the amphibole, thus adjusting the values based on equilibrium non-pressure dependent Al^{VI} content in the amphiboles. D) Calculated pressures using our Mg# barometer (equation 1). Plotted are all of the experiments in Table 4.4 but excluding those not in the range of amphibole Mg# >0.72 and experimental pressures outside the 50-950 MPa range. E) The average of the calculated pressures in plots (B) and (D), the independent empirical barometers.

Figure 11: Histogram of amphibole phenocryst Mg#'s from Mt. Shasta lavas from Grove et al. [2005]. Also plotted are the experimental amphiboles we have produced in this study. Each experimental amphibole is labeled with its pressure in kbar, and the estimated H_2O content necessary to precipitate it. Experimental amphiboles range in f_{O_2} and are both PMA and BA. It is clear that the high-Mg# peak in the Mt. Shasta region amphiboles indicates deep and H_2O -rich fractionation.

Figure 12: Dissolved H_2O content and magmatic temperatures are estimated for the parental magmas crystallizing high-Mg# amphiboles in Mt. Shasta lavas. Experimental amphibole Mg# and temperatures were used to make a calibration curve

to determine the temperature of parental magma to the Shasta amphiboles in Table 4.5. Pressure estimates come from the amphibole Mg# barometer calibrated for these specific magmas. Pressure estimates were then converted to H₂O contents assuming water saturation and using VolatileCalc of a mixture of 75% basalt and 25% rhyolite solubilities at 1000°C. The trend defined by the Mt. Shasta samples (diamonds) defines an H₂O saturated crystallization trend of magmas as they ascend through the crust, so the high-H₂O, high T samples are the deepest and the low H₂O and low T are the shallowest. The HAB and BA trend of S. Cascades lavas is from Sisson and Grove [1993] and represents variable melting processes that produce variable water contents for mantle derived melts.

Table 4.1: Starting materials for experiments

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total	Mg#
85-41c	57.79	0.6	14.46	5.74	0.11	9.14	8.17	3.11	0.71	0.15	99.98	0.74
85-44	51.68	0.6	16.40	7.93	0.16	10.79	9.67	2.24	0.42	0.11	100	0.71

Table 4.2: Run conditions and products for hydrous experiments in Au capsules

Run #	Starting Material [‡]	H ₂ O saturated [†]	T °C	MPa	Duration (hrs)	<i>f</i> _{O₂}	Phases*	% $\Delta\text{Fe}^{\S}$
B1038	RP	Yes	1050	800	7.4	85-41c NNO	olv(7) + opx(1) + cpx(9) + liq(81)	-16.7
B1133	RP	Yes	1000	800	26	NNO	olv(<1) + opx(9) + cpx(11) + amph(14) + liq(66)	-1.8
B1160	RP	Yes	1000	800	9.5	NNO	olv(4) + opx(7) + cpx(15) + amph(-2) + liq(75)	-6.5
41c-101	RP	Yes	1070	203	25	NNO	olv + spnl	
41c-102	G	8.9/1.7	945	489	101	NNO	opx + cpx + amph + liq	
41c-103a	G	Yes	945	489	101	NNO	opx + cpx + amph + liq	
41c-103b	RP	Yes	945	489	101	NNO	opx(9) + cpx(11) + amph(18) + liq(61)	-0.7
41c-106	G	7.7/6.0	975	490	66	NNO	opx(12) + cpx(14) + amph(3) + liq(70)	0.5
41c-107a	G	Yes	975	490	66	NNO	olv(14) + opx(-10) + cpx(16) + liq(79)	1.0
41c-107b	RP	Yes	975	490	66	NNO	olv(12) + opx(-7) + cpx(15) + spnl(<1) + liq(80)	-4.0
41c-108a	G	Yes	1000	476	73	NNO	olv(8) + cpx(10) + liq(80)	-6.6
41c-108b	RP	Yes	1000	476	73	NNO	olv(7) + cpx(10) + spnl(<1) + liq(82)	-6.7
41c-110	G	7.4/6.2	1000	476	73	NNO	opx(12) + cpx(13) + liq(75)	-7.3
41c-111a	G	Yes	1025	485	69	NNO	olv(7) + cpx(6) + spnl(<1) + liq(85)	-6.5
41c-111b	RP	Yes	1025	485	69	NNO	olv(7) + cpx(6) + liq(86)	-12.3
41c-116b	RP	Yes	950	500	75	NNO+3	opx(4) + cpx(4) + amph(34) + spnl(<1) + liq(57)	-0.8
41c-117	G	7.7/2.4	975	500	52	NNO+3	opx(6) + cpx(8) + amph(19) + mag(<1) + liq(67)	-0.3
41c-118	G	6.4/6.4	975	500	52	NNO+3	opx(10) + cpx(12) + amph(13) + mag + liq(65)	-0.5
41c-119b	RP	Yes	975	500	52	NNO+3	opx(6) + cpx(8) + amph(14) + mag(1) + liq(72)	-0.3
41c-129	RP	Yes	915	201	47	NNO	opx(15) + cpx(10) + amph(22) + plag(23) + liq(30)	1.8
41c-141	RP	Yes	930	208	35	RRO	opx(13) + cpx(4) + amph(20) + plag(14) + liq(49)	2.8
44-100	G	Yes	1000	476	73	85-44 NNO	olv(12) + cpx(7) + liq(80)	-7.1
44-101	G	Yes	1025	485	69	NNO	olv(11) + cpx(2) + liq(87)	-8.0
44-102	G	Yes	1000	500	55	NNO+3	olv(3) + cpx(6) + amph(18) + mag(3) + liq(71)	0.2

[‡] RP is a crushed rock powder starting material, and G is the glassed rock powder that was crushed and sieved

[†] Yes = experiment is H₂O saturated and wt% H₂O/wt%Ag₂C₂O₄ = experiments that are vapor saturated but mixtures of CO₂ and H₂O

* numbers in parentheses are the calculated modes of a particular phase calculated with a least squares linear regression mass balance

[§] percent of relative Fe loss or gain from the starting material based on the difference between

Table 4.3: EMP analyses of experimental run products in oxide weight percents

Run	Phase	n*	SiO ₂ [†]	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total											
B1038	glass	20	55.0	1.0	0.63	0.08	16.11	0.61	0.03	0.02	3.8	0.3	0.04	4.6	0.3	6.87	0.40	1.91	0.13	0.83	0.08	0.16	0.05	90.0	
	oliv	10	39.9	0.9	0.00	0.01	0.03	0.02	0.04	0.01	12.6	1.1	0.17	0.01	46.2	0.9	0.16	0.02						99.0	
	cpx	18	53.5	1.0	0.26	0.08	1.84	0.51	0.55	0.20	4.6	0.9	0.12	0.04	18.5	0.6	20.38	0.80	0.25	0.05				100.1	
B1133	opx	9	56.3	0.6	0.13	0.03	1.11	0.27	0.29	0.15	9.4	1.1	0.19	0.03	30.8	1.1	1.72	0.37	0.00	0.00				100.0	
	glass	19	57.5	0.5	0.43	0.06	17.84	0.16	0.01	0.01	4.3	0.1	0.10	0.02	2.9	0.2	5.96	0.23	2.89	0.30	0.32	0.09	0.13	0.04	92.4
	oliv	13	39.0	0.5	0.01	0.01	0.02	0.01	0.03	0.02	16.7	0.7	0.21	0.03	44.6	0.9	0.13	0.04						100.6	
B1160	cpx	20	53.3	0.7	0.26	0.06	2.10	0.46	0.36	0.10	6.0	0.4	0.14	0.02	18.3	0.9	19.67	1.18	0.24	0.04				100.3	
	opx	2	55.6	0.6	0.11	0.02	1.40	0.06	0.25	0.04	10.8	0.3	0.19	0.01	31.0	0.1	1.51	0.15	0.03	0.02				100.8	
	amph	12	45.1	0.6	1.31	0.20	11.57	0.37	0.54	0.34	7.2	0.5	0.11	0.02	17.8	0.3	11.44	0.34	2.29	0.06	0.19	0.02		97.5	
B1160	glass	19	54.1	0.9	0.64	0.07	17.42	0.26	0.04	0.02	4.0	0.2	0.10	0.02	3.5	0.4	6.61	0.37	2.12	0.46	0.60	0.06	0.17	0.03	89.2
	oliv	2	39.4	1.2	0.02	0.00	0.06	0.01	0.01	0.01	15.4	1.2	0.14	0.03	45.0	2.6	0.21	0.04						100.2	
	cpx	11	53.7	0.7	0.29	0.05	2.22	0.31	0.15	0.14	5.6	0.7	0.15	0.04	17.9	1.1	20.20	1.27	0.25	0.06				100.5	
41c-101	opx	7	55.9	0.7	0.14	0.04	1.76	0.59	0.08	0.05	10.1	0.5	0.20	0.04	30.2	0.8	1.71	0.59	0.04	0.03				100.1	
	amph	16	47.0	0.8	1.04	0.24	11.77	0.81	0.37	0.22	6.8	0.7	0.11	0.03	17.3	0.8	11.50	0.45	1.96	0.22	0.26	0.02		98.1	
	glass																								
41c-101	spnl	3	0.2	0.1	0.73	0.08	11.85	2.51	47.51	0.45	20.0	2.6	0.30	0.03	17.8	0.5	0.19	0.12							98.6
	oliv	8	40.6	0.4	0.0	0.0	0.03	0.01	0.02	0.02	9.38	1.05	0.19	0.02	49.05	1.05	0.19	0.02							99.50
41c-102	glass																								
	cpx	19	53.3	0.6	0.28	0.04	2.38	0.45	0.18	0.04	6.4	0.6	0.22	0.04	17.1	0.4	20.66	0.71	0.27	0.05				100.8	
41c-102	opx	11	55.3	0.4	0.15	0.03	2.36	0.44	0.21	0.03	12.1	0.3	0.29	0.03	28.5	0.4	1.59	0.24	0.03	0.03				100.5	
	amph	10	47.5	0.5	1.14	0.26	10.23	0.65	0.31	0.14	7.5	0.6	0.10	0.01	17.8	0.6	11.08	0.38	2.26	0.12	0.22	0.03			
	glass																								
41c-103a	cpx	12	54.6	0.5	0.26	0.05	1.83	0.40	0.24	0.07	6.3	0.5	0.14	0.03	17.6	0.5	19.60	0.83	0.19	0.05				100.7	
	opx	11	56.0	0.7	0.13	0.03	1.44	0.37	0.15	0.04	11.4	0.2	0.24	0.03	28.5	0.6	1.72	0.28	0.01	0.01				99.6	
	amph	9	47.9	0.2	0.97	0.12	10.15	0.30	0.21	0.09	7.5	0.5	0.12	0.03	17.8	0.3	11.15	0.31	2.15	0.08	0.22	0.01		98.2	
41c-103b	glass	10	58.2	0.3	0.42	0.04	17.85	0.14	0.03	0.02	3.7	0.1	0.05	0.01	2.4	0.1	5.56	0.26	2.93	0.90	0.74	0.05	0.26	0.07	92.1
	cpx	12	52.7	0.4	0.33	0.08	2.76	0.31	0.16	0.08	6.5	0.7	0.16	0.03	16.8	0.4	20.45	0.56	0.30	0.07				100.3	
	opx	12	55.1	0.7	0.15	0.05	1.86	0.85	0.06	0.03	12.6	0.9	0.20	0.02	29.3	0.6	1.66	0.46	0.03	0.02				101.0	
41c-106	amph	12	45.3	0.5	1.78	0.27	12.38	0.36	0.16	0.14	7.6	0.2	0.07	0.02	16.9	0.5	11.30	0.24	2.40	0.08	0.27	0.03		98.2	
	glass	10	55.9	0.7	0.54	0.05	17.43	0.18	0.01	0.01	4.2	0.2	0.09	0.02	3.3	0.2	6.33	0.20	3.59	0.17	0.89	0.02	0.19	0.42	92.5
	cpx	20	51.2	0.8	0.48	0.11	3.64	0.58	0.33	0.07	6.6	0.6	0.12	0.02	17.2	1.0	20.09	0.97	0.44	0.08				100.1	
41c-107a	opx	12	53.4	0.7	0.32	0.07	3.27	0.55	0.41	0.09	11.1	0.6	0.26	0.03	29.7	0.7	1.43	0.32	0.09	0.05				100.0	
	amph	16	44.5	0.6	1.33	0.22	10.72	0.59	0.20	0.07	9.2	0.3	0.10	0.03	16.8	0.4	11.42	0.76	2.10	0.13	0.33	0.08		96.7	
	glass	10	56.6	0.3	0.60	0.06	16.60	0.12	0.01	0.01	4.0	0.1	0.04	0.02	3.6	0.2	6.01	0.14	2.36	0.20	0.91	0.17	0.19	0.03	90.9
41c-107a	oliv	25	39.6	0.2	0.01	0.01	0.00	0.00	0.04	0.02	16.1	0.4	0.20	0.03	43.7	0.7	0.11	0.02						99.8	
	cpx	12	53.8	0.5	0.32	0.07	2.47	0.52	0.56	0.13	5.5	0.5	0.13	0.02	17.4	0.6	20.04	0.86	0.26	0.05				100.5	
	opx	9	56.2	0.5	0.10	0.04	2.06	0.54	0.23	0.08	8.7	0.5	0.16	0.04	30.4	0.5	1.71	0.13	0.03	0.02				99.6	
41c-107b	glass	14	55.6	0.6	0.62	0.04	16.39	0.19	0.03	0.02	4.2	0.1	0.05	0.02	3.9	0.1	6.09	0.09	2.91	0.20	0.68	0.03	0.25	0.04	90.8
	spnl	6	0.2	0.1	0.70	0.09	14.44	1.39	46.3	1.4	27.5	1.1	0.31	0.02	9.6	0.4	0.22	0.06						99.3	
	oliv	9	40.1	0.3	0.00	0.01	0.01	0.02	0.03	0.02	13.2	1.3	0.17	0.03	46.4	1.2	0.15	0.02						100.1	

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Table 4.3 – Continued

Run	Phase	n*	SiO ₂ [‡]	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total													
41c-108a	cpx	19	54.0	0.4	0.29	0.08	1.77	0.28	0.51	0.22	5.5	1.4	0.13	0.04	17.9	1.0	20.13	0.78	0.29	0.09	100.5						
	opx	2	56.3	1.6	0.07	0.01	1.37	0.68	0.31	0.12	8.1	2.1	0.14	0.03	32.8	1.1	1.58	0.06	0.07	0.02	100.6						
	glass	7	56.2	0.4	0.56	0.06	15.79	0.14	0.02	0.01	4.2	0.2	0.06	0.02	4.2	0.1	6.61	0.26	2.29	0.15	0.83	0.03	0.19	0.04	90.9		
	oliv	12	40.1	0.3	0.02	0.01	0.02	0.01	0.04	0.03	14.7	0.3	0.19	0.03	44.2	0.7	0.13	0.03			99.3						
41c-108b	cpx	16	54.2	0.4	0.27	0.04	2.11	0.41	0.55	0.14	4.9	0.4	0.13	0.04	18.0	0.6	20.25	0.77	0.23	0.06	100.6						
	glass	14	54.9	0.5	0.63	0.04	15.69	0.13	0.04	0.02	4.4	0.1	0.05	0.02	4.5	0.1	6.45	0.29	2.79	0.14	0.67	0.04	0.23	0.03	90.4		
	spnl	8	0.2	0.1	0.61	0.13	12.16	1.25	48.7	2.3	25.3	1.4	0.29	0.03	10.2	0.4	0.23	0.04			97.6						
	oliv	10	40.5	0.3	0.01	0.01	0.04	0.06	0.02	0.01	12.9	0.7	0.17	0.03	46.7	0.9	0.14	0.03			100.6						
41c-110	cpx	14	53.7	0.5	0.24	0.07	1.82	0.56	0.67	0.25	4.6	0.9	0.11	0.03	17.7	0.3	21.40	0.80	0.27	0.07	100.5						
	glass	19	55.8	0.3	0.60	0.06	16.89	0.15	0.02	0.03	4.4	0.3	0.08	0.03	4.0	0.2	6.58	0.09	3.65	0.16	0.85	0.02	0.21	0.02	93.1		
	cpx	20	52.6	0.7	0.43	0.07	3.14	0.45	0.36	0.05	5.9	0.5	0.15	0.03	17.3	0.8	19.91	1.03	0.37	0.08				100.1			
	opx	10	55.6	0.7	0.18	0.03	2.14	0.64	0.25	0.06	9.1	0.7	0.20	0.01	30.6	0.6	1.81	0.55	0.07	0.07	99.9						
41c-111a	glass	14	55.8	0.2	0.59	0.08	15.07	0.08	0.00	0.01	4.5	0.1	0.09	0.02	5.2	0.1	7.03	0.09	2.27	0.19	0.81	0.04	0.16	0.03	91.5		
	spnl	7	0.2	0.1	1.19	0.12	14.33	0.71	46.8	1.0	23.3	0.5	0.26	0.02	11.5	0.3	0.27	0.02			97.8						
	oliv	17	40.1	0.5	0.01	0.01	0.01	0.04	0.07	0.04	12.3	0.6	0.14	0.02	46.6	1.0	0.25	0.43			99.5						
	cpx	10	54.4	0.4	0.15	0.03	1.42	0.33	0.72	0.19	4.1	0.4	0.11	0.03	18.6	0.7	20.58	1.20	0.26	0.05				100.4			
41c-111b	glass	15	55.5	0.4	0.62	0.11	15.05	0.07	0.03	0.04	4.2	0.2	0.08	0.02	5.3	0.1	6.94	0.19	2.44	0.15	0.78	0.05	0.18	0.02	91.1		
	oliv	9	39.9	0.3	0.03	0.01	0.04	0.01	0.04	0.02	12.5	0.3	0.18	0.03	47.2	0.6	0.18	0.03			100.0						
	cpx	15	54.2	0.2	0.17	0.03	1.36	0.16	0.81	0.07	3.8	0.3	0.10	0.02	18.1	0.3	21.73	0.40	0.28	0.05				100.5			
	glass	15	62.0	0.5	0.34	0.05	16.67	0.13	0.00	0.00	3.4	0.2	0.09	0.02	2.4	0.3	5.42	0.19	3.38	0.10	0.63	0.10	0.13	0.04	94.5		
41c-116b	spnl	6	0.1	0.0	0.53	0.13	10.47	1.70	44.8	1.2	31.9	2.7	0.40	0.03	8.5	0.4	0.23	0.04			96.9						
	cpx	14	52.6	0.6	0.33	0.09	3.48	0.45	0.30	0.27	6.3	0.5	0.16	0.03	16.7	1.1	20.64	0.97	0.33	0.06				100.8			
	opx	10	55.5	0.7	0.15	0.05	2.48	0.79	0.09	0.03	11.5	0.6	0.22	0.03	29.4	0.8	1.34	0.36	0.06	0.04				100.7			
	amph	16	45.4	0.3	1.37	0.28	12.01	0.38	0.09	0.04	8.4	0.4	0.11	0.02	16.7	0.4	11.21	0.24	2.04	0.08	0.22	0.02		97.5			
41c-117	glass	15	57.8	1.1	0.60	0.10	16.67	0.05	0.02	0.01	4.2	0.1	0.10	0.04	3.6	0.1	5.91	0.27	2.82	0.68	0.82	0.15	0.25	0.03	92.8		
	cpx	7	51.2	0.6	0.42	0.07	4.03	0.29	0.24	0.04	6.2	0.3	0.18	0.03	16.3	0.3	20.86	0.29	0.40	0.03				99.8			
	opx	8	55.4	0.8	0.18	0.03	2.64	0.84	0.16	0.05	8.5	0.4	0.24	0.03	31.7	0.6	1.60	0.19	0.04	0.02				100.5			
	amph	10	45.0	0.4	1.16	0.07	10.58	0.46	0.32	0.03	7.9	0.5	0.06	0.03	17.6	0.3	11.37	0.30	2.22	0.07	0.26	0.03		96.5			
41c-118	mag	7	0.2	0.0	1.79	0.01	5.85	0.08	1.71	0.35	76.1	1.4	0.23	0.03	6.8	0.2	0.18	0.03			92.9						
	glass	15	59.0	0.3	0.47	0.09	17.22	0.14	0.02	0.02	3.9	0.2	0.09	0.01	3.2	0.1	5.92	0.18	3.40	0.14	0.93	0.02	0.18	0.02	94.3		
	cpx	7	50.0	0.7	0.57	0.05	5.34	0.42	0.27	0.05	7.5	0.2	0.11	0.03	15.5	0.7	20.44	0.56	0.54	0.03				100.3			
	opx	8	53.9	0.7	0.19	0.02	4.07	0.33	0.19	0.01	9.9	0.2	0.16	0.02	30.3	0.2	1.40	0.15	0.08	0.02				100.2			
41c-119b	amph	11	44.0	0.4	1.44	0.05	11.96	0.24	0.26	0.06	8.7	0.3	0.13	0.06	16.7	0.2	11.43	0.27	2.30	0.06	0.27	0.02	0.75	0.04	0.23	0.06	97.2
	glass	28	55.2	1.0	0.56	0.06	16.05	0.18	0.02	0.02	4.4	0.1	0.06	0.02	4.1	0.1	6.14	0.12	2.84	0.22	0.75	0.04	0.23	0.06	90.3		
	cpx	15	52.9	0.7	0.26	0.06	2.15	0.48	0.44	0.29	4.7	0.6	0.11	0.01	17.6	0.8	20.96	0.81	0.31	0.06				99.4			
	opx	10	56.8	0.5	0.10	0.02	1.45	0.31	0.24	0.13	7.4	0.5	0.17	0.03	32.8	0.8	1.23	0.24	0.04	0.01				100.2			
41c-129	amph	19	45.2	0.4	0.97	0.06	10.45	0.39	0.14	0.08	7.4	0.4	0.07	0.04	18.3	0.3	11.38	0.28	2.12	0.08	0.23	0.02			96.3		
	mag	10	0.2	0.0	1.47	0.13	5.03	0.37	4.89	2.55	72.4	2.8	0.27	0.03	7.6	0.4	0.21	0.03			92.1						
	glass																										
	cpx	12	53.0	0.7	0.47	0.09	2.13	0.39	0.26	0.13	7.2	0.6	0.18	0.02	16.5	0.6	19.96	0.91	0.23	0.10				99.9			
41c-129	opx	8	54.4	0.8	0.22	0.05	1.29	0.69	0.07	0.02	15.6	0.7	0.30	0.03	26.2	0.9	1.48	0.21	0.03	0.05				99.5			

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Table 4.3 – Continued

Run	Phase	n*	SiO ₂ [‡]	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total											
41c-141	plag	10	54.5	0.7	29.10	0.57	0.7	0.1	0.2	0.0	11.75	0.47	4.44	0.33	0.14	0.02	100.9								
	amph	13	44.7	1.1	2.70	0.38	0.15	9.5	0.3	0.11	0.03	15.7	0.6	11.26	0.63	2.17	0.13	0.28	0.03	96.6					
	glass	34	61.1	1.1	0.73	0.09	15.04	0.39	0.02	0.02	3.8	0.3	0.06	0.02	2.3	0.7	5.61	0.29	2.70	0.49	0.68	0.10	0.23	0.03	92.4
	cpx	13	52.7	0.5	0.55	0.09	2.30	0.34	0.21	0.06	6.7	0.3	0.17	0.03	16.7	0.5	20.59	0.74	0.27	0.04					100.1
	opx	10	55.3	0.5	0.18	0.04	0.92	0.33	0.07	0.03	13.4	0.6	0.28	0.03	28.9	0.7	1.47	0.31	0.03	0.02					100.5
44-100	plag	17	50.2	0.7	31.66	0.52	0.5	0.1	0.1	0.0	14.48	0.37	3.09	0.21	0.06	0.01	100.2								
	amph	17	45.8	1.1	2.60	0.29	9.75	0.94	0.21	0.18	8.9	0.5	0.11	0.03	16.7	0.7	10.98	0.51	2.02	0.21	0.24	0.02			97.3
	glass	35	49.4	0.4	0.58	0.06	17.80	0.11	0.03	0.03	5.8	0.2	0.10	0.03	5.0	0.2	8.74	0.21	2.61	0.21	0.39	0.02	0.13	0.04	90.6
	oliv	23	39.3	0.6	0.02	0.01	0.04	0.15	0.07	0.03	15.6	0.7	0.20	0.06	44.3	0.6	0.20	0.11							99.8
	cpx	20	52.2	1.0	0.34	0.09	3.39	0.79	0.50	0.24	5.4	0.7	0.14	0.02	16.8	0.7	21.07	1.06	0.29	0.06					100.1
44-101	glass	15	49.3	0.4	0.61	0.08	16.96	0.12	0.02	0.01	6.1	0.2	0.14	0.03	5.9	0.1	9.32	0.14	2.28	0.14	0.43	0.02	0.17	0.02	91.2
	oliv	9	39.8	0.3	0.03	0.01	0.03	0.01	0.05	0.02	13.9	0.5	0.23	0.02	46.2	0.7	0.21	0.02							100.4
	cpx	15	52.4	0.4	0.30	0.05	3.04	0.49	0.77	0.18	4.6	0.4	0.11	0.03	16.8	0.6	22.23	0.75	0.27	0.04					100.6
	glass	15	49.3	0.5	0.55	0.05	17.27	0.16	0.01	0.01	4.8	0.1	0.14	0.02	5.5	0.2	7.93	0.30	2.55	0.28	0.65	0.18	0.14	0.03	88.8
	oliv	8	40.3	1.9	0.00	0.00	0.02	0.02	0.01	8.3	1.1	0.25	0.03	51.3	2.9	0.12	0.01								100.3
44-102	cpx	15	50.6	2.1	0.34	0.14	4.16	1.46	0.10	0.04	5.6	1.0	0.15	0.03	16.3	1.2	22.14	0.43	0.30	0.05					99.8
	amph	18	44.4	0.6	0.72	0.05	11.18	0.55	0.30	0.08	7.8	0.2	0.06	0.02	18.3	0.5	11.03	0.38	2.37	0.09	0.18	0.02			96.3
	mag	3	0.2	0.0	1.17	0.05	8.57	0.33	2.14	0.62	70.6	0.8	0.35	0.01	9.7	0.7	0.10	0.04							92.8

* n=number of probe analyses.

† columns directly following the oxide wt% are 1- σ errors from replicate analyses.

Table 4.4: Comparison of empirical amphibole barometers

Source	P (MPa)	Mg# ^a	ΔNNO	Al ^{VI} ^b	Al ₂ O ₃ ^c	LC ^d	ΔP ^e	adj LC ^f	ΔP	Al ₂ O ₃ ^g	ΔP	Mg# ^h	ΔP	avei	ΔP
This study	800	0.815	0	0.334	19.31	582	-218	511	-289	562	-238	729	-71	620	-180
	800	0.819	0	0.529	19.52	930	130	838	38	836	36	785	-15	812	12
	489	0.809	0	0.362		633	144	559	70			652	163	606	117
	489	0.807	0	0.390		682	193	606	117			628	139	617	128
	489	0.799	0	0.443	19.36	777	288	695	206	711	222	540	51	617	128
	490	0.763	0	0.225	18.81	388	-102	329	-161	379	-111				
	500	0.781	3	0.451	17.62	790	290	707	207	582	82				
	500	0.798	3	0.254	17.97	439	-61	377	-123	350	-150				
	500	0.773	3	0.315	18.24	548	48	479	-21	452	-48				
	500	0.815	3	0.240	17.73	415	-85	354	-146	313	-187	481	-19	418	-82
G et al. 2003	201	0.747	0	0.197		338	137	282	81			195	-6	239	38
	208	0.770	2	0.188	16.22	322	114	267	59	124	-84	231	23	249	41
	500	0.806	3	0.256	19.44	442	-58	380	-120	469	-31	405	-95	392	-108
	800	0.793	0	0.513	17.60	902	102	811	11	663	-137				
Ba and C 2004	800	0.782	0	0.527	19.68	926	126	834	34	846	46				
	200	0.692	0.5	0.160	18.46	272	72	221	21	266	66				
	155	0.700	0.5	0.134	18.06	224	69	176	21	199	44				
	221	0.758	1.3	0.103	17.57	170	-51	125	-96	120	-101	201	-20	163	-58
P and M 2007	121	0.744	2	0.142	17.58	239	118	189	68	171	50	136	15	163	42
	104	0.752	1.8	0.118	18.52	197	93	150	46	215	111	166	62	158	54
	94	0.751	3	0.028	18.30	36	-58	-1	-95	79	-15	135	41	67	-27
	54	0.745	1.7	0.118	19.06	197	143	150	96	258	204	145	91	148	94
Bl and C 2001	958	0.810	2.1	0.414	22.61	725	-233	645	-313	931	-27				
	958	0.818	2.2	0.442	22.10	776	-182	693	-265	928	-30				
	194	0.770	0.81	0.233	18.43	402	208	343	149	359	165	276	82	310	116
	228	0.791	1.64	0.160	17.61	272	44	221	-7	198	-30	371	143	296	68
Bl and C 1998	297	0.812	0.57	0.224	17.57	386	89	328	31	279	-18	634	337	481	184
	132	0.769	0.62	0.278	16.19	482	350	417	285	240	108	276	144	347	215
	292	0.794	3.13	0.233	16.93	401	109	342	50	239	-53	314	22	328	36
	205	0.771	3	0.250	17.41	433	228	371	166	300	95	205	0	288	83
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Table 4.4 – Continued

Source	P (MPa)	Mg# ^a	Δ NNO	Al ^{VI} ^b	Al ₂ O ₃ ^c	LC ^d	Δ P ^e	adj LC ^f	Δ P	Al ₂ O ₃ ^g	Δ P	Mg# ^h	Δ P	ave ⁱ	Δ P
M et al. 2001	252	0.778	3.49	0.199	17.47	342	90	286	34	239	-13	218	-34	252	0
	145	0.774	3.17	0.207	17.28	356	211	299	154	234	89	208	63	254	109
	1200	0.752	0	0.705	20.19	1245	45	1133	-67	1122	-78				
	1200	0.741	0	0.753	20.79	1330	130	1213	13	1233	33				

^a Mg# of experimental amphibole^b Al^{VI} calculated by method of Leake et al. [1997].^c This is the Al₂O₃ of the melt in equilibrium with the amphibole, with the melt normalized anhydrous to 100% total.^d Barometer of Larocque and Canil [2010]: Al^{VI}=0.056*P+0.008 (P is in kbar not MPa).^e Difference in MPa of calculated pressure from previous column and the experimental pressure.^f A new barometer calibrated by the same method of Larocque and Canil [2010] but adding ours and experiments Grove et al. [2003], Müntener et al. [2001], Barclay and Carmichael [2004], Blatter and Carmichael [1998, 2001], Pichavant and MacDonald [2007] to the calibration.^g new calibration following the method of Larocque and Canil [2010] but with a term added to account for non-P dependent Al^{VI} content.^h Mg# barometer of this paper (equation 1).ⁱ average pressure from the adjusted LC and Mg# barometers.

Table 4.5: Calculated crystallization pressures of Mt. Shasta high-Mg# amphiboles

Sample	Amph Mg#	ΔNNO	Al^{VI}	adj LC	Mg#	average
82-85	0.833	0.5	0.164	226	949	588
82-85	0.813	0.5	0.194	277	656	467
82-88a	0.768	0.5	0.195	278	276	277
85-59	0.782	0.5	0.242	358	363	361
83-56	0.800	0.5	0.313	476	514	495
96-5	0.800	0.5	0.245	362	514	438
96-11b	0.812	0.5	0.309	469	644	556
97-1f	0.797	0.5	0.244	361	485	423

All pressures in MPa, amphibole compositions and f_{O_2} from Grove et al. [2005]

Figure 4-1: Design for hydrous piston cylinder experiments

Figure 4-2: Backscattered electron images of experiments

Figure 4-3: Al site assignment variations in experimental amphiboles

Figure 4-4: Summary of isobaric crystallization experiments

Figure 4-6: Experimental liquid lines of descent

Figure 4-7: Pseudo-ternary projections of experimental liquids

Figure 4-9: Calibration of amphibole Mg# hygrometer

Figure 4-10: Comparison of Al in hornblende and Mg in hornblende barometers

Amphibole analyses from Mt. Shasta Lavas

Figure 4-11: Distribution of amphibole $Mg\#$'s in Mt. Shasta andesite and dacite lavas

Figure 4-12: Magmatic H₂O content as a function of temperature

Chapter 5

Deep magma mixing and fractionation of primitive hydrous magmas beneath Mt. Shasta, CA

5.1 Introduction

Here we present a petrologic study of a suite of 82 quenched magmatic inclusions collected from andesite and dacite lavas of Mt. Shasta volcano. Experimental evidence suggests that primitive magnesian andesites and basaltic andesites from the Shasta region could be parental melts to evolved andesites and dacites that make up erupted material at Mt. Shasta. We demonstrate that these inclusions represent quenched liquids intermediate in composition between the PMA and BA lavas and the Shasta andesite and dacite lavas. They provide evidence that links the primitive andesites and basaltic andesites in the formation of the volumetrically important but compositionally complicated Shasta main group lavas. We use phase equilibrium arguments to show that some of these inclusions contained up to 14 wt% H₂O in order to stabilize the mineral assemblages present, and record polybaric magma fractionation, assimilation, and mixing processes that are occurring through the entire crustal column down to Moho depths in the Mt. Shasta plumbing system. In this paper we investigate

the relationship of the primitive magnesian andesite sample number 85-41c (PMA, chapter 4) and a primitive basaltic andesite 85-44 (BA of Baker et al. [1994]), to the mixed main group andesite and dacite lavas that typify Shasta volcanism. The H_2O saturated phase relations of the PMA have been determined for the full range of crustal pressures (0-0.8 GPa, chapter 4) and comparison of the amphibole compositions in the quenched magmatic inclusions provide constraints on pre-eruptive P_{H_2O} , and depth of formation in the crust.

Mt. Shasta CA, is a stratocone volcano that is constructed solely by lavas that are mixed and evolved andesites and dacites. A key question is what is/are the melt(s) parental to these voluminous mixed magmas. Mt. Shasta is an important volcano in the context of global subduction zone magmatism because primitive melts in equilibrium with a mantle mineral assemblage are preserved at monogenetic cinder cones in the greater Shasta region [Baker et al., 1994, Grove et al., 2002], and the fact that high pre-eruptive H_2O contents have been inferred for lavas erupted from Shastina (a large vent on the flank of Mt. Shasta) by melt inclusion studies [Anderson, 1974], the primitive lavas by melt inclusions [Ruscitto et al., 2010], the petrology of the primitive magmas [Grove et al., 2005], and experiments [McCanta et al., 2007]. However there is still debate as to whether the high H_2O contents of these melt inclusions, and the origin of primitive Mg-rich andesites and basaltic andesites are related to the voluminous cone building lavas. Streck et al. [2007] proposed that the primitive lavas are actually a product of mixing of a Shasta dacite with entrained ultramafic material, and thus represent an anomalous group of magmas not directly related to the formation of large volumes of calc-alkaline magmatism. However a number of authors have questioned the validity of the Streck et al. [2007] conclusions, and support the idea of the primitive lavas being parental to the evolved andesites and dacites.

5.2 Geologic Setting and Sampling

Mt. Shasta, largest of the Cascade stratocone volcanoes, has erupted $\sim 500 \text{ km}^3$ of andesitic-dacitic lava (58-66 wt% SiO_2 , Baker [1988]), over the last 250,000 years. These lavas (referred to hereafter as the Shasta main group lavas) erupted from vents associated with the construction of the main Mt. Shasta edifice and show complicated histories of fractionation, mixing, and assimilation [Grove et al., 2005]. Mt. Shasta is located at the southern end of the Cascades chain, just south of the CA-OR border. Early work on Mt. Shasta has shown there to be 4 major eruptive episodes that built the main cone [Christiansen et al., 1977]. Ordered by age these episodes are Sargents Ridge (~ 250 – $\sim 130 \text{ ka}$), Misery Hill (80–10 ka), Shastina (10–9.4 ka) and Hotlum (6–2 ka) (Fig 5-1). Also erupted during the two early phases are the satellite vents where the PMA and BA have been collected and described [Baker et al., 1994].

Glassy and microcrystalline quenched magmatic inclusions ranging in size from 10 cm - 1 m were collected. They are usually of ellipsoid shape and easily distinguished in the field from the relatively lighter in color and phenocryst rich host andesites and dacites. Most of the inclusions are smooth and rounded, vesicular, and diktytaxitic. Some form irregular cusped or crenulated boundaries on the mm scale with the host magma. Inclusions were sampled from lava flows spanning all 4 eruptive periods, and come from 5 main localities that cover most of the main Shasta cone (Fig 5-1). Red Butte and North Gate are satellite dacite domes assigned to the Sargents Ridge eruptive period [Christiansen et al., 1977]. Inclusions from these localities were extracted from fresh dacite blocks exposed on the edges of flow fronts. Red Butte is situated on the southern flank of Mt. Shasta and North Gate is located on the northern flank. Shastina is a large volcano located directly on the western flank of Mt. Shasta proper. Inclusions from Shastina were collected from flows near the vent. The other two inclusion localities sampled for this paper come from lava flows that issued directly from Shasta's central vent. The andesite of Cold Creek is an inclusion-rich Misery Hill flow on the southeast side of the volcano. The Cold Creek andesite flows has been glacially eroded and offer relatively unweathered exposures. Hotlum

aged inclusions come from a flow near Gravel Creek on the east-northeast side of Mt. Shasta.

5.3 Analytical Methods

Inclusions were removed from their host lava and chipped in the field. Then chips of rock were handpicked to remove chips that were weathered, contained pieces of the host, or had hammer marks to avoid contamination. The picked over chips were boiled in purified, deionized water and ultrasounded to remove dust from porous samples. 100-200 grams of chips were then crushed using an Al₂O₃ shatter box and an agate mortar for fine grinding. Major and trace element whole rock analyses were obtained on samples with 05, 06, or 07 prefix by X-ray fluorescence and ICPMS at the Geoanalytic Lab at Washington State University. Samples with other than 05, 06, and 07 prefix were analyzed for major and trace elements by XRF at the USGS in Menlo Park (Tables 5.1 to 5.9). Compositions of minerals in the inclusions as well as experiments were obtained using a five-spectrometer JEOL 733 Superprobe at MIT (Table 5.10 to 5.15). All of the analyses used 15 kV acceleration voltage and a 10 nA beam current.

5.4 Petrology of Magmatic Inclusions

5.4.1 Cumulate and Granoblastic Inclusions

The collection of magmatic inclusions has been classified based on distinctive phenocryst assemblages and textures. The two main textural types of magmatic inclusions we designate are quenched liquid, and cumulate or recrystallized (granoblastic). Cumulate inclusions include two subtypes, plagioclase/pyroxene cumulates or plagioclase/amphibole cumulates. Amphibole bearing cumulates are porphyritic in texture, containing large euhedral, 5-10 mm (maximum length) blades of amphibole, surrounded by slightly smaller subhedral plagioclase grains, and smaller subhedral orthopyroxene (Fig 5-3). Some of the cumulates are the most magnesian rocks ana-

lyzed in the collection, at bulk contents of 10-12 wt% MgO (Table 5.9), a result of accumulated amphibole and pyroxene. Pyroxene bearing cumulates are porphyritic with phenocrysts up to 2-4 mm of plagioclase and pyroxene. These cumulates are sometimes porous, with glass filling many of the vesicles, and have orthopyroxene (opx) and clinopyroxene (cpx) and lack amphibole. Pyroxene and plagioclase rich cumulates often are similar in appearance to other quenched liquid inclusions, but can be distinguished using bulk major element variations because of lower K₂O contents and enrichments in FeO relative to MgO, and do not lie on liquid lines of descent from primitive end member lavas (Fig 5-2).

Granoblastic inclusions are the rarest variety with only 3 samples identified. These rocks have a recrystallized texture with plagioclase grains on the order of 10 microns, with well developed triple junctions. Pyroxene grains are also on the order of 10 microns, but are interstitial with respect to the plagioclase and far less abundant (Fig 5-3). On the hand sample scale it is often possible to make out a fabric in the granoblastic inclusions that may be a remnant of magmatic foliation or recrystallized melt veins. It is likely that the granoblastic and cumulate inclusions are remnants of wall rock or reheated bed rock that was incorporated as xenoliths in the host lava.

The main focus of this paper will be on the 65 ‘quenched liquid’ type inclusions. These inclusions make up the vast majority of what has been collected, and are typically microcrystalline to glassy, vesicular, and diktytaxitic in texture. We have classified the quenched liquid type inclusions into 4 different subgroups based on distinctive microphenocryst mineralogy and texture. These subgroups are petrographically determined; however it will be shown that each subgroup has its own typical bulk chemical characteristics. The four subgroups are: amphibole and plagioclase dominated samples which are the most common and found in the Red Butte, North Gate, and Cold creek localities; amphibole and olivine bearing samples which have rare but ubiquitous olivine microphenocrysts and are found at both Red Butte and Cold Creek; pyroxene and plagioclase dominated samples which have pyroxene in subequal or greater abundance to amphibole phenocrysts, and are found at the Red Butte, Cold Creek, and Gravel Creek sites; plagioclase and olivine bearing inclusions

which have small euhedral olivine microphenocrysts and are found only in the Cold Creek locality. The mineralogy of this inclusion suite is the same or similar across the inclusion types, but the abundance and textural relationships are very distinct.

5.4.2 Quenched Liquid Magmatic Inclusions

All quenched liquid type inclusions collected for study range in size from approximately 10-100 cm in diameter, although in the field their size range extends all the way down to single xenocrysts in the host lava from disaggregated inclusions. These inclusions are remarkable for their uniform, aphanitic textures, with no zoning or heterogeneities visible on the cm scale, in stark contrast to their highly porphyritic host lavas. Crenulated margins on the mm scale at the boundary between the host lava and the quenched inclusions are common features, but all display a distinct smooth ellipsoid shape. All inclusions contain a quenched glass or microlite-rich groundmass. They are vesicular, with vesicle boundaries often defined by glass, but sometimes by plagioclase or amphibole crystals in a diktytaxitic manner.

Amphibole and plagioclase dominated (AMPL) inclusions

These inclusions exhibit a pilotaxitic texture with needle like amphibole and plagioclase as the dominant microphenocrysts, and they range in grain size from almost aphyric to medium grained (1-5 mm xtals in longest direction, Fig 5-4). Amphibole makes up about 30-40 percent of the crystalline material in the inclusion and is either the first phase to crystallize and shows well developed euhedral boundaries or co-crystallizes with the plagioclase which makes up the remaining 60-70 percent of crystals. Often the two crystal types interpenetrate one another (Fig 5-5). Rare orthopyroxene (opx) and clinopyroxene (cpx) microphenocrysts are found in this variety of inclusion. Glass is abundant and usually makes up the majority of the mesostasis with plag and amphibole microlites making up the groundmass assemblage. The amphiboles are variably opacitized and range in color from dark green-brown to dark red, to completely opaque. The opacitization is a mineral breakdown to a fine grained

mixture of plagioclase+pyroxene+oxide due to the inclusion experiencing high temperatures for a prolonged period at pressures below amphibole stability.

Amphibole-olivine (AMOL) dominated inclusions

These inclusions are distinguished by rare ($<<1\%$) but ubiquitous sub mm olivine microphenocrysts surrounded by a rim of amphibole and/or opx (Fig 5-5). Plagioclase, cpx and opx phenocrysts are also found in this variety of inclusion. Rare inclusions of amphibole and cpx are found inside olivine and opx phenocrysts, further indicating these are early crystallizing phases. Grain size ranges from fine to medium grained. These samples are often so amphibole rich they are reddish-brown in hand sample, with 50 percent of the crystalline material being amphibole and the remaining 50 percent being plagioclase. Quenched vesiculated glass with amphibole, pyroxene, and hopper-type plagioclase microlites make up the mesostasis (Fig 5-5). Phenocrysts of apatite are found in this variety of inclusion and can range up to several mm in length in the maximum growth direction, as well as abundant microcrystals of magnetite and ilmenite and rarely biotite as a late stage crystallization phase.

Plagioclase-olivine (PLOL) dominated inclusions

Euhedral microphenocrysts of olivine and plagioclase are the dominant feature of these inclusions, and range from 100-1000 microns. Glomerocrysts of plagioclase and olivine are common and are less than 5 mm in diameter (Fig 5-6). Plagioclase is about 80-90 percent of the crystalline material and olivine and opx are 10-20 percent. Rare opx phenocrysts are present as well as some rare Fe-rich opx xenocrysts which are embayed and reacted cores with Mg-rich overgrowth rims. Plagioclase phenocrysts 1-2 mm in diameter have An poor cores, and are probably mixed in from host lava (Fig 5-6). The samples are all fine grained and vesicular, often with late stage plagioclase crystals extending into the vesicles in a diktytaxitic manner.

Plagioclase-pyroxene (PLPX) dominated inclusions

Plagioclase, cpx, and opx and are the dominant phenocrysts in these samples. Amphibole is sometimes present but in lesser abundance (<10 percent of crystalline material) than the AMOL or AMPL types. Plagioclase phenocrysts range in size from 0.5-3 mm and many of the large phenocrysts have sieve-textured cores with a normally zoned rim overgrowth. Olivine is occasionally present as a remnant reacted core with opx overgrowths (Fig 5-7). Amphibole phenocrysts are often oxidized and/or completely opacitized, or have a decompression breakdown rim. Where amphibole is preserved it shows a dark reddish-brown to light brown pleochroism (Fig 5-7). When present the amphibole is always co-crystallizing with plagioclase, and plagioclase inclusions in amphibole are common. Clinopyroxene and orthopyroxene are common phenocrysts, and some samples contain complexly zoned pyroxenes. The crystallinity of these samples varies from some that are over 50% quenched glass, to some that are completely crystalline. Plagioclase and pyroxene and rarely amphibole are groundmass minerals.

5.5 Mineral Chemistry

5.5.1 Olivine

The cores of olivine grains range in forsterite content from a high of Fo_{90.4} in phenocryst cores from an AMOL sample down to Fo_{78.2} in a PLPX sample (Table 5.10). Olivine in the PLOL type inclusions has a more restricted range in composition from Fo₈₈ to Fo₈₅ (Table 5.10). Nickel content in the olivine is highly variable. Low Ni contents in the PLPX and PLOL olivine grains are common and range from undetectable on the microprobe to 2000 ppm. High nickel olivines are found in the in AMOL samples and are typically around 5000 ppm with the highest found being 5600 ppm. High Ni contents combined with the most Fo-rich olivines suggest a parental melt in equilibrium with mantle olivine. The nickel contents also indicate that olivine crystallized from a high SiO₂ composition such as the BA or PMA melt, not a basalt [Hart and Davis, 1978].

5.5.2 Plagioclase

The anorthite (An) content of plagioclase cores in the AMOL and AMPL inclusions within a single sample usually have a narrow range of only several percent and are normally zoned. The cores in different samples range from 50.5 to 69.7% An. Simple zoning patterns with smooth composition variation from core to rim are typical in the AMOL samples and range from 34.4 at the rim to 67.5 in the cores (Table 5.11). PLPX inclusions have much more complexly zoned plagioclase crystals that show patchy zoning, sieve textures, and reverse zoning. Anorthite content ranges from 43.3 to 77.7 in single crystals with a high-An spike surrounding a low An core. A typical zoning profile for one of the complexly zoned crystals is shown in Fig 5-8. The plagioclase in these inclusions resemble some in the host rock, and may represent some physical mixing. However the plagioclase in the host lavas is heterogeneous and all populations of plagioclase did not crystallize from the same liquid composition, and so mixing is required to form plagioclase populations in the host and inclusions.

5.5.3 Pyroxene

Both opx and cpx are present as phenocrysts or xenocrysts in all of the classes of inclusions, although opx is more abundant, and pyroxenes are most common in the PLPX class of inclusions. Orthopyroxene cores in the AMOL samples have enstatite contents up to $\text{En}_{92.4}$ and range down to $\text{En}_{85.4}$. These are the most primitive orthopyroxene crystals and with this Mg# would be expected to be in equilibrium with the $\text{Fo}_{90.4}$ to $\text{Fo}_{84.0}$. Mg# is defined as the molar ratio of MgO in a mineral to the total of MgO and FeO, $(\text{MgO}/[\text{MgO}+\text{FeO}])$ assuming all Fe is ferrous. Zoning in the pyroxene is typically normal with high-Mg cores low low-Mg rims, although there are some Fe-rich pyroxene cores that show a clear reaction relationship with the host magma in the AMOL and PLPX class of inclusions. These rims range down to Mg# 0.641.

Clinopyroxene crystals show a more limited range in composition from Mg# 0.910 in the AMOL samples to 0.756 in the PLPX samples. Clinopyroxene is less abundant

than the opx, and exhibits much less zoning. The cpx phenocrysts are typically low Al_2O_3 (<2 wt%) and low Na_2O (Table 5.12).

5.5.4 Amphibole

Amphibole zoning varies widely in these samples. Cores of amphibole microphenocrysts range in Mg# from 0.645 to 0.833 and in Al_2O_3 content from 8.0 to 13.5 wt%. In the AMOL and AMPL inclusions the amphiboles have extremely fine scale oscillatory zoning. Figure 5-9 shows an electron microprobe transect across the length of an amphibole microphenocryst, and there is >20 oscillations per mm length of crystal. The maximum Mg# for the particular amphibole in Fig 5-9 is 0.782 and the minimum is 0.714, and there is an overall decreasing Mg# from core to rim overprinted on the oscillatory zoning. Although plagioclase in the same sample is sub-equal in size and habit, it is An poor and simply normally zoned suggesting that the amphibole crystallized in an earlier plag free crystallizing environment. Other samples show some reverse zoning in the amphiboles, suggesting xenocrysts mixed into the magmas, and others show simple or 2 stage normal zoning.

Amphibole in the cumulate inclusions shows very little zoning, despite the crystals being much larger. The Mg# range is 0.705 to 0.730 from rim to core, and the Al_2O_3 content does not vary and is about 11.7 wt%. These values are similar for the phenocrysts in the PLPX samples. Both the cumulate amphibole inclusions and PLPX amphibole phenocrysts crystallize late in the crystallization sequence.

5.5.5 Biotite

Rare groundmass biotite is present in a few samples, 2 are AMOL and one is PLPX. The compositions range from Mg# 0.828 to 0.734 (Table 5.13). There is no zoning present, and it is a late crystallizing phase.

5.6 Whole Rock geochemistry

The quenched liquid type inclusions are the most MgO-rich liquid compositions erupted from the central vent at Mt. Shasta. Most range from basaltic andesite to andesite in composition (Fig 5-10) with the notable exception of the AMOL inclusions which have more alkalis and are borderline between the andesite-trachyandesite transitions [Le Bas et al., 1992]. The quenched liquid type inclusions range from 53.6 wt% to 61.5 wt% SiO₂. MgO ranges from 2.24 to 7.41 wt%, and the Mg# varies from 0.42 to 0.69. There is a peak in the bulk rock compositions at 58% SiO₂, 18-18.5 wt% Al₂O₃, and 2 peaks in Mg# frequency, one at 0.52 and one at 0.64 (Fig 5-11).

Major element whole rock analyses show the best evidence that the quenched magmatic inclusions are preserving liquid compositions. Variation diagrams, particularly in SiO₂ v. MgO and CaO v. MgO show a crystallization controlled liquid line of descent (LLD) for all of the quenched magmatic inclusions. Plotted in Figure 5-12 are the bulk major element contents of the inclusions along with the experimentally determined LLD's of primitive BA and PMA at various crustal pressures. The Al₂O₃ v. MgO and FeO v. MgO diagrams are especially indicative that a single LLD is not sufficient to explain the total chemical variation amongst the quenched magmatic inclusions (Fig 5-12).

5.7 Trace Element Geochemistry

The rare earth elements (REE) patterns for the quenched magmatic inclusions are plotted in Fig 5-13. The AMOL group shows extreme light-REE (LREE) enrichment (La/Sm>4, MORB normalized from Sun and McDonough [1989]) and a constantly negatively sloping pattern. The AMOL inclusions are some of the most LREE enriched magmas at Mt. Shasta and extend the range of trace element patterns observed in Grove et al. [2003] which examined the slab fluid contributions to primitive Mt. Shasta lavas. The AMPL group has a slight LREE enrichment (2<La/Sm<4) and the overall pattern has a constant negative slope. The PLPX group has complete overlap

with the AMPL group in both slope and abundance. The PLOL group has overlap with the AMPL and PLPX groups as well, but there is more spread in the LREE compositions ($10-30\times$ chondrite) than the heavy-REE ($10-11\times$ chondrite). There are thus two distinct groups of REE patterns observed in the inclusion suite, the AMPL, PLPX, and PLOL groups have constantly negative slopes that are flatter than the AMOL group. The flatter pattern groups have an affinity to the less enriched REE pattern of the BA while the AMOL group is more enriched like the PMA (Fig 5-13). A major difference between the AMOL class and as the PMA is that the AMOL samples have a negative slope in the HREE as well as the LREE.

Mt. Shasta lavas have been compared to the erupted products from the Setouchi belt in Japan, which have adakitic type high-Mg andesites. We plot the Ba/La ratios of the Shasta lavas and Setouchi lavas [Tatsumi and Ishizaka, 1982] and compare them to the slope of the LREE elements (La/Sm), and show that the inclusions fall within the range of the Shasta lavas with the exception of one of the AMOL inclusions which has a slightly steeper slope in the LREE (Fig 5-14). There is also overlap with the Setouchi samples. For comparison basalts from the Marianas are also plotted, and have very flat LREE (La/Sm <2) element patterns and much higher Ba/La ratios, interpreted as a fluid component as the carrier for Ba relative to the LREE [Elliott et al., 1997].

When plotting Pb/Ce ratios (another indicator of slab fluid) vs. Th/Nb (indicators of sediment melt input) the inclusions overlap the Shasta lavas in Th/Nb space, ranging from 0.3 to 0.9. However in Pb/Ce, the Shasta lavas are mostly below 0.2 where as the inclusions are up to 0.35. These values are similar to the range of the Marianas lavas, and very much different than the Setouchi values which are higher in both Pb/Ca and Th/Nb and plot of the scale in Fig 5-15.

Elliott et al. [1997] interpreted the high Pb/Ce ratios as a high content of a slab fluid trace element signature. Thus it is possible that the inclusions record similar sediment input as their host magmas (i.e. the Shasta lavas), but possibly even higher 'slab fluid' component. However the AMOL group of inclusions has some of the lowest Pb/Ce ratios of all the inclusions, and as will be discussed later, has to be extremely

H₂O rich in order to form their mineral assemblages and compositions. And so a lack of slab fluid does not equate to a lack of H₂O.

5.8 Discussion

5.8.1 Bulk Compositional Characteristics of Inclusions

The suite of magmatic inclusions presented here ranges to significantly more magnesium-rich compositions than the main group Shasta andesites. Main group andesites, while still relatively magnesium-rich themselves at 3-4 wt% MgO, are less primitive than the inclusions which are 3-7 wt% MgO (Table 5.9). There is a significant gap in composition plots (i.e. Fig 5-10) between primitive compositions and the main group andesites, and that gap is bridged by the inclusions. The liquids produced in isobaric crystallization experiments on Shasta region primitive lavas show the down temperature progression followed during differentiation. Using the experiments at 200, 500, and 800 MPa, the resultant LLD's form boundaries that parallel the trend seen in the suite of magmatic inclusions (Fig 5-12). The LLD's in the Al₂O₃ vs. MgO diagram (Fig 5-12) have a distinct kink at low P_{H₂O} (200 MPa) when plagioclase becomes a saturating phase, thus limiting liquid compositions to less than 19 wt% Al₂O₃. At higher P_{H₂O} plagioclase crystallization is suppressed and liquids can evolve to have at least 20 wt% Al₂O₃. This is a useful way to use bulk compositions to show high P_{H₂O} but only a couple of the inclusions are evolved enough that they would lie to the left of the plag kink on the Al₂O₃ v. MgO diagram. Inclusions that plot along the LLD on the MgO-rich side of this plagioclase kink presumably have seen fractionation of olivine+cpx+opx+amph, but not plagioclase, and pressure cannot be distinguished in this manner. This agrees with the fact that only extremely small if any europium anomalies are present in the REE patterns (Fig 5-13).

The MgO rich nature of the inclusions, although preventing the determination of pressure of last equilibration, is ideal for determining their relationships to parental magmas. The experimentally determined LLD's for both the PMA and BA merge

together on the low MgO side of LLD's, and thus evolved magmas may come from any number of primitive parents. The compositional spread of inclusions, and the fact that the LLD's from the PMA and BA parallel them, is evidence that the inclusions are mixtures of different magma types; yet they must come from magmas that are high in both MgO and SiO₂. The fine grain size, uniformity of texture, and low phenocryst contents corroborate that these quenched inclusions are indeed liquids. The existence of these quenched liquid inclusions in the evolved andesite and dacite lava flows is direct evidence that the primitive magmas erupted at satellite vents [Grove et al., 2002, 2005] are the dominant primary magmatic inputs into the Shasta plumbing system.

5.8.2 Crystallization Sequence

Olivine is the first phase to crystallize from melts that are hydrous and parental to the Mt. Shasta lavas. Olivine microphenocrysts are found in the AMOL, PLOL, and PLPX samples. The next phase to crystallize depends mainly on H₂O content, but also on melt composition. For the PLOL samples plagioclase crystallizes with the olivine, and cores of plagioclase are about An₆₅ (Fig 5-16). Using the bulk rock sample as the liquid composition in equilibrium with the plagioclase gives a $K_D^{Na-Ca}=1.6$, suggesting that these samples crystallized with ~2 wt% dissolved H₂O [Sisson and Grove, 1993]. Opx is the next phase to crystallize in these samples, and often forms rims around the normally zoned olivine phenocrysts (Fig 5-16). Cpx is a very minor phase, and also late in the crystallization, either coeval with or after opx.

Olivine microphenocrysts in the AMOL class of inclusions crystallized from magmas with much higher H₂O contents. Amphibole and both cpx and opx are the next phases to crystallize with olivine, forming rims around the olivine phenocrysts and rare inclusions in olivine (Fig 5-17). These inclusions are dominated by plagioclase which makes up over 50% of the crystalline material but is an An₅₀ plagioclase which is clearly a late stage crystal that crystallized from a Na-rich residual melt and low P_{H₂O} contents. At high H₂O contents this is to be expected because plagioclase does not crystallize until temperatures lower than 945°C at 500 MPa and above (Fig 4-5).

Liquid lines of descent for the PMA and BA at various pressures overlap significantly with each other. This means that from bulk rock chemistry alone will not be distinctive over any particular depth range of crystallization. However from the mineralogy of the inclusions and in particular the Mg#’s of amphiboles it is possible to infer the pressure range over which they were crystallizing. The crystallization temperature of the first amphibole increases monotonically with increasing P_{H_2O} . Our interpretation of these high Mg# amphiboles is that they record conditions of formation and come from magmas where amphibole with these compositions is stable. Using the Mg# barometer-hygrometer developed in chapter 4, an amphibole with Mg# above 80 must be in equilibrium with a magma containing at least ~ 10 wt% H_2O at depths greater than 500 MPa (Fig 4-9). These high H_2O contents have been previously reported in extremely rare melt inclusions in opx from a Shastina lava flow [Anderson, 1974], and estimated amphibole antecrysts from Mt. Shasta lavas (Fig 4-12), however the high Mg# amphiboles in the quenched magmatic inclusions give conclusive evidence that H_2O contents of input magmas into main conduit system can be just as rich in H_2O .

The PLPX class of inclusions also has olivine as the first phase to crystallize. Olivines are not always present in the PLPX samples, however when they are present it is as embayed cores surrounded by rims of normally zoned opx. In one case there was an intergrowth of amphibole+cpx+opx+olivine included in one of the reacted olivine microphenocrysts (Fig 5-18). The Amphibole Mg# was 0.833 and the highest recorded by any inclusions. Thus high dissolved H_2O contents are not limited to the parental melts for the AMOL class of inclusions. Following olivine, plagioclase co-crystallizes with opx and cpx as the next phases in the PLPX samples. On some occasions amphibole is a late crystallizing phenocryst phase (Fig 5-7), and often has inclusions of pyroxene and plag. Amphibole can be of similar abundance to opx in some of the rocks.

The AMPL class of inclusions is the most compositionally evolved, and no olivine has been found in these samples. These samples are the lowest in MgO content of the inclusion suite and the bulk compositions of the AMPL samples overlap compositionally with some of the main group Shasta lavas (Fig 5-10). Thus some of the

AMPL liquids might be Mt. Shasta main group andesites. A main difference between the AMPL samples and main group andesites is that amphibole is the first phase to crystallize in these samples, and is often found as inclusions in plagioclase (Fig 5-5). According to our experimental results, the crystallization sequence of amphibole before plagioclase requires pressures of 300 MPa or more and H₂O concentrations of greater than 8 wt%. Evolved magmas with amphibole crystallizing as the liquidus phase have been found in the greater Shasta region at Black Butte, a satellite vent several km's to the west of Shastina. These Black Butte samples have been experimentally investigated and require pressures of 400 MPa and water contents of 8 wt% to form [McCanta et al., 2007]. The magmas represented by the AMPL inclusions may be the same magmas producing the plagioclase bearing andesites common at Mt. Shasta, but crystallized at higher pressures prior to degassing their magmatic H₂O contents. These quenched inclusions are evidence that the erupted andesites may have had higher pre-eruptive H₂O contents, but degassed and crystallized in shallow magma chambers.

5.8.3 Quenched magmatic inclusions and magma mixing

In the suite of inclusions presented here many of the magmatic inclusions do not plot directly on the LLD from the PMA, and yet we still interpret these inclusions to represent liquid compositions. Mixing and/or different parental magmas are required to explain the departure from the observed LLDs. As mentioned earlier there is at least three different possible reasons why the quenched magmatic inclusions, which are derived from primitive mantle melts, do not lie directly on the LLD's in the Harker diagrams. 1) Different primary mantle melts are producing a variety of LLD's. 2) Mixing of only a few primary end members to produce hybrid magmas and thus LLD's that span the gap between PMA and BA on the variation diagrams 3) Magma mixing between variably differentiated magmas.

The first and second mechanisms for producing liquids on intermediate LLD's relates to the spectrum of primitive mantle melts that intrude into the crust beneath Mt. Shasta. Examples of candidates for end members of the primitive spectrum are

the basaltic andesite composition 85-44 of Grove et al. [2005] as well as the primitive magnesian andesite 85-41c. Using just these two primitive magmas, almost all of the major element compositional variability of the liquid type inclusions can be explained by mixing of these different primary end members to create a hybrid primitive magma that will have a LLD intersecting the fields of inclusions (Fig 5-12). However there are other eruptive products, such as a basaltic andesite from a vent on the north flank of Mt. Shasta. Sampled as 82-94 and published in by Baker et al. [1994], Grove et al. [2002], it has an Mg# of 0.72 and has intermediate MgO and SiO₂ between the BA and PMA investigated here. The 82-94 sample is a lava composition that represents a liquid in equilibrium with the mantle [Baker et al., 1994]. Thus we cannot rule out a continuum of primary end members produced by slightly different mantle melting conditions which might have LLDs that could produce the inclusion suite.

The third mechanism to produce the inclusions as derivative liquids not on the BA and PMA LLD's would be if both of these magmas fractionated along their respective LLD's, and then the evolved liquids mixed with each other, as well as mixing back with more primitive compositions. When plotting the inclusions on a pseudo-ternary diagram it is clear that mixing must play a role because almost none of the inclusion compositions could be explained as derived from the PMA alone. Primitive end members 85-44, 85-41c, and 82-94 are plotted in the Oliv-Plag-Qtz mineral component diagram in oxygen units (Fig 5-19). Olivine and then olivine+cpx are the early fractionating phases from the primitive magmas under H₂O saturated conditions. Thus primitive liquids will evolve away from the olivine apex in the ternary space (black arrows in Fig 5-19). It is clear from the high plag component contents of the AMOL and PLOL groups that they require a dominant amount of the BA parental component to form. The fractionation path of olivine and olivine+cpx will be followed until another cotectic is encountered. In addition to the other primitive lavas found around Mt. Shasta including contemporaneous high-alumina olivine tholeiites (also plotted in the ternary diagrams), and that composition as one of the mixing end members cannot be ruled out. It is likely that some mixture of all three of these mechanisms is playing a role. Indeed the inclusions themselves are evidence for mingling of evolved

liquids in the Mt. Shasta plumbing system, creating mixtures of mixtures. High H_2O content that is present in the primitive magmas may also enhance their mixing capabilities near their respective mantle sources. There is no doubt that extensive mixing at all crustal levels must be playing a role in the development of the inclusions, and by extension the main group andesites at Mt. Shasta.

5.9 Model for the Mt. Shasta Magmatic System

The suite of inclusions presented here in addition to the experiments conducted at mid to lower crustal pressures, and previous work on the mixed andesites and primitive mantle melts of the Mt. Shasta area, creates a clearer picture of the crustal differentiation processes that have influenced lavas at Mt. Shasta, and provide some limits on the depths of differentiation.

1. The down going Juan de Fuca slab dehydrates and injects H_2O , sediment melts, and basaltic crust melts into the mantle wedge providing much of the trace element budget [Grove et al., 2003]. This ultimately leads to primary mantle melts with different major, REE and trace element ratios.
2. At the deepest levels of the crust (near the Moho) at 25-35 km [Zucca et al., 1986], primary hydrous melts of the mantle wedge are injected into the plumbing system of Mt. Shasta. Analyses of the petrology [Grove et al., 2002, 2005] and melt inclusions in these samples [Ruscitto et al., 2010] suggest they have at least 6-8 wt% H_2O . Some of these magmas bypass the main conduit system and erupt as satellite vents.
3. Magmas that do not bypass the main conduit system fractionate at depth before rising. In the lower crust, fractionation occurs and magmas with up to 14 wt% H_2O are recorded by Mg-rich amphiboles found in association with olivine microphenocrysts. However these amphiboles are located in inclusions with intermediate compositions between the PMA and BA, thus suggesting that extensive mixing of the primitive melts from the mantle has already started in the

lower most crust, and magma mingling is common at these depths. We cannot rule out partial crystallization at even higher pressure (i.e. in the mantle).

4. At mid crustal (300-500 MPa) levels, further fractionation of hydrous magmas is taking place. Evolved inclusions with high H₂O contents as recorded by the AMPL class of inclusions most likely originate from these depths because of the distinctive textures indicating amphibole crystallizing before plagioclase. There is also evidence for degassed H₂O poor magmas at this depth, recorded by PLOL class of magmatic inclusions.
5. Extensive mixing of magmas is required at shallow levels (<200MPa) in addition to the deeper mixing, and lower H₂O contents (<5 wt%) are required to produce the relatively homogenous andesites (with respect to bulk composition) and mixed plagioclase and pyroxene phenocrysts assemblages of lava erupted at Mt. Shasta. In addition there are injections of hotter, and variably H₂O-rich primitive material into this shallow chamber that freeze in and create the inclusions we have collected for study. Some of these injections are mixed efficiently into the evolved shallow magmas, with evidence for this in single xenocrysts of primitive olivine and amphibole, as well as multiple populations of pyroxene and plagioclase crystals in the main group Mt. Shasta andesites. Injection of this hotter material might be a trigger for eruptions at the volcano.

Thus mixing of hydrous primitive melts, and crystal fractionation occurs throughout the entire crustal column at Mt. Shasta (Fig 5-20). Mg-rich amphiboles require some magmas to be extremely enriched in H₂O, and amphibole-free inclusions show that H₂O-poor magmas are also being processed in the same conduit system. The quenched magmatic inclusions show us that the primitive melts erupted as satellite vents are indeed the parental magmas to Mt. Shasta andesites. The ultra efficient mixing and fractionation that occurs in the crustal system beneath Mt. Shasta is capable of transforming this variety of primitive inputs into the homogenous but extensively mixed erupted products that make up the vast majority of the volume of Mt. Shasta.

5.10 Figure Captions

Figure 5-1: Geologic map showing the major eruptive units from vents that make up the main edifice at Mt. Shasta adapted from the map of Christiansen et al. [1977]. The flows containing the inclusions collected for this study stand out in bolded colors and a black line and span all of the eruptive time periods.

Figure 5-2: Potassium contents of all the inclusions plotted vs. MgO content. Dark arrows show the experimental liquid lines of descent from the BA and PMA magmas. Outliers on this plot are the cumulate and granoblastic inclusions which are in green and blue.

Figure 5-3: Photomicrographs of a typical amphibole-plagioclase cumulate, and granoblastic inclusion. A+B) Plane and crossed polarized light pictures of amphibole-rich cumulate inclusion 97-13A. Note the 2 mm unzoned amphiboles surrounded by a matrix of plagioclase and pyroxene. C+D) plane and crossed polarized light pictures of granoblastic inclusion 07-23H. The pyroxene grains stand out in high relief compared to the recrystallized plagioclase matrix.

Figure 5-4: Four photomicrographs taken at the magnification of four different AMPL samples in plane polarized light. The grain sizes range from 50 microns to >1 mm in the longest direction for amphibole crystals. The relative abundance and textural relationship of amphibole to plagioclase is similar in all the samples.

Figure 5-5: Photomicrographs of typical AMPL and AMOL inclusions. A+B) Plane and crossed polarized light pictures of AMPL sample 06-11C. Notice that amphibole crystallizes before and together with the plagioclase as indicated by the amphiboles included in the plagioclase. C+D) Plane and polarized light pictures of two different areas of the 06-13A sample. C) In the center of the figure is an olivine microphenocryst with a rim of amphibole overgrowth. This is the distinguishing feature of the AMOL class of inclusions.

Figure 5-6: Photo micrographs in crossed polarized light of two PLOL samples. A) millimeter sized plagioclase phenocryst set in the matrix of plagioclase and olivine microphenocrysts. B) 2 mm glomerocryst made up of smaller olivine and plagioclase

microphenocrysts. C) Typical diktytaxitic PLOL texture that dominates all of these inclusions. The olivine intergrows with plagioclase and is sometimes rimmed with opx.

Figure 5-7: Photomicrographs displaying some of the range in texture in the PLPX class of inculsions. A+B) Plane and crossed polarized picture of sample 89-21C displaying reacted olivine surrounded by rims of opx co-crystallizing with plagioclase. Dark crystals in (A) are amphibole that has been partially opacitized. C+D) Plane and crossed polarized pictures of sample 07-23G. Pyroxene and plagioclase are equigranular and about 0.5 mm in diameter. Glass and microlite rich groundmass make up about 30 percent of the sample.

Figure 5-8: A) Backscattered electron picture of a plagioclase phenocryst in PLPX sample. The plagioclase has inclusions of Fe-rich cpx and opx in a core that is low An content, overgrown by a rime of normally zoned plagioclase. B) A transect of electron microprobe analyses from the core to the rim of the plagioclase phenocryst displaying the An content of the crystal. The yellow line in (A) shows the location of the transect.

Figure 5-9: A) Backscattered electron picture of a amphibole grain from AMOL sample 06-13D. The zoning is oscillatory and has the highest MgO content in the core of the crystal. B) electron microprobe transect across the amphibole crystal where the blue line is located in (A). Mg# varies from 0.78 in the core to less than 0.7 at the rim.

Figure 5-10: Compositions of all of the inclusions in a total alkalis vs. SiO_2 diagram from Le Bas et al. [1992]. Also shown are the primitive end members that have been found at satellite vents around Mt. Shasta (stars) and the main group Shasta andesites (green ellipse). The inclusions bridge the compositional gap between both groups. Symbols are the same as in Fig 5-12.

Figure 5-11: Histograms of three different compositional parameters for the entire suite of the quenched liquid type inclusions. A) Distribution of bulk SiO_2 content of the inclusions showing a peak at 58 wt% SiO_2 . B) Distribution of bulk Al_2O_3 contents of the inclusions with a peak centered at 18 wt%. C) Distribution of bulk Mg# of

the quenched liquid inclusions, two peaks are evident, one at 0.52 and the other at 0.64.

Figure 5-12: Major element Harker variation diagrams for the suite of quenched liquid type inclusions. For reference the liquid lines of descent from isobaric crystallization experiments on primitive end members are shown as black arrows, and parallel the trends defined by the inclusions. The numbers 200, 500 and 800 refer to the pressure in MPa of the experiments that define a particular LLD. Note that not any single primitive end member can account for the complete chemical distribution of the quenched liquid inclusions.

Figure 5-13: Six panels showing the variation in bulk sample rare Earth element contents of the quenched magmatic inclusions. REE patterns for the (A) AMOL inclusions, (B) AMPL inclusions, (C) PLPX inclusions, (D) PLOL inclusions. E) overlays the span of REE concentrations for all 4 groups. The AMOL group is more enriched in LREE than the other three groups. F) REE patterns for primitive lavas in the Mt. Shasta region from Baker et al. [1994].

Figure 5-14: Trace element variation diagram showing range of Ba/La ratios versus the normalized ratios of La/Sm. The inclusions overlap with the main group Mt. Shasta andesites except for one AMOL inclusions that has a high La/Sm value. Also shown for comparison are arc magmas from the Marianas which are known to have hydrous parental magmas, and high-Mg andesites from the Setouchi belt in Japan. The Marianas lavas extend to much higher Ba/La ratios.

Figure 5-15: Th/Nb ratios of the quenched inclusions overlap with the main group Shasta lavas, but the Pb/Ce ratios in the quenched magmatic inclusions extend to much higher values. They are comparable at values up to 0.4 with the Marianas lavas. The Setouchi belt magmas plot off the scale here with Th/Nb over 1 and Pb/Ce over 0.5.

Figure 5-16: Backscattered electron image of PLOL sample 05-7E. Normally zoned olivines are co-crystallizing with An₆₅ plagioclase, surrounded by late stage interstitial opx and cpx.

Figure 5-17: Backscattered electron image of sample 06-13A. Shown is an olivine

microphenocryst with inclusions of Mg-rich opx and cpx surrounded by a reaction rim of amphibole. Equilibrium boundaries between the amphibole and olivine are preserved suggesting both were in equilibrium with each other at the time of crystallization.

Figure 5-18: Backscattered electron image of a normally zoned olivine crystal surrounded by a rim of normally zoned opx in PLPX sample 07-23D. Enlarged area is an inclusion within the olivine crystal of cpx+opx+amphibole intergrowth. The amphibole Mg# of this sample is 0.833, the highest found in the inclusion sample suite.

Figure 5-19: Pseudo-ternary diagram showing the compositions of the quenched liquid inclusions recast into the mineral components Oliv-Plag-Cpx-Qtz according to the methods of Tormey et al. [1987], and projected onto the olivine-plagioclase-quartz plane. Primitive end member compositions are shown as stars, and olivine controlled fractionation lines are black arrows. The samples are all plotting close to the plagioclase apex, and show that they have not undergone extensive plagioclase fractionation. It is apparent that the PMA cannot be the sole parental melt to any of these inclusions, and magma mixing is required to make the trends observed.

Figure 5-20: Cross section of the crust beneath Mt. Shasta (drawn to scale 4 km above sea level). Minimum pressures of crystallization are shown for inclusions with amphibole microphenocrysts as determined by the Mg# hygrometer of chapter 4. Plotted alongside the inclusion pressures are those recorded by amphibole antecrysts found in lavas from Mt. Shasta as reported in chapter 4. There is complete overlap of the two data sets, supporting the hypothesis that the quenched liquid inclusions are progenitors of the Mt. Shasta main group andesites. This also strongly suggests that magma mixing is happening very deep under Mt. Shasta, possibly even in the mantle.

Table 5.1: Trace Element Whole Rock Analyses

	NG97-13C AMPL	NG97-13D AMPL	NG97-13E AMPL	NG97-13F AMPL	NG06-11A AMPL	NG06-11B AMPL	NG06-11C AMPL	NG06-11D AMPL
<i>ICPMS</i>								
La	11.38	12.94	11.38	10.23	11.43	11.43	11.54	11.40
Ce	22.87	26.04	23.29	21.26	24.15	24.45	24.53	24.80
Pr	2.83	3.25	2.97	2.71	3.17	3.24	3.20	3.33
Nd	12.42	14.00	13.07	12.18	13.83	14.10	13.92	14.49
Sm	3.22	3.52	3.49	3.19	3.37	3.47	3.38	3.59
Eu	1.06	1.14	1.12	1.03	1.14	1.13	1.09	1.15
Gd	3.21	3.31	3.36	3.07	3.45	3.56	3.35	3.44
Tb	0.51	0.52	0.55	0.49	0.55	0.56	0.55	0.56
Dy	3.02	3.00	3.18	2.78	3.30	3.37	3.26	3.32
Ho	0.60	0.59	0.63	0.54	0.65	0.67	0.63	0.65
Er	1.60	1.56	1.66	1.42	1.72	1.76	1.68	1.75
Tm	0.23	0.23	0.24	0.20	0.25	0.26	0.25	0.25
Yb	1.45	1.39	1.48	1.27	1.52	1.55	1.55	1.56
Lu	0.22	0.23	0.24	0.20	0.23	0.24	0.23	0.24
Ba	343	393	338	303	357	346	344	325
Th	2.38	2.41	1.98	2.06	2.18	2.27	2.17	3.25
Nb	4.85	5.41	4.90	4.39	4.67	4.58	4.79	5.12
Y	15.80	15.81	16.79	14.68	15.66	16.05	15.54	16.30
Hf	2.78	3.04	2.77	2.73	2.86	2.92	2.92	2.47
Ta	0.37	0.38	0.34	0.31	0.33	0.32	0.34	0.38
U	0.86	0.93	0.71	0.85	0.86	0.89	0.98	1.32
Pb	5.72	6.36	5.34	6.56	8.42	5.65	5.49	5.87
Rb	27.56	24.34	20.74	31.46	29.71	25.73	23.69	29.90
Cs	1.66	1.37	1.09	2.54	1.67	1.42	1.27	2.10
Sr	554	586	563	554	568	576	568	598
Sc	17.59	10.91	17.41	15.42	15.06	15.83	15.37	14.84
Zr	93.9	105.2	95.1	90.2	98.9	97.5	100.3	72.7
<i>XRF</i>								
Ni	34	2	20	23	26	27	27	20
Cr					48	48	48	11
V					107	113	108	110
Ba								
Rb								
Sr								
Zr								
Y								
Ga					17	19	19	18
Cu					30	21	24	32
Zn					70	69	68	66

Table 5.2: Trace Element Whole Rock Analyses continued...

	NG06-11E-1 AMPL	NG06-11E-2 AMPL	NG06-11F AMPL	NG96-6E AMPL	NG96-6C AMPL	RB89-21A AMPL	RB97-1B AMPL	RB97-1C AMPL
<i>ICPMS</i>								
La	11.24	11.50	9.79		8.92		9.69	
Ce	24.11	24.46	21.38		19.20		19.80	
Pr	3.22	3.27	2.93		2.55		2.47	
Nd	13.83	14.05	12.97		12.16		11.04	
Sm	3.43	3.41	3.26		3.60		2.89	
Eu	1.12	1.13	1.08		1.17		0.89	
Gd	3.29	3.43	3.28		3.76		2.83	
Tb	0.54	0.55	0.52		0.61		0.46	
Dy	3.19	3.20	3.15		3.64		2.77	
Ho	0.65	0.65	0.62		0.71		0.57	
Er	1.66	1.70	1.65		1.87		1.48	
Tm	0.25	0.25	0.24		0.27		0.21	
Yb	1.48	1.51	1.45		1.60		1.29	
Lu	0.23	0.24	0.23		0.24		0.21	
Ba	341	339	311		267		265	
Th	2.00	2.05	1.79		1.46		2.64	
Nb	4.59	4.77	3.99		4.23		4.09	
Y	15.68	15.83	15.33		19.21		14.69	
Hf	2.79	2.88	2.60		2.35		1.72	
Ta	0.31	0.32	0.29		0.29		0.33	
U	0.77	0.77	0.70		0.56		1.03	
Pb	5.30	5.43	4.88		4.32		6.32	
Rb	21.62	21.09	18.26		14.72		24.20	
Cs	1.13	1.12	1.01		0.77		1.75	
Sr	569	573	503		536		518	
Sc	16.00	16.20	22.62		30.33		21.47	
Zr	94.1	96.9	85.0		77.9		54.3	
<i>XRF</i>								
Ni	28	30	69	24	47			58
Cr	50	50	172					
V	111	114	145					
Ba				339				262
Rb				29		35		28
Sr				551		553		549
Zr				100				58
Y						12		12
Ga	18	18	19			18		
Cu	19	22	28					
Zn	71	73	75					

Table 5.3: Trace Element Whole Rock Analyses continued...

	RB06-13G AMPL	CC05-5B AMPL	CC06-14F AMPL+PLOL	RB89-21C PLPX+AMPL	RB97-1F AMOL	RB99-8C AMOL	RB06-13A AMOL	RB06-13C AMOL
<i>ICPMS</i>								
La	9.87	11.33	6.64		33.66	33.30	31.44	10.58
Ce	19.87	23.50	15.51		66.46	61.71	65.59	24.94
Pr	2.54	2.96	2.26		8.07	7.01	8.51	3.59
Nd	10.22	13.02	10.18		33.22	27.63	34.23	15.67
Sm	2.45	3.36	2.64		6.70	5.30	6.45	3.94
Eu	0.85	1.10	0.98		1.80	1.45	1.74	1.19
Gd	2.23	3.47	2.96		5.01	3.94	4.65	3.81
Tb	0.37	0.57	0.50		0.62	0.51	0.61	0.64
Dy	2.12	3.44	3.15		3.13	2.68	3.00	3.85
Ho	0.44	0.71	0.68		0.56	0.48	0.53	0.78
Er	1.14	1.90	1.86		1.34	1.19	1.31	2.11
Tm	0.17	0.28	0.27		0.18	0.16	0.18	0.31
Yb	1.09	1.70	1.64		1.07	1.00	1.06	1.86
Lu	0.18	0.27	0.27		0.17	0.16	0.16	0.29
Ba	353	292	188		746	550	751	276
Th	3.31	2.75	1.29		5.67	6.25	5.53	2.39
Nb	3.33	4.75	1.53		7.42	9.61	6.88	3.68
Y	10.99	19.18	16.95		15.11	13.16	13.84	19.92
Hf	2.68	2.86	2.05		5.17	4.66	4.85	2.44
Ta	0.26	0.34	0.12		0.43	0.55	0.38	0.27
U	1.17	0.95	0.47		1.61	1.57	1.69	0.95
Pb	6.46	5.23	3.09		9.30	7.00	7.91	5.79
Rb	32.01	25.03	13.65		30.78	32.78	29.93	22.58
Cs	2.30	1.52	0.72		1.22	1.36	1.23	1.56
Sr	539	571	628		1247	1112	1359	529
Sc	13.78	23.02	26.92		18.10	16.89	16.94	22.34
Zr	94.0	98.3	70.5		193.8	184.0	182.3	76.4
<i>XRF</i>								
Ni	43	11	73			97	97	17
Cr	44	41	176			126	128	53
V	109	111	173			122	147	164
Ba								
Rb				20				
Sr				502				
Zr								
Y				21				
Ga	17	18	18	19		22	21	19
Cu	42	22	63			35	34	46
Zn	62	72	58			81	76	66

Table 5.4: Trace Element Whole Rock Analyses continued...

	RB06-13D	RB06-13H	RB96-2B	RB96-2D	RB97-1E	RB89-21D	CC05-5C	CC05-5D
	AMOL	AMOL	AMOL	AMOL	AMOL	PLPX	PLPX	PLPX
<i>ICPMS</i>								
La	33.06	35.24			31.68		10.48	10.24
Ce	67.74	73.55			61.69		21.44	21.31
Pr	8.60	9.43			7.39		2.63	2.68
Nd	33.82	37.45			30.36		11.41	11.90
Sm	6.21	7.05			6.07		2.88	3.06
Eu	1.68	1.92			1.67		1.06	0.99
Gd	4.47	4.91			4.48		2.93	3.09
Tb	0.58	0.63			0.56		0.49	0.53
Dy	2.87	3.08			2.87		2.99	3.23
Ho	0.52	0.54			0.51		0.62	0.67
Er	1.30	1.35			1.25		1.71	1.82
Tm	0.17	0.18			0.17		0.25	0.27
Yb	1.03	1.09			1.04		1.57	1.71
Lu	0.16	0.16			0.16		0.25	0.27
Ba	777	810			731		280	228
Th	6.34	6.76			5.44		2.55	2.34
Nb	6.99	7.28			7.10		4.30	4.07
Y	13.54	14.44			14.13		16.47	18.03
Hf	4.80	5.18			4.61		2.60	2.64
Ta	0.40	0.40			0.40		0.31	0.30
U	1.94	2.05			1.54		0.94	0.87
Pb	8.52	8.51			8.06		4.34	3.63
Rb	31.74	31.30			30.15		26.72	23.01
Cs	1.41	1.26			1.25		1.55	1.61
Sr	1221	1278			1214		569	590
Sc	15.07	15.91			16.28		24.64	27.58
Zr	185.8	201.6			177.0		91.5	92.5
<i>XRF</i>								
Ni	70	97	68	83			16	22
Cr	83	130					132	106
V	135	146					135	168
Ba			757	737				
Rb			47	51		23		
Sr			1250	1210		548		
Zr			211	201				
Y						8		
Ga	19	19				18	18	17
Cu	25	44					32	42
Zn	79	82	85	81			70	70

Table 5.5: Trace Element Whole Rock Analyses continued...

	CC05-5E PLPX	CC05-5G PLPX	CC05-5I PLPX	GC722 PLPX	GC07-23A PLPX	GC07-23B PLPX	GC07-23G PLPX	GC07-23C PLPX
<i>ICPMS</i>								
La	10.20	6.97	8.53	6.64	6.80	8.27	7.14	7.37
Ce	23.27	14.84	17.26	14.36	14.52	18.21	15.65	15.89
Pr	3.17	1.93	2.24	1.91	1.91	2.47	2.14	2.13
Nd	14.49	8.82	10.26	8.03	8.08	10.69	9.25	9.27
Sm	3.87	2.40	3.03	1.96	1.98	2.60	2.39	2.36
Eu	1.15	0.86	0.91	0.65	0.68	0.87	0.79	0.84
Gd	3.91	2.55	3.10	2.05	2.00	2.44	2.45	2.42
Tb	0.64	0.43	0.52	0.33	0.33	0.38	0.40	0.39
Dy	4.00	2.73	3.18	2.07	2.01	2.26	2.47	2.37
Ho	0.81	0.57	0.63	0.42	0.42	0.45	0.49	0.48
Er	2.26	1.57	1.66	1.13	1.11	1.21	1.33	1.29
Tm	0.33	0.23	0.24	0.16	0.17	0.18	0.19	0.19
Yb	2.06	1.42	1.50	1.07	1.01	1.08	1.23	1.16
Lu	0.32	0.23	0.23	0.17	0.16	0.17	0.19	0.18
Ba	263	235	240	185	200	205	209	210
Th	2.36	1.52	2.08	1.71	1.73	1.78	1.90	1.65
Nb	3.39	1.94	3.26	2.12	2.09	1.94	1.96	2.22
Y	22.53	15.06	16.22	10.69	10.24	11.31	12.18	11.83
Hf	1.96	2.09	1.62	1.68	1.67	1.76	1.86	1.72
Ta	0.24	0.14	0.25	0.16	0.17	0.15	0.16	0.17
U	0.92	0.62	0.79	0.68	0.68	0.69	0.75	0.66
Pb	4.66	2.72	3.52	3.49	4.44	3.51	4.11	3.81
Rb	20.22	11.31	26.49	14.74	15.21	15.64	16.60	14.81
Cs	1.52	0.62	3.28	0.98	0.98	0.98	1.08	0.94
Sr	479	662	468	458	525	624	521	550
Sc	27.33	28.36	29.18	28.63	26.23	28.39	31.07	31.17
Zr	56.2	72.5	52.0	56.9	57.3	59.7	61.6	57.2
<i>XRF</i>								
Ni	30	53	30	43	43	83	47	45
Cr	52	98	197	318	318	430	246	146
V	193	152	163	209	167	149	159	187
Ba								
Rb								
Sr								
Zr								
Y								
Ga	20	17	16	14	16	16	15	17
Cu	56	15	65	98	50	114	63	55
Zn	70	52	83	57	58	77	75	70

Table 5.6: Trace Element Whole Rock Analyses continued...

	GC07-23D PLPX	GC07-23E PLPX	GC07-23F PLPX	GC07-23I PLPX	RB99-8D PLPX	RB97-1A PLPX	CC05-7C PLOL	CC05-7D PLOL
<i>ICPMS</i>								
La	11.42	7.84	6.46	7.03	8.80	9.07	7.63	6.63
Ce	26.41	16.89	14.02	15.10	18.22	19.70	16.29	14.72
Pr	3.70	2.19	1.84	2.01	2.33	2.63	2.10	2.00
Nd	16.28	9.12	7.59	8.37	10.41	12.29	9.57	9.28
Sm	3.66	2.14	1.83	1.96	2.84	3.47	2.54	2.67
Eu	1.05	0.70	0.69	0.70	0.93	0.97	0.93	0.97
Gd	3.27	2.09	1.82	1.95	3.01	3.56	2.73	2.96
Tb	0.49	0.34	0.30	0.32	0.50	0.58	0.46	0.51
Dy	2.82	2.11	1.86	1.91	3.10	3.33	2.88	3.21
Ho	0.56	0.42	0.38	0.39	0.64	0.67	0.60	0.66
Er	1.49	1.17	1.06	1.10	1.76	1.75	1.63	1.87
Tm	0.21	0.17	0.15	0.16	0.26	0.25	0.24	0.27
Yb	1.33	1.08	0.96	1.00	1.62	1.50	1.53	1.72
Lu	0.21	0.17	0.15	0.16	0.25	0.23	0.25	0.27
Ba	247	226	181	200	233	237	247	226
Th	2.33	2.10	1.61	1.79	2.12	2.05	1.66	1.29
Nb	2.92	2.20	1.79	1.96	3.33	4.05	2.04	1.81
Y	14.26	10.72	9.65	9.80	17.20	17.45	15.91	17.92
Hf	2.39	1.94	1.52	1.76	1.93	1.72	2.31	2.21
Ta	0.22	0.18	0.14	0.16	0.25	0.29	0.16	0.13
U	0.89	0.84	0.64	0.71	0.77	0.79	0.60	0.46
Pb	4.48	4.30	6.17	3.63	4.58	4.81	3.43	3.25
Rb	20.13	18.88	14.12	16.14	17.77	16.04	12.79	12.09
Cs	1.28	1.22	0.89	1.01	1.30	1.22	0.69	0.56
Sr	595	516	517	537	504	493	637	573
Sc	28.21	24.96	26.47	25.14	23.64	29.71	26.79	29.67
Zr	78.5	66.3	52.1	58.9	63.0	54.8	78.1	77.7
<i>XRF</i>								
Ni	61	44	30	61	17		57	64
Cr	317	213	367	260	15		109	133
V	183	133	178	162	92		150	155
Ba								
Rb								
Sr								
Zr								
Y								
Ga	16	15	16	15	21		18	16
Cu	33	76	117	43	69		58	44
Zn	62	57	56	67	64		56	56

Table 5.7: Trace Element Whole Rock Analyses continued...

	CC05-7E	CC05-7F	CC05-7G	CC05-7I	CC05-5K	CC06-14A	CC06-14B	CC06-14C
	PLOL	PLOL	PLOL	PLOL	PLOL	PLOL	PLOL	PLOL
<i>ICPMS</i>								
La	5.74	8.78	6.97	6.97	10.50	6.93	7.83	7.04
Ce	12.98	18.22	14.87	15.00	21.42	15.39	17.29	15.35
Pr	1.78	2.31	1.94	1.98	2.61	2.14	2.35	2.12
Nd	8.48	10.23	8.89	9.16	11.29	9.30	10.29	9.30
Sm	2.45	2.59	2.49	2.54	2.86	2.40	2.48	2.34
Eu	0.94	0.91	0.91	0.96	0.90	0.92	0.90	0.88
Gd	2.72	2.64	2.60	2.75	2.82	2.60	2.76	2.61
Tb	0.48	0.43	0.45	0.47	0.47	0.45	0.45	0.44
Dy	3.05	2.66	2.82	2.99	2.87	2.77	2.87	2.75
Ho	0.63	0.54	0.59	0.63	0.58	0.60	0.61	0.59
Er	1.75	1.51	1.63	1.72	1.61	1.67	1.63	1.63
Tm	0.26	0.23	0.24	0.25	0.23	0.24	0.24	0.24
Yb	1.61	1.38	1.50	1.61	1.45	1.47	1.52	1.51
Lu	0.26	0.22	0.24	0.25	0.23	0.23	0.24	0.24
Ba	204	279	236	236	287	240	263	242
Th	1.05	1.99	1.50	1.43	3.18	1.45	1.68	1.48
Nb	1.57	2.35	1.88	1.87	4.01	1.83	2.09	1.85
Y	16.85	14.72	15.68	16.62	15.56	14.86	15.04	14.87
Hf	1.95	2.33	2.09	2.17	2.50	2.20	2.36	2.15
Ta	0.11	0.18	0.15	0.14	0.33	0.13	0.16	0.14
U	0.37	0.73	0.53	0.52	1.15	0.56	0.64	0.55
Pb	2.77	4.28	3.47	3.47	5.96	2.94	3.07	3.04
Rb	9.04	17.76	13.26	12.80	30.29	14.35	15.48	13.72
Cs	0.39	1.04	0.70	0.64	2.07	0.70	0.77	0.62
Sr	598	675	621	602	482	673	667	664
Sc	31.10	24.26	28.27	28.71	23.43	23.87	22.67	23.70
Zr	68.1	80.4	74.0	76.1	85.1	74.7	79.8	75.3
<i>XRF</i>								
Ni	61	50	64	58	29	57	51	53
Cr	127	94	119	114	247	93	85	88
V	162	147	150	162	132	152	144	154
Ba								
Rb								
Sr								
Zr								
Y								
Ga	16	17	17	18	18	16	17	17
Cu	30	28	32	28	22	38	21	36
Zn	58	58	56	58	63	54	53	54

Table 5.8: Trace Element Whole Rock Analyses continued...

	CC06-14D	CC06-14E	NG97-13A	NG97-13B	RB06-13B	NG06-11I	RB06-13E	GC721	GC07-23H
	PLOL	PLOL	CI	CI	CI	CI	GB	GB	GB
<i>ICPMS</i>									
La	7.66	6.59	7.26	7.66	8.61	11.11	15.30	0.99	3.01
Ce	16.80	15.00	14.65	15.56	19.67	24.96	37.31	2.76	7.44
Pr	2.33	2.11	1.84	1.98	2.91	3.29	5.43	0.59	1.19
Nd	10.10	9.42	8.18	8.78	13.25	13.52	23.66	3.52	6.10
Sm	2.53	2.41	2.20	2.39	3.59	3.20	5.18	1.47	2.10
Eu	0.95	0.91	0.72	0.76	1.08	1.08	1.48	0.73	0.68
Gd	2.69	2.79	2.24	2.32	3.71	3.21	4.48	2.21	2.74
Tb	0.46	0.46	0.36	0.38	0.64	0.55	0.67	0.44	0.51
Dy	2.89	2.91	2.17	2.27	3.85	3.20	3.77	3.17	3.36
Ho	0.61	0.62	0.43	0.46	0.79	0.67	0.73	0.76	0.70
Er	1.73	1.71	1.15	1.22	2.04	1.83	1.90	2.35	1.95
Tm	0.25	0.25	0.17	0.17	0.30	0.28	0.26	0.36	0.29
Yb	1.56	1.57	1.04	1.07	1.84	1.79	1.58	2.40	1.74
Lu	0.25	0.25	0.16	0.17	0.29	0.29	0.24	0.40	0.26
Ba	262	231	217	238	196	167	167	103	114
Th	1.65	1.34	1.36	1.54	1.35	1.87	1.62	0.11	0.38
Nb	2.08	1.75	2.87	3.09	2.75	3.52	4.76	0.19	0.53
Y	15.33	15.36	11.36	11.84	18.94	16.79	18.48	23.60	17.49
Hf	2.31	2.11	1.77	1.93	1.37	1.69	3.58	0.80	1.24
Ta	0.15	0.13	0.21	0.22	0.20	0.26	0.32	0.02	0.05
U	0.64	0.50	0.52	0.64	0.56	0.72	0.75	0.08	0.21
Pb	3.51	2.73	3.23	5.55	4.09	5.28	4.19	2.56	2.38
Rb	15.95	12.71	12.61	16.05	11.52	8.96	5.24	2.85	1.28
Cs	0.78	0.58	0.71	0.94	0.84	0.68	0.34	0.30	0.07
Sr	648	648	329	373	467	505	544	225	449
Sc	23.31	25.39	31.52	29.44	38.29	29.18	19.87	29.39	34.95
Zr	81.5	70.3	60.0	64.5	37.7	46.7	132.4	21.9	39.2
<i>XRF</i>									
Ni	51	56	215	153	61	37	152	58	37
Cr	83	94			341	199	380	135	228
V	155	162			180	133	159	223	245
Ba									
Rb									
Sr									
Zr									
Y									
Ga	15	17			18	17	17	14	14
Cu	28	47			98	39	25	85	219
Zn	57	56			111	93	99	95	54

Table 5.9: Whole rock major element analyses in oxide weight percents

Sample	Type	SiO ₂	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total	Mg#
NG97-13C	AMPL	60.1	0.79	18.4	5.48	-	3.38	6.53	3.81	1.21	0.23	99.9	0.52
NG97-13D	AMPL	61.5	0.79	18.4	5.47	-	2.24	5.77	4.30	1.20	0.26	99.9	0.42
NG97-13E	AMPL	59.2	0.81	18.6	5.80	-	3.49	6.76	3.97	1.06	0.20	99.9	0.52
NG97-13F	AMPL	59.7	0.73	18.5	5.72	-	3.50	6.66	3.70	1.23	0.21	99.9	0.52
NG06-11A	AMPL	58.5	0.76	18.0	5.41	0.10	3.20	6.53	3.80	1.26	0.18	97.7	0.51
NG06-11B	AMPL	58.4	0.77	18.0	5.48	0.10	3.33	6.63	3.95	1.15	0.17	98.0	0.52
NG06-11C	AMPL	58.9	0.77	17.9	5.40	0.10	3.26	6.47	3.98	1.07	0.18	98.0	0.52
NG06-11D	AMPL	59.1	0.80	18.1	5.38	0.09	2.75	6.60	3.80	1.25	0.17	98.1	0.48
NG06-11E-1	AMPL	58.7	0.78	17.8	5.57	0.10	3.35	6.64	3.82	0.99	0.18	98.0	0.52
NG06-11E-2	AMPL	58.2	0.79	18.1	5.70	0.10	3.40	6.72	3.91	0.99	0.18	98.2	0.52
NG06-11F	AMPL	56.3	0.81	16.9	6.42	0.12	5.52	6.95	3.48	0.88	0.14	97.6	0.61
NG96-6B	AMPL	58.0	0.88	18.4	6.51	-	3.81	7.08	4.00	1.07	0.19	99.9	0.51
NG96-6D	AMPL	61.0	0.74	18.1	5.10	-	3.04	6.31	4.21	1.22	0.19	99.9	0.52
NG96-6E	AMPL	59.6	0.83	18.5	5.64	-	3.31	6.91	3.81	1.07	0.21	99.9	0.51
NG96-6C	AMPL	55.5	1.05	18.7	6.60	-	5.31	8.16	3.63	0.78	0.19	99.9	0.59
RB89-21A	AMPL	59.5	0.61	18.6	5.15	-	4.20	6.81	3.63	1.43	0.02	100.0	0.59
RB97-1B	AMPL	58.2	0.73	18.9	6.06	-	3.94	7.00	3.81	0.98	0.19	99.9	0.54
RB97-1C	AMPL	57.7	0.68	18.9	6.11	-	4.36	7.30	3.77	0.85	0.16	99.9	0.56
RB06-13G	AMPL	59.5	0.61	17.9	5.12	0.09	3.72	6.36	3.82	1.26	0.11	98.5	0.56
CC05-5B	AMPL	57.6	0.85	18.5	6.23	0.11	4.19	7.54	3.51	1.09	0.15	99.8	0.55
CC06-14F	AMPL+PLOL	53.6	0.79	17.4	6.59	0.12	6.56	9.21	3.02	0.72	0.11	98.1	0.64
RB97-1F	AMOL	57.6	0.92	16.8	5.57	-	5.11	7.31	4.23	1.81	0.48	99.9	0.62
RB99-8C	AMOL	58.0	0.82	16.6	5.51	-	5.37	7.11	4.20	1.76	0.51	99.9	0.63
RB06-13A	AMOL	55.6	0.91	16.3	5.67	0.08	5.29	7.29	4.16	1.67	0.43	97.4	0.62
RB06-13C	AMOL	57.2	0.67	18.3	5.63	0.09	4.37	7.83	3.80	0.96	0.12	99.0	0.58
RB06-13D	AMOL	57.0	0.83	16.8	5.37	0.08	4.40	6.80	4.30	1.77	0.38	97.8	0.59

Continued on Next Page...

Table 5.9 – Continued

Sample	Type	SiO ₂	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total	Mg#
RB06-13H	AMOL	56.0	0.90	16.2	5.60	0.09	5.18	7.23	4.19	1.78	0.42	97.6	0.62
CC05-5H	AMOL	0.0	0.00	0.0	0.00	-	0.00	0.00	0.00	0.00	0.00	0.0	0.00
RB96-2A	AMOL	57.5	0.91	17.2	5.53	-	4.74	7.37	4.39	1.82	0.43	99.9	0.60
RB96-2B	AMOL	58.4	0.89	16.8	5.37	-	4.82	7.08	4.26	1.82	0.45	99.9	0.62
RB96-2D	AMOL	57.6	0.92	16.9	5.53	-	5.15	7.27	4.33	1.72	0.45	99.9	0.62
RB97-1E	AMOL	58.0	0.87	17.4	5.41	-	4.57	7.05	4.46	1.75	0.44	99.9	0.60
RB89-21C	PLPX+AMPL	57.4	0.51	17.5	6.63	-	5.75	7.54	3.76	0.82	0.10	100.0	0.61
RB89-21D	PLPX	58.0	0.60	19.2	5.64	-	4.46	7.57	3.61	0.88	0.12	100.0	0.58
RB89-21G	PLPX	58.3	0.71	19.3	6.08	-	3.35	6.56	3.98	0.83	0.17	99.3	0.50
CC05-5C	PLPX	58.1	0.82	17.8	6.24	0.12	4.96	7.93	3.40	1.05	0.14	100.6	0.59
CC05-5D	PLPX	57.0	0.90	17.9	6.50	0.12	5.34	8.53	3.20	0.86	0.14	100.5	0.59
CC05-5E	PLPX	57.8	0.59	18.2	6.11	0.10	4.79	8.20	3.82	0.83	0.11	100.6	0.58
CC05-5G	PLPX	57.4	0.71	18.3	5.47	0.11	5.87	8.94	3.20	0.51	0.11	100.6	0.66
CC05-5I	PLPX	57.4	0.58	17.4	6.50	0.12	5.65	7.99	3.44	0.78	0.11	100.0	0.61
GC99-12A	PLPX	57.8	0.37	17.4	5.46	-	5.99	8.96	3.08	0.75	0.13	99.9	0.66
GC7-22	PLPX	56.4	0.52	16.9	5.90	0.11	7.12	9.33	2.77	0.69	0.10	99.8	0.68
GC07-23A	PLPX	57.2	0.46	17.2	5.62	0.11	6.22	8.85	3.10	0.70	0.12	99.5	0.66
GC07-23B	PLPX	57.1	0.46	15.3	6.50	0.13	7.36	8.77	3.02	0.71	0.12	99.5	0.67
GC07-23G	PLPX	57.1	0.41	14.8	6.53	0.14	7.02	9.14	2.87	0.75	0.08	98.8	0.66
GC07-23C	PLPX	56.6	0.64	16.8	6.48	0.13	5.97	8.92	3.31	0.67	0.13	99.6	0.62
GC07-23D	PLPX	57.5	0.69	15.2	5.88	0.11	7.41	8.99	3.04	0.89	0.21	99.9	0.69
GC07-23E	PLPX	58.4	0.36	17.2	5.23	0.10	5.81	8.44	3.20	0.85	0.10	99.7	0.66
GC07-23F	PLPX	56.8	0.37	17.5	5.41	0.11	6.40	9.27	2.95	0.66	0.11	99.5	0.68
GC07-23I	PLPX	57.2	0.42	16.7	6.06	0.12	6.47	8.49	2.98	0.74	0.10	99.2	0.66
RB99-8D	PLPX	56.3	0.68	19.2	6.63	-	4.92	7.79	3.43	0.74	0.19	99.9	0.57
RB97-1A	PLPX	57.2	0.64	18.7	6.21	-	5.05	7.50	3.72	0.69	0.14	99.9	0.59
CC05-7C	PLOL	56.4	0.72	18.1	5.94	0.11	5.68	8.59	3.62	0.75	0.13	100.1	0.63
CC05-7D	PLOL	55.4	0.74	17.9	6.20	0.12	6.38	9.22	3.44	0.73	0.11	100.3	0.65

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Table 5.9 – Continued

Sample	Type	SiO ₂	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total	Mg#
CC05-7E	PLOL	54.4	0.75	18.1	6.43	0.12	6.47	9.56	3.40	0.61	0.10	100.0	0.64
CC05-7F	PLOL	58.0	0.70	17.8	5.60	0.10	5.20	7.96	3.77	0.94	0.13	100.2	0.62
CC05-7G	PLOL	56.2	0.70	17.9	6.02	0.11	6.11	8.88	3.56	0.76	0.11	100.4	0.64
CC05-7I	PLOL	56.0	0.77	17.9	6.31	0.12	5.97	8.91	3.63	0.75	0.11	100.5	0.63
CC05-5K	PLOL	59.2	0.70	16.9	5.96	0.11	5.81	7.40	3.18	1.15	0.13	100.5	0.63
CC06-14A	PLOL	55.9	0.68	17.8	5.77	0.11	5.74	8.73	3.57	0.77	0.10	99.1	0.64
CC06-14B	PLOL	56.6	0.69	17.6	5.55	0.10	5.28	8.19	3.72	0.84	0.11	98.6	0.63
CC06-14C	PLOL	56.1	0.69	17.8	5.79	0.11	5.63	8.64	3.59	0.74	0.10	99.2	0.63
CC06-14D	PLOL	56.5	0.72	17.5	5.87	0.11	5.37	8.27	3.69	0.86	0.10	98.9	0.62
CC06-14E	PLOL	55.2	0.74	17.7	6.12	0.11	5.83	8.85	3.57	0.72	0.10	99.0	0.63
NG97-13A	CI	57.3	0.58	12.3	8.34	-	11.84	6.26	2.43	0.63	0.14	99.8	0.72
NG97-13B	CI	57.6	0.60	13.9	7.58	-	9.87	6.72	2.68	0.73	0.16	99.9	0.70
GC99-12B	CI	56.5	0.55	17.0	6.66	-	6.17	9.37	2.92	0.49	0.13	99.9	0.62
RB06-13B	CI	55.3	0.62	15.3	8.94	0.17	6.86	8.00	3.35	0.54	0.09	99.2	0.58
NG06-11I	CI	55.8	0.53	16.6	7.28	0.16	5.61	7.95	3.72	0.61	0.11	98.4	0.58
RB06-13E	GB	54.0	0.83	15.9	7.49	0.15	8.15	8.42	3.58	0.38	0.28	99.2	0.66
GC7-21	GB	52.0	0.46	15.3	8.45	0.24	8.48	12.32	2.33	0.21	0.04	99.8	0.64
GC07-23H	GB	54.1	0.69	17.4	5.59	0.14	6.54	11.01	3.51	0.17	0.07	99.2	0.68

footnote

Table 5.10: Representative olivine EMP analyses

	96-2D	96-2D	05-7E	06-13A	06-13A	06-13D	06-13D	06-13H	06-13H	07-23C	07-23D
SiO ₂	40.3	39.9	39.6	40.4	39.6	39.6	39.5	40.0	39.7	38.0	39.9
TiO ₂	0.00	0.03	0.01	0.00	0.03	0.02	0.04	0.01	0.00	0.00	0.00
Al ₂ O ₃	0.02	0.00	0.03	0.00	0.03	0.00	0.01	0.00	0.00	0.00	0.01
Cr ₂ O ₃	0.00	0.03	0.02	0.00	0.04	0.02	0.04	0.02	0.02	0.02	0.01
FeO	10.1	14.0	12.2	9.3	15.1	14.7	15.0	12.8	14.1	20.4	13.0
MnO	0.25	0.18	0.15	0.15	0.18	0.27	0.17	0.20	0.22	0.06	0.18
MgO	48.3	45.7	47.1	49.1	44.3	45.1	44.9	45.2	44.5	41.1	46.2
CaO	0.15	0.05	0.17	0.03	0.12	0.09	0.09	0.12	0.06	0.05	0.06
NiO	-	0.46	0.20	0.44	0.50	0.35	0.50	0.50	0.56	0.02	0.20
Total	99.1	100.3	99.5	99.4	99.8	100.1	100.3	98.9	99.2	99.6	99.6
Fo	89.5	85.4	87.3	90.4	84.0	84.6	84.2	86.3	84.9	78.2	86.3

Table 5.11: Representative plagioclase EMP analyses

	96-6C	05-7E	05-7E	06-13A	06-13A	06-13D	06-13D	06-13H	06-13H	07-23C	07-23C
SiO ₂	51.0	51.1	52.6	57.4	60.1	51.0	54.2	55.6	59.4	48.4	56.8
Al ₂ O ₃	31.7	30.5	29.7	26.7	25.1	30.8	29.1	28.4	25.1	33.2	26.9
FeO	0.41	0.46	0.77	0.68	0.63	0.62	0.58	0.21	0.53	0.46	0.38
MgO	0.06	0.10	0.11	0.07	0.04	0.07	0.06	0.02	0.03	0.05	0.04
CaO	14.37	13.52	12.57	10.28	7.25	13.56	11.75	10.30	7.23	15.91	8.90
Na ₂ O	3.41	3.98	4.08	5.06	7.21	3.55	4.99	5.38	7.20	2.49	6.32
K ₂ O	0.07	0.07	0.11	0.73	0.65	0.10	0.17	0.31	0.63	0.04	0.19
Total	100.9	99.7	99.9	100.9	101.0	99.7	100.8	100.2	100.1	100.5	99.5
An	69.7	65.0	62.6	50.6	34.4	67.5	56.0	50.5	34.4	77.7	43.3

Table 5.12: Representative clinopyroxene EMP analyses

	06-13A	06-13F-1	07-23C	07-23D	07-23D
SiO ₂	53.3	53.4	51.3	53.6	51.4
TiO ₂	0.35	0.19	0.25	0.15	0.47
Al ₂ O ₃	1.93	0.62	1.46	1.32	3.22
Cr ₂ O ₃	0.42	0.04	0.02	0.42	0.59
FeO	4.79	6.38	8.81	3.12	5.01
MnO	0.12	0.15	0.01	0.14	0.13
MgO	17.4	16.3	15.3	17.8	16.9
CaO	21.6	21.8	21.1	23.4	21.5
Na ₂ O	0.29	0.14	0.42	0.17	0.27
Total	100.3	98.9	98.7	100.1	99.5
Mg#	0.866	0.820	0.756	0.910	0.858

Table 5.13: Representative biotite EMP analyses

	06-13C	06-13D	07-23C
SiO ₂	38.1	39.2	37.2
TiO ₂	0.22	2.28	0.34
Al ₂ O ₃	16.4	14.5	16.0
Cr ₂ O ₃	0.04	0.00	0.19
FeO	7.46	11.62	10.15
MnO	0.04	0.12	0.00
MgO	20.1	18.0	19.2
CaO	0.01	0.05	0.00
Na ₂ O	0.73	0.91	0.80
K ₂ O	7.73	8.62	8.59
F	-	-	1.69
Total	90.8	95.3	94.1
Mg#	0.828	0.734	0.771

Table 5.14: Representative orthopyroxene EMP analyses

	96-6C	05-7E	06-13A	06-13D	06-13D	06-13F-1	07-23C	07-23C	07-23D	07-23D
SiO ₂	55.8	54.3	57.2	55.0	53.7	53.7	53.7	52.4	54.8	55.2
TiO ₂	0.12	0.21	0.03	0.13	0.14	0.21	0.13	0.14	0.34	0.12
Al ₂ O ₃	1.14	1.82	1.38	1.76	0.78	0.78	1.43	0.85	2.26	1.71
Cr ₂ O ₃	0.28	0.00	0.42	0.47	0.06	0.05	0.03	0.02	0.31	0.22
FeO	12.7	15.3	5.1	9.4	22.5	16.3	13.5	19.9	8.7	10.5
MnO	0.24	0.29	0.15	0.22	0.50	0.43	0.08	0.04	0.19	0.28
MgO	29.1	27.1	34.6	30.8	22.5	26.2	29.3	24.1	31.9	30.5
CaO	1.33	1.07	0.42	1.49	0.98	1.74	1.21	1.27	1.13	1.36
Na ₂ O	0.03	0.01	0.00	0.05	0.00	0.00	0.07	0.02	0.00	0.10
Total	100.7	100.1	99.4	99.3	101.1	99.4	99.4	98.7	99.5	100.0
Mg#	0.804	0.759	0.924	0.854	0.641	0.741	0.795	0.684	0.868	0.838

Table 5.15: Representative amphibole EMP analyses

	96-2D	96-6A	96-6C	97-13A	97-13B	97-13D	99-8C	99-8C
SiO ₂	44.3	42.8	42.6	43.6	44.3	43.8	46.4	45.3
TiO ₂	1.66	2.03	2.66	2.61	2.34	2.51	2.05	2.09
Al ₂ O ₃	10.81	13.49	13.03	11.62	11.75	12.15	9.25	9.97
Cr ₂ O ₃	0.05	0.83	0.03	0.10	0.16	0.00	0.16	0.08
FeO	8.49	7.97	9.88	9.95	11.10	11.43	8.02	8.31
MnO	0.08	0.07	0.14	0.12	0.12	0.14	0.04	0.09
MgO	16.9	16.1	14.6	15.1	14.9	15.2	17.7	17.3
CaO	11.2	11.7	11.4	11.4	11.3	11.3	11.4	11.1
Na ₂ O	2.53	2.62	2.39	2.51	2.37	2.56	2.38	2.25
K ₂ O	0.45	0.18	0.30	0.26	0.27	0.25	0.38	0.41
Total	96.5	97.9	97.1	97.2	98.6	99.3	97.7	96.9
Mg#	0.780	0.783	0.725	0.730	0.705	0.704	0.797	0.788
Al ^{VI}	0.340	0.468	0.479	0.366	0.397	0.355	0.226	0.274
	06-13A	06-13A	06-13C	06-13D	06-13D	06-13H	07-23C	07-23D
SiO ₂	45.5	43.9	45.8	46.2	44.0	45.2	42.1	45.9
TiO ₂	2.01	1.87	2.15	2.14	2.06	1.89	1.75	0.51
Al ₂ O ₃	10.00	10.82	8.03	8.75	10.42	9.97	10.75	10.37
Cr ₂ O ₃	0.08	1.05	0.00	0.18	0.02	0.22	0.03	0.91
FeO	8.10	7.56	13.84	7.75	8.33	7.81	10.03	6.62
MnO	0.07	0.11	0.21	0.11	0.04	0.09	0.08	0.08
MgO	17.4	17.4	14.1	17.7	16.8	17.7	16.1	18.5
CaO	11.6	11.7	11.0	11.2	11.2	11.2	11.2	11.7
Na ₂ O	2.35	2.32	1.65	2.44	2.84	2.43	2.44	2.26
K ₂ O	0.46	0.55	0.37	0.48	0.46	0.41	0.49	0.23
Total	97.5	97.2	97.1	96.9	96.1	97.0	94.9	97.0
Mg#	0.793	0.804	0.645	0.803	0.782	0.802	0.740	0.833
Al ^{VI}	0.265	0.224	0.183	0.177	0.269	0.249	0.235	0.356

Figure 5-1: Geologic map of Mt. Shasta volcano

Figure 5-2: Potassium contents of magmatic inclusions

97-13A

07-23H

Figure 5-3: Photomicrographs of cumulate and granoblastic inclusions

Figure 5-4: Photomicrographs of AMPL inclusions of varying grainsize

06-11C

06-13A

Figure 5-5: Photomicrographs of AMPL and AMOL inclusions

06-14C

05-7E

Figure 5-6: Photomicrographs of PLOL inclusions

89-21C

07-23G

Figure 5-7: Photomicrographs of PLPX inclusions

Figure 5-8: Electron backscatter image and probe transect for a zoned plagioclase

Figure 5-9: Electron backscatter image and probe transect for a zoned amphibole

IUGS Classification for extrusive rocks

Figure 5-10: Total alkalis v. Silica

Figure 5-11: Histograms of bulk chemical properties for quenched magmatic inclusions

Figure 5-12: Harker variation diagrams of magmatic inclusion compositions

Figure 5-13: REE patterns of magmatic inclusions and primitive lavas

Figure 5-14: Ba/La vs. La/Sm ratios

Figure 5-15: Pb/Ce vs. Th/Nb ratios

05-7E spot #1a 3/1/11

Figure 5-16: Electron backscatter image of olivine in a PLOL inclusion

Figure 5-17: Electron backscatter image of olivine microphenocryst surrounded by amphibole in an AMOL inclusion

Figure 5-18: Electron backscatter image of a cpx-opx-olivine-amphibole intergrowth in a PLPX inclusion

Figure 5-19: Pseudo-ternary quartz-plagioclase-olivine projection of inclusion compositions

Figure 5-20: Depths of crystallization under Mt. Shasta as recorded by amphibole compositions

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