

Experimental investigations into shergottite formation

By

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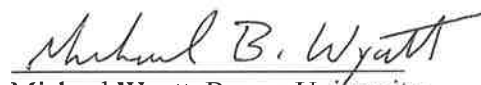
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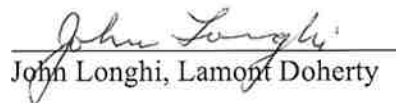
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Introduction

Based on age, mineralogy, and isotopes, martian meteorites have been divided into 4 groups: shergottites, nakhlites, chassignites, and the single meteorite ALH 84001. Of these four groups, the shergottites have the youngest crystallization ages and comprise the largest group of martian meteorites with approximately 23 unique members. The shergottites are further subdivided into basaltic, olivine-phyric, and lherzolitic end members (Goodrich, 2003). With the advent of analyses from the martian rovers, Spirit and Opportunity, many researches have drawn analogies between the rocks at the surface of Mars with the bulk rock chemistry and mineralogy found in the shergottites (McSween et al., 2006). Thus understanding the magmatic composition of the shergottites and their petrogenetic evolution could potentially shed light on large-scale process on Mars. This thesis describes studies shergottite petrogenesis that use a variety of experimental and analytical techniques and attempt to apply the results of these studies to obtain a better understanding of the basaltic rocks found on Mars.

In Chapter 1, a series of experiments are described that define the parental magma of lherzolitic shergottites ALH 77005 (ALH). The lherzolitic shergottites are cumulate rocks composed primarily of olivine and low-Ca pyroxene with minor amounts of plagioclase, high-Ca pyroxene, chromite, phosphate, and ilmenite (McSween et al., 1979). From petrographic studies, the crystallization sequence of these rocks has been defined as chromite followed by olivine and low-Ca pyroxene. High-Ca pyroxene, plagioclase, phosphates and ilmenite are thought to have filled in the interstitial regions between the olivine and low-Ca pyroxene.

In basaltic rocks, the groundmass liquid combined with the phenocrysts can sometimes be interpreted as the magmatic composition from which the melt grew. However cumulate rocks often represent crystals that settled out of a larger magma chamber, thus the phenocrysts assemblages combined with any remaining interstitial glass almost never represent a true liquid composition for the parental melt.

ALH, with > 80% volume euhedral olivine and low-Ca pyroxene is readily identified texturally as a cumulate rock and has defied attempts to estimate its parent melt. This study developed a new technique for rehomogenizing melt inclusions. Melt inclusions are melt pockets that became trapped during rapid crystal growth. In ALH, slow-cooling allowed daughter crystals to form within the melt inclusions. The experiments in this study remelted the daughter phases with temperatures ranging from 1140 to 1185°C and then analyzed olivine- and chromite-hosted melt inclusions. Because olivine and chromite were the first two phases on the liquidus, these melt compositions give us the best estimates of the parental magma of ALH and are the focus of this project. The most primitive parental melt determined from the melt inclusions found in chromite have an MgO concentration of ~7.5 wt % while the most primitive composition found in olivine-hosted conclusion have MgO concentrations of ~7.1 wt %.

In Chapter 2, crystallization experiments are performed on the ALH parental melt defined in Chapter 1 by the chromite-hosted melt inclusions. The crystallization experiments were performed between 35 and 200 MPa under both hydrous and anhydrous conditions and at oxygen fugacities ranging from QFM – 3.6 to QFM – 1.7. The crystallization experiments confirmed the parental melt composition by producing

the same mineral assemblage found in ALH. In addition, the crystallization experiments allowed the liquidus temperatures of the various mineral phases to be determined as well as the liquid line of descent for both a dry and hydrous magma.

From the various experiments, it was determined that the presence of olivine in the rocks was highly dependent on the pressure of the experiment. At pressures greater than 400 bars, olivine was not observed in the experiments whereas at pressures below 400 bars olivine was observed and was sometimes found to be in a reaction relationship with low-Ca pyroxene. This observation implies that the parental melt of ALH is very close to the boundary curve that separates olivine from low-Ca pyroxene and the composition of the melt closely constrains the position of the phase boundary. This observation also leads to the conclusion that because olivine is prevalent in ALH, the rock must have crystallized at low pressures very near the surface of Mars. Because all the members of the lherzolitic shergottite family have generally similar mineral abundances and mineral compositions, the parental melt defined in Chapter 1 and the liquid line of descent and phase diagram developed in Chapter 2 should be broadly applicable to the other shergottites.

Chapter 3 examines more closely an anomaly found in Chapter 1. In examining olivine-hosted melt inclusions, it was found that some inclusions contained anomalously high P_2O_5 concentrations (up to 8 wt %). While several theories were addressed in Chapter 1, without further investigation it was difficult to say with any certainty what the origin of these P_2O_5 anomalies were. If the high P_2O_5 concentrations found in martian meteorites are magmatic, this would have a significant effect on the magma in that P

competes with Si for other cations (like Ca) thereby increasing the Si-O-Si bonds in the melt and moving the boundary curve between olivine and low-Ca pyroxene such that low-Ca pyroxene crystallization is favored (Ryerson and Hess, 1980; Hess, 1995). If the high P_2O_5 concentrations were the result of secondary processes such as contamination through sedimentary processes or shock, this would call into question the interpretation of the REE in ALH as the phosphates are the major reservoir of REE in this rock.

Thus this chapter takes two approaches to addressing this question. First, the phosphate saturation point in the ALH magma is experimentally determined under dry conditions. These experiments were performed similar to those in Chapter 2 however the synthesis was doped with 5 wt % P_2O_5 . The analyzed melt inclusions in Chapter 1 fall along the phosphate saturation curve defined in this study. The second approach was to analyze the REE concentrations of various reheated melt inclusions in ALH. It was found that while absolute REE concentration does not change with increasing concentrations of P_2O_5 , however a LREE enrichment is correlated to increased P_2O_5 concentration. Crozaz and Wadwha (2003) found that LREE enrichment could be caused by terrestrial sedimentary contamination. The correlation between the LREE enrichment and increased P_2O_5 suggests that there was significant secondary contamination and that the bulk rock major and trace element geochemistry of the lherzolitic shergottites should be questioned.

Finally, Chapter 4 expands the study of shergottites to include EETA 79001 Lithology A (EETA). EETA 79001 (EETA) is unique among the martian meteorites in that it has a linear contact that separates two lithologies (McSween and Jarosewich,

1983). Lithology A (lith A) is a vesicular basalt containing crystals of plagioclase and pyroxene. Lithology B is coarser grained than lithology A and composed primarily of phenocrysts of pigeonite, augite, and maskelynite. Based on the mineralogy and grain sizes, lith A is grouped with the olivine-phyric shergottites while lith B is grouped with the basaltic shergottites. In addition, Lithology A contains megacrysts (lith X) of olivine, orthopyroxene, and chromite that are petrologically similar to lherzolitic shergottites ALH 77005 (ALH) and LEW 88516 (LEW) (Treiman, 1993). Thus developing the relationships between lith A, lith B, and lith X can shed light on the relationships between the basaltic, olivine-phyric, and lherzolitic shergottites.

Chapter 4 examines two different types of experiments. The first set of experiments are crystallization experiments that were performed by John Jones and Laura Wasylenski at Johnson Space Center. These experiments crystallized the Eg composition (Longhi and Pan, 1989), which is thought to be a parental melt of Lith A, under dry conditions at 1 atmosphere and QFM. The crystallization experiments defined the liquid line of descent for Eg through plagioclase and low-Ca pyroxene crystallization. The second set of experiments reheated chips of EETA using the same experimental methods used in Chapter 1. These experiments produced melts in equilibrium with various mineral assemblages that could then be compared with the crystallization experiments performed by Jones and Wasylenski. In addition, because Lith X in EETA is very similar both in mineralogy and composition to the lherzolitic shergottites, the liquid line of descent for ALH determined in Chapter 2 can be compared with that for EETA to make larger inferences about the relationships of the shergottites.

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**Chapter 1: The parental melt of lherzolitic shergottite ALH 77005: a study of
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Abstract

Lherzolithic Shergottite ALH 77005 is one of the most primitive martian meteorites. To characterize the parental melt of this primitive meteorite, olivine and chromite-hosted melt inclusions have been experimentally rehomogenized. The rehomogenization was performed with hydrostatic pressures (800-1000 bars) of CO₂ +CO gas along with finely-powdered graphite at temperatures of 1150-1185°C. Equilibrium between the host and inclusion melt was determined based on the lack of zonation in the host surrounding the melt inclusion, equilibrium K_d values of host and melt inclusions, and textures of the melt inclusion. Chromite-hosted melt inclusions where chromite is poikilitically enclosed by olivine contain ~7.5 wt % MgO. This composition most closely reflects the parental melt of ALH 77005. The melts trapped in Fo₇₅ olivine contain ~7.1 wt % MgO when brought to equilibrium with the host. This olivine-hosted melt inclusion composition has lower SiO₂ (~50 vs. 53.9 wt %) and higher Cr₂O₃ (~1.2 vs. 0.2 wt %) and P₂O₅ (~1.2 vs. 0.5 wt %) than previous estimates for ALH 77005. In addition, compared with the chromite-hosted inclusions the olivine-hosted inclusions have higher Al₂O₃ and lower CaO than can be explained through crystallization of phases known to be on the liquidus. This suggests that magma mixing occurred between chromite and olivine crystallization or olivine-hosted inclusions were contaminated by secondary minerals such as phosphate. Both olivine- and chromite-hosted melt inclusions in ALH 77005 have slightly higher Al₂O₃ than olivine inclusions in Chassigny but significantly higher Al₂O₃ than nakhlites such as MIL 03346 and Nakhla at comparable MgO.

Keywords: ALH 77005, SNC meteorite, melt inclusion, parent melt, lherzolitic shergottite, olivine, chromite

Introduction

The martian meteorite collection (SNC) has been studied extensively for clues to the nature and petrogenesis of igneous rocks on Mars (e.g., McSween 1985; Longhi and Pan 1989; Jagoutz 1991; Treiman 2003). One way these studies can provide information about martian magmatism is by characterizing the parental melts of the SNC meteorites. Defining the chemical characteristics of these magmas has the potential to provide important clues about the interior of Mars, processes involved in magma generation, the timing of these processes, and the relationship between the meteorites. However, the SNC meteorites are comprised of both mafic cumulate and basaltic igneous rocks and the methods for determining the parental melt for cumulate and basaltic meteorites differ. For fine-grained basaltic shergottites such as Shergotty and Zagami, the quenched glass and phenocrysts are believed to have cooled in a closed system (e.g., Treiman, 1986, McCoy et al., 1992; Wadhwa et al. 1994). Therefore, the bulk rock may represent the composition of the magma that erupted. In contrast, minerals present in cumulate meteorites, such as lherzolitic shergottite ALH 77005, have separated from the parental melt through processes such as crystal settling. The bulk rock of cumulate igneous rocks is not generally equal to the composition of the parent magma.

In the quest for parental magma compositions in cumulate meteorites, melt inclusions provide an alternative to studying interstitial melts, which are not preserved in these rocks. Melt inclusions form when melt is trapped by a growing crystal and is eventually cut off from the bulk of the magma (Roedder 1984 and references therein).

Therefore, melt inclusions in cumulus minerals may provide a window into the crystallization history of a cumulate rock by trapping magma at various stages of parent magma evolution. If the crystal cools rapidly after entrapment, the trapped melt will quench to a glass. However, if the rock cools slowly, daughter crystals may begin to form within the melt inclusion and material may be added to or removed from the host phenocryst. In order to determine the parental melt compositions for cumulate SNC meteorites, several investigators have analyzed melt inclusions (e.g., Johnson et al. 1991; Ikeda 1998; Varela et al. 2000; Stockstill et al. 2002) through modal analysis of melt inclusion phases, defocused beam analysis, or rehomogenization using a heating stage. As will be discussed later, these methods present problems for slowly cooled igneous rocks and we have developed an alternative method for reestablishing crystal-melt equilibrium between a crystalline melt inclusion and the host phenocryst.

The focus of this study is on melt inclusions in lherzolitic shergottite ALH 77005. Based on the Mg # of olivines and melts found in the SNC meteorite collection, ALH 77005 is one of the most primitive martian meteorites and may provide insight into the petrology and composition of the primitive martian mantle. ALH 77005 contains two distinct textures (McSween et al. 1979; Lundberg et al. 1990). The first texture is composed chiefly of euhedral chromite and olivine, poikilitically enclosed by low-Ca pyroxene with minor interstitial maskelynite and high-Ca pyroxene (Figure 1). The second texture consists of subhedral olivine with pyroxene, interstitial maskelynite, Ti-rich chromite, ilmenite, troilite, and merrillite. This paper focuses on the first textural domain in which chromites are found partially or completely enclosed by olivine suggesting that chromite crystallized early followed by olivine and then low- and high-Ca

pyroxene. Chromites trapped in olivines, low-Ca pyroxene and interstitial regions have four different zonation patterns depending on the host (Ikeda 1998). However, in general the cores of chromites are Cr-rich ($\sim\text{Chrm}_{81}\text{Sp}_{14}\text{Us}_2\text{Mt}_3$) with increasing amounts of titanium and/or aluminum toward the rim. Olivine is unzoned in major element but the Mg # varies from 70 to 75 in different grains (Ikeda 1994). Orthopyroxene crystals have low CaO, magnesian-rich cores ($\text{En}_{74}\text{Wo}_6\text{Fs}_{20}$) that zone towards ferroan pigeonite rims ($\text{En}_{53}\text{Wo}_{25}\text{Fs}_{22}$). Textures and REE data suggest that plagioclase ($\text{An}_{52}\text{Ab}_{46}\text{Or}_2$) and whitlockite (or other phosphate) crystallized late in the sequence (Lundberg et al. 1990). Plagioclase has been largely converted to maskelynite by shock.

Chromite-hosted melt inclusions in ALH 77005 contain pyroxene and high- SiO_2 glass (Goodrich and Harvey 2002), however no complete chromite-hosted melt inclusion compositions have been reported. Previous studies of this rock have instead focused primarily on olivine-hosted melt inclusions in the poikilitic lithology such as those in Figure 2 (Ikeda 1994; Ikeda 1998; Zipfel and Goodrich 2001; Stockstill et al. 2002). Textural and chemical analysis of these melt inclusions highlights several interesting aspects of this meteorite. Some melt inclusions found in olivine are highly crystallized (Figure 2a) and contain small ($<5\text{ }\mu\text{m}$), SiO_2 -rich regions as well as crystals of high-Ca pyroxene and plagioclase (Jagoutz 1989; Ikeda 1998). Ikeda (1998) analyzed the major and minor elements of the phases contained in the olivine-hosted melt inclusions and used this together with the modal abundance to calculate a parental melt (melt inclusion composition) having between 54 and 60 wt % SiO_2 (Ikeda 1998). Recognizing that this composition was too silica-rich for an olivine-hosted melt inclusion, he added olivine host at various percentages to achieve a better estimate of the parental melt composition.

Edmunson et al. (2005) looked at REE in olivine and olivine-hosted melt inclusions to identify possible causes of Sm-Nd disequilibrium in this meteorite. They determined Sm-Nd in olivine may have been altered by additions of impact melt. Based on studies of melt inclusions in ALH 77005, several authors have discussed the possibilities that these melt inclusions represent assimilated crustal material, remnants of mixed magmas, or immiscible melts (Harvey et al. 1993; Ikeda 1998).

In an effort to clarify the origin of these unusual olivine-hosted melt inclusions and to better understand the nature of the parental magma of ALH 77005, we experimentally rehomogenized melt inclusions in olivine and chromite. Rehomogenization eliminates several potential problems in melt inclusion analysis by melting all of the daughter phases to form a homogenous glass that can then be analyzed. Analyses of rehomogenized glass inclusions eliminate sources of error that arise from analysis of a multiphase melt inclusion such as erroneous estimates of phase abundance, host-melt inclusion interactions, and zoning in small melt inclusion crystals. Determining the major and minor element composition of chromite- and olivine-hosted melt inclusions allows comparison of melts present during two early stages of the crystallization of this rock. The new melt inclusion data also allow comparisons between ALH 77005 primitive melt and those determined for other martian meteorites. Specifically, we compare ALH 77005 with melts with those determined for Chassigny and the nahklites MIL 03346 and Nahkla.

Methods

Rehomogenization experiments were performed on 0.1 gm chips of natural samples of ALH 77005 (ALHA77005,12). The chips of poikilitic textured ALH 77005

were surrounded with packed graphite powder and sealed in platinum tubing. The graphite fixes the oxygen fugacity at QFM -2.9 ± 0.1 for the experimental pressure (800-1000 bars) and temperature range used (1140-1185°C) by allowing the terrestrially oxidized sample to react with carbon to achieve graphite-gas buffering (Eugster and Skippen 1967). This oxidation state is within the range estimated for shergottites by Wadhwa (2001) and Herd et al. (2002). The graphite also prevents the chips from reacting with the platinum sample tube which would result in Fe-loss from the sample. The tubes were placed in TZM pressure vessels and brought to pressures of either 800 or 1000 bars. These pressures were chosen to fix the fO_2 , prevent incongruent melting of olivine to produce orthopyroxene and melt (Morse 1994 and references therein), and maintain the structural integrity of melt inclusions that had not been otherwise compromised by post-magmatic exchange of volatiles with the surrounding. The one disadvantage of this rehomogenization technique is that it precludes analysis of elements such as sulfur that partition into the CO_2+CO gas phase generated during the experiment. However melt inclusions totally isolated within a host crystal may retain the original abundance of these elements, particularly for those that diffuse slowly in olivine and basaltic melt. No attempt was made to determine the H_2O in the homogenized melt inclusions in this study. ALH 77005, like all SNC samples, is highly shocked and fractured, and it is likely that volatile species such as H_2O were partially or completely lost during the shock event (Boctor et al., 2003). Additionally, ALH 77005 melt inclusions do not contain nominally hydrous phases such as amphibole. This is in contrast to Chassigny (Floran et al., 1978) and Nakhla (Treiman, 1986), and suggests that

the shergottite parent melt contained a lower abundance of water than has been estimated for the nakhlites and Chassigny (Watson et al., 1994).

After pressurization, each chip was brought to temperature and held at the final pressure and temperature for 3 hours to 72 hours (Table 1). Initial experiments were run for a relatively short duration. After the initial experiments, it was determined that experiments run for 24+ hours closely approached Fe and Mg exchange equilibrium between the olivine host and the melt inclusion. Samples were quenched by immersing the pressure vessel in H₂O and thick sections were made. Chips from the experiments were polished until a melt inclusion was exposed. Once exposed, the melt inclusions were analyzed for major, minor, and some trace elements. The associated host and any daughter and/or rim minerals remaining in the inclusion were also analyzed for the same suite of major and minor elements. After analysis, thick sections were polished to expose new melt inclusions. Individual samples were polished and analyzed between 1 and 24 times.

Microprobe analyses were performed on a Cameca SX100 electron microprobe. An accelerating voltage of 15 kV and a focused beam (1-2 μm) were used for all analyses. Glasses were analyzed with a 10 nA beam. The following standards were used to calibrate for glass standards: SiO₂, Al₂O₃, CaO, TiO₂, and FeO (basaltic glass VG-A99, USNM 113498), MgO (Kakanui hornblende, USNM 143965), Cr₂O₃ (chromite, USNM 117075), P₂O₅ (Al-phosphate, American Museum of Natural History), NaO₂ (omphacite, USNM 110607), CaO (labradorite, USNM 115900), MnO (rhodanite, American Museum of Natural History), and K₂O (orthoclase, American Museum of Natural History). References to USNM standards can be found in Jarosewich et al.

(1979). Because P_2O_5 was particularly high in these glasses and there was interference using the TAP crystal, analyses were done using the PET crystal (Mandeville, 2004). Standardizations were checked using test analyses on basaltic glass VG-A99 (USNM 113498) and basaltic glass VG-2 (USNM 111240/52). Olivine and pyroxene were analyzed using a 15 nA beam and were calibrated using the following standards: SiO_2 and FeO (Olivine Fo₉₀, USNM 111312/444,), MgO (Olivine Fo₈₃, USNM 2566), Al_2O_3 (chrome-augite, benchstandard from Eugene Jarosewich at the Smithsonian Institution), CaO and Na_2O (omphacite, USNM 110607), MnO (rhodanite, American Museum of Natural History), TiO_2 (Kakanui hornblende, USNM 143965), Cr_2O_3 (chromite, USNM 117075), and K_2O (orthoclase, American Museum of Natural History). Standardizations were checked using test analyses on olivine Fo₈₃ (USNM 2566) and chrome-augite (benchstandard from Eugene Jarosewich at the Smithsonian Institution).

Two polished thin sections of ALH 77005 were also used in this study: 117 and 54 from NASA Johnson Space Center in Houston, TX. In addition, one chip of the natural sample (ALH 77005,12) was made into a thick section in an effort to develop a three dimensional picture of unhomogenized melt inclusions. The host phenocrysts, daughter crystals, glass matrix, and pyroxene rims associated with each melt inclusion were analyzed for major and minor elements using a Cameca SX-100 electron microprobe.

Comparison of methods for investigating melt inclusion compositions

There are several techniques used for estimating the composition of partially or completely crystallized melt inclusions. Non-destructive techniques such as modal analyses and wide-beam microprobe techniques are reviewed in Roedder (1984) and

references therein. Two destructive techniques are also employed: the heating stage method (e.g., Sobolev et al. 1980; Zapunyy et al. 1989) and rehomogenization in a 1 atm, gas-flow furnace (e.g., Zapunyy et al. 1989; Gaetani and Watson 2000; Hauri 2002). Each of these techniques has advantages and drawbacks. In the case of ALH 77005, non-destructive techniques are particularly problematic as the size and highly crystallized nature of the melt inclusions often preclude getting an appropriate cross-section for accurate modal abundances of phases (Figure 2).

A survey of existing rehomogenization techniques showed that they would not be the most appropriate for ALH 77005. Heating stage rehomogenization commonly uses the vapor bubble as a guide to completion of the rehomogenization (Danyushevsky et al. 2002 and references therein). As the daughter phases melt, the volume of the melt expands causing a decrease in the volume of the vapor bubble. However, consistent with previous melt inclusion analyses on SNC meteorites (Stockstill et al. 2005), melt inclusions in ALH 77005 rarely contain a vapor bubble as a guide for completion. In addition, any loss of the vapor phase after entrapment and cooling of the melt inclusion would change the remaining volume of the vapor phase and result in overheating of the melt inclusion during rehomogenization. As ALH 77005 suffered severe shock upon ejection from Mars, we suspect the vapor phase may have been lost from some inclusions (Johnson et al. 1991). Finally analyses on a heating stage would be difficult if not impossible for highly-fractured, sample material such as ALH 77005.

Rehomogenizing melt inclusions in a 1 atm, gas-flow furnace involves placing the sample in a furnace at a temperature above the liquidus for duration of ~ 10 minutes (Hauri, 2002). The sample is immediately quenched. However, the kinetics of these

reactions in coarsely crystallized melt inclusions such as those in ALH 77005 are slow and require longer durations in the furnace. Given the highly fractured nature of host crystals in ALH 77005, a high-pressure method was considered preferable.

The method we developed to rehomogenize melt inclusions under pressure takes into account the highly-crystallized nature of the melt inclusions, the fragile nature of the sample, and the low f_{O_2} conditions at the time of crystallization. Our method fixes the oxidation state of the sample at a desired level based on the graphite-gas equilibrium and prevents exchange between the sample and the platinum container. The possible loss of some volatiles from the sample was a secondary concern to that of achieving crystal melt equilibrium and therefore we rehomogenized our melt inclusions in relatively long duration experiments. As will be explained later, textural and chemical criteria were used to make the determination of equilibrium between the trapped melt and host crystal.

Results

ALH 77005 Petrology

A thin section created from a chip of the same aliquot of ALH 77005 used in the experiments illustrates that it is predominantly composed of chromite and olivine poikilitically enclosed by low-Ca pyroxene (Figure 1) as described by McSween et al. (1979). Although melt inclusions have been reported in olivine, chromite, and orthopyroxene, they are most common in olivine. No chromite-hosted melt inclusions were found in thin sections of the natural sample used for this study. Olivine-hosted melt inclusions that are magmatic in origin have undergone extensive crystallization and fall into two textural groups. One group consists of large ($> 100 \mu\text{m}$ diameter) inclusions with high- and low-Ca pyroxene and high- SiO_2 ($> 90 \text{ wt\% SiO}_2$) daughter phases while

the other group consists of smaller ($<50\text{ }\mu\text{m}$) and considerably less crystallized inclusions, with low-Ca pyroxene rims adjacent to the olivine host and no other observable daughter phases (Figure 2); (Ikeda 1998). In addition, our analyses have shown that while pyroxene rims are formed adjacent to the inclusion-host contact in inclusions of both types, the large, highly crystallized melt inclusions have high-Ca pyroxene rims while the small, crystal-poor melt inclusions have low-Ca pyroxene rims. One of the goals of melt inclusion rehomogenization was to determine what factors produce the two melt inclusion crystallization paths.

Results from rehomogenization experiments

Overview of Experiments

Table 1 shows the run conditions for fourteen rehomogenization experiments conducted on ALH 77005 chips. The first two experiments, performed at 1185°C and 1000 bars for different periods of time, melted large portions of olivine, low-Ca pyroxene, and chromite to produce pockets of melt. It was determined that these experiments were run at too high a temperature to reasonably expect melt inclusions to remain isolated from these melt pockets. Subsequent experiments were run at lower temperatures and produced melt inclusions in various stages of rehomogenization depending on the temperature and run duration.

Olivine-Hosted Melt Inclusions

Olivine melt inclusions analyzed after rehomogenization experiments are categorized into one of three groups: partly homogenized with a variety of daughter crystals remaining in the melt inclusion, partly homogenized with only low-Ca pyroxene remaining visible in the melt inclusions, and nearly or fully homogenized melt inclusions

which do not contain visible daughter crystals. Experiment #3, which was run at 1150°C for 12 hours, falls into the first category of olivine-hosted melt inclusions that contained daughter phases of pyroxene, plagioclase, chromite, high-SiO₂ phases and/or phosphates as well as pyroxene rims (Figure 3a). The texture and compositions of the daughter phases mimic those in the natural thin section and these crystals are interpreted to be residual phases produced during melt inclusion crystallization that have not completely rehomogenized. Inclusions in experiments #4, #7, #8 and #11 fall into the second category. These melt inclusions contain euhedral pyroxene daughter crystals (En₇₄Fs₂₁Wo₅) but no longer retain pyroxene rims separating the host and melt, (Figure 3b). Finally, experiments #6, #12, #13, and # 14 contain nearly or fully rehomogenized melt inclusions that do not contain visible rims or daughter crystals (Figure 3c).

Comparisons of glass compositions from melt inclusions in various stages of rehomogenization (Figure 4 and Table 2) reveal that with decreasing MgO (lower degrees of rehomogenization), SiO₂ increases while CaO and FeO decrease. At the same time, Al₂O₃ contents increase from 11 wt % to a peak at ~18 wt % (~3 wt % MgO) before beginning to decrease. Comparison of other major and minor elements shows that K₂O and Na₂O increase while FeO and TiO₂ decrease with decreasing MgO. There is a sharp decrease in FeO at MgO < 4 wt %. P₂O₅ increases with increasing MgO (rehomogenization), however it is quite variable in olivine-hosted melt inclusions at MgO values of 6-7 wt %. As in the natural sample, individual host olivines exhibit no Fe, Mg, or Ca zoning (Table 3) but have Mg #s ranging from 70-75. Cr₂O₃ contents in olivine are less than 0.1 wt %. CaO, ranging between 0.13 and 0.23 wt %, is uniform within a single olivine crystal.

Chromite-Hosted Melt Inclusions

Glass compositions of rehomogenized melt inclusions in chromite are shown in Table 4. All melt inclusions found in chromite were in chromites poikilitically enclosed in olivine and are free of daughter crystals. When compared with completely rehomogenized olivine-hosted melt inclusions, the chromite-hosted melt inclusions have a higher MgO. SiO₂, Na₂O, FeO, K₂O, and TiO₂ concentrations are comparable to olivine-hosted melt inclusions with MgO values between 6 and 7 wt %. CaO and P₂O₅ are slightly lower while Al₂O₃ is slightly elevated in chromite-hosted melt inclusions.

Chromite zoning is discussed extensively by Ikeda (1998) and will not be described here. However, minor zoning of chromite hosts at the margins of melt inclusions show increases in Al₂O₃ and TiO₂ (< 1 wt %) and decreases in Cr₂O₃ (~3 wt %) at the host-melt inclusion contact. Figure 5 compares chromites analyzed in our experiments with those determined by Ikeda (1998).

Discussion

Chromite-hosted melt inclusions: the parental magma of ALH 77005

Chromites poikilitically enclosed by olivine were the first crystallizing phase (McSween et al. 1979), suggesting that the parental melt composition of ALH 77005 may be best approximated by a chromite-hosted melt inclusion (Table 4). Compared with the olivine-hosted melt inclusions discussed in the following sections, chromite-hosted melt inclusions are less susceptible to post-entrapment effects such as reequilibration with the host and crystallization along the margin of the host-melt interface (Kamenetsky 1996). This is demonstrated in ALH 77005 by the preservation of distinct zoning patterns found in chromites enclosed by low-Ca pyroxene and olivine (Ikeda, 1998).

Accordingly, we suggest that melt inclusion 7-10 found in Table 4 represents the parental melt composition of ALH 77005 at the time of chromite crystallization. However, this composition has a Cr_2O_3 concentration of 1.35 wt % which is anomalously high compared with terrestrial basalts and may reflect excess melting of the chromite host. The Cr_2O_3 contents of chromite-hosted melt inclusions are particularly sensitive to small changes in the melting of the chromite host because the Cr_2O_3 of the chromite is so much greater than the coexisting melt. Once chromite begins to crystallize in the ALH 77005 magma, the Cr_2O_3 of the melt begins to decrease (i.e., McCallum, 1996), and thus the olivine-hosted melt inclusions trapped slightly later in the crystallization sequence are expected to contain lower Cr_2O_3 . We have modeled possible corrections in the Cr_2O_3 (and other oxides) of the chromite-hosted melt inclusion using the Cr_2O_3 of olivine-hosted inclusions (0.2-0.4 wt %) as the lower limit on the melt trapped by chromite in ALH 77005. The results of these calculations are shown in Table 5. To reach the upper limit of Cr_2O_3 concentration observed in olivine inclusions, an excess of 1 and 2 % of the chromite host would need to be remelted into the chromite inclusion. The recalculation to account for the excess Cr_2O_3 (1 wt%) in MI 7-10 increases the SiO_2 concentration of the parental melt by 1 wt%, CaO by 0.2 wt %, and decreases FeO by 0.2 wt %.

The recalculated chromite-hosted melt inclusion 7-10 (Table 5) is probably the best estimate of the parental melt for ALH 77005. This composition contains ~ 7.6 wt % MgO and 49.9 wt % SiO_2 . The P_2O_5 in this melt (1.1 wt %) is an order of magnitude larger than previous estimates of either the parental melt or the melt inclusion compositions in ALH 77005. This high P_2O_5 is considered more reliable as it is consistent with both the chromite- and olivine-hosted melt inclusions analyzed in this

study. It suggests that the ALH 77005 magma is a partial melt of a cumulate zone that contained phosphates or an evolved trapped melt as well as olivine and low-Ca pyroxene (Borg and Draper 2003). The Cr_2O_3 for this parental melt (0.2 wt %) is also an order of magnitude larger than previous estimates for ALH 77005 olivine-hosted melt inclusions. The relatively high Cr_2O_3 in the parental melt indicates that the cumulate source of the magma may also have contained chromite.

Post-crystallization magmatic equilibration of major elements in ALH 77005

Before considering the results of the experiments with respect to olivine-hosted melt inclusions, it is necessary to address the possibility that olivine hosts and their entrained melt inclusions experienced significant reequilibration of Fe and Mg and possibly minor elements in post-entrapment magmatic events on Mars. Should such reequilibration have occurred, it may have significantly changed the composition of the melt inclusion. Of particular importance are Fe and Mg, which diffuse quickly through olivine relative to the other cations (Danyushevsky et al. 2000; Gaetani and Watson 2000; Gaetani and Watson 2002). Significant exchange of Fe^{2+} and Mg^{2+} would produce either a) zoned olivine if reequilibration was not complete and the quench was rapid or b) neighboring olivine crystals with the same Mg # if the reequilibration occurred over an extended period of time. Consistent with previous studies of ALH 77005 (Ikeda 1994), we found that olivine in this rock is not zoned for any major elements but individual homogenous grains do vary from Fo_{69} - Fo_{75} within the same sample (Figure 1). The fact that adjacent crystals retain different Mg #s indicates no late magmatic event changed the MgO/FeO ratio post-crystallization. The homogeneous nature of the olivines together with the grain to grain differences in Mg# does suggest that the grains were zoned at the

time of entrapment in low-Ca pyroxene, and experienced diffusional reequilibration within each crystal. The grain to grain variability suggests that this reequilibration was limited to changes within the single grain and not to exchanges with other olivines or with a larger magmatic system.

Although there is also no detectable zoning in Al or Cr in ALH 77005 olivine, there is a prominent cyclic growth zoning of P (Figure 7b). The formation of cyclic P zoning in olivine has been attributed to differences in growth rate in terrestrial olivines (Milman-Barris et al. 2008). Zones of fast-growing olivine incorporate higher P_2O_5 into their lattice compared with slow-growth cycles because the slow-moving, highly-charged cations (P, Cr, V) concentrate around the growth front. This zoning can presumably develop without zoning of Mg in Fe which diffuse much more rapidly in the melt, but in this case, the crystals probably were zoned in Fe-Mg as discussed in the previous paragraph. The fact that the cyclic, growth-induced zoning is preserved in the natural sample and in the olivines after rehomogenization (Figure 7d) supports our conclusion that ALH 77005 did not experience post-crystallization magmatic reequilibration.

Validation of rehomogenization technique

We have already addressed the necessity to develop a new technique for rehomogenizing melt inclusions in ALH 77005. However, to validate and understand the data obtained from rehomogenized melt inclusions in this study, two questions must be addressed. Did the melt inclusions 1) achieve equilibrium with the host during the course of the experiment? and 2) completely rehomogenize?

Traditional melt inclusion rehomogenization techniques rehomogenize melt inclusions as quickly as possible to avoid exchange between the melt inclusion and the

host (e.g., Frezzotti 2001; Danyushevsky et al. 2002; Hauri 2002). The short duration heating in these experiments is based on two goals: 1) to find entrapment temperatures by observing changes in the vapor bubble over the course of reheating and 2) to avoid any diffusion of major or minor elements between the host and the melt inclusion. We have made no attempt to determine the entrapment temperature here and therefore the first point is not relevant to this study. In regards to the second point, if the host changed composition after the melt inclusion was trapped, this chemical change could be transferred to the melt inclusion during rehomogenization. However, as discussed above, ALH 77005 olivine hosts appear not to have undergone major reequilibration after crystallization and chromite hosts are particularly insensitive to changes in major and minor elements as the diffusion of most elements through the lattice is limited (Kamenetsky 1996). Therefore changes in the melt inclusion composition due to equilibration with the host over the course of the experiments are not a significant concern with ALH 77005.

Unlike other methods that require mathematical corrections to olivine-hosted melt inclusion compositions to account for Fe-Mg equilibrium with the host (Danyushevsky et al. 2000), the rehomogenization technique used in this study reestablishes the initial equilibrium between the trapped melt and the host phenocryst. Four criteria were used to determine equilibrium: the length of the experiment, texture of host and associated daughter phases, melt-olivine K_d , and the composition of coexisting olivine-hosts and low-Ca pyroxene daughter crystals. Only experiments that had been run for 48 to 72 hours were considered as possibly achieving phase equilibrium. This period of time is long enough for MgO and FeO to reach diffusive Fe-Mg equilibrium in olivine

(Danyushevsky et al. 2000; Gaetani and Watson 2000; Gaetani and Watson 2002). In addition, for melt inclusions that retained daughter phases, equilibrium between the host, melt, and daughter crystals in the melt inclusions was interpreted to be approximated if the melt inclusion's low-Ca pyroxene daughter crystals were euhedral. Olivine-hosted inclusions in our experiments that are texturally near equilibrium have a K_d in the range from 0.26-0.3 with most inclusions having a K_d of 0.27. The K_d for melts in equilibrium with olivine are generally near 0.30 (Roeder 1974), however they can range from 0.25-0.35 since K_d varies with temperature, pressure, oxidation state, and composition (e.g., Mysen 1975; Ulmer 1989). Finally, the composition of the coexisting olivine and low-Ca pyroxene daughter crystals were compared for experiments that contained low-Ca pyroxene daughter crystals (Figure 8). Tie lines connecting coexisting olivine, low-Ca pyroxene, and melt are shown as dashed lines. The melt composition was normalized to the pyroxene quadrilateral so that it can be plotted along with the pyroxenes. If the melt was out of equilibrium with the mineral phases, olivine would have diffusively reequilibrated faster than low-Ca pyroxene (Ganguly and Tazzoli, 1994; Jurewicz and Watson, 1988). The fact that the tie lines don't cross suggests that the melt, olivine, and low-Ca pyroxene approach compositional equilibrium in these experiments.

The second question to be addressed is whether any melt inclusions were completely homogenized. Of the ~ 100 olivine-hosted melt inclusions analyzed, only melt inclusions without daughter crystals could be considered completely homogenized. However, to identify whether the melt inclusion had fully homogenized or had been taken past homogenization by incorporating host material, we compare the olivine-hosted melt inclusion compositions with those from chromite-hosted melt inclusions (Figure 9 and

Table 2 and 3), none of which contain visible daughter crystals. In this plot (Figure 9), the various oxides are plotted against MgO, which is a proxy for extent of crystallization. As will be discussed in the next section, the MgO content of the chromite-hosted melt inclusions is well constrained. Since the chromites are poikilitically enclosed in olivine, it is expected that they should have slightly higher MgO contents than their olivine counterparts and this is the case.

To confirm these interpretations, we started with an olivine-hosted melt inclusion containing 7.1 wt % MgO and modeled its evolution as host olivine was remelted (Table 5). The results of this addition are shown in Figure 6 along with the analogous data for chromite remelting. Olivine was added to the olivine-hosted melt composition in increments of 1, 2, 3, and 4 wt %. After each increment, the Mg # of the melt was allowed to equilibrate with the host olivine using the Fe-Mg K_d of 0.27. Given the relatively small volume of the melt inclusions (<300 μm), we treated the olivine as an infinite reservoir whereby the Mg # of the host would not change. As already discussed, the compositional evidence suggests the olivine-hosts were not significantly modified after entrapment. Therefore, we conclude that the melt trapped by ALH 77005 olivine phenocrysts is close to the composition reported here and it was unlikely to have been significantly modified by post-entrapment effects.

P₂O₅ in olivine-hosted melt inclusions

Several important points regarding the appearance of phosphate are indicated from the comparison of olivine-hosted melt inclusions as P₂O₅ shows significantly more variation at a given MgO than the other oxides (Figure 10). Specifically, P₂O₅ is high in melt inclusions from experiments 8, 14, 15, and 17. The variation in P₂O₅ at ~6 wt %

MgO is positively correlated with CaO suggesting phosphates were incorporated into early crystallizing phases through one of three possible mechanisms. First, secondary phosphates found in cracks may have been mobilized during rehomogenization and incorporated into some melt inclusions. This would artificially raise the CaO and P_2O_5 in these inclusions. Second, P_2O_5 may be the result of olivine's incorporation of the boundary layer at a fast moving growth front. The components of the phosphates are trapped in melt inclusions as part of the boundary layer and saturate during cooling and crystallization within the melt inclusion. However, entrapment of the boundary layer should enrich other slow diffusing cations such as Al_2O_3 and TiO_2 in the inclusion and this is not observed. Finally, phosphates may have saturated prior to being incorporated into the melt inclusion. P_2O_5 diffuses slowly relative to other cations in a natural silicate melt such that P_2O_5 may build up and apatite begins to nucleate and grow at the margin of a fast growing phenocryst (Harrison and Watson 1984). P x-ray maps of both natural and experimental samples show P zoning in olivine (Figure 7), suggesting variation in olivine growth rate (Milman-Barris et al. 2008). The saturation of phosphates during olivine crystallization would be a significant departure from the crystallization sequence defined by Lundberg et al. (1990), who suggested that saturation of phosphates occurred at the end of the crystallization sequence.

Comparing olivine- and chromite-hosted melt inclusion compositions

The composition of the completely rehomogenized olivine and chromite-hosted melt inclusions differ significantly from each other in the case of some oxides (figure 9). For example, SiO_2 and Al_2O_3 are significantly lower while CaO and P_2O_5 are higher in olivine-hosted melt inclusions than in chromite-hosted melt inclusions that differ by only

1 wt % in MgO (figure 9). Of specific interest are P_2O_5 , CaO, and Al_2O_3 as they are not significant components in the only two phases known to be on the liquidus as the melt evolved from the chromite- to the olivine-hosted melt inclusion composition. Figure 11 shows the evolution of the chromite-hosted melt inclusion composition assuming olivine and chromite crystallize in various percentages. It reveals that no percentage of chromite + olivine crystallization will produce a liquid line of descent that connects the magmas contained in chromite- and olivine-hosted inclusions. Even assuming crystallization of low-Ca pyroxene and plagioclase of the composition found in ALH 77005, there is no melt evolution path that brings the chromite-hosted melt inclusion composition to the olivine-hosted melt inclusions (figure 11). While Al_2O_3 is incorporated into chromite, it is incorporated in such small quantities that chromite crystallization can not account for the lower Al_2O_3 observed in olivine-hosted melt inclusions.

This above discrepancy in melt inclusion composition may be explained by one or more magmatic processes including, magmatic reequilibration of olivine, entrapment of a boundary layer during phenocryst growth, and magma mixing between chromite and olivine crystallization. It has already been shown that ALH 77005 olivine did not suffer significant modification of the Fe/Mg ratio therefore the first possibility is considered unlikely. However, increasing MgO to the degree that it is consistent with chromite-hosted melt inclusions still produces an olivine-hosted melt composition that is inconsistent in Al_2O_3 , CaO, P_2O_5 and SiO_2 with the melt trapped by chromite. If olivine and/or chromite-hosted melt inclusions trapped the boundary layer as they crystallized, slow-moving cations such as P_2O_5 could have been trapped in higher than average proportions. However, the slow-moving cations Al_2O_3 and TiO_2 are too low in the

olivine-hosted melt inclusions suggesting that the discrepancy can not be solely attributed to this affect. Finally, the composition difference may be evidence of injection of or mixing with a magma that is lower in SiO_2 and Al_2O_3 . Several studies have already addressed whether ALH 77005 crystallized in an open or closed system (Lundberg et al. 1990; Harvey et al. 1993; Borg and Draper 2002). Ikeda (1998) suggested that a high K magma was introduced to the ALH 77005 magma during olivine crystallization but prior to low-Ca pyroxene crystallization. From our study of olivine-hosted melt inclusions, there does not appear to be a significant change in the K/Na ratio of olivine-hosted melt inclusions prior to the formation of plagioclase daughter crystals, however our results could be explained by an injection of magma that is higher in CaO and P_2O_5 and lower in SiO_2 and Al_2O_3 between chromite and olivine-hosted melt inclusion entrapment.

A non-magmatic origin for this discrepancy could be contamination by phosphates which would artificially raise the P_2O_5 and CaO of the olivine-hosted melt inclusion composition. As discussed in the previous section, CaO and P_2O_5 enrichment in some inclusions may reflect secondary contamination by phosphates found in veinlets and cracks in the natural sample. If olivine-hosted melt inclusion compositions were modified to reflect the CaO and P_2O_5 content of the chromite-hosted melt inclusions, all other oxides would increase accordingly. Therefore Al_2O_3 and SiO_2 would increase such that they are consistent with the projected path of the melt composition assuming olivine crystallization (Figure 11). After this correction, the only major oxide that does not become consistent between the two types of melt inclusions is FeO. As seen in Figure 9, the FeO concentration varied for olivine-hosted melt inclusions. This may reflect small changes in the Fe/Mg ratio of the magma during olivine crystallization. Olivine-hosted

melt inclusions were in equilibrium with their olivine hosts; however the hosts' Mg # ranged between 70 and 75. Therefore, the high FeO concentration of this particular melt inclusion may reflect a point in the magmatic evolution and entrapment where the MgO/FeO ratio had decreased.

Comparison of Rehomogenized Olivine-Hosted Melt Inclusions with Previous Studies of ALH 77005

The purpose of experimentally rehomogenizing melt inclusions was to eliminate the effect of post-entrapment crystallization on our analyses. Comparing our results with previous melt inclusion studies of ALH 77005 (Table 6), it is clear that the experimentally rehomogenized olivine-hosted melt inclusion compositions have lower SiO₂ values (48 wt %) than most previous mode-based estimates. Unlike previous studies (McSween 1987; Jagoutz 1989; Harvey et al. 1993; Ikeda 1998), the SiO₂ contents of the olivine-hosted melt inclusions (~48 wt % SiO₂ at MgO of 6 wt %) from this study are demonstrated to be in equilibrium with a magma crystallizing olivine. In addition, the MgO value obtained by Ikeda (1998) is at least 4 wt % higher than the MgO values for the chromite melt inclusions obtained in this study (Table 4). As chromite was one of the first crystallizing phases and was co-crystallizing with olivine (McSween et al. 1979), it is unlikely that the olivine-hosted melt inclusions could have obtained MgO contents higher than chromite without significant reequilibration of the host olivine which we have established was unlikely. The Cr₂O₃ of early ALH 77005 melts appears to have been underestimated in previous studies possibly because the abundance of chromite in trapped melts was underestimated. As chromite incorporates, Fe, Mg, Al, and Ti in addition to Cr, it is important to accurately account for the trapped chromite

found in melt inclusions when estimating melt inclusion bulk compositions. In addition, small increases in Cr_2O_3 in a magma have significant effects on the stability field of olivine and spinel, which expand at the expense of pyroxene and plagioclase (Onuma and Tohara 1983). Therefore underestimating Cr_2O_3 can significantly impact models that estimate where minerals are likely to appear on the liquidus.

Our P_2O_5 concentrations in olivine-hosted melt inclusions, while showing considerable variability at higher MgO concentrations, are also considerably higher ($\sim 2.5 \pm 1$ wt % P_2O_5 at 6 wt % MgO) than those calculated by previous studies (~ 1 wt %). Regardless of the cause of the CaO and P_2O_5 enrichment, prior studies have underestimated the role of phosphates when calculating their compositions. This observation has significant implications for the REE signatures analyzed in olivine-hosted melt inclusions as the REE may reflect the phosphates contained in the inclusions and not the magmatic composition.

One final point can be made from looking at the olivine-hosted melt inclusions. It has been suggested that the two different types of magmatic olivine-hosted melt inclusions (Figure 2) described earlier were produced by differences in their trapped melt composition, assimilation of crustal rocks, silicate immiscibility and/or magma mixing (Jagoutz 1989; Harvey et al. 1993; Ikeda 1998). Some of these models also explained the high SiO_2 content determined for the melt inclusions. The results of our work show the two types of melt inclusions have the same SiO_2 contents after rehomogenization. In fact, all the major and minor elements are similar in the fully rehomogenized melt inclusions with the exception of P_2O_5 . Several other possibilities exist to explain the physical differences in these melt inclusions. First, they may have been trapped at

different stages of magmatic evolution. Second, they could have had different initial trapped volatile contents. Finally, they may have evolved differently due to differences in their cooling rate. However with the exception of Ca and P_2O_5 , the melt inclusion analyses of this study do not support a conclusion that these melt inclusions are fundamentally different in their trapped melt composition.

ALH 77005's parental magma compared with other SNC meteorites

We have compared the rehomogenized olivine-hosted melt inclusions and the parental melt determined from chromite-hosted melt inclusions with studies of melt inclusions in two other classes of martian meteorites, chassignites and nakhlites (Table 7 and Figure 12). Chassignites, dunites with > 93 % olivine, are thought to be cumulates (Florán et al. 1978). Varela et al. (2000) rehomogenized olivine-hosted melt inclusions in Chassigny using a heating stage. The melt inclusion composition determined by Varela et al. (2000) is very close to the evolved composition we determined from partially rehomogenized melt inclusions in ALH 77005. That they obtained olivine-hosted melt inclusions with compositions in excess of 69 wt % SiO_2 seems to indicate that they were not analyzing a parental melt for Chassigny and this composition will not be considered further. Using modal data and phase compositions, Johnson et al. (1991) constrained olivine-hosted melt inclusion compositions in Chassigny. The melt in equilibrium with Fo_{68} olivine is identified as the Chassigny A* composition and is slightly lower in MgO than the parental melt of ALH 77005. Like the olivines found in ALH 77005, if A* is projected to higher MgO, assuming the parental melt experienced olivine crystallization, Al_2O_3 is significantly lower and FeO is significantly higher than ALH 77005 suggesting a source composition that is different from that found in the chromites in ALH 77005.

Three melt inclusion rehomogenization studies have been performed on nakhlites (Varela et al. 2001; Rutherford et al. 2005; Stockstill et al. 2005) which contain high-Ca pyroxene and olivine in a fine-grained groundmass that makes up 25-60% of the rock (e.g., Treiman et al., 2005). The phenocryst compositions are essentially identical in the different nakhlites. Rehomogenization experiments on nakhlites MIL 03346 were performed in the same manner as those in our study (Rutherford et al. 2005). The compositions of the melt inclusions in olivine and high-Ca pyroxene are identical to the interstitial melt at the conditions of complete melt inclusion rehomogenization (very low- Al_2O_3 , high FeO at 3.5 - 4.0 wt % MgO). This suggests no significant fractionation affected the magma after melt inclusion entrapment. Stockstill et al. (2005) and Varela et al. (2001) both utilized heating stages to rehomogenize melt inclusions in Nakhla. The composition for Nakhla determined by Varela et al. (2001) is higher in SiO_2 and Al_2O_3 but lower in FeO than Stockstill et al. (2005). A projection line drawn through the rehomogenized melt inclusions analyzed for MIL 03346 is consistent with a melt inclusion composition determined by Stockstill et al. (2005). Therefore, we compare the parental melt of ALH 77005 with the Nahklite compositions determined from the studies of Stockstill et al. (2005) and Rutherford et al. (2005). If projected to the same MgO composition as ALH 77005 chromite-hosted melt inclusions, the Nahklite parent melts would be substantially lower in Al_2O_3 and SiO_2 and higher in FeO than either the chromite-hosted melt inclusions but also the olivine-hosted melt inclusion compositions found in ALH 77005 and in Chassigny. This indicates the source region of the nakhlites is significantly depleted in Al-bearing phases relative to ALH 77005's source region. It is also notable that the P_2O_5 in the Nakhla and MIL 03346 melts is quite low relative to

the amounts determined for ALH 77005. However, both Varela et al. (2001) and Stockstill et al. (2005) present a wide range of P_2O_5 concentrations, up to 1 wt %.

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Figure Captions

Figure 1. Backscatter images of a) thin section of ALH77005 and b) an experimental chip of ALH 77005 (Expt #4). White areas are chromite. Light grey areas are olivine poikilitically enclosed in low-Ca pyroxene (dark grey). High-Ca pyroxene is also found interstitially. Mg numbers of olivine are shown. Images confirm lack of Fe-Mg zoning determined from electron microprobe profiles. Variation in Mg # between homogeneous grains indicates lack of late magmatic or post-magmatic exchange between crystals.

Figure 2. Backscatter images of a thin section of ALH 77005 showing the two different types of olivine-hosted melt inclusions. a. Large, highly crystallized melt inclusion with a very thin high-Ca pyroxene rim. The light grey areas within the melt inclusions are also high-Ca pyroxene. The black spots are high-silica phases that may be quartz polymorphs. The interstitial region is glass. b. Small melt inclusion with low-Ca pyroxene rim (light grey) along the outer margin of the melt inclusion. The dark grey material in the interior is glass.

Figure 3. Backscatter image of olivine-hosted melt inclusions in three experiments. a. Melt inclusion that did not obtain equilibrium (12 hours at 1150°C). The rim is predominantly high-Ca pyroxene. Dark areas within the melt inclusion are high-silica phases surrounded by glass. b. Melt inclusion that obtained olivine-melt equilibrium based on Fe-Mg exchange but did not fully rehomogenize. The dark grey, euhedral crystals are daughter crystals of low-Ca pyroxene. c. Fully rehomogenized melt

inclusion that obtained equilibrium with its olivine host. The bright, spherical objects are quenched FeS-rich melts that were present in the sample prior to rehomogenization.

Figure 4. Glass compositions for olivine-hosted melt inclusions in various stages of rehomogenization. Open diamonds: Melts from partially rehomogenized melt inclusions. These inclusions retain visible remnants of pyroxene rims, pyroxene daughter crystals, plagioclase, phosphates, and chromites. Solid Circle: Plot of melt compositions from inclusions that retain only low-Ca pyroxene daughter crystals. Open Squares: Glass compositions from melt inclusions that show no visible daughter crystals and are interpreted to be nearly or completely rehomogenized and in equilibrium with their host olivine.

Figure 5. Plot of chromite compositions. Grey regions show two trends observed by Ikeda (1998). Black squares are analyses from this study, which are consistent the trends of Ikeda (1998).

Figure 6. Compositions for rehomogenized olivine (solid circles) and chromite-hosted (solid triangles) melt inclusions. Host olivine is added into the olivine-hosted melt inclusion and allowed to reequilibrate. The open circles are a projection of melt composition as the host olivine was added to the rehomogenized melt in various percentages. Open triangles represent this projection of the chromite-hosted melt composition as chromite-host is added back into the melt in various percentages.

Figure 7. Comparisons of thin sections of the natural sample and thick sections of experimental samples. a. Backscatter image of an olivine hosted melt inclusion in a thin section of the natural sample. b. P x-ray map of the same olivine-hosted melt inclusion in a thin section of ALH 77005. Bright areas are zones of high P_2O_5 . The

bright areas within the melt inclusion are phosphates that were either trapped with the melt or formed as the crystal grew. Oscillating zones of P_2O_5 content in the olivine may represent different growth rates of the olivine crystal (Milman-Barris et al. 2008). c. Backscatter image of an olivine (light grey) surrounded by low-Ca pyroxene (dark grey) in experimental sample CC1-05-3. d. X-ray map of the same experimental sample. P zoning was been preserved throughout the course of the experiment and defines the edges of the olivine grains.

Figure 8. Coexisting pyroxene (circles), olivine (dark filled squares) and melt (light filled squares) compositions for minerals in equilibrium with melt at pressures ranging from 800-1000 bars and temperatures ranging from 1155 to 1165 °C and with fO_2 between QFM – 2.7 to QFM – 3.0. Melt composition was normalized to the pyroxene quadrilateral such that it would plot in the same location as a pyroxene with the same FeO-MgO-CaO ratio. Because the lines connecting these coexisting pairs do not cross, these phases were near equilibrium with each other.

Figure 9. Composition of olivine-hosted melt inclusions (circles) that are nearly or completely rehomogenized (i.e., retain no observable daughter crystals) plotted along with chromite-hosted melt inclusions (triangles).

Figure 10. Chromite and olivine-hosted melt inclusions. Triangles represent the chromite-hosted melt inclusions. Olivine-hosted melt inclusions have been divided into high- P_2O_5 bearing inclusions (squares) and those with lower P_2O_5 contents (circles). High- P_2O_5 bearing melt inclusions are higher in CaO but lower in SiO_2 than low P_2O_5 bearing inclusions. The correlation with high CaO suggests that high- P_2O_5 bearing melt inclusions contain remelted phosphates. As the oxide contents are normalized to 100,

SiO₂ contents of these melt inclusions are low as a result of having anomalously high P₂O₅ values in the melt. Errors for these analyses are smaller than the symbol size and can be found in Table 2.

Figure 11. Various possible crystallization paths starting with the melt composition found in chromite-hosted melt inclusions (solid triangle). Open diamonds represent the path of crystallization if only chromite crystallized from this melt. The open circles represent the crystallization path assuming only olivine crystallized from this melt. Open diamonds represent a 50/50 mix of chromite and olivine crystallization from this starting composition. The solid circle represents the composition of a rehomogenized olivine-hosted melt inclusion. It is not possible to form a liquid line of descent from the chromite-hosted melt inclusion to the olivine-hosted melt inclusion through crystallization of olivine and chromite alone. The star represents a corrected olivine composition assuming the high P₂O₅ and CaO concentrations are due to secondary phosphate contamination.

Figure 12. Comparison of the melt composition for rehomogenized olivine-hosted melt inclusions in ALH 77005 with other martian meteorites. Blue triangles are chromite-hosted melt inclusions suggested to represent the parental melt composition of ALH 77005. The solid blue line is a fitted curve to ALH 77005 melt inclusions. Rehomogenized melt compositions for Nahkla are shown as red triangles (Stockstill et al., 2005). Rehomogenized melt compositions from primitive Nahklite MIL 00346 are plotted as squares (Rutherford et al. 2005). The A* composition determined from Chassigny melt inclusions is shown as a star (Johnson et al. 1991).

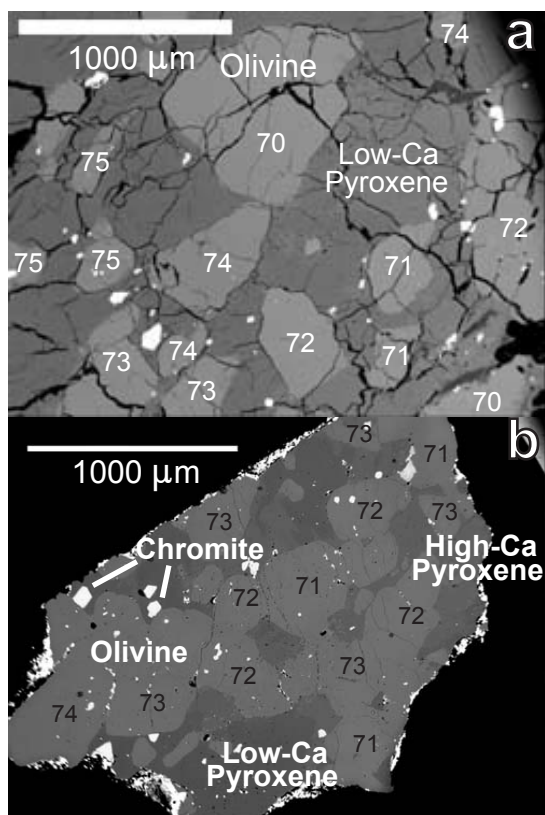


Figure 1

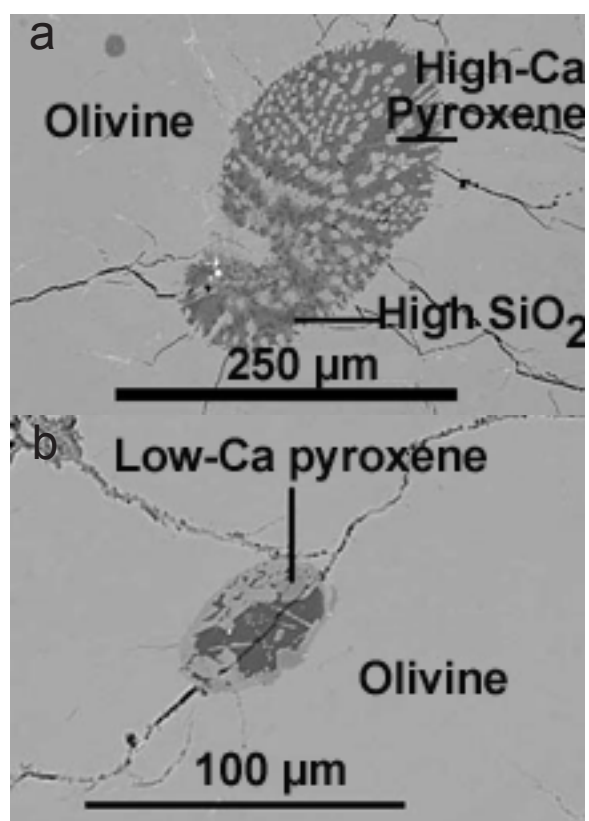


Figure 2

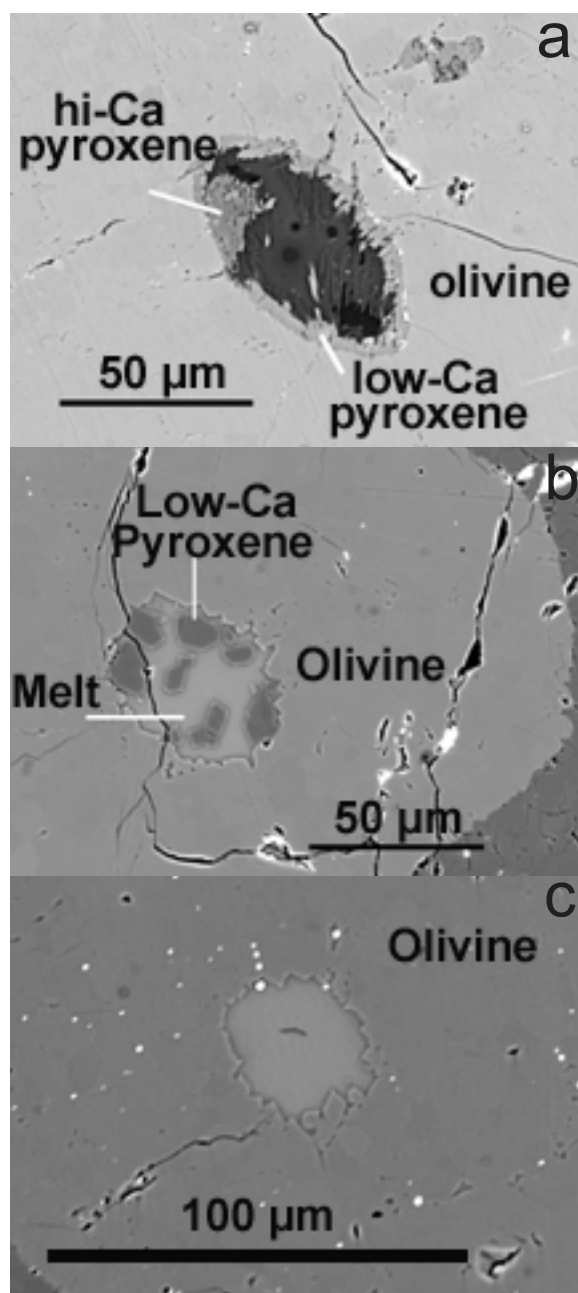


Figure 3

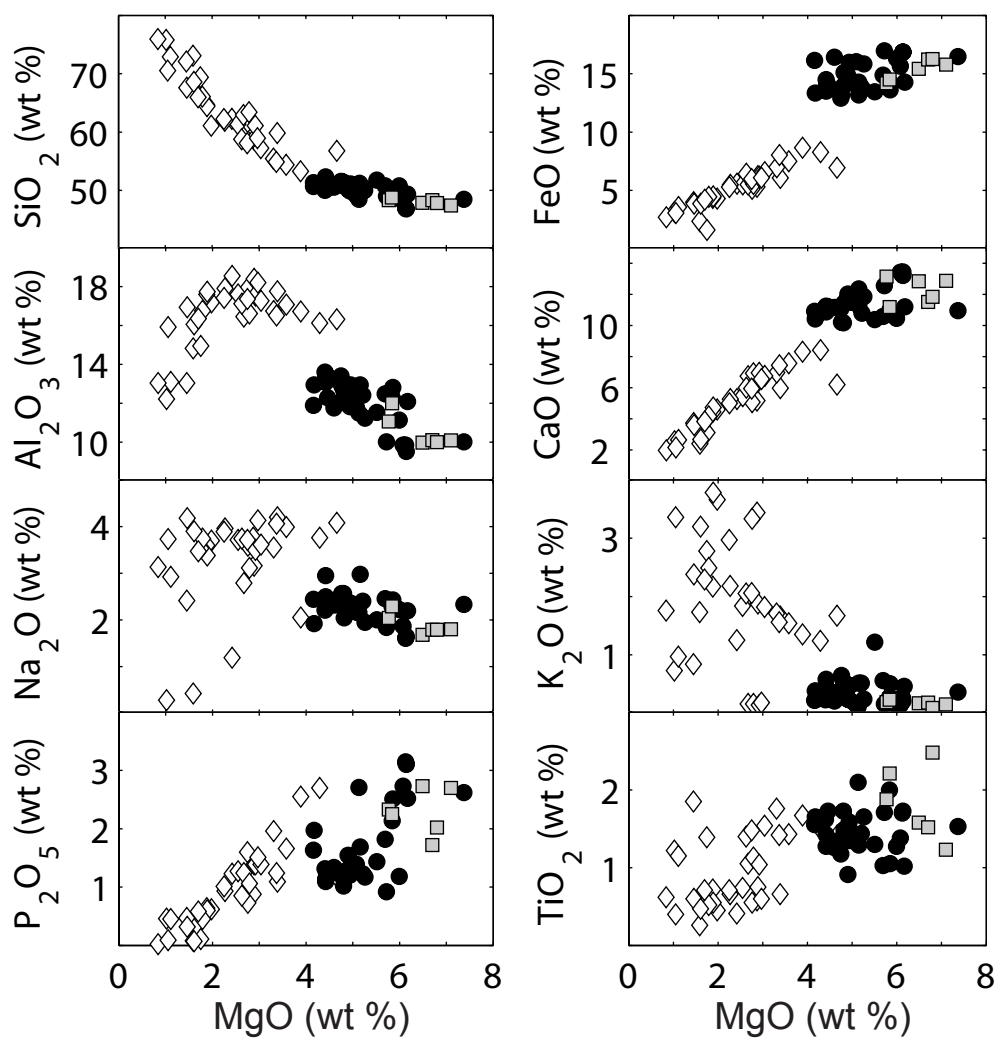


Figure 4

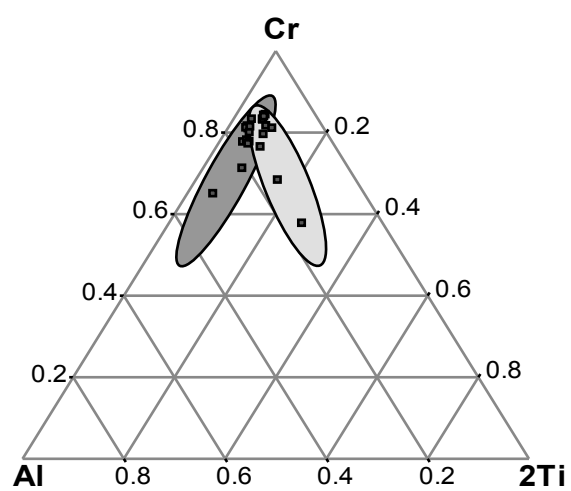


Figure 5

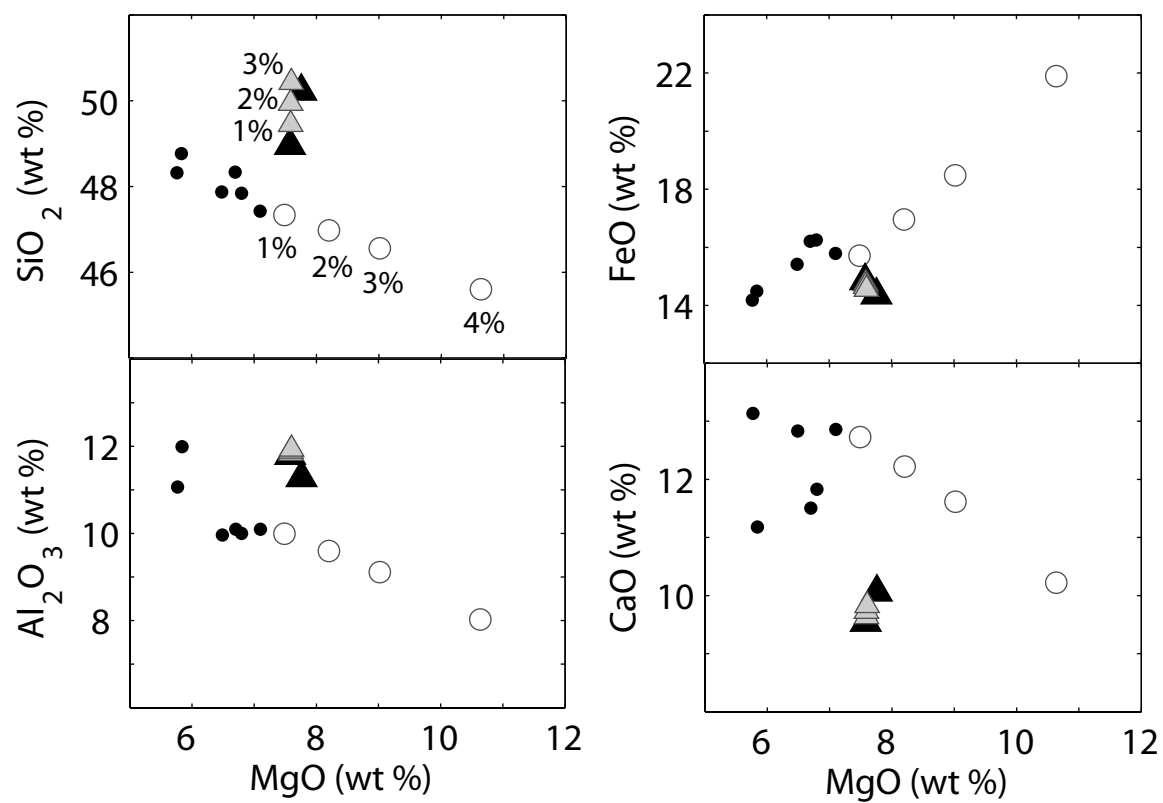


Figure 6

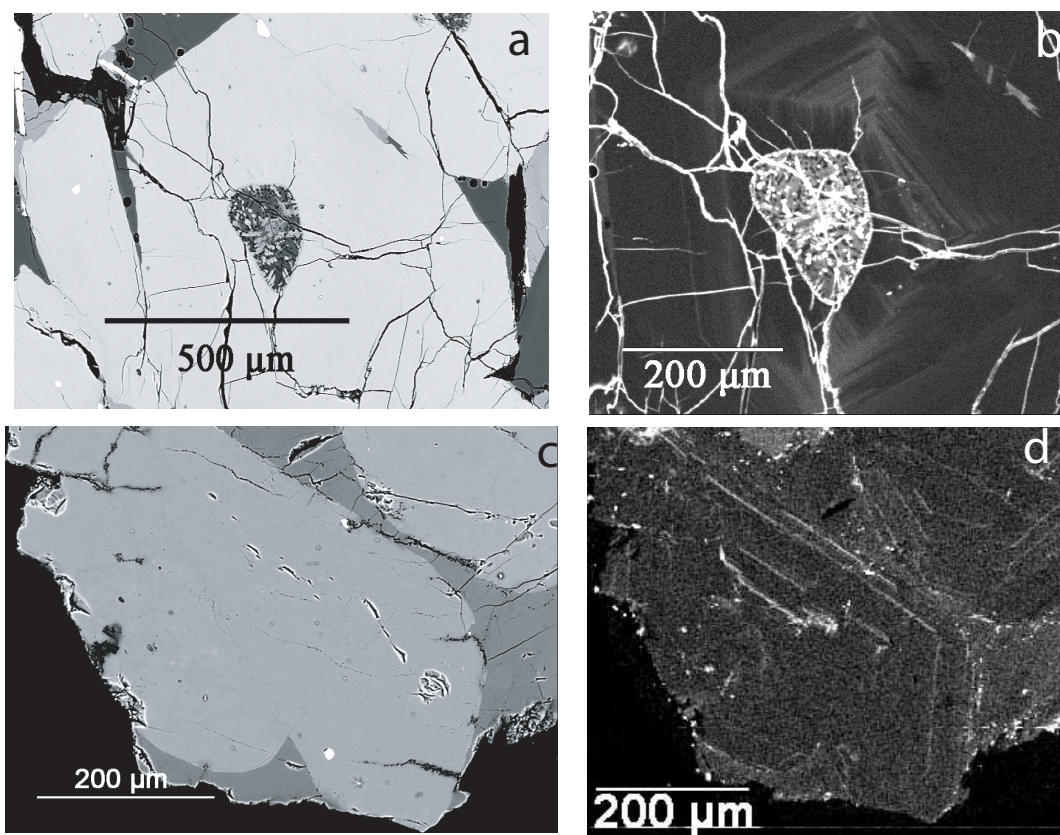


Figure 7

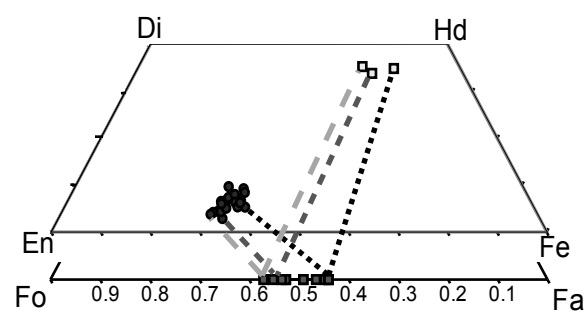


Figure 8

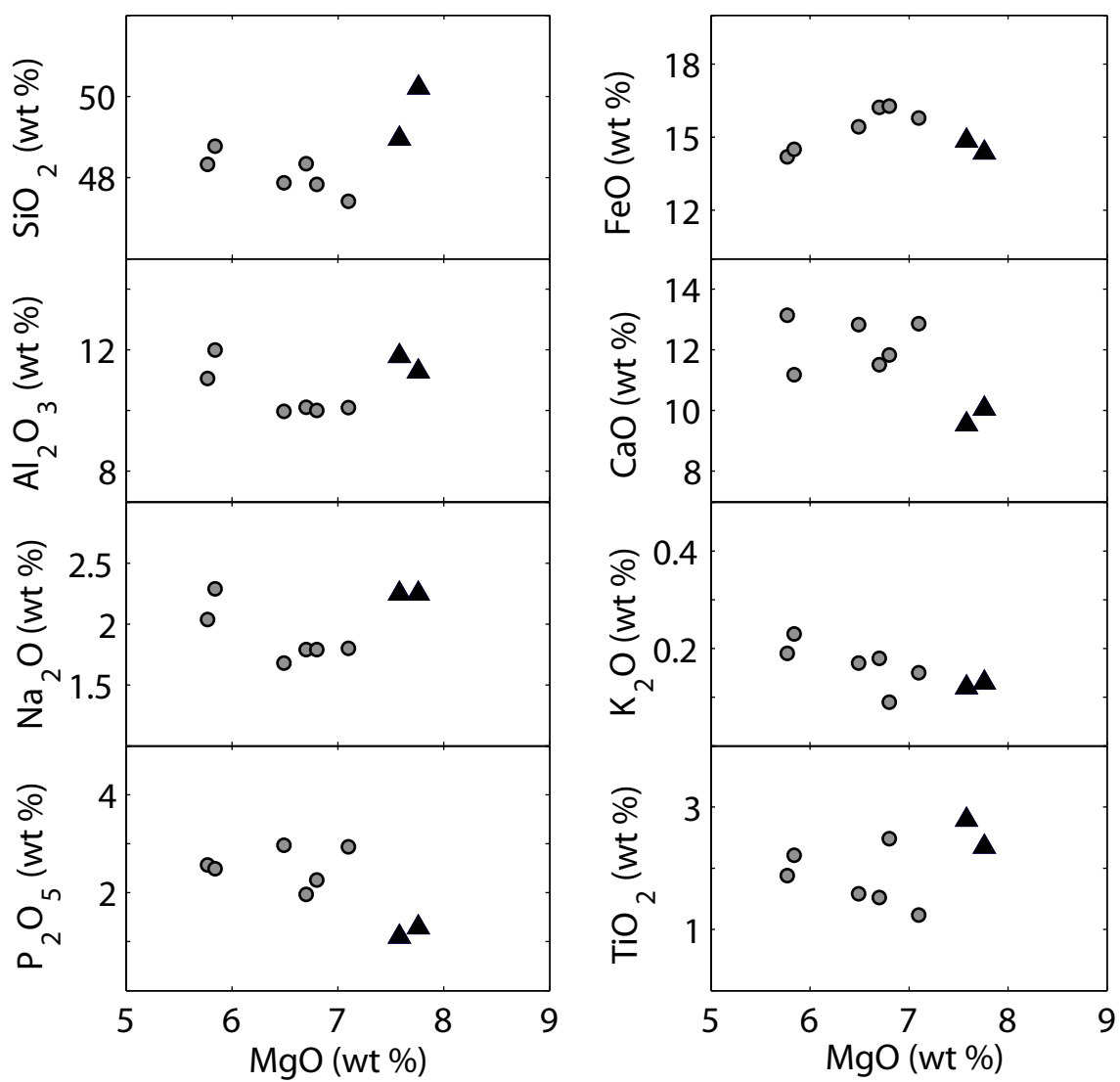


Figure 9

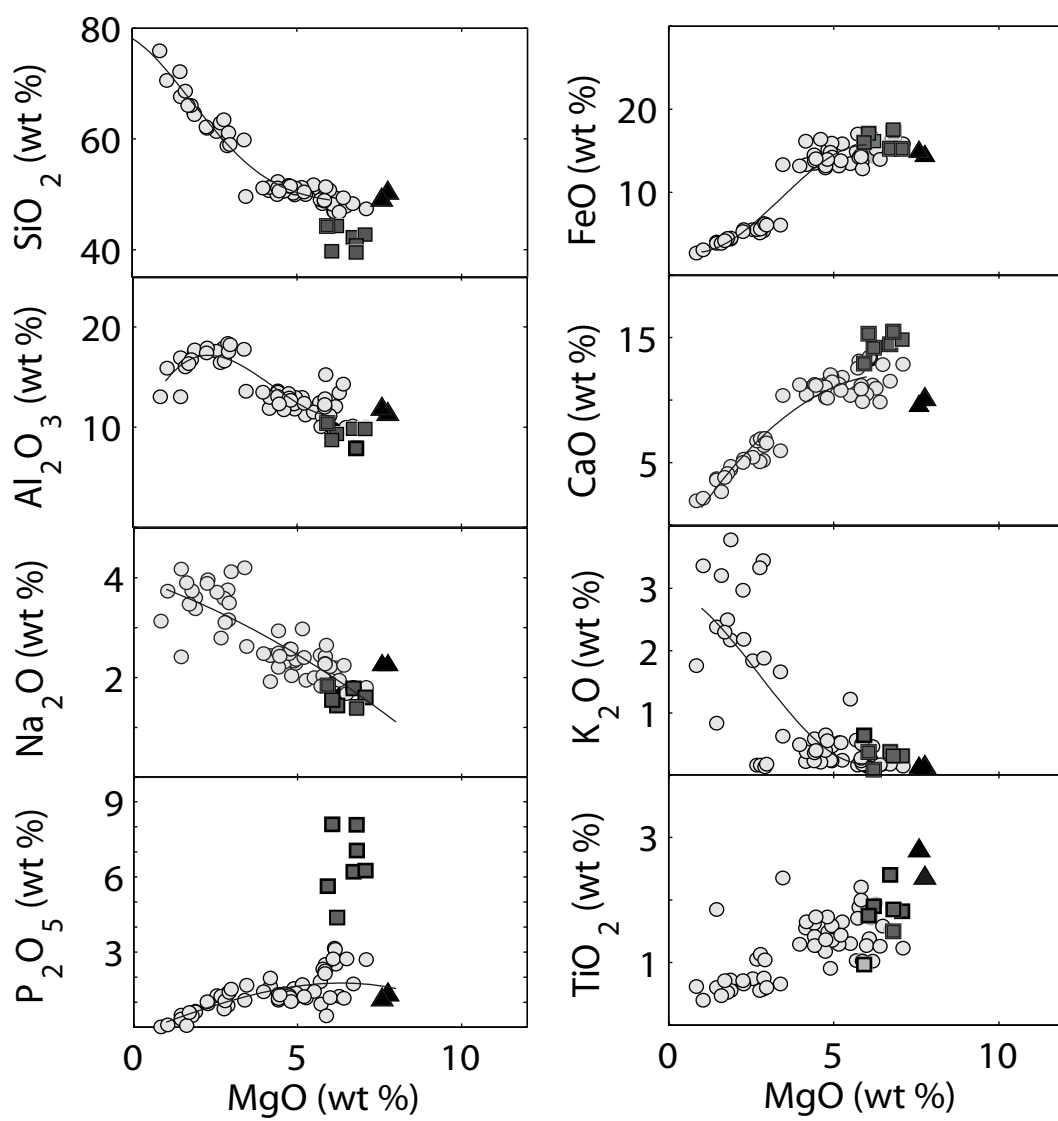


Figure 10

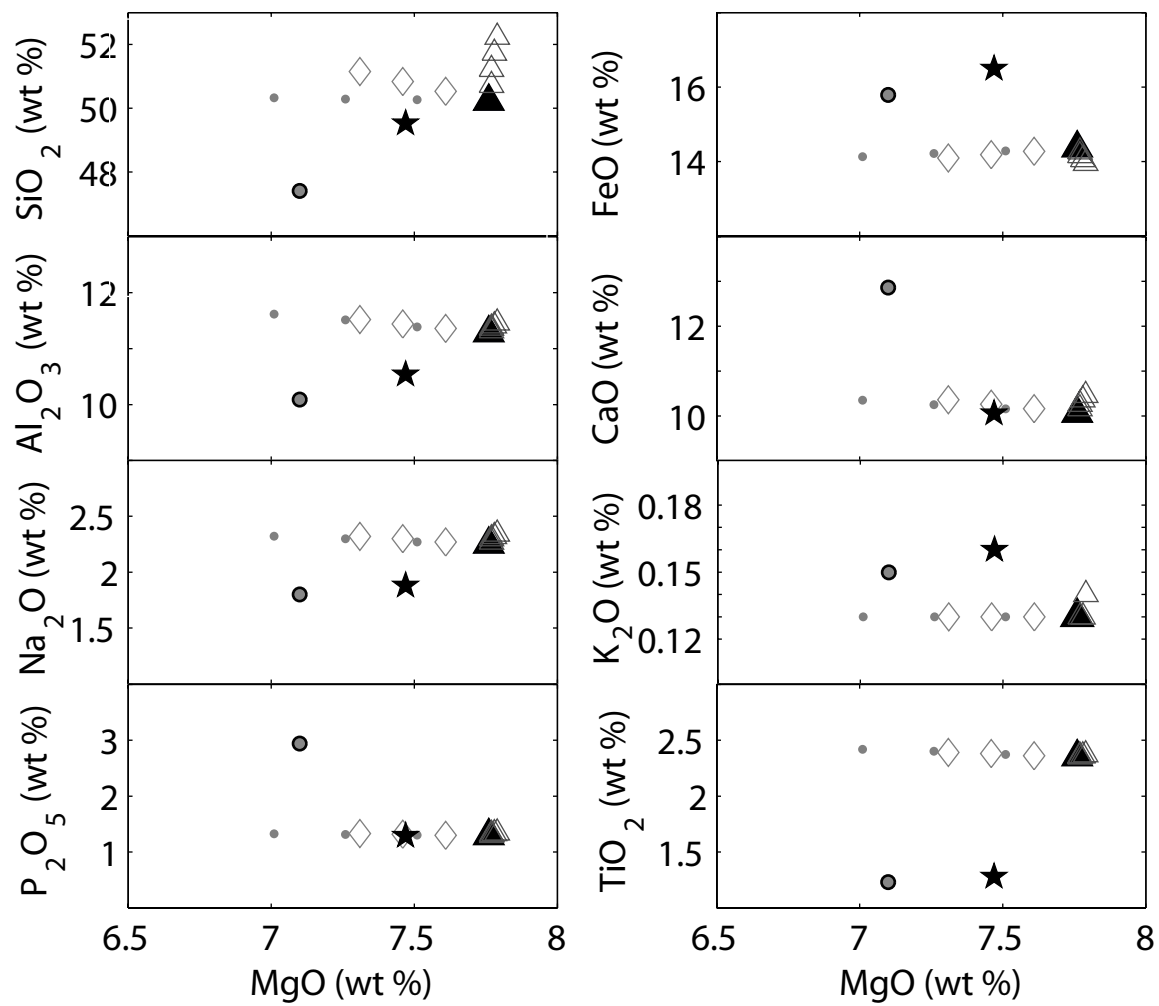


Figure 11

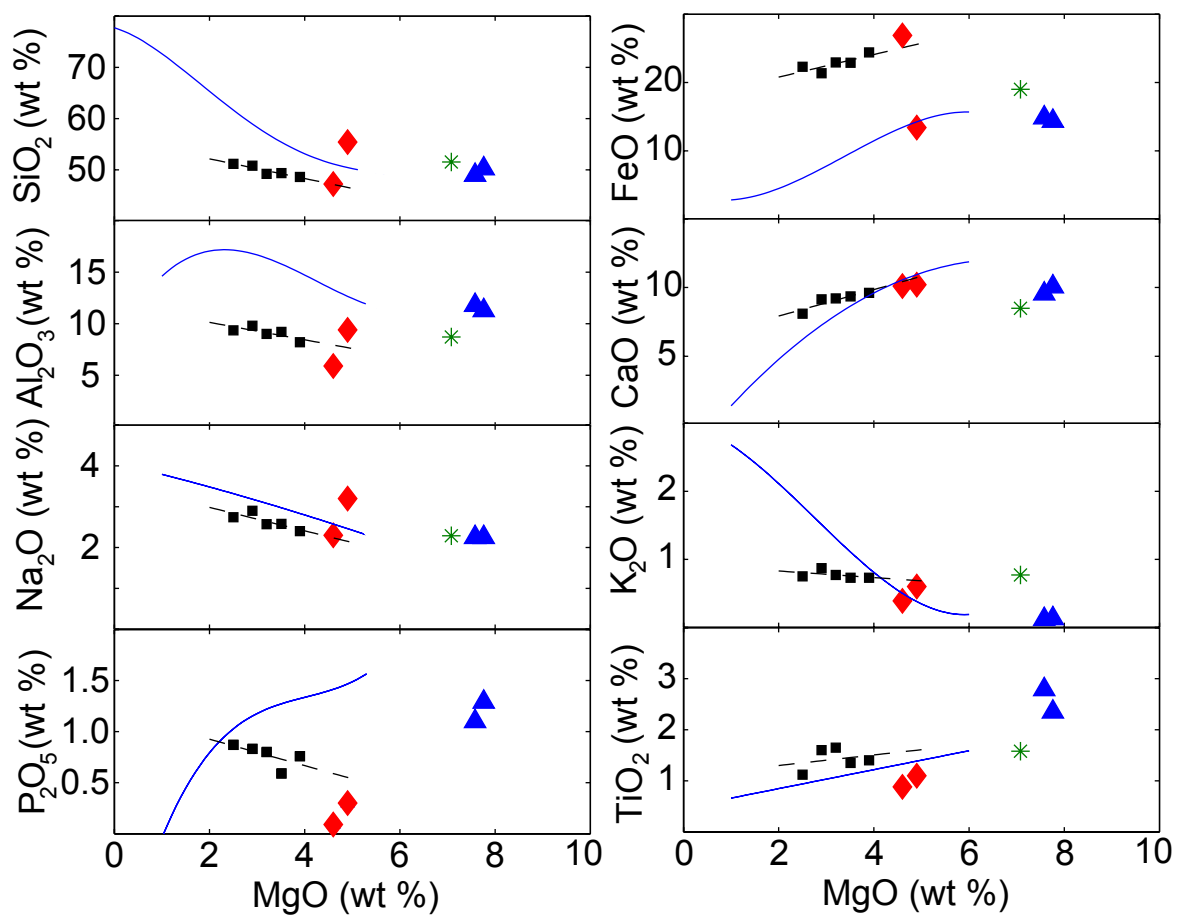


Figure 12

Table 1: Experimental run conditions.

Run #	Temp	Pressure (in bars)	Time (in hours)	fO_2	Mineral Assemblage ¹ (in olivine-hosted melt inclusions)
1b	1185	1000	3	QFM - 2.8	No inclusions
2	1185	1000	6	QFM - 2.8	No inclusions
3	1150	1000	12	QFM - 2.7	plag, chrm, opx, cpx, si, phos, gl
4	1165	1000	72	QFM - 2.8	opx, gl
6	1165	800	23	QFM - 3.0	opx, gl
7	1160	800	24	QFM - 3.0	gl
8	1150	800	70	QFM - 2.9	opx, gl
9	1155	800	48	QFM - 2.9	No inclusions
11	1150	800	48	QFM - 2.9	opx, gl
12	1155	800	48	QFM - 2.9	opx, gl
13	1155	800	48	QFM - 2.9	No inclusions
14	1157	800	47	QFM - 2.9	gl
15	1140	800	72	QFM - 2.9	plag, opx, si, gl
17	1140	800	48	QFM - 2.9	opx, si, phos, gl

¹ Phases present are olivine = olv, low-Ca pyroxene = opx, high-Ca pyroxene = cpx, phosphate = phos, plagioclase = plag, high-Si phase = si, chromite = chrm, and glass = gl.

Table 2: Representative melt inclusion analyses. The first number in the melt inclusion number is the corresponding experiment's number.

Experiment	3	3	4	6	7	8	12	
Melt Inclusion	3-11	3-12	4-5	6-1	7-7	8-2	12-2	Std Dev
SiO ₂	64.42	72.11	49.32	47.42	51.10	42.72	48.90	0.75
TiO ₂	0.55	1.85	1.02	1.23	1.31	1.82	2.00	0.06
Al ₂ O ₃	17.73	13.03	12.08	10.09	11.50	9.81	12.28	0.13
Cr ₂ O ₃	0.02	0.02	0.04	0.28	0.02	0.17	0.09	0.02
FeO	4.49	3.99	14.29	15.79	16.51	15.22	14.28	0.14
MnO	0.07	0.09	0.47	0.51	0.44	0.37	0.39	0.81
MgO	1.89	1.45	6.17	7.10	5.90	7.07	5.84	0.13
CaO	4.72	3.72	11.21	12.86	10.23	14.84	10.89	0.11
Na ₂ O	3.38	2.41	2.19	1.80	2.44	1.60	2.27	0.17
P ₂ O ₅	0.60	0.47	2.52	2.94	1.27	6.49	2.38	0.02
K ₂ O	3.78	0.84	0.46	0.15	0.14	0.31	0.27	0.03
Cl	0.02	0.07	not meas	0.47	0.09	0.66	0.17	
Mg_Num	43	39	43	44	39	45	42	
Total	101.65	99.98	99.77	99.98	100.03	99.23	99.78	
Host Mineral	Olivine	Olivine	Olivine	Olivine	Olivine	Olivine	Olivine	
Host Mg #	73	74	75	73	70	74	71	
K _d (ol-melt)	0.26	0.22	0.27	0.27	0.26	0.27	0.30	
Daughter Phases Remaining	Pyroxene, Phosphate	Pyroxene, Plagioclase, Phosphate, Chromite	Low-Ca Pyroxene	None	Phosphate	Low-Ca pyroxene, Phosphate	None	
# of analyses	2	2	2	2	1	2	1	

Table 3: Representative host mineral compositions from experimental runs.

Experiment	3	4	6	12	3	3
Host Mineral	Olivine	Olivine	Olivine	Olivine	Cpx	Opx
SiO₂	37.93	38.24	37.80	37.85	51.80	55.14
FeO	23.13	22.08	23.08	25.08	8.13	13.90
MgO	37.95	38.31	37.92	36.50	16.96	27.27
Al₂O₃	----	----	----	----	3.05	0.45
Na₂O	----	----	----	----	0.31	0.03
MnO	0.60	0.57	0.49	0.51	0.36	0.57
TiO₂	----	----	----	----	0.60	0.07
Cr₂O₃	0.04	0.07	0.16	0.10	0.96	0.39
CaO	0.17	0.32	0.29	0.29	17.73	2.08
Mg_Num	75	76	75	72	79	78
Total	99.96	99.63	99.76	100.34	99.95	99.91

Table 4. Chromite-hosted melt inclusion compositions that best represent the parental melt composition of ALH 77005.

Sample	7-1	7-10
Temp (in C)	1160	1160
Pressure (in bars)	800	800
Time (in hours)	24	24
SiO₂	50.22	48.96
TiO₂	2.35	2.79
Al₂O₃	11.28	11.79
Cr₂O₃	1.42	1.35
FeO	14.36	14.85
MnO	0.41	0.41
MgO	7.76	7.58
CaO	10.06	9.54
Na₂O	2.25	2.25
P₂O₅	1.29	1.10
K₂O	0.13	0.12
Sulfur (wt %)	0.16	0.10
Chlorine (wt %)	<i>not meas</i>	0.07
Total	101.54	100.76

Host Mineral	Chromite	Chromite
FeO	24.42	24.56
MgO	7.28	7.04
Al₂O₃	7.72	6.88
MnO	0.18	0.16
TiO₂	2.48	1.96
Cr₂O₃	56.95	59.05
Total	99.02	99.65

Table 5. Recalculated parental melt composition. Chromite-hosted melt inclusion 7-10 (Table 3) and olivine-hosted melt inclusion 6-1 (Table 2) are modeled assuming the host composition in adsorbed in ratios of 99:1, 98:2, and 97:3 (melt:host). * represents the chromite hosted melt inclusion that most closely represents the parental melt based on the Cr_2O_3 concentration found in olivine-hosted melt inclusions.

Mixing Ratio	MI 7-10	99:1	98:2*	97:3	MI 6-1	99:1	98:2	97:3	96:4
SiO₂	48.96	49.45	49.94	50.43	47.42	47.33	47.23	47.14	47.04
TiO₂	2.79	2.80	2.81	2.81	1.23	1.22	1.21	1.19	1.18
Al₂O₃	11.79	11.84	11.89	11.94	10.09	9.99	9.89	9.79	9.69
Cr₂O₃	1.35	0.77	0.20	-0.38	0.28	0.28	0.28	0.27	0.27
FeO	14.85	14.75	14.66	14.56	15.79	16.05	16.32	16.58	16.84
MnO	0.41	0.41	0.42	0.42	0.51	0.51	0.51	0.51	0.51
MgO	7.58	7.59	7.59	7.60	7.1	7.22	7.34	7.46	7.57
CaO	9.54	9.64	9.73	9.83	12.86	12.73	12.61	12.48	12.35
Na₂O	2.25	2.27	2.30	2.32	1.8	1.78	1.76	1.75	1.73
P₂O₅	1.1	1.11	1.12	1.13	2.94	2.91	2.88	2.85	2.82
K₂O	0.12	0.12	0.12	0.12	0.15	0.15	0.15	0.15	0.14
Total	100.76	100.75	100.76	100.77	99.98	100.17	100.16	100.16	100.16

Table 6: Prior studies of olivine-hosted melt inclusion compositions in ALH 77005 and estimates of the parental composition of LEW 88516.

Sample	ALH 77005 MI	ALH 77005 MI	ALH 77005 MI	LEW Parental
SiO₂	49.94	63.6	53.9	53.72 - 54.89
TiO₂	2.81	0.91	0.92	0.06 - 0.86
Al₂O₃	11.89	16.6	10.69	6.06 - 9.27
Cr₂O₃	0.20	0.03	0.02	
FeO	14.66	3.62	9.39	12.58 - 15.72
MnO	0.42	0.1	0.25	
MgO	7.59	1.41	12.67	9.33 - 12.43
CaO	9.73	10.63	9.44	7.83 - 11.55
Na₂O	2.30	2.35	1.72	1.05 - 0.91
P₂O₅	1.12	1.44	0.48	
K₂O	0.12	0.17	0.52	0.05 - 0.09
Mg#	47	41	71	
Total	100.76	100.86	100.00	98.11 - 98.36
Reference	This Study	Jagoutz (1989)	Ikeda (1998)	Harvey et al. (1993)
Method	Rehomogenized	Wide Beam electron microprobe	Calculated	Calculated

Table 7: Prior studies of magmatic compositions from other SNC meteorites. In cases where more than one melt inclusion composition was reported in the original study, the most primitive (lowest SiO₂) content is reported here.

Meteorite	Chassigny [Chassignite]	Chassigny (A*) [Chassignite]	Yamato 980459 [Basaltic Shergottite]	MIL 03346 [Nahklite]	Nahkla [Nahklite]	Nahkla [Nahklite]
SiO₂	69.1	51.52	49.40	49.34	47.2	55.4
TiO₂	0.12	1.58	0.48	1.35	0.88	1.1
Al₂O₃	16.7	8.72	6.00	9.2	5.9	9.4
Cr₂O₃	0.00	---	0.71	0.03	---	0.2
FeO	3.12	19.02	15.80	22.89	26.9	13.4
MnO	0.07	0.53	0.43	0.44	0.71	0.2
MgO	1.32	7.08	18.10	3.51	4.6	4.9
CaO	1.24	8.49	7.20	9.35	10.1	10.2
Na₂O	4.11	2.29	0.80	2.58	2.3	3.2
P₂O₅	---	---	0.31	0.59	0.09	0.3
K₂O	3.33	0.77	0.02	0.73	0.39	0.6
Mg_Num	43	40	67	21	23	39
Total	99.1		99.54	100.01	99.1	98.9
Reference	Varela et al. (2000)	Johnson et al. (1991)	Dalton et al. (2005)	Rutherford et al. (2005)	Stockstill et al. (2006)	Varela et al. (2001)
Method	Rehomogenized	Calculated	Bulk	Rehomogenized	Rehomogenized	Rehomogenized (mean of 6)

Chapter 2: Crystallization conditions of martian meteorite ALH 77005

C. Calvin and M. Rutherford

Abstract

Hydrous and anhydrous crystallization experiments were performed on the parental melt of lherzolitic shergottite ALH 77005 in order to characterize the conditions under which the rock crystallized. The parental melt was synthesized and crystallization experiments were performed between 1060 and 1185°C at pressures ranging between 35 and 200 MPa. A graphite buffer was used to control the oxidation state between QFM – 1.7 and QFM -3.4. The addition of water via the OH(G-COH) buffering system lowered the liquidus temperature for olivine in these experiments from 1165 to 1140°C. Increasing the pressure of the experiments above 50 MPa prevented the appearance of olivine on the liquidus suggesting that for olivine to appear in the abundance that it does, the lherzolitic shergottites must have crystallized below 50 MPa or (< 1km from the surface). The crystallization experiments also allowed the phase diagram of the ALH 77005 parental melt to be constructed for anhydrous conditions at low pressures. Because the lherzolitic shergottites are all very similar in their mineralogy and composition, the phase equilibrium is applicable to all the meteorites of this class.

Introduction

Lherzolitic shergottite ALH 77005 is an ultramafic martian meteorite. With Fo₇₅ olivines (McSween et al., 1979), ALH 77005 is one of the most primitive martian meteorites with only Yamato 980459 (Greshake et al., 2004) and NWA 2737 (Beck et al., 2006) containing melts and/or olivines with higher MgO and Mg#. Thus ALH 77005 may provide important information about the martian interior and the magmatic processes that shaped the planet's surface. In addition, similarities in the mineral

compositions and modal abundance of minerals found in the lherzolitic shergottites suggests that understanding the petrology and evolution of ALH 77005 will produce better understandings of all of the lherzolitic shergottites.

ALH 77005 contains two lithologies (McSween et al., 1979). The first lithology is composed chiefly of euhedral chromite and olivine, poikilitically enclosed by low-Ca pyroxene with some interstitial maskelynite and high-Ca pyroxene (Figure 1). The second lithology has less pyroxene than the first and is composed of subhedral olivine with interstitial maskelynite, Ti-rich chromite, ilmenite, troilite, and merrillite. Petrologic and geochemical analysis suggests that ALH 77005 is a cumulate rock formed from a martian magma (Wood and Ashwal, 1980; McSween et al., 1979). In both lithologies chromite is thought to come on the liquidus early followed by olivine, low-Ca pyroxene, and eventually high-Ca pyroxene and plagioclase. However, the gap in MgO concentration between olivine- and chromite-hosted melt inclusions suggests that some magmatic reequilibration may have altered the MgO/FeO ratio of the host phases.

The most primitive olivine-hosted melt inclusion composition has MgO of 7.1 wt % while chromite-hosted melt inclusions have MgO concentrations of 7.5 wt %. Because petrographic studies suggest that olivine closely follows chromite on the liquidus of this meteorite {McSween, 1979 #2}, the discrepancy in MgO concentrations between the two melt inclusions suggests that either MgO concentrations were modified in olivine or that the earliest MgO concentration for the olivine-hosted melt inclusions was not found in that study. In addition, some but not all of the olivine-hosted melt inclusions contained rims of low- and high-Ca pyroxene {Calvin, 2008 #56; Ikeda, 1998 #4}. The rims may have controlled the magmatic evolution of the melt inclusions as they would have

prevented or minimized post-magmatic reequilibration with the olivine host in some inclusions. This prevents some challenges in using the olivine-hosted melt inclusion compositions for developing a liquid line of descent for ALH 77005.

This study takes two new approaches to understanding and integrating the magmatic and petrologic history of the Iherzolitic shergottites. First, hydrous and anhydrous crystallization experiments are performed on a synthesized parental melt composition (ALH –PM) determined from chromite-hosted melt inclusions in ALH 77005 (Calvin and Rutherford, 2008). The crystallization experiments reported here highlight the effect of pressure, temperature, oxidation state, and water content on the appearance of mineral phases on the liquidus of the ALH 77005 parental melt.

Comparing the results of the crystallization experiments with phenocrysts in the natural sample allows the crystallization conditions of ALH 77005 to be examined more closely. Second, this study reports the compositions of remelted pyroxene-hosted melt inclusions. Prior melt inclusion studies (Calvin and Rutherford, 2008; Ikeda, 1998; Goodrich and Harvey, 2003) have focused almost exclusively on chromite- and olivine-hosted melt inclusions and studying the pyroxene-hosted melt inclusions allows a later-stage magma to be characterized. Combining the results of the crystallization experiments with the melt inclusion data allows for the evaluation of the conditions of phenocryst crystallization including depth of crystallization, volatiles in the magma, and oxygen fugacity. In addition, studying the changes in the magmatic composition under various conditions both in the crystallization experiments and through melt inclusions in early- and late-crystallizing phases makes it possible to construct phase diagrams for this magma as it evolved.

Methods

Experiments:

Crystallization experiments Crystallization experiments were performed on a synthesized parental melt composition (Table 3) that is equivalent to the glass composition in chromite-hosted melt inclusions (Calvin and Rutherford, 2008). To make the synthesis, reagent-grade oxides and carbonates were dried overnight in an oven at 140°C. Reagents were combined and mixed with a mortar and pestle and ethanol. The resulting synthesis was reduced at 900°C with a mixture of H₂ and CO₂ for two hours to drive off the carbonate and to set the oxidation state of the powder closer to the oxidation state at which the experiments would be run.

Crystallization experiments were performed on aliquots of the synthesis that were pressed into a pellet and placed in a platinum tube lined with graphite. The platinum tube was placed in a TZM pressure vessel and subjected to Argon pressures between 35 and 180 MPa. Samples were initially taken above the liquidus temperature, which was determined to be near 1185°C in the rehomogenization experiments of Calvin and Rutherford (2008). The temperature was subsequently dropped in a series of time steps so that the sample was allowed to crystallize. In these experiments, graphite holds the oxidation state below QFM through generation of a CO-rich gas phase and prevents the sample from touching the platinum tube which would have resulted in Fe-loss. Using a graphite-CO buffer, which is sensitive to changes in pressure, produced variations in f_{O_2} between QFM -2.6 in high pressure experiments (160-180 MPa) to QFM – 3.7 in low

pressure experiments (35-50 MPa). These f_{O_2} values are within the range suggested for shergottites by (Wadhwa, 2001; Herd et al., 2002). In addition, two reversal experiments were performed. After achieving a low final temperature, the temperature of the reversal experiments were increased to 1150 and 1165 °C and held there for a period of 24 hours. The complete list of experimental run conditions can be found in Table 1.

Hydrous experiments were performed with a two buffer technique described by Eugster and Skippen (1967). An inner capsule contained a pressed pellet of ALH-PM powder surrounded in graphite and enough oxalic acid ($H_2C_2O_4$) to saturate the melt with 1 wt % water. The outer capsule contained Ni and NiO. The use of graphite and oxalic acid with a NiNiO outer capsule held the oxidation state between QFM -3.2 and -1.7. As with the anhydrous experiments, the samples were placed in TZM pressure vessels, pressurized with Argon, and taken above the liquidus for 3 hours. The experimental temperature was then lowered to a final temperature where the experiment was allowed to crystallize for between 3 and 72 hours. The final temperatures ranged from 1100 to 1175°C, with the hydrous experiments crystallizing at lower temperatures than the dry experiments. Thin sections were made for analysis on a Cameca SX100 electron microprobe at Brown University. Glasses and minerals were analyzed for major, minor, and some trace elements. The methods for mineral and glass analysis are identical to those used by Calvin and Rutherford (2008).

ALH 77005 partial melting experiments Experiments to rehomogenize melt inclusions were performed on 1 mm chips of the poikilitic textured ALH 77005. Chips were surrounded with powdered graphite and sealed in platinum tubing for experiments in

TZM pressure vessels at pressures of either 80 or 100 MPa and temperatures ranging from 1150 to 1185°C. Detailed methods and experimental run conditions can be found in Calvin and Rutherford (2008). Cl, F, and H₂O analyses were performed on the melt inclusions using the IMF 3F at Woods Hole Oceanographic Institution following the procedures of (Shimizu and Hart, 1982).

Results

Results from crystallization experiments

Dry Crystallization Experiments. All dry crystallization experiments initially crystallized chromite, followed by low-Ca pyroxene, high-Ca pyroxene, plagioclase and eventually FeTi oxide at lower temperatures. The appearance of mineral phases with respect to temperature is shown in Figure 2a. Chromite, the first phase to appear in the cooling melt, begins crystallizing between 1165 and 1185°C. By 1165°C and at pressures less than 50 MPa, olivine appears on the liquidus (Figure 3a). Low-Ca pyroxene appears after olivine at ~1165°C at pressures < 50 MPa, and in some cases small olivine crystals are poikilitically enclosed in low-Ca pyroxene (Figure 3b). At pressures above 50 MPa, low-Ca pyroxene appears instead of olivine. Plagioclase begins crystallization at 1140°C. The last phase to appear is an FeTi oxide, which is present at temperatures below 1070°C. Experiments with durations of at least 24 hours were less likely to contain olivine than shorter duration experiments.

Mineral phases were analyzed for all experiments and compositions are given in Table 2. The chromites produced are often small and difficult to analyze by EMP; only

experiments S27 (dry), S41 (anhydrous reversal), and S44 (hydrous reversal) produced chromites large enough to analyze. Cr/Al ratios range between 4.1 and 3.2 and decrease with increasing degrees of crystallization. Olivine Mg #s range between 68 and 77 (Table 2). In several experiments, pyroxene is zoned from low-Ca (5 wt %) in the core to higher-Ca pyroxene (15 wt %) at the rim (Figure 3c). The composition of the first crystallizing low-Ca pyroxene does not vary significantly based on the presence or absence of olivine. Plagioclase ($\text{An}_{65}\text{Ab}_{35}$) was found only in experiments that were run at temperatures of 1140°C or less.

Representative residual glass compositions are given in Table 3 and Figure 4. With decreasing temperature, melt compositions decreased in MgO and increased in FeO. Several short duration experiments run at 1100°C showed higher MgO and lower FeO than the long duration experiments run at the same temperature. In addition, melts from experiments that contained olivine had lower FeO concentrations.

The temperature of the two reversal experiments was taken to 1125°C before being raised to 1155° and 1165°C at 35 MPa. Both experiments contained chromite, low- and high-Ca pyroxene, and plagioclase along with the quenched melt phase. Pyroxene in these samples shows wide variability in Ca content from $\text{En}_{72}\text{Fs}_{20}\text{Wo}_7$ to $\text{En}_{48}\text{Fs}_{12}\text{Wo}_{40}$. The reversal experiment that was run at a lower final temperature (S40) has a larger proportion of high-Ca pyroxene and shows extensive zoning from high-Mg, low-Ca pyroxene cores to low-Mg, high-Ca rims (Figure 3c). High-Ca plagioclase ($\text{An}_{65}\text{Ab}_{35}$) was present in both experiments as euhedral lath-shaped crystals and were not strongly zoned. Representative chromite, low-Ca pyroxene, and olivine compositions for the

reversal experiments are given in Table 2. The glass compositions are plotted with the crystallization experiments in Figure 4.

Water-bearing Crystallization Experiments. The experimental run conditions for hydrous crystallization and the phases present in the run products are given in Table 1. As with the dry crystallization experiments, chromite appeared at temperatures above 1140°C. It was the first phase to crystallize in all experiments. Chromite was followed by olivine crystallization at 1140°C if the pressure was less than or equal to 50 MPa (Figure 2). Experiments performed at higher pressure did not contain olivine, instead crystallizing low-Ca pyroxene at 1140°C, directly after chromite. As shown in Table 2, the Mg # for olivine in these experiments ranges from 66 to 74. Hydrous experiments failed to produce the very low-Ca pyroxene found in dry experiments. Instead pyroxene ranged in composition from pigeonite ($\text{En}_{67}\text{Fs}_{24}\text{Wo}_9$) to augite ($\text{En}_{55}\text{Fs}_{21}\text{Wo}_{24}$). The first crystallizing plagioclase (1125°C) is Ca-rich ($\text{An}_{63}\text{Ab}_{37}$). FeTi oxide follows plagioclase on the liquidus at temperatures below 1125°C.

The residual melt compositions are shown in Table 3. The water concentration in the melts varied from 300 to 700 ppm. Figure 4 displays the FeO and MgO concentration of experiments versus time. With decreasing temperature, the MgO decreased. FeO increased with decreasing temperature until 1110°C when FeO decreases. Experiments run at 1110°C showed a range in FeO and MgO concentration. Residual melts in long duration runs contain lower MgO and higher FeO than melts from short duration runs. The temperature at which phases appeared in the experiments is shown in Figure 2.

Two reversal experiments produced glass in equilibrium with chromite, pyroxene, and plagioclase. In addition, experiment S44 also produced olivine (Fo₆₆) although the olivine appears to be in disequilibrium with the surrounding melt based on the subhedral and embayed characteristics of the olivine crystals (Figure 3d). Low-Ca pyroxene compositions ranged from En₆₅Fs₁₇Wo₁₇ to En₄₀Fs₁₆Wo₄₃. Plagioclase compositions were An₆₁Ab₃₈Or₁.

Results from ALH 77005 reheating experiments

The results of seventeen rehomogenization experiments on chips of ALH 77005 were presented in Calvin and Rutherford (2008). However, the data for pyroxene-hosted melt inclusions was not reported there because the focus of the paper was to determine the parental melt in equilibrium with early crystallizing phases such as olivine and chromite. Texturally, low-Ca and high-Ca pyroxene appear later in the ALH 77005 crystallization sequence and this is indicated by the crystallization experiments.

However, some glassy pyroxene-hosted melt inclusions were produced during one of the low temperature rehomogenization experiments and they were analyzed as part of this project for comparison with residual melts produced in the liquid line of descent. Many inclusions retained a daughter phase of Cl-apatite and/or olivine (Figure 5a).

Pyroxene-hosted melt inclusions have MgO contents between 1.7 and 4.7 wt %. The range in MgO concentration is correlated to variability in the CaO concentration of the pyroxene which ranges from 2.63 to 17.73 wt % and partly to the presence of daughter phases of olivine in that low-Ca pyroxene-hosted inclusions that contain olivine daughter phases have lower MgO concentrations. As shown in Table 4, the CaO, FeO,

and TiO_2 all decrease with decreasing MgO . In addition, SiO_2 and K_2O increase with decreasing MgO . There is some variability in the minor elements. P_2O_5 ranges from < 1 wt % to > 2.5 wt % at comparable MgO . Na_2O remains consistently high between 3 and 4 wt % but there is one significantly lower data points near 2 wt %.

Determining Equilibrium

Before discussing the implications of the crystallization experiments, it is necessary to address whether the glass obtained equilibrium with the mineral phases during these experimental runs. All experiments spent from 3 to 24 hours at their final temperature with the short durations occurring at the highest temperatures. Experiments run at the high end of this temperature range should allow crystals to reach an equilibrium state with the melt based on previous studies of this melt composition {Calvin, 2008 #56}. Figure 4 shows that experiments run for short durations in both the dry and hydrous experiments were more likely to have high MgO concentrations and are not in equilibrium. However even in long duration runs, pyroxenes and plagioclase may sometimes have become zoned during crystallization.

To test for equilibrium in long duration experiments, the K_d values between melt and olivine crystals was analyzed (Table 2). The K_d varied between 0.24 and 0.36 with the hydrous experiments and dry experiments containing high-Ca pyroxene having K_d values on the higher end of the spectrum. K_d s for melts in equilibrium with olivine are generally accepted near 0.30 (Roeder, 1974), however they can range from 0.25-0.35, varying with temperature, pressure, oxidation state, and composition (e.g., Mysen, 1975; Ulmer, 1989).

Euhedral olivine and low-Ca pyroxene crystals in several experiments provides textural support that the mineral phases approach equilibrium with the melt (Figure 2a). However some experiments have olivine that is embayed and/or appears to be breaking down (Figure 3b and 3d), suggesting that these olivines are out of equilibrium. As will be discussed below, these olivines suggest a reaction relationship with the melt to form pyroxene. In addition, reversal experiments were run to determine if similar phenocryst and melt compositions could be achieved from both directions. The results of the reversals are shown graphically in Figure 4. As can be seen in this figure, when the experimental run is taken below the final temperature and then raised to its final temperature, the residual melt composition still falls close to the liquid line of descent defined by the long duration crystallization experiments. The similarity between the liquids in the crystallization experiments and the reversals supports the conclusion that there is a relatively close approach to crystal-melt equilibrium in the crystallization experiments.

Discussion

The parental melt composition and equilibrium mineral assemblage.

If the Calvin and Rutherford (2008) estimate of the ALH 77005 parental melt is correct, the crystallization experiments should initially produce minerals that are identical to the phenocrysts found in the meteorite. Chromites, which crystallized first in ALH 77005, have 4 different zoning patterns depending on where the chromites are located in ALH 77005 (Ikeda 1998). Chromites in the crystallization experiments are plotted with

the range of chromite compositions presented by Ikeda (1998) in Figure 6. The crystallization experiments produce compositions consistent with the cores of chromites trapped in olivine, which are interpreted to be the earliest crystallizing chromites. In addition, the chromites crystallizing in these experiments tend to follow the pattern of increasing Ti with respect to Al and Cr. This is consistent with a buildup of Ti in the magma prior to FeTi oxide crystallization. Al-bearing phases, such as pyroxene and plagioclase, begin crystallizing within 15° and 40°C after chromite. Therefore Al would not be expected to increase as dramatically as Ti in the chromite.

For experiments that crystallize olivine and low-Ca pyroxene, the compositions of these phases are comparable to analyses performed on a natural sample of ALH 77005 (Figure 7). The Mg# of olivine in ALH 77005 ranges between Fo₇₀ and Fo₇₅ (McSween et al., 1979) (Figure 1), but individual olivine crystals are homogenous. Olivines that formed during the crystallization experiments have a slightly larger range in Mg # (Fo₆₈ to Fo₇₇). Likewise, ALH 77005 has low CaO, magnesian-rich cores (En₇₄Fs₂₀Wo₆) that zone towards ferroan pigeonite rims (En₅₃Fs₂₂Wo₂₅) (Ikeda, 1994), whereas the first crystallizing low-Ca pyroxene in our experiments has a composition range from En₆₄Wo₁₁Fs₂₄ to En₆₃Wo₁₇Fs₁₉ to En₅₈Wo₁₃Fs₂₉ (Figure 7). While no pyroxenes found in the dry and hydrous crystallization experiments have the lowest-Ca content found in thin sections of ALH 77005, they fall within the range of pyroxene found in the rock. The reversal experiments do contain low-Ca pyroxene as seen in the natural sample. This suggests that the first crystallizing pyroxene may be a pigeonite that inverts to low-Ca pyroxene as crystallization continues. As will be discussed later, pyroxene composition and formation is part of a reaction relationship with olivine. The similarity of the early

crystallizing phases in the crystallization experiments to those found in ALH 77005 both in the sequence and the composition, suggest the Calvin and Rutherford (2008) parental melt composition is a good match to one that exists in the natural ALH 77005 sample.

The Liquid Line of Descent

The residual melt compositions in dry crystallization experiments are shown in Figure 8. Peaks in Al_2O_3 and TiO_2 represent the onset of plagioclase and FeTi oxide crystallization respectively. Variability in the FeO and CaO concentration is due to the variation in the duration of the experimental run time as well as the presence or absence of plagioclase also effect the FeO concentration of the melt. The residual melt compositions for hydrous experiments are shown in Figure 9. As in the dry crystallization experiments, the peak in FeO and TiO_2 indicates the onset of FeTi oxide crystallization while the peak in Al_2O_3 indicates the onset of plagioclase crystallization.

The residual melt compositions from both the dry and hydrous experiments are summarized in Figure 10. The best fit curves define two possible liquid lines of descent for this magma. These lines are consistent in their K_2O , CaO, Na_2O , and P_2O_5 but differ in the FeO, TiO_2 , SiO_2 , and Al_2O_3 . The increase in SiO_2 and the delayed decrease in Al_2O_3 in the hydrated samples are consistent with the depolymerization of a melt with the addition of water {Kushiro, 1969 #87; Kushiro, 1975 #88; Wasserburg, 1957 #89}. The decrease in FeO and TiO_2 in the hydrous liquid line of descent at low MgO concentrations is interpreted to represent the onset of FeTi oxide crystallization. This result is somewhat surprising given only 700 ppm of H_2O was measured in the hydrated glass. However, it is possible that this concentration represents the lower limit of water found in the experiment due to loss of water over the course of the experiment. In

addition, the liquid lines of descent for the dry and anhydrous melts are consistent with the lowered solidus temperature of plagioclase and FeTi oxide crystallization in the hydrous experiments as observed in Figure 2.

The residual melts in the experiments can also be compared with olivine-hosted melt inclusion compositions from Calvin and Rutherford (2008) in Figure 10. The olivine-hosted melt inclusion line is defined by various melt inclusions in different stages of remelting. Therefore the high MgO region of this line is consistent with a melt that is in equilibrium with olivine and chromite but not pyroxene. In the early stages of crystallization, the residual melt in the crystallization experiments is consistent with the evolution of olivine-hosted melt inclusions in ALH 77005 for most major elements. However, as the crystallization experiments continue to lower temperatures, the liquid lines of descent for the experiments diverge significantly from the line defined by the olivine-hosted inclusions. Specifically, the olivine-hosted inclusions show large increase in Al_2O_3 before the onset of plagioclase crystallization. In addition, TiO_2 decreases in both the dry and hydrous crystallization experiments suggesting the onset of an FeTi oxide in the crystallization experiments but not in the inclusions. The decrease in TiO_2 is not observed in the olivine-hosted melt inclusions. The discrepancies between these experiments and those performed on the natural sample in Calvin and Rutherford (2008) may have one or more of the following explanations. First, the delayed onset of plagioclase and the lower TiO_2 in the olivine-hosted melt inclusions may reflect a different level of water in the magma. The low levels of dissolved water used in this study resulted in FeTi oxides crystallizing earlier and plagioclase crystallizing later. Significantly more water might produce an exaggerated effect where FeTi oxides were

crystallizing very early and plagioclase was significantly delayed. Thermal differences might also contribute to these differences. The crystallization experiments experienced a steady decrease in temperature over a period of several hours or days. If the melt inclusions were held above the liquidus of plagioclase for an extended period of time, crystallization of pyroxene and olivine might have continued for a longer period of time delaying the appearance of plagioclase. In addition, the melts contained in olivine-hosted melt inclusions are buffered by the olivine host. However, some hosts have low- and/or high-Ca pyroxene rims which may have buffered the melt inclusion from changes in the FeO/MgO ratio as the olivine reequilibrated with the surrounding melt. Finally, a low fO_2 was selected for these experiments based on the recent work by Wadhwa (2001) and Herd et al. (2002). However, if the experiments had been run at higher fO_2 this might produce a liquid line of descent closer to that found in the olivine-hosted inclusions.

Determining the depth of ALH 77005 crystallization

The appearance of olivine in ALH 77005 is very well constrained by petrographic analyses (McSween et al., 1979), and therefore it is possible to use the relationship of olivine and low-Ca pyroxene at various experimental pressures to help constrain the depth of crystallization. Experiments run at pressures greater than 50 MPa failed to crystallize olivine, crystallizing low-Ca pyroxene immediately after chromite. Experiments run at pressures of 35 MPa or less did crystallize olivine immediately following the crystallization of chromite. In some cases (Figure 3b), the olivines appeared as small crystals within larger pyroxene. Anhydrous experiments had a lower pressure limit for olivine crystallization implying that a small addition of H_2O increases the pressure range at which olivine could have formed.

Among characteristics such as melt composition including H₂O concentration, the placement and nature of the boundary curve between olivine and low-Ca pyroxene is sensitive to pressure (Morse, 1994 and references therein). Decreases in pressure expand the olivine field with respect to the low-Ca pyroxene field and these experiments place the ALH 77005 parental melt composition on different sides of the olivine and low-Ca pyroxene boundary. The boundary curve can be either a cotectic or a peritectic relationship. For example, in experiments run at pressures greater than 50 MPa where olivine is not present, it is possible that the absence of olivine means that the olivine was resorbed and that the boundary curve is a peritectic. However, the poikilitic texture of ALH 77005 shows large euhedral olivines (no dissolution) surrounded by low-Ca pyroxene (Figure 5) which implies that olivine not only crystallized but was stable as low-Ca pyroxene crystallized, suggesting a cotectic relationship. Either way in order to retain olivine, ALH 77005 phenocrysts must have crystallized at pressures below 50 MPa which corresponds to depths < 5 km on Mars (Longhi et al., 1992).

Implications for primary magmas

A primary magma is a magma that has not differentiated significantly since separating from its source region. Primary magmas are particularly interesting as they may give clues to the martian mantle. One of the assumptions that is generally made for a primary magma is that the melt was probably multisaturated with at least two minerals as biminerals have lower melting temperatures than monomineralic rocks. Based on high pressure experiments and modeling for martian basalts, these minerals are likely pyroxene and olivine (Bertka and Fei, 1997; Elkins-Tanton et al., 2003). If the chromite-hosted melt inclusion composition is representative of a primary melt, the source depth

would be the point at which olivine, orthopyroxene, and chromite are simultaneously on the liquidus for this composition. However, the crystallization experiments presented in this study show that olivine only coexists with orthopyroxene at pressures less than 50 MPa. This observation suggests one of three possibilities. First, the chromite-hosted melt inclusions are derivatives of a mantle composition that did not contain olivine. Because orthopyroxene is prominent in this rock, the source region would have contained orthopyroxene. It is difficult to conceive of a heterogeneous martian mantle devoid of olivine so this possibility implies that ALH 77005's parental melt came from a layered deposit. The second possibility is that the source of ALH 77005 could have been a partial melt of a shallow intrusion (<1km) that contained olivine. Alternatively, the parental melt could represent a magma that has evolved from an olivine source but has undergone significant fractional crystallization and/or assimilation of surrounding rocks. Assuming that olivine crystallization took place, the MgO concentration of the primary magma and source region would be significantly higher than the MgO concentration in the melt inclusions. The most likely of these scenarios is the last option which is consistent with the magmatic compositions of primitive shergottite Yamato 980459 which has olivines with Mg# of 84 (Greshake et al., 2004). Y98's high Mg # olivines imply that at least part of the martian interior is capable of generating high MgO basalts.

Water and the Temperature of Crystallization

The presence of water in martian magmas has been the subject of considerable study (eg. {Dann, 2001 #90; Johnson, 1991 #7; Leshin, 1996 #91; McSween, 2001 #93; Mysen, 1998 #94}), in part due to the discovery of surface features that suggest fluids ({Carr, 1996 #117} and reference therein) and in part due to the discovery of normally

hydrous phases such as amphibole and apatite in SNC meteorites (eg. {Johnson, 1991 #7; McSween, 1993 #114; Treiman, 1985 #116; Watson, 1994 #115}). Although there has been no evidence for hydrous phases in crystallized melt inclusions in ALH 77005, for completeness sake, this study examined the effect of small amounts of dissolved H₂O on the crystallization sequence of the parental melt of ALH 77005. Adding H₂O to a magma depolymerizes the melt resulting in a decreased liquidus temperature (particularly for more polymerized silicates) and changes to the order in which phases appear on the liquidus (Wasserburg, 1957; Kushiro, 1969; Kushiro, 1975). For example, plagioclase appearance on the liquidus is delayed whereas the onset of FeTi oxide crystals occurs earlier in the presence of a water-saturated melt relative to a dry magma. To explore the effect of H₂O on the crystallization of this parental melt of ALH 77005, H₂O was added to the synthesized composition following the COH buffering system defined in (Eugster and Skippen, 1967). This system generates a water-bearing vapor phase while maintaining the low f_{O_2} suggested by recent studies of f_{O_2} in shergottites (Wadhwa, 2001; Herd et al., 2002). The resulting partial pressure of H₂O was significantly less than 10% of the total vapor pressure. Ion probe measurements indicate that hydrous crystallization experiments at 35 MPa had between 0.03 and 0.07 wt % H₂O in the glass which translates to 0.1 and 0.3 mole % H₂O. Despite the small concentration of H₂O in the melts, the delayed appearance of mineral phases on the liquidus (figure 2) suggests that the addition of H₂O lowered the liquidus temperature of this magma by as much as 20°C.

As shown above, both the dry and anhydrous experiments produced mineral phases and coexisting melts that are compositionally consistent with phases found in

ALH 77005. The coexisting melt compositions varied slightly between the hydrous and anhydrous experiments at increased crystallization. Specifically, there was a decrease in Na_2O , SiO_2 , and Al_2O_3 in the hydrous experiments that was not observed in the anhydrous experiments that suggests that plagioclase crystallization either occurred earlier in the crystallization process or crystallized in higher abundance in the hydrous experiments. Therefore the addition of water to the melt affected the temperature at which minerals crystallized and their relative proportions in the rock but did not significantly effect the composition of the phases that initially crystallized. This is consistent with the low partial pressure of H_2O in the vapor phase.

Magma Composition During Late-Stage Crystallization

Low-Ca pyroxene-hosted melt inclusions in ALH 77005 were not addressed by previous studies in part because olivine-hosted melt inclusions occur in significantly higher abundance than those in any other mineral phase and in part because low-Ca pyroxene-hosted melt inclusions represent a later stage liquid. This study adds to the existing melt inclusion literature for ALH 77005 by addressing low-Ca pyroxene-hosted melt inclusions. Because low-Ca pyroxene poikilitically encloses olivine, the melts trapped by low-Ca pyroxene likely represent a more evolved magma and certainly provide a window into the changes that occurred in the residual melt as ALH 77005 crystallized. One rehomogenization experiment (R03) produced low-Ca pyroxene-hosted melt inclusions, some of which retained Cl-apatite and/or olivine daughter phases (Figure 5a). In other experiments (Calvin and Rutherford, 2008), equilibrium was established in part using long duration experiments; this was not a long duration run. However, some indications of equilibrium were achieved in that olivine and apatite

daughter crystals are euhedral. In addition, the Kd values between melts and olivine daughter crystals are consistent with the established equilibrium Kd value for this magma (Calvin and Rutherford, 2008).

The glass compositions found in the low-ca pyroxene melt inclusions are shown in Figure 11 with those of olivine-hosted melt inclusions in various degrees of remelting (Calvin and Rutherford, 2008). In this figure, glass compositions evolve from high MgO in the primitive chromite-hosted melt inclusions towards low MgO in the later crystallizing olivine and low-Ca pyroxene-hosted melt inclusions. Melt inclusions that contained daughter olivine crystals occur in the range of 2.5 to 5 wt % MgO while inclusions without olivine daughter crystals occur at lower MgO concentrations. The trend is consistent with the crystallization sequence of chromite, followed by olivine and finally low-Ca pyroxene that was identified by (McSween et al., 1979; Lundberg et al., 1990).

FeO, CaO, K₂O, and TiO₂ are consistent between the different types of melt inclusions. The low FeO and TiO₂ suggest these melts represent a magma that has crystallized FeTi oxides. P₂O₅ shows considerable variability. In part, this is likely the result of residual phosphates remaining in some melt inclusions, possibly of secondary origin as suggested in Calvin and Rutherford (2008). Na₂O in one inclusion shows significantly lower values than either the other olivine-hosted inclusions or the remainder of the low-Ca pyroxene-hosted inclusions but are more consistent with the liquid line of descent defined by the crystallization experiments. This is due to residual plagioclase that had not achieved equilibrium with the melt composition.

In general, the consistent trend between the low-Ca pyroxene, olivine, and chromite-hosted melt inclusions may argue for continuous crystallization in a magma system. However, the discrepancy between the liquid line of descent determined from melt inclusions and that determined from the crystallization experiments requires some explanation. In the olivine and low-Ca pyroxene-hosted inclusions, the melt remain in contact with the host phase through at least the early cooling stages. This means that the melts are forced into equilibrium with a large crystal reservoir and not allowed to evolve the way they might in an open magma chamber or in the crystallization experiments.

Phase Equilibria Constraints on shergottite crystallization

The crystallization of chromite followed by olivine and low-Ca pyroxene implies that the ALH 77005 parental magma started crystallizing in the olivine + chromite field and evolved away from olivine to cross the boundary curve that separates olivine from low-Ca pyroxene (Figure 12). Plagioclase appears on the liquidus after low-ca pyroxene based both in the crystallization experiments performed on a ALH 77005 parental melt composition and based on textures in thin sections of ALH 77005 (McSween et al., 1979). After saturation of plagioclase, the residual ALH 77005 melt moved along the low-Ca pyroxene + plagioclase cotectic towards SiO₂ saturation. High-Ca pyroxene and FeTi oxide began to crystallize during this period. The crystallization path outlined above is shown on a generic phase diagram (Figure 12), where crystallization began in the olivine field, moved through the pyroxene towards the plagioclase field and then moved along the low-Ca pyroxene + plagioclase cotectic towards the cristobalite field. In this phase diagram the boundary curve between olivine and low-Ca pyroxene is treated as a cotectic rather than a peritectic.

However, combining the crystallization experiments performed in this study with the rehomogenization experiments performed by Calvin and Rutherford (2008) allows the phase diagram for ALH 77005's parental magma composition to be refined. As previously discussed, olivine is only retained in experiments with pressures less than 50 MPa. This suggests that between 35 and 50 MPa, the boundary curve between the low-Ca pyroxene and olivine fields a) crosses the parental melt composition and/or b) changes from a peritectic to a cotectic (Figure 13). The nature of the boundary curve separating olivine and low-Ca pyroxene can be either a peritectic or cotectic depending on whether olivine is consumed to make low-Ca pyroxene or olivine and low-Ca pyroxene are cocrystallizing. Textural evidence from some experiments shows that olivine may have been resorbing to form pyroxene (Figure 1a), suggesting that this boundary curve is a peritectic rather than a cotectic. However, some experiments appear to show olivine in equilibrium with pyroxene (Figure 1b). Likewise, evidence exists for both euhedral olivines and resorbing olivines in textural analysis of thin sections of ALH 77005 (McSween et al., 1979). Reversal experiments failed to show olivine regardless of the pressure at which they were run which suggests that any olivine that may have crystallized was resorbed to make pyroxene. In addition, while all dry experiments show olivine in run conditions below 50 MPa, two hydrous experiments run at pressures below 50 MPa failed to crystallize olivine. This indicates that this magmatic composition is extremely close to the boundary at which small changes in temperature, pressure, cooling rate, oxygen fugacity, and hydration state cause the boundary to change from a peritectic to a cotectic. However, the crystallization experiments performed in this study and analyses of thin sections suggest that the relationship between olivine and low-Ca

pyroxene is a peritectic rather than a cotectic during most of the crystallization of ALH 77005. As a result, in the Figure 13 phase diagram this curve is drawn as a peritectic rather than a eutectic.

ALH 77005 has more than one texture. Assigning the boundary curve as a peritectic is consistent with textural evidence in studies that suggests olivine is subhedral {McSween, 1979 #2}; however some olivines in ALH 77005 appear euhedral. The different olivine textures in the natural sample may indicate different pressures of crystallization or slightly different water concentrations. For example, if water was lost during crystallization the boundary curve would move towards the SiO_2 field, expanding the olivine field. Olivine that had been involved in a reaction relationship would then be crystallizing in the olivine field and would be more likely to form euhedral crystals. Likewise, olivine that crystallized at or near 350 bars might appear embayed as they reacted to form melt and pyroxene while olivine that crystallized at the surface would appear euhedral. The heterogeneity found in ALH 77005 may be revealing different crystallization conditions.

Conclusions

Rehomogenization experiments performed on chips of martian meteorite ALH 77005 and crystallization experiments performed on a synthesized parental melt of ALH 77005, indicate the following:

- 1) The crystallization sequence of the melt trapped in ALH 77005 chromite and olivine phenocrysts mimics the sequence and composition of phases crystallizing in the natural rock. Mineral phases began crystallizing at 1165°C at 35 MPa.

- 2) Low- and high- Ca pyroxene-hosted melt inclusions are consistent with the low MgO region of the liquid line of descent defined by rehomogenized olivine-hosted melt inclusions. The pyroxene-hosted melt inclusions are also consistently at low MgO contents where they would be expected since petrographic analyses indicate that low and high-Ca pyroxene crystallized after olivine and chromite.
- 3) Olivine appears on the liquidus only at pressures lower than 50 MPa. This pressure is decreased to 35 MPa if the system was anhydrous. 50 MPa corresponds to depths of < 5 km below Mars' surface and suggests that ALH 77005 formed as part of a shallow intrusion.

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Figure Captions

Figure 1. Backscatter images of thin section of ALH77005. White areas are chromite. Light grey areas are olivine poikilitically enclosed in low-Ca pyroxene (dark grey). High-Ca pyroxene is also found interstitially. Mg numbers of olivine are shown. Images confirm lack of Fe-Mg zoning determined from electron microprobe profiles. Variation in Mg # between homogeneous grains indicates lack of late magmatic or post-magmatic exchange between crystals.

Figure 2. The appearance of different crystals is plotted against the final temperature of the crystallization experiment. Dry experiments represented were all conducted ≤ 35 MPa while hydrous experiments were all conducted ≤ 50 MPa. Dry experiments have higher liquidus temperatures than hydrous experiments suggesting that while the partial pressure of water is low in the hydrous experiments, it is still significant enough to have lowered the liquidus temperature in those experiments.

Figure 3. Backscatter images of four crystallization experiments. A. In the dry crystallization experiment S33, olivine appears euhedral and stable while crystallizing with low-ca pyroxene. B. In hydrous crystallization experiment S26, olivine appears to be out of equilibrium and possibly breaking down in a reaction relationship with low-ca pyroxene. C. In experiment S40, a dry reversal experiment, highly zoned pyroxene shows high-Ca pyroxene rims around a low-Ca pyroxene core. There is no evidence for olivine crystallization. D. In experiment S44, a hydrous reversal experiment, olivine, low-

Ca pyroxene, and plagioclase all appear to be breaking down. Ol = olivine, Lpyx = low-Ca pyroxene, Hpyx = High-Ca pyroxene, Plg = Plagioclase.

Figure 4. A. MgO concentration of the residual melt in crystallization experiments vs. the temperature of the experiment. B. FeO concentration of the residual melt in crystallization experiments vs. the temperature of the experiment. In both figures, the filled circles represent the dry crystallization experiments while the open circles represent the dry reversal experiments. The filled squares represent the hydrous crystallization experiments while the open squares represent the hydrous reversal experiments.

Figure 5. Backscatter images of low-Ca pyroxene-hosted and olivine-hosted melt inclusions. A. The melt inclusion retains olivine and apatite daughter phases. B. Highly crystallized olivine-hosted melt inclusion from thin section of ALH 77005.

Figure 6. Two different zones of chromite compositions as presented by Ikeda (1998) are shown as grey bubbles. All early crystallizing chromites were high in Cr/Al. Chromites trapped in pyroxene tend to zone towards higher Al while those trapped in olivine zone towards higher Ti. Chromite compositions from Calvin and Rutherford (2008) are shown as small squares. The chromite composition of the first crystallizing chromite in crystallization experiments are shown as large squares.

Figure 7. The composition of low-Ca pyroxene and olivine crystals are compared for a) dry experiments and b) hydrous experiments. In both cases, large grey circles represent

mineral compositions from the natural sample (McSween et al., 1979; Ikeda, 1994). a) Small black circles represent compositions of crystals found in dry crystallization experiments. Squares represent pyroxene found in reversal experiments. No olivine was found in reversal experiments. Both olivine and low-ca pyroxene crystallized in the crystallization experiments fall within the accepted range of compositions found in the natural sample. b) Olivine and pyroxene in hydrous experiments are shown as squares with grey circles representing compositions of those minerals from the natural sample.

Figure 8. Oxide contents of residual glass in dry crystallization (dark circles) and dry reversal experiments (light circles) are plotted with the chromite-hosted melt inclusion composition (triangle) used as the starting material. The line is the best fit curve for olivine-hosted melt inclusions in ALH 77005 (Calvin and Rutherford, 2008).

Figure 9. Oxide contents of residual glass in hydrous crystallization (dark squares) and hydrous reversal experiments (light squares) are plotted with the chromite-hosted melt inclusion composition (triangles). The line is the best fit curve for olivine-hosted melt inclusions in ALH 77005 (Calvin and Rutherford, 2008).

Figure 10. Liquid line of descent for dry (red) and hydrous (green) crystallization experiments of ALH-PM as well as olivine-hosted melt inclusions (blue). The lines are the best fit curves to the residual melt compositions in the crystallization experiments from Figures 4 and 5. The olivine-hosted melt inclusion line was obtained from Calvin and Rutherford (2008).

Figure 11. Harker diagrams showing the glass composition of low-Ca pyroxene-hosted melt inclusions (stars). Triangles represent chromite-hosted melt inclusions from Calvin and Rutherford (submitted). The line reflects the trend of olivine-hosted melt inclusions presented by Calvin and Rutherford (submitted). Olivine-hosted melt inclusions with high MgO are fully rehomogenized while those with low MgO retain daughter crystals to various degrees.

Figure 12. Generic phase diagram of system showing the evolution of an olivine-saturated melt. The melt begins in the olivine field. Crystallization of olivine moves the melt composition to the boundary curve with low-Ca pyroxene. The melt remains on the boundary curve and moves towards the plagioclase field at which point plagioclase comes on the liquidus. Crystallization of plagioclase will move the melt towards the boundary curve with cristobalite.

Figure 13. Phase diagram showing the boundary curves as determined by crystallization experiments and rehomogenization experiments.

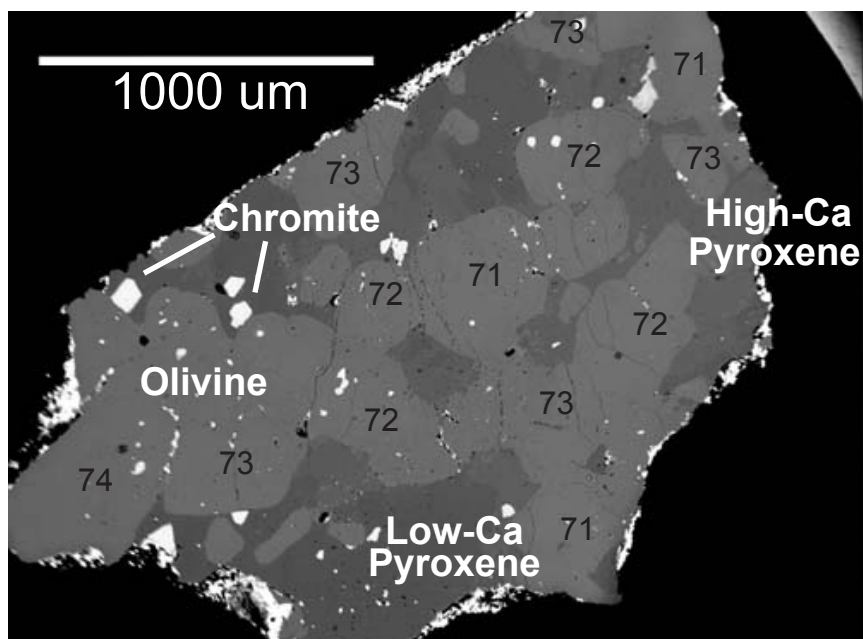


Figure 1

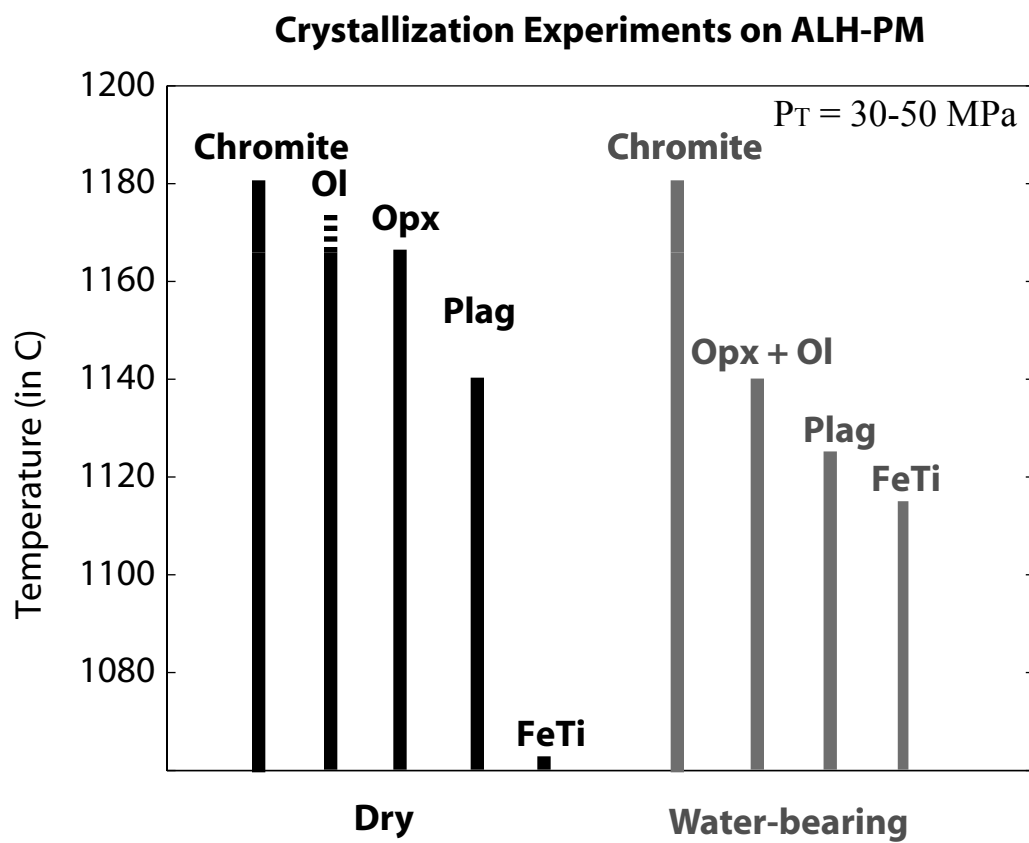


Figure 2

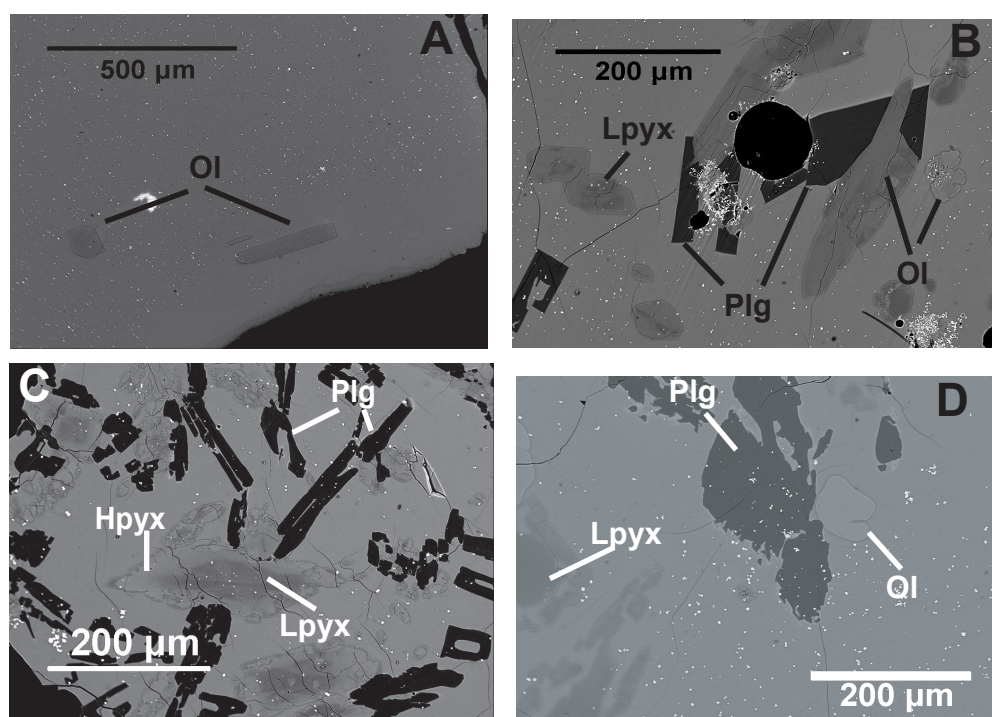


Figure 3

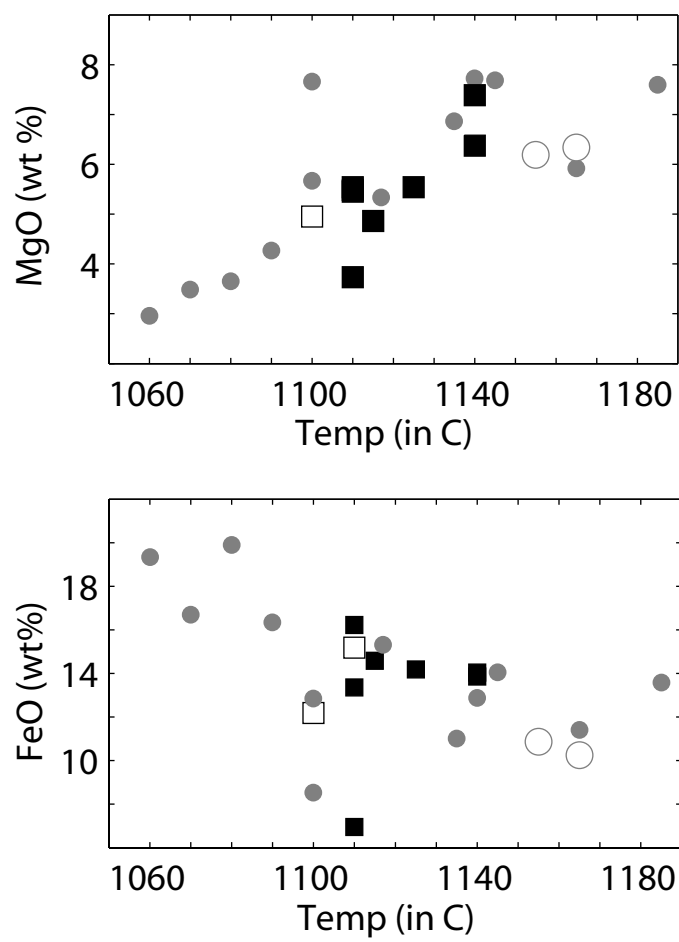


Figure 4

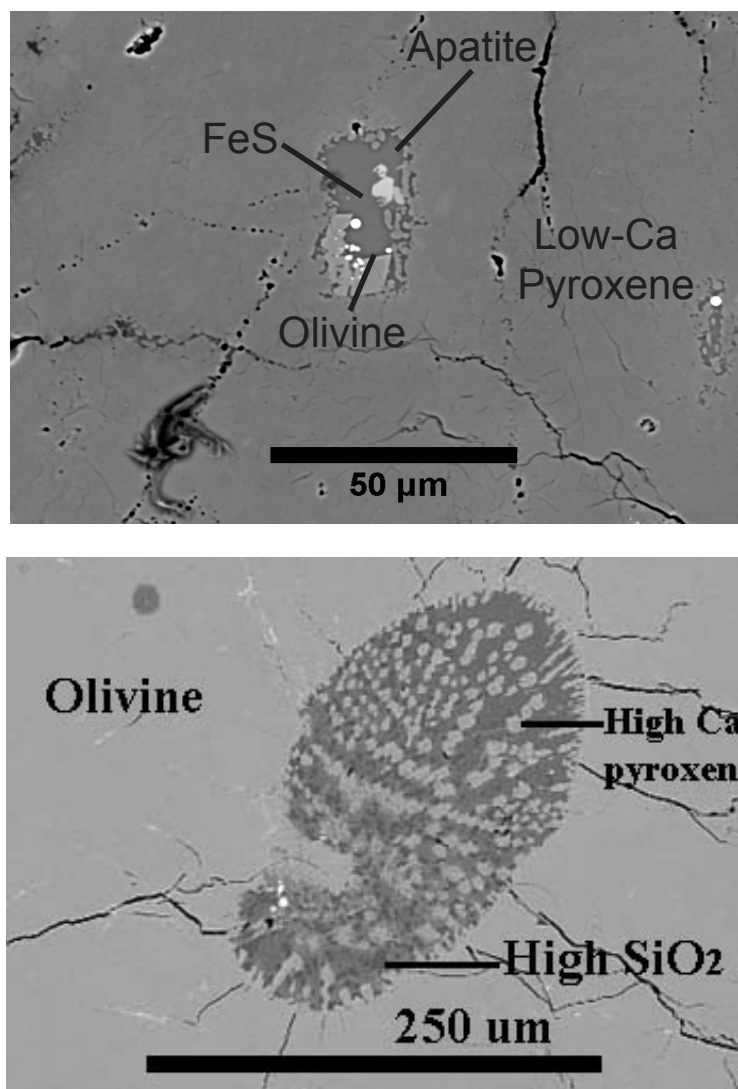


Figure 5

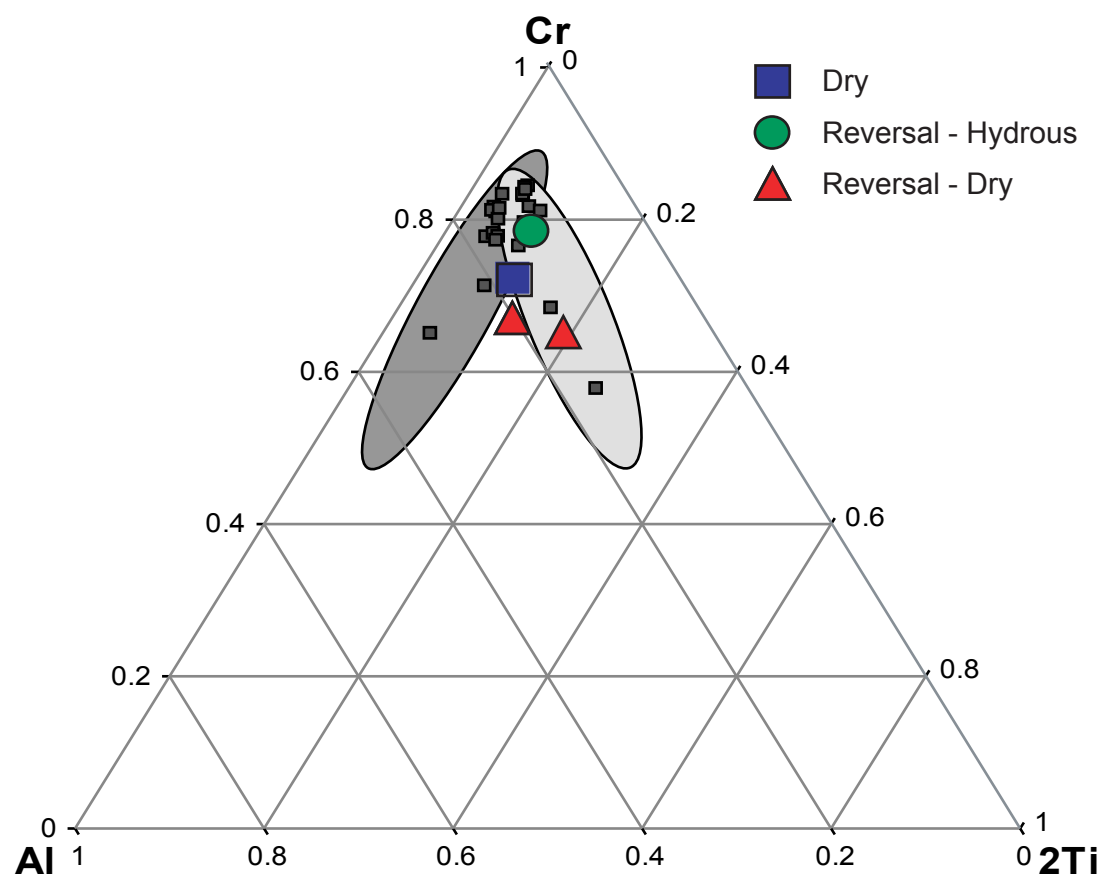


Figure 6

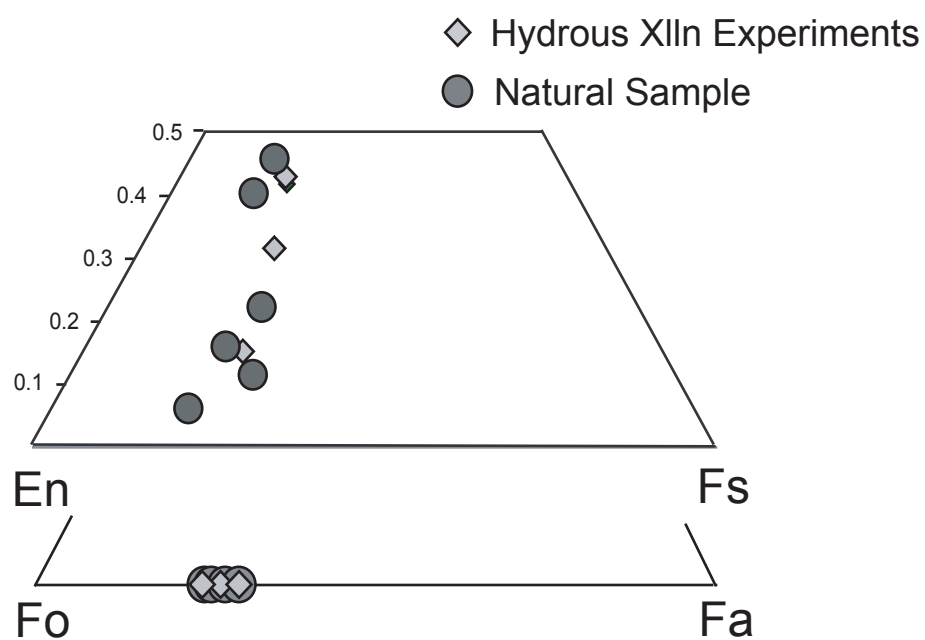
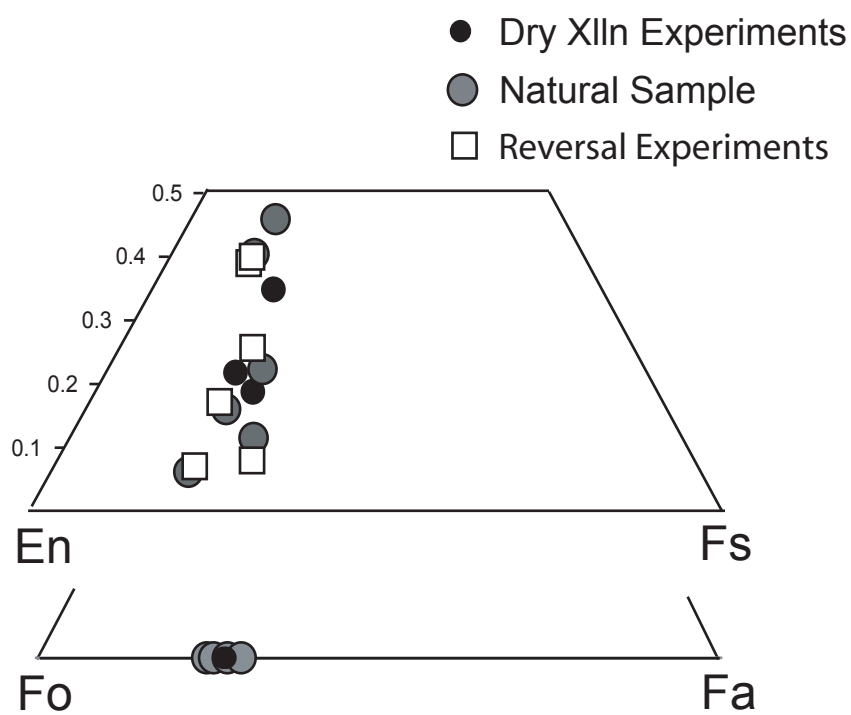


Figure 7

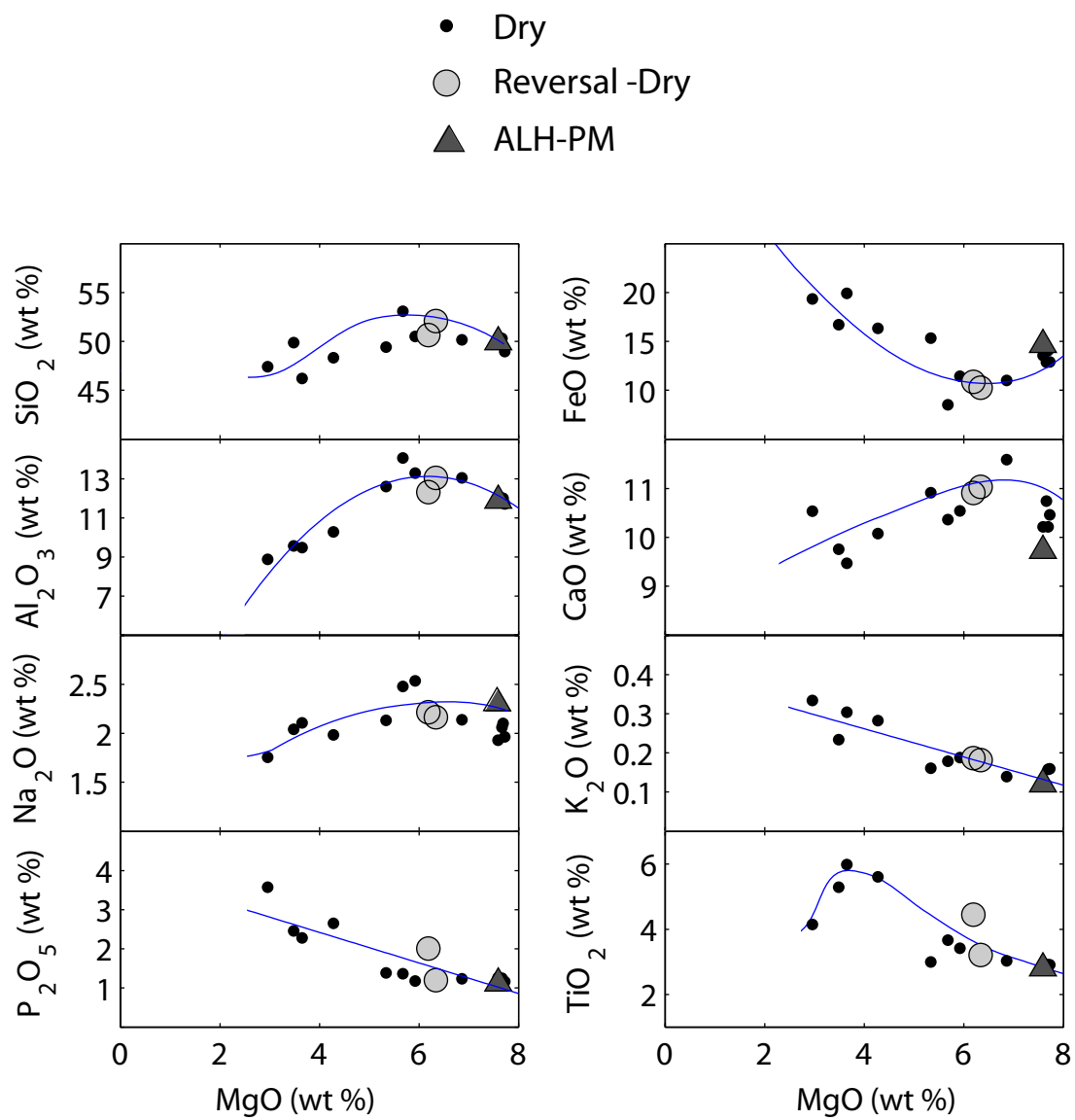


Figure 8

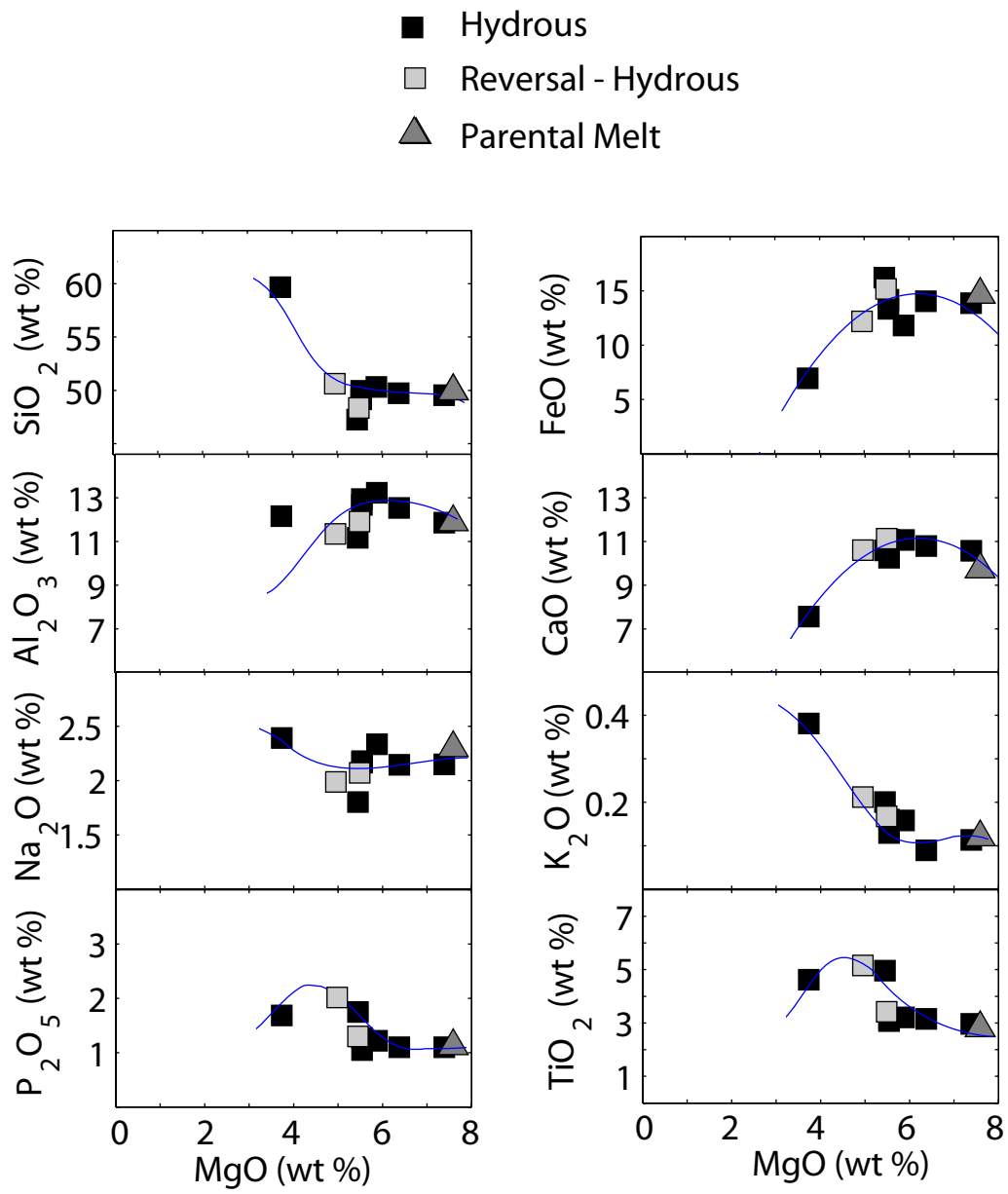


Figure 9

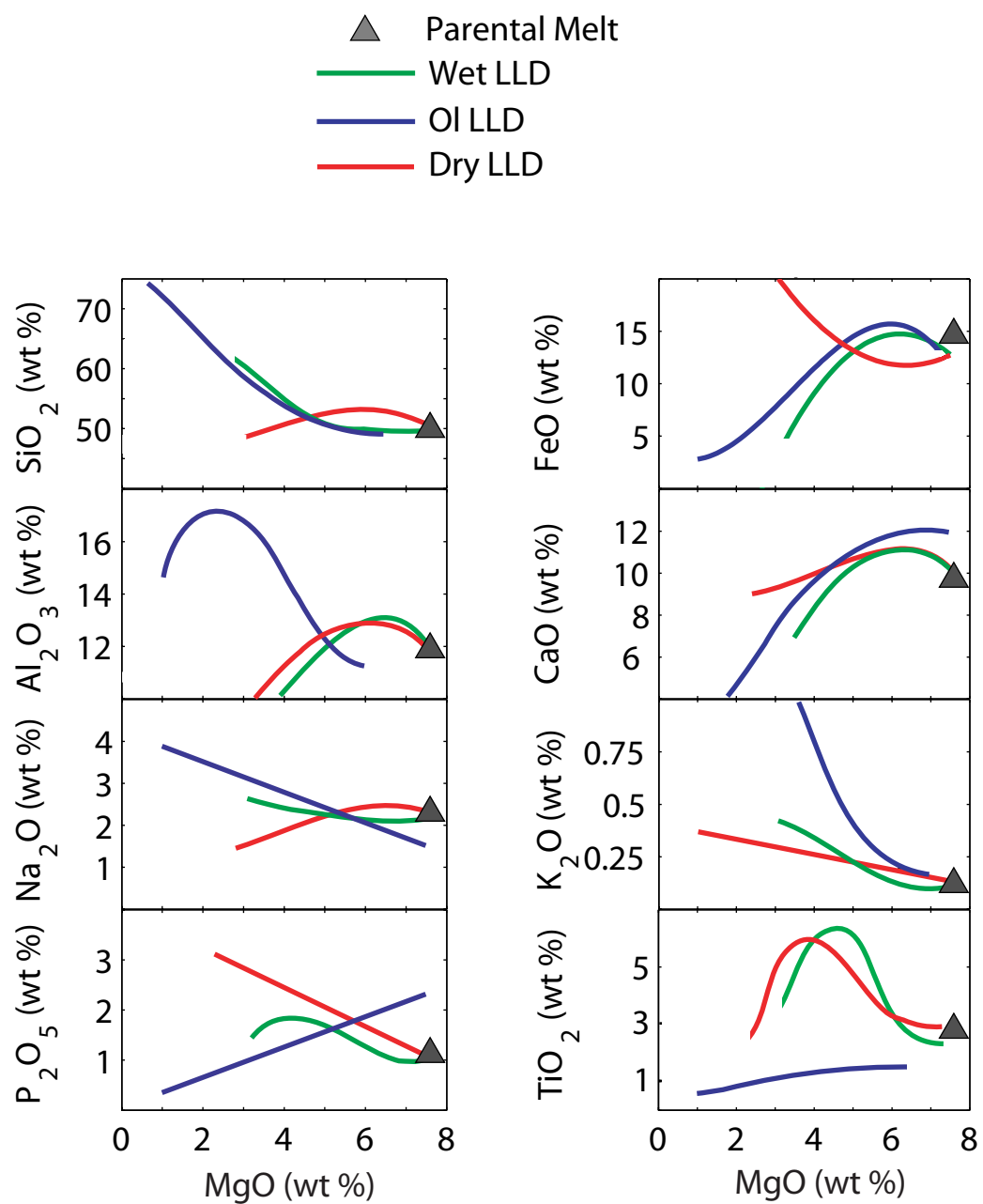


Figure 10

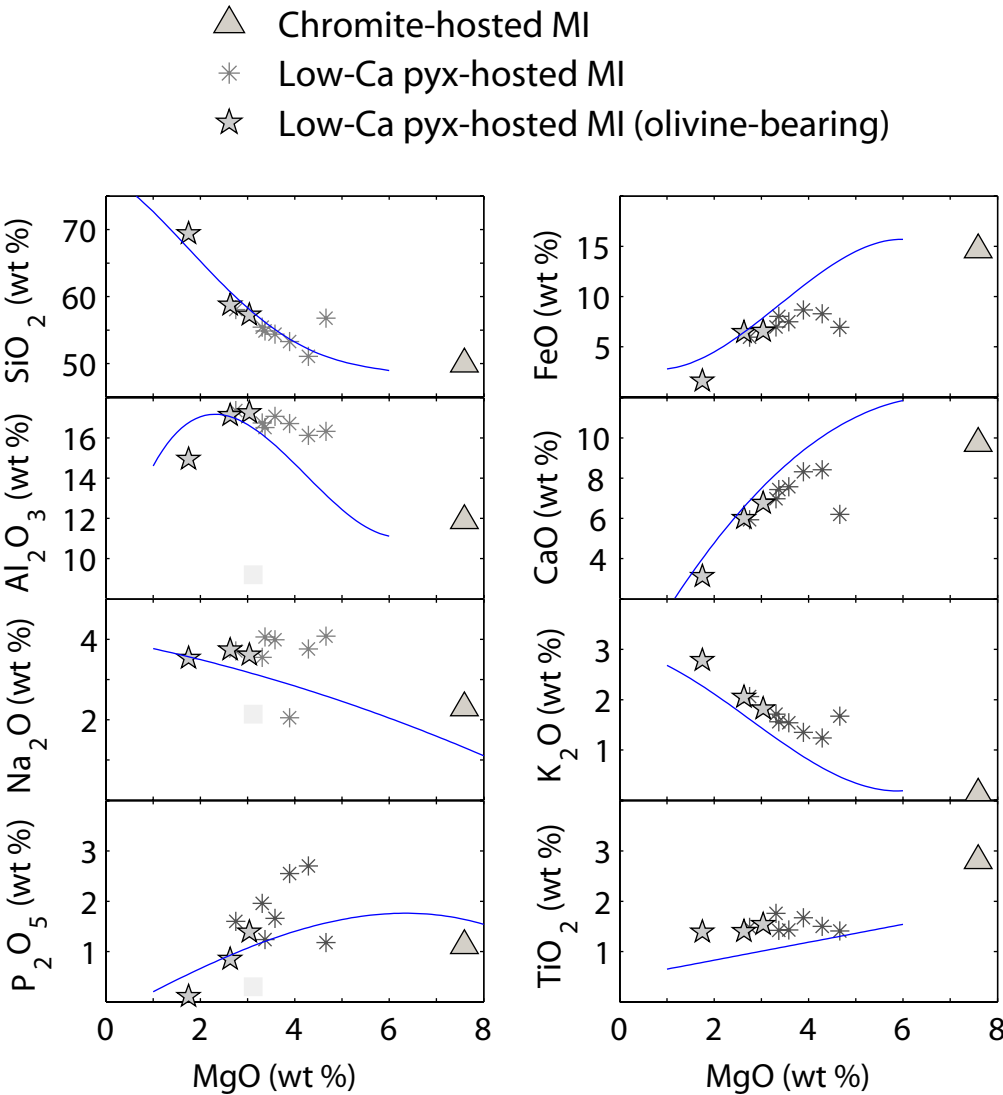
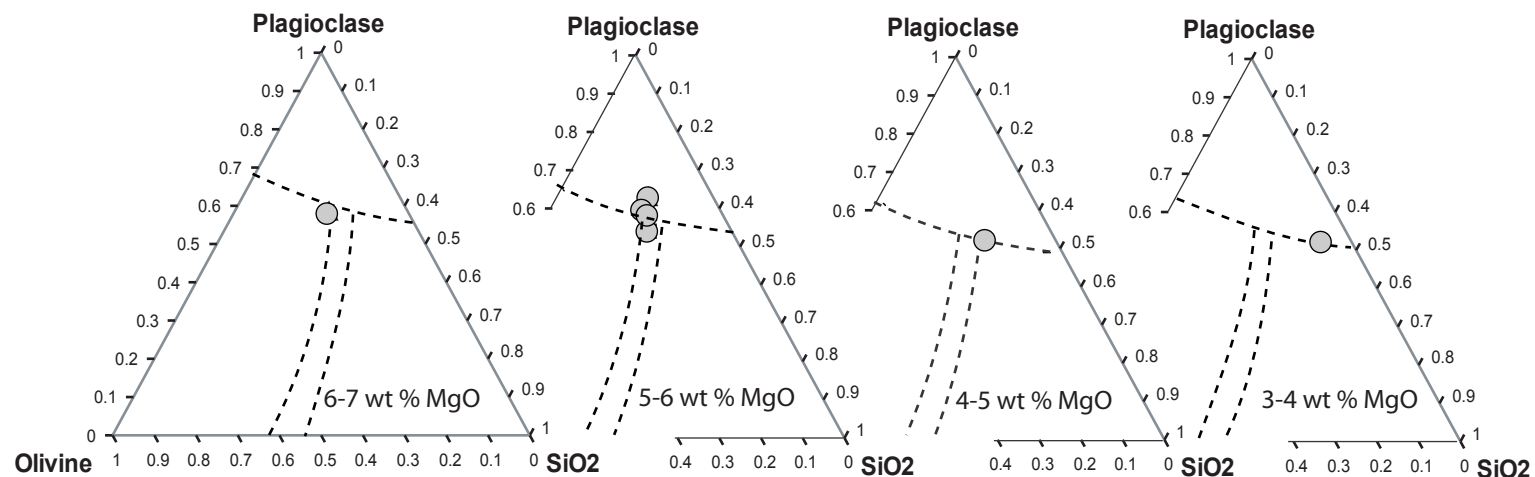


Figure 11

Diopside Projection of glass composition from hydrous crystallization experiments. All points contain plagioclase.



Diopside Projection of glass composition from crystallization experiments

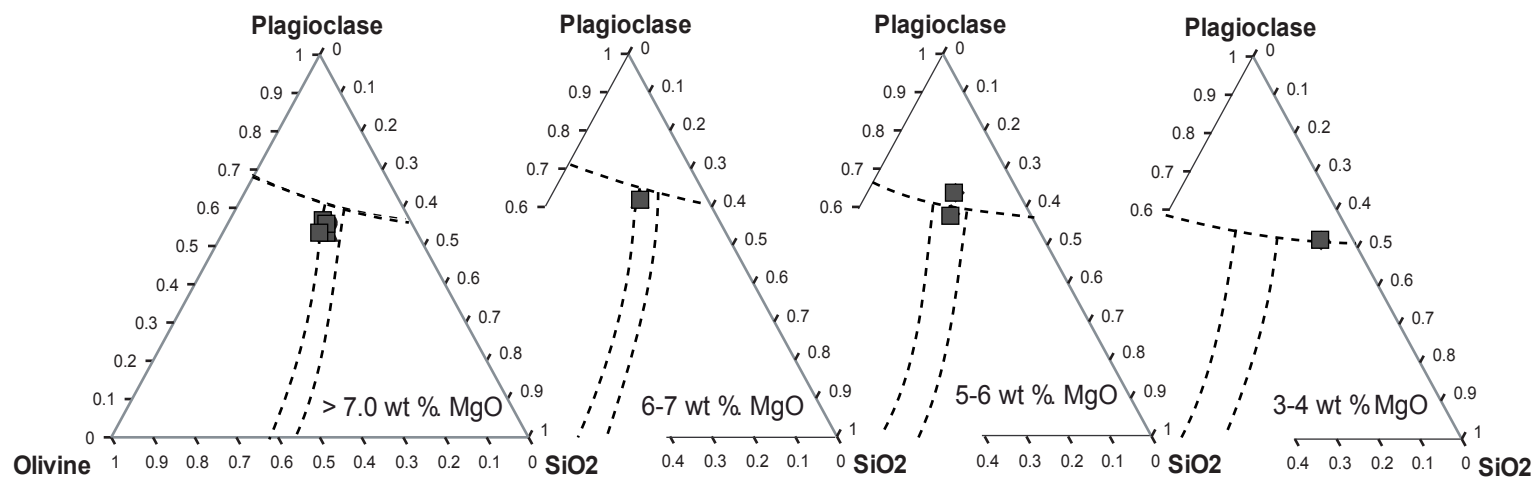


Figure 13

Table 1: Run conditions for crystallization and rehomogenization experiments.

Expt #	Final Temp (in °C)	Pressure (in MPa)	Duration (in hours)	Oxidation**	Expt Type	Minerals Present*	Olivine Texture
S15	1185	80	3	QFM – 3.4	Dry Xln	lpx	N/A
S13	1140	80	22	QFM – 3.0	Dry Xln	none	N/A
S22	1145	40	4.5	QFM – 3.4	Dry Xln	lpx	N/A
S43	1110	36	74	QFM – 3.4	Dry Xln	lpx, plag	N/A
S27	1180	35	22	QFM – 3.4	Dry Xln	None	N/A
S32	1165	35	18	QFM – 3.7	Dry Xln	ol, lpx	subhedral; all ol embedded in pyx
S33	1140	35	22	QFM – 3.6	Dry Xln	lpx, plag	N/A
S23	1135	35	5	QFM – 3.5	Dry Xln	ol, lpx	euhedral
S53	1090	37	72	QFM – 3.1	Dry Xln	ol, lpx, hpx, plag	subhedral; all ol embedded in pyx
S46	1080	35	71	QFM – 3.0	Dry Xln	ol, lpx, hpx, plag	subhedral; some ol embedded in pyx
S47	1070	35	74	QFM – 3.0	Dry Xln	lpx, hpx, plag	N/A
S52	1060	37	77	QFM - 2.9	Dry Xln	ol, lpx, hpx, plag, FeTi	subhedral; some ol embedded in pyx
S41	1165	35	68	QFM – 3.7	Dry Rev	chrm, lpx, plag	N/A
S40	1155	35	72	QFM – 3.7	Dry Rev	chrm, lpx, plag	N/A
S12	1110	200	21	QFM – 1.7	Hydrous Xln	lpx, plag	N/A
S25	1140	50	10	QFM – 3.1	Hydrous Xln	ol, lpx	euhedral
S26	1125	50	12.5	QFM – 3.0	Hydrous Xln	ol, lpx, plag	subhedral - euhedral
S24	1110	50	13	QFM – 2.9	Hydrous Xln	ol, lpx, plag	subhedral; some ol embedded in pyx
S37	1115	47	32	QFM – 2.9	Hydrous Xln	ol, lpx, plag, FeTi	subhedral; some ol embedded in pyx
S34	1140	35	24	QFM – 3.2	Hydrous Xln	lpx, plag	N/A
S35	1110	35	30	QFM – 3.0	Hydrous Xln	lpx, plag	N/A
S44	1110	36	73	QFM – 3.0	Hydrous Rev	ol, lpx, plag	anhedral
S45	1100	37	100	QFM – 3.0	Hydrous Rev	lpx, plag	N/A
R03	1150	100	12	QFM – 2.7	Rehomog	Variable mineralogy	N/A

*All crystallization experiments contained chromite.

** Oxidation states calculated from (Eugster and Skippen, 1967) and (Fogel and Rutherford, 1995).

Rev = reversal experiment; lpx = low-Ca pyroxene; hpx = high-Ca pyroxene, ol = olivine; pl = plagioclase; FeTi = FeTi oxide; chromite = chrm

Table 2: Table of representative mineral compositions from both dry and hydrous crystallization experiments.

Expt #	S27	S23		S41 Reversal (Dry)		S24		S26		S25		S44 Reversal (Hydrous)	
Hydration	Dry	Dry				Hydrous		Hydrous		Hydrous			
Temp (°C)	1100	1135		1165		1110		1125		1140		1110	
Press (MPa)	35	35		37		50		50		50		36	
Mineral	Chrm	Pyx	Ol	Chrm	Pyx	Pyx	Ol	Pyx	Ol	Pyx	Ol	Pyx	Ol
SiO ₂	--	52.05	38.34	--	54.38	49.69	36.88	51.11	37.22	52.49	37.7	52.32	36.65
Al ₂ O ₃	12.28	2.61	0.07	13.84	0.72	4.78	0.03	2.75	0.06	1.75	0.06	2.09	0.03
TiO ₂	3.75	1.13	0.07	4.44	0.37	1.74	0.07	1.06	0.12	0.62	0.08	0.61	0.06
FeO	24.77	11.9	20.19	24.16	13.35	9.45	30.04	12.66	27.36	14.85	24.68	15.3	29.56
MnO	0.14	0	0.03	0.2	0.03	0.07	0	0.01	0.01	0.03	0.03	0.03	0
MgO	8.38	23.28	40.21	9.79	26.6	14.96	31.63	19.05	33.75	23.87	36.65	21.74	31.74
CaO	--	6.95	0.34	--	3.7	17.81	0.41	11.33	0.42	4.57	0.29	5.69	0.33
K ₂ O	--	0.01	0.02	--	0	0	0	0.01	0.01	0.01	0	0	0.02
Na ₂ O	--	0.1	0	--	0.05	0.25	0.02	0.18	0.01	0.07	0.03	0	0
Cr ₂ O ₃	49.96	1.2	0.36	45.43	0.55	1.28	0.15	1.06	0.15	0.75	0.18	0.76	0.11
Kd	N/A	0.25	0.24	N/A	0.29	0.31	0.36	0.31	0.32	0.26	0.26	0.23	0.31
Total	99.29	99.23	99.62	97.86	99.75	99.24	100.02	99.22	99.1	99.01	99.7	98.53	98.49

Table 3: Major and minor element compositions for the starting composition and residual glasses in crystallization experiments.

Experiment	Starting Composition	S15	S21	S22	S41	S41	S12	S24	S25	S35	S44
		Dry	Dry	Dry	Dry	Reversal (Dry)	Hydrous	Hydrous	Hydrous	Hydrous	Reversal (Hydrous)
Hydration Temperature (°C)		1185	1117	1145	1165	1165	1110	1110	1140	1110	1110
Pressure (MPa)		80	40	40	37	35	200	50	50	35	36
SiO ₂	49.94	49.82	49.41	49.54	52.09	51.63	49.16	47.26	49.72	59.67	48.36
TiO ₂	2.81	2.86	3	2.91	3.22	3.37	3.15	4.96	3.15	4.62	3.42
Al ₂ O ₃	11.89	12.01	12.61	12	13.06	13.21	12.94	11.17	12.54	12.16	11.92
FeO	14.66	13.57	15.31	14.06	10.25	10.34	13.36	16.23	14.04	6.95	15.18
MnO	0.42	0.07	0.03	0.01	0	0.0	0	0	0.04	0.01	0.01
MgO	7.59	7.59	5.34	7.69	6.34	6.48	5.54	5.45	6.38	3.73	5.49
CaO	9.73	10.21	10.92	10.22	11.04	10.91	10.26	10.6	10.8	7.56	11.13
Na ₂ O	2.3	1.93	2.13	2.1	2.16	2.31	2.18	1.8	2.14	2.39	2.07
P ₂ O ₅	1.12	1.26	1.38	1.1	1.20	1.26	1.27	1.75	1.1	1.68	1.29
K ₂ O	0.12	0.13	0.16	0.16	0.18	0.16	0.16	0.2	0.09	0.38	0.17
Total	100.76	99.42	100.29	99.79	99.54	99.67	99.02	99.42	100	99.15	99.14

* Hydrous crystallization experiments at 35 MPa had between 500 and 700 ppm H₂O.

Table 4: Representative glass compositions from pyroxene-hosted melt inclusion analyses (this study) compared with chromite and olivine-hosted melt inclusions from Calvin and Rutherford (2008). In the melt inclusion field, the number preceding the dash refers to the experimental run. The number following the dash refers to the melt inclusion analyzed.

Melt inclusion	3-4	3-34	3-42	3-46	3-48	7-10	6-1
SiO₂	53.29	69.40	57.24	54.39	56.78	48.96	47.72
TiO₂	1.67	1.39	1.54	1.43	1.41	2.79	1.23
Al₂O₃	16.71	14.94	17.26	17.07	16.32	11.79	10.09
Cr₂O₃	0.06	0.04	0.04	0.04	0.06	1.35	0.28
FeO	8.66	1.61	6.56	7.49	6.94	14.85	15.79
MnO	0.24	0.08	0.18	0.22	0.16	0.41	0.51
MgO	3.89	1.75	3.04	3.58	4.66	7.59	7.1
CaO	8.31	3.11	6.75	7.57	6.19	9.64	12.86
Na₂O	2.05	3.53	3.61	3.99	4.08	2.27	1.8
P₂O₅	2.55	0.11	1.39	1.66	1.18	1.11	2.94
K₂O	1.35	2.78	1.82	1.54	1.67	0.12	0.15
Chlorine	<i>not meas</i>	0.82	0.51	<i>not meas</i>	<i>not meas</i>	0.07	0.47
Mg_Num	43	65	44	45	53	58	43
Total	98.79	98.74	99.47	98.97	99.42	100.75	99.98
# of analyses	2	2	2	1	1	2	2

Host Mineral	High -Ca pyx	Low-Ca pyx	Low-Ca pyx	Low-Ca pyx	Low-Ca pyx	Chromite	Olivine
SiO₂	51.80	54.90	53.86	53.86	53.86	--	37.80
FeO	8.13	13.15	13.54	13.54	13.54	24.56	32.08
MgO	16.96	26.63	27.49	27.49	27.49	7.04	37.92
Al₂O₃	3.05	0.72	0.54	0.54	0.54	6.88	--
Na₂O	0.31	0.09	0.02	0.02	0.02	--	--
MnO	0.36	0.61	0.44	0.44	0.44	0.16	0.49
TiO₂	0.60	0.14	0.10	0.10	0.10	1.96	--
Cr₂O₃	0.96	0.52	0.44	0.44	0.44	59.95	0.16
CaO	17.73	4.46	2.63	2.63	2.63	--	0.29
Mg_Num	78	77	78	78	78	N/A	74
Total	99.95	101.20	99.08	99.08	99.08	99.65	99.76
Associated Phases	FeS	Cl-apatite, olivine	olivine, FeS	Cl-apatite, FeS	Cl-apatite	None	None

Appendix 1: Glass compositions for crystallization experiments.

Experiment	Pressure	Final Temperature	Hydrated	SiO ₂	Al ₂ O ₃	TiO ₂	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅
S12	2000	1110	Yes	49.16	12.94	3.15	13.36	0.00	5.54	10.26	2.18	0.16	1.27
S13	800	1140	No	48.94	11.71	2.90	12.88	0.00	7.72	10.46	1.96	0.16	1.16
S15	800	1185	No	49.82	12.01	2.86	13.57	0.07	7.59	10.21	1.93	0.13	1.26
S22	400	1145	No	49.54	12.00	2.91	14.06	0.01	7.69	10.22	2.10	0.16	1.10
S23	350	1135	No	50.18	13.04	3.03	11.01	0.00	6.86	11.59	2.14	0.14	1.24
S24	500	1110	Yes	47.26	11.17	4.96	16.23	0.00	5.45	10.60	1.80	0.20	1.75
S25	500	1140	Yes	49.72	12.54	3.15	14.04	0.04	6.38	10.80	2.14	0.09	1.10
S26	500	1125	Yes	49.96	12.67	3.07	14.18	0.01	5.54	11.07	2.17	0.13	1.04
S27	350	1100	No	50.30	12.01	2.91	12.86	0.01	7.66	10.75	2.06	0.12	1.25
S32	350	1165	No	50.50	13.29	3.42	11.42	0.00	5.92	10.54	2.53	0.19	1.18
S33	350	1140	Yes	49.54	11.86	2.97	13.86	0.01	7.39	10.57	2.15	0.11	1.10
S34	350	1140	Yes	50.32	13.23	3.21	11.81	0.00	5.88	11.07	0.16	2.33	1.22
S35	350	1110	Yes	59.67	12.16	4.62	6.95	0.01	3.73	7.56	2.39	0.38	1.68
S37	470	1115	Yes	47.37	10.25	6.14	14.58	0.00	4.86	10.98	1.82	0.25	3.03
S40	390	1155	No	50.65	12.32	4.44	10.86	0.00	6.19	10.91	2.22	0.19	2.00
S41	370	1165	No	52.09	13.06	3.22	10.25	0.00	6.34	11.04	2.16	0.18	1.20
S43	360	1100	No	53.07	14.07	3.67	8.54	0.00	5.67	10.37	2.48	0.18	1.37
S44	360	1110	Yes	48.36	11.92	3.42	15.18	0.01	5.49	11.13	2.07	0.17	1.29
S45	370	1100	Yes	50.63	11.35	5.16	12.19	0.02	4.95	10.60	1.99	0.21	2.04
S46	350	1080	No	46.21	9.48	5.98	19.90	0.04	3.65	9.47	2.11	0.30	2.28
S47	350	1070	No	49.86	9.56	5.29	16.70	0.35	3.48	9.76	2.04	0.23	2.46
S52	370	1060	No	47.40	8.88	4.15	19.35	0.00	2.96	10.53	1.75	0.33	3.58
S53	360	1090	No	48.31	10.27	5.61	16.34	0.00	4.27	10.08	1.98	0.28	2.65

Appendix 2. Olivine composition for crystallization experiments.

Expt #	Pressure	Final Temp	Hydrated	SiO ₂	Al ₂ O ₃	TiO ₂	FeO	MnO	MgO	CaO	K ₂ O	Na ₂ O	Cr ₂ O ₃
S23	1135	35	Yes	38.67	0.02	0.10	18.97	0.00	40.84	0.31	0.02	0.00	0.39
S24	1110	50	No	36.88	0.04	0.07	30.04	0.00	31.63	0.41	0.00	0.02	0.15
S25	1140	50	No	37.70	0.06	0.08	24.68	0.03	36.65	0.29	0.00	0.03	0.18
S26	1125	50	No	37.22	0.06	0.12	27.36	0.01	33.75	0.42	0.01	0.01	0.15
S32	1165	35	Yes										
S33	1140	35	Yes										
S37	1115	47	Yes	37.48	0.05	0.13	25.83	0.02	35.33	0.36	---	0.01	0.12
S43	1110	36	Yes										
S44	1110	36	No	36.65	0.03	0.06	29.56	0.00	31.74	0.33	0.02	0.00	0.11
S45	1100	37	No										
S46	1080	35	Yes	35.68	0.03	0.07	34.63	0.01	27.92	0.34	0.00	0.00	0.10
S52	1060	37	Yes	35.01	0.02	0.06	38.46	0.01	24.98	0.32	0.00	0.00	0.07
S53	1090	37	Yes	36.84	0.05	0.06	26.73	0.04	34.42	0.32	0.02	0.01	0.21

Appendix 3: Pyroxene compositions from crystallization experiments.

Expt #	Pressure	Final Temp	Hydrated	SiO ₂	Al ₂ O ₃	TiO ₂	FeO	MnO	MgO	CaO	K ₂ O	Na ₂ O	Cr ₂ O ₃
S12	1110	200	Yes										
S15	1185	80	No										
S22	1145	40	No	53.61	1.76	0.62	12.37	0.03	26.65	3.92	---	0.07	0.90
S23	1135	35	No	52.05	2.61	1.13	11.90	0.00	23.28	6.95	0.01	0.10	1.20
S24	1110	50	Yes	49.69	4.78	1.74	9.45	0.07	14.96	17.81	0.00	0.25	1.28
S25	1140	50	Yes	52.49	1.75	0.62	14.85	0.03	23.87	4.57	0.01	0.07	0.75
S26	1125	50	Yes	51.11	2.75	1.06	12.66	0.01	19.05	11.33	0.01	0.18	1.06
S32	1165	35	No	53.03	1.66	0.56	13.87	0.00	25.68	3.39	---	0.05	0.78
S33	1140	35	No	51.55	2.72	1.01	12.32	0.00	23.11	7.27	---	0.09	1.06
S34	1140	35	Yes	53.40	1.32	0.45	13.82	0.00	25.89	3.74	---	0.03	0.72
S35	1110	35	Yes	54.03	1.51	0.63	10.63	0.01	26.85	5.08	---	0.06	0.87
S37	1115	47	Yes	51.34	1.93	1.25	17.34	0.03	21.07	4.89	---	0.06	0.63
S40	1155	35	No	52.99	1.75	0.69	11.26	0.00	24.68	6.91	0.02	0.10	0.94
S41	1165	35	No	54.38	0.72	0.37	13.35	0.03	26.60	3.70	0.00	0.05	0.55
S44	1110	36	Yes	52.32	2.09	0.61	15.30	0.03	21.74	5.69	0.00	0.00	0.76
S45	1100	37	Yes	52.99	2.23	0.67	11.63	0.00	25.32	4.87	0.01	0.00	0.92
S46	1080	35	No	52.30	1.65	0.60	15.43	0.00	23.77	4.31	0.00	0.05	0.72
S47	1070	35	No	53.82	1.53	0.54	14.22	0.39	26.23	2.75	0.01	0.06	0.76
S52	1060	37	No	52.79	2.11	0.61	14.05	0.02	25.45	3.46	0.00	0.07	0.91
S53	1090	37	No	53.24	1.65	0.59	13.10	0.03	25.25	4.42	0.01	0.06	0.82

Appendix 4: Plagioclase composition for crystallization experiments.

Experiment	Final Temperature	Pressure	Hydration	SiO ₂	Al ₂ O ₃	CaO	Na ₂ O	K ₂ O	FeO
S12	1110	200	No						
S24	1110	50	No						
S26	1125	50	No	53.95	28.98	12.42	4.03	0.05	0.43
S33	1140	35	Yes	54.35	28.50	12.22	3.69	0.03	0.42
S34	1140	35	No	52.57	29.31	13.04	3.81	0.04	0.58
S35	1110	35	No	55.03	26.83	10.94	4.67	0.05	0.42
S37	1115	47	No	54.86	27.71	11.24	4.61	0.08	0.66
S40	1155	35	Yes	53.45	28.65	12.34	4.10	0.06	0.41
S41	1165	35	Yes	53.99	28.32	11.93	3.60	0.04	0.61
S43	1110	36	Yes						
S44	1110	36	No	54.73	28.59	11.66	4.19	0.06	0.70
S45	1100	37	No	54.96	28.40	11.73	4.25	0.07	0.55
S46	1080	35	Yes	54.09	28.74	11.97	4.23	0.07	0.61
S47	1070	35	Yes	55.64	28.48	11.71	4.61	0.05	0.51
S52	1060	37	Yes	55.09	28.26	11.77	4.41	0.07	0.53
S53	1090	37	Yes	54.93	27.78	11.31	4.63	0.09	0.70

Chapter 3: Origin of phosphates in shergottite meteorites

Abstract

P₂O₅ was found to be anomalously high (>8 wt % P₂O₅) in early crystallized melt inclusions in ALH 77005 and these high-P₂O₅ concentrations were correlated with CaO suggesting the presence of extra phosphates in these inclusions (Calvin and Rutherford, 2008). In addition, shergottites have shown a wide range of bulk rock REE patterns and concentrations (Symes et al., 2008). Treiman 2003 noted that among the basaltic shergottites, P and La in the bulk rock values showed different compatibilities in different samples. This study was undertaken to determine the origin and implications of high P₂O₅-bearing melt inclusions and distinguish the relationship with the REE. Two approaches were taken: experimentally determining the P₂O₅ saturation values for the ALH 77005 parent melt and analyzing the REE patterns and concentrations for melt inclusions over a range of P₂O₅ concentrations. Saturation was determined to be at 7.2 wt % P₂O₅ at MgO concentrations of 7.7 wt % and 1.9 wt % P₂O₅ at MgO concentrations of 2.1 wt %. MREE and HREE concentrations and patterns were unchanged between melt inclusions with low P₂O₅ (0.6 wt %) and high P₂O₅ (8.1 wt %). LREE became increasingly enriched with increasing P₂O₅ concentration however they did not change as significantly as would be expected if the high-P₂O₅ concentrations were the result of melting of magmatic phosphates. Thus, this research suggests that the high-P₂O₅ concentrations are the result of secondary contamination that increased the P₂O₅ without significantly changing the concentration of the MREE and HREE.

Introduction

Bulk rock measurements of phosphorous in basaltic shergottites vary considerably (Lodders, 1998; Treiman, 2003 and references therein). As P_2O_5 is not incorporated in significant quantities into any of the major mineral phases found in shergottites, the variation in phosphorous is due to differences in the modal abundance of phosphates in the groundmass. However, P_2O_5 appears to be decoupled from the LREE in that La/P ratios in some basaltic shergottites suggest P_2O_5 is more compatible than La while in others it seems less compatible (Treiman, 2003). This is puzzling as phosphates are the major REE reservoir in shergottites (Laul et al., 1986; Wadhwa et al., 1994) and might be expected to have consistent compatibility between different samples if the phosphates were all derived from a shergottite magma. Yet some shergottites have flat bulk REE patterns while others have LREE depleted patterns (eg. Symes et al., 2008). Complicating matters, some deviations in LREE have been attributed to terrestrial weathering (Crozaz and Wadhwa, 2001; Crozaz et al., 2003). Thus, the variability in REE make it hard to quantify the role of P_2O_5 , the nature of phosphates, and the phosphates control (or lack thereof) on the absolute concentration and pattern of REE during shergottite petrogenesis.

This study examines phosphates in lherzolitic shergottite ALH 77005 where phosphates are thought to crystallize late (Lundberg et al., 1990; Ikeda, 1994). However, Calvin and Rutherford (2008) showed that some reheated olivine-hosted melt inclusions in ALH 77005 did not contain consistent P_2O_5 values. Some melt inclusions were enriched by as much as 5 wt % P_2O_5 relative to melt inclusions at the same MgO concentration (Figure 1). The appearance of variable P_2O_5 concentrations in melt inclusions in olivine raises the possibility that some phosphates are not magmatic in

origin or have been mobilized during secondary processes such as weathering and/or shock. If so, this may potentially effect the interpretation of REE in the shergottites. Likewise, if the P_2O_5 -enriched melts are representative of the magma at the time of crystallization, this may contribute to the larger understanding of shergottite petrogenesis in that P increases network forming bonds in a melt, favoring crystallization of pyroxene over olivine (Ryerson, 1985; Hess, 1995), significantly lowering the liquidus temperature of the magma (Ryerson and Hess, 1980), and increasing the potential for liquid immiscibility (Longhi, 1990).

To examine the origin of the phosphates in shergottites, this study takes two approaches. First, phosphate saturation for the ALH 77005 parent melt has been experimentally determined as a function of temperature. This allows high- P_2O_5 bearing melts in ALH 77005 to be examined from a magmatic perspective while also providing a more general guideline for evaluating the origin of phosphates in shergottites where the magmatic composition is well constrained. Second, the REE concentration of high- and low- P_2O_5 melts were measured in rehomogenized melt inclusions from ALH 77005. This allows the relationship between REE and P_2O_5 concentrations in melt inclusions to be examined.

Methods

Phosphate saturation experiments. The ALH 77005 parental melt composition (Calvin and Rutherford, 2008) was synthesized and doped with 7 wt % P_2O_5 in the form of $CaHPO_4$. The powder did not contain Cl or F. An aliquot of this powder was then pressed into a pellet, surrounded in graphite and placed in a platinum capsule. The fO_2 of

the experiments was controlled by the graphite at QFM – 3.7 for the pressure of these experiments. Using a TZM pressure vessel, the sample was taken above the liquidus (1185 °C) for >3 hours at pressures of 350 bars. The temperature was then dropped to the final temperature over a series of increments and held at that temperature for durations of time between 25 and 72 hours. The experiments were immediately quenched. In addition, one reversal experiment was conducted as above. However, after the temperature was reduced to 1065 °C, the temperature was raised to 1080°C where it was held for 24 hours. Run conditions for individual experiments can be found in Table 1.

Ion Probe Analyses. REE were analyzed on three reheated experimental chips of ALH 77005: R03, R06, and R08 (Calvin and Rutherford, 2008). The chips had been reheated using a graphite buffer at temperatures of 1150, 1165, and 1150°C and 100, 80, and 80 MPa respectively for durations between 12 and 70 hours. Analyses were performed using the Cameca 3f SIMS at Woods Hole Oceanographic Institute with an O- beam with about 2 nA and -60V (offset ± 10 V). The spot size was ~ 15 microns. The basaltic glass standard KL2G was used to convert intensity data to concentrations. Reproducibility is to within 10%. Analytical uncertainties are $\pm 10\sim 15\%$.

Results

All experiments produced at least two mineral phases in equilibrium with a melt: phosphate and chromite. Chromites are too small to analyze by electron microprobe. Phosphates were Ca-rich with variable amounts of MgO and FeO (Table 2). Following chromite and phosphate crystallization, pyroxene, plagioclase, a high-SiO₂ phase, and

finally FeTi oxide (Table 2) appear on the liquidus with decreasing temperature of the experiment (Figure 2). The FeTi oxide has a molar ratio of 1.01, consistent with ilmenite. Representative melt and their associated mineral compositions are presented in Table 3. As shown in Figure 3, P_2O_5 concentrations in the melt decrease with increasing crystallization (represented by decreasing MgO) and decreasing temperature.

REE compositions from rehomogenized melt inclusions and remelted melt pockets adjacent to olivine (Calvin and Rutherford, 2008) are presented in Table 4. The REEs varied both in their concentration and pattern with some showing minor LREE enrichment while others were LREE depleted. Increased P_2O_5 in the melt inclusion corresponded with increased LREE.

Determining Equilibrium in the experiments.

Equilibrium in these experiments was established in three ways. First, samples were examined to determine if the minerals were euhedral. All experiments appear to have euhedral crystals that grew from and are approaching equilibrium with the surrounding melt (Figure 4). Secondly, a reversal experiment was conducted to approach equilibrium from the opposite direction. The reversal experiment, as shown in Figure 3, falls on the saturation line defined by the other experiments, suggesting that the experiments approached the same equilibrium conditions. Finally, in experiments that contained minerals other than phosphate and chromite, the equilibrium relationship was established by examining the K_d of the Mg-Fe in the mineral phase with that of the melt. The K_d values of the pyroxene rims range between 0.28 and 0.30 with the higher values being for higher concentrations of CaO. These values are consistent with the pyroxene

equilibrium established for this magma in the dry crystallization experiments reported in Calvin and Rutherford (Chapter 2). Thus the combination of textural evidence, similarities of reversal experiments to the crystallization experiments, lacking of detectable zoning in minerals other than pyroxene and the K_d values of minerals in the low temperature runs, provides a convincing argument that the mineral phases in these experiments achieved equilibrium with the surrounding melts.

Identification of phosphates

There are several phosphate minerals found in magmatic rocks. Because the phosphates in these experiments are CaO-rich, this narrows the identification of the phosphates down to apatite, merrillite, and whitlockite. Electron microprobe analyses of the phosphates (Table 2) indicate that they have a CaO to P_2O_5 molar ratio of 2.5, consistent with the chemical formula for whitlockite and merrillite and not apatite which has a ratio of 3.3. In addition, the incorporation of FeO and MgO into the phosphate structure is consistent with the phosphates being merrillite or whitlockite. Merrillite and whitlockite are often distinguished by whitlockite's incorporation of H into the structure (Dowty, 1977; Hughes et al., 2006). Based on our electron microprobe analyses, it is difficult to distinguish between merrillite and whitlockite, however the experiments in this study were performed under dry conditions and thus the phosphates should not have little to no H to incorporate into the structure. In addition, the halogen free phosphates found in ALH 77005 have been identified as merrillite. Therefore, for the purposes of this paper, the phosphates discussed from these experiments will be identified as merrillite.

Discussion

Phosphate Saturation in ALH 77005

The purpose of the crystallization experiments was to determine the P_2O_5 concentration of a phosphate-saturated (merrillite) shergottite magma. The ALH 77005 parental melt (Calvin and Rutherford, 2008) was chosen for the experiments because it is one of the most primitive shergottites and because ALH 77005 was shown to have significant P_2O_5 variability in melts trapped in early crystallizing phases. In a metaluminous melt such as ALH 77005, saturation is dependent on the composition of the melt and the temperature (Harrison and Watson, 1984; Piccoli and Candela, 2002). In the experiments performed in our study, a decrease in the dissolved P_2O_5 at phosphate saturation is correlated with decreasing MgO concentration and increasing in the crystallinity as shown in Figure 3a. The decrease in P_2O_5 is also consistent with a decrease in the final temperature of the experiment as shown in Figure 3b. Decreasing temperature and the accompanying evolution of the melt favors the crystallization of phosphates and therefore lowers the required P_2O_5 to create phosphate (Piccoli and Candela, 2002). In addition, increased crystallization of the early crystallizing phases in this magma (chromite and low-Ca pyroxene) increase the available CaO in the melt which also favors phosphate saturation.

To compare the melts at phosphate saturation in these experiments to those found in rehomogenized melt inclusions of ALH 77005, the P_2O_5 melt data have been plotted against MgO in Figure 5. Melts in the reheating experiments were analyzed from both chromite- and olivine-hosted inclusions. Representative inclusion compositions are given in Table 3. Texturally, chromite is the first phase to appear in ALH 77005 and chromite-

hosted melt inclusions have the highest MgO melts in this rock. The P_2O_5 concentration in these inclusions ranged between 1.10 and 1.29 wt %. Olivine was the next phase on the liquidus and reheated olivine-hosted melt inclusions had a considerable range of major and minor element chemistries depending in part on which phases remained as daughter crystals inside the inclusion. In general, the P_2O_5 concentration in olivine-hosted melt inclusions are within analytical error of a line fit through the data at $MgO < 5$ wt %. However the variability and the absolute concentration of P_2O_5 increased dramatically above 6 wt % MgO. Possible explanations for this will be discussed later. P_2O_5 concentrations at MgO concentrations < 5 wt % are in part due to the presence of phosphates in melt inclusions which buffer the P_2O_5 in the associated melt. Low-Ca pyroxene, which often contains phosphates as well, followed chromite and olivine on the ALH 77005 liquidus. These melt inclusions contained P_2O_5 concentrations between 1 and 3 wt % P_2O_5 .

The P_2O_5 solubility at saturation determined from these experiments is slightly higher than the P_2O_5 measured in phosphate saturated inclusions at low MgO and slightly lower at high MgO. At low MgO this may be explained in that the reheated experiments may not have achieved equilibrium. As will be shown in the next paragraph, there was a significant amount of Cl in some of these inclusions and therefore the P_2O_5 may represent the saturation of Cl-apatite rather than merrillite.

It should be noted that olivine does not appear in the crystallization experiments despite being abundant in ALH 77005. As shown in Calvin and Rutherford (Chapter 2), the ALH 77005 parent melt is very close to the boundary curve between olivine and low-Ca pyroxene. Since P_2O_5 favors Si-O-Si bonds, the boundary curve would shift in favor

of low-Ca pyroxene over olivine in these experiments (Ryerson, 1985; Hess, 1995). The pyroxene composition is consistent with the pyroxene found in crystallization experiments in Calvin and Rutherford (Chapter 2) where olivine did not crystallize.

Another point to be made is that the starting material for this study did not contain F or Cl and the experiments were performed under anhydrous conditions. Thus the saturation data discussed are for an anhydrous, halogen-free phosphate and might vary in a water-saturated magma although this has not been shown to be the case for all magmas (Harrison and Watson, 1984). The magma might also saturate at different points if it contained a significant halogen component. However, F was below the detectability range in ALH 77005 chromite-hosted melt inclusions and Cl range from 600 – 740 ppm (Calvin and Rutherford, 2008). In olivine-hosted melt inclusions of ALH 77005, F ranged between 165 and 957 ppm and Cl between 157 and 5319 ppm (Figure 6). The low concentration of F in the natural sample makes the absence of F in this study appropriate. Cl increases over the course of crystallization from chromite in the early stages to low-Ca pyroxene in the late stages. Because Cl can be held in phosphates, this may explain the correlation seen between Cl and P_2O_5 are correlated (Figure 6). However Cl increases an order of magnitude between chromite and low-ca pyroxene crystallization. To increase an order of magnitude, the melt would have to crystallize more than 90% and Cl would have to behave incompatibly. However, low-Ca pyroxene melt inclusions often contain Cl-apatite so Cl is not behaving incompatibly. Furthermore, the MgO concentrations in the low-Ca pyroxene melt inclusions do not support extensive crystallization of the melt. This observation suggests that the Cl in these inclusions may not be magmatic in origin. Because of the uncertainty in the origin of the Cl, it was not

included in the synthesized starting material. Low-Ca and olivine-hosted melt inclusions that contain a phosphate while not always in equilibrium with their host can still provide a guideline for the saturation point of this magma at low MgO values.

The origin of ALH 77005 merrillites.

Three possible explanations for phosphate-saturated melts in ALH 77005 have been identified. First, the very high- P_2O_5 melts (8 wt %) could represent the magmatic composition present in the magma chamber or localized chemistry in the magma chamber at the time of entrapment. Second, phosphates crystallized elsewhere in the rock were mobilized and recrystallized during shock and subsequent reheating experiments. Third, the phosphates represent a weathering phase that is not magmatic in origin but was incorporated into the melt during reheating. Each of these possibilities will be discussed below.

Magmatic Origin. Calvin and Rutherford (2008) performed a phosphorous x-ray map on a thin section of ALH 77005 (Figure 1). The presence of phosphates in these magmatic inclusions suggests that the phosphates may be of magmatic origin (Figure 1). As these inclusions are highly crystallized, the melt inclusions could have achieved phosphate saturation after extensive crystallization. However, the P_2O_5 concentrations of reheated olivine-hosted melt inclusions show considerable variation at the same MgO concentration and are not necessarily consistent with having formed after, immediately after or concurrently with chromite, which contained melt inclusions with between 1.1 and 1.3 wt % P_2O_5 . Having defined the P_2O_5 concentration in the melt at phosphate

saturation for a given MgO, it is clear that while some inclusions are saturated with phosphates, many inclusions were clearly undersaturated. If phosphates saturated during olivine crystallization, the P_2O_5 concentration within magmatic inclusions would be expected to remain high throughout the early olivine crystallization. However, the presence of undersaturated inclusions at the same and lower MgO values suggests that many olivine-hosted inclusions were not saturated in phosphate.

If the phosphates are still assumed to be magmatic in origin, the presence of P_2O_5 undersaturated melt inclusions requires an additional magmatic process. Assimilation or mixing with high P_2O_5 material during olivine crystallization could produce melt inclusions that contained high- P_2O_5 . However, when normalized to the same P_2O_5 (3 wt %) and CaO concentrations (Figure 7), the inclusions appear very similar and thus the magma would be almost identical for the increased P_2O_5 and CaO. A second possibility is that the P_2O_5 represents a local environment within the larger magma chamber. This might be achieved in that P_2O_5 diffuses very slowly relative to other cations (Harrison and Watson, 1984) and P_2O_5 is trapped at the boundary layer of a fast-moving crystal growth front. However, a localized buildup of P_2O_5 would also be expected to produce anomalously high concentrations in other slow diffusing cations such as TiO_2 and Al_2O_3 . As shown in Figure 7, when the effect of the high- P_2O_5 is removed, no such buildup is observed. Additionally, it seems highly unlikely that P_2O_5 buildup from 3 to 8 wt % would be produced by such a process.

Mobilization by impact or reheating. Phosphates that were formed during a later stage of crystallization could also have been mobilized during shock or the reheating experiments

so that they are no longer distributed evenly throughout the rock. Evidence from a phosphorous x-ray map (Figure 8) shows that Ca-phosphates appear in fractures within the rock (Calvin and Rutherford, 2008), which may indicate remobilization during a shock event. Shock-melt in ALH 77005 has also been shown to contain recrystallized phosphates and some shock melts contained as much as 8 wt % P_2O_5 (Edmunson et al., 2005). Fusion crusts have also been shown to contain up to four times more phosphates relative to the interior of the meteorite (Mautner and Sinaj, 2002). And while this suggests that phosphates can be concentrated under extreme pressures and temperatures, the presence of phosphates in highly-crystallized olivine-hosted melt inclusions prior to reheating (Figure 8) suggests that some inclusions contained phosphates prior to reheating and that reheating in these experiments alone is not responsible for their P_2O_5 concentration. In addition, the melt inclusions studied were in sections of the rock that were texturally less shocked and were not in obvious contact with shocked melt pockets. This makes impact less likely to be the sole cause of the enriched melt inclusions.

Low temperature origin. Finally, there is the potential that the phosphates studied are the product of low-temperature alteration or hydrothermal activity. Phosphorous has been found in the soils and rocks at the surface of Mars (Rieder et al., 2004; Gellert et al., 2006) and the removal of weathering rinds on surface rocks shows a depletion in phosphate phases on the exterior relative to the interior (Gellert et al., 2006). The absence of P_2O_5 in the outer rims of Gusev crater rocks is consistent with weathering of martian basalts under acidic martian conditions where phosphates weather faster than olivine, the fastest weathering major mineral phase in martian rocks (Guidry and

Mackenzie, 2003; Tang et al., 2003; Hurowitz et al., 2006). However extended exposure to high P-bearing fluids will increase the likelihood that P will react with Ca to replace existing carbonates in rocks (Knudsen and Gunter, 2002) and references therein) which in SNC meteorites could then operate as a P_2O_5 sink in fractures (Mautner and Sinaj, 2002).

Based on the above information it can be inferred that for phosphates to have been preserved in ALH 77005 and other martian rocks, one of two scenarios must be true: the phosphates are indeed magmatic and experienced almost no weathering or the rocks have been modified by exposure to a P-rich fluid. While alteration products in ALH 77005 are rare and of questionable origin (McSween et al., 1979; Smith and Steele, 1984; Burgess et al., 1989; Wentworth and Gooding, 1993), stable isotopic analyses of hydrous phases in shergottites indicate interaction with martian surficial water (Leshin et al., 1996). If this scenario is correct, we can presume that there would be a correlation between other signatures of weathering. Figure 6 shows the correlation of P_2O_5 with Cl and S, which for surface rocks and soils is thought to indicate weathered terrains in an early acidic hydrosphere on Mars (Greenwood and Blake, 2006). The increase in Cl and P suggests these may be linked. In addition, the presence of phosphates in the cracks of ALH 77005 (Figure 1) suggest that these phosphates recrystallized in the fractures as this is not where phosphates would be found if they were magmatic in origin. Having ruled out the possibility that all the phosphates formed magmatically, this strongly supports the presence of additional phosphates from alteration.

REE patterns and P₂O₅ concentrations in ALH 77005

REE concentrations and patterns in phosphates are determined by the elements incorporated into their structure (Pan and Fleet, 2002 and reference therein). Na-rich phosphates would therefore have a different REE pattern than Ca-rich phosphates. In addition, elements such as H, Cl, and F effect the structure of the apatite crystal and therefore change the partitioning behavior of REE. Having said this, REE patterns for ALH 77005 have been previously determined by performing leaching experiments (Laul et al., 1986), wide beam analyses on melt inclusions and shock melts (Edmunson et al., 2005), and ion probe analyses of various mineral phases (Lundberg et al., 1990). REE in a few ALH 77005 reheated melt inclusions were also analyzed by McCanta et al. (submitted) but without the comparison to P₂O₅ concentration. These previous studies are compared with the REE patterns determined from reheated melt inclusions and melt pockets in this study (Figure 9a). The REE patterns determined in these previous studies have the same shape as the whole rock pattern in that they are light REE depleted and slightly enriched in the middle REE relative to the heavy REE. The melt inclusion with the lowest P₂O₅ concentration has the same relative REE abundance as the whole rock values although the concentration in the inclusion is higher. However, the melt inclusions with higher P₂O₅ concentrations are light REE enriched up to 20 times the whole rock value and yet remain relatively consistent with the whole rock value through the middle and heavy REE (Figure 9b).

Since the high CaO and P₂O₅ concentrations found in some melt inclusions imply that a phosphate had to melt during the reheating process, it would be reasonable to expect that if the phosphates are all magmatic, the magma would show a comparable

increase in the concentration of REE to correspond with the CaO and P_2O_5 . However the middle and heavy REE show relatively small increase in concentration in the high- P_2O_5 melts and the light REE show only a mild increase. This implies that the increase in CaO and P_2O_5 was not caused by the melting of a magmatic mineral phase or that the magmatic phase was formed in a melt that contained low concentrations of REE.

As discussed above, there is evidence to support the conclusion that some of the phosphates in these melt inclusions are secondary low-temperature phases. If the high- P_2O_5 bearing melt inclusions are the product of melting of a secondary phosphate, the phosphates would have to be nearly devoid of REE as the successive melting of the phosphates does not produce a comparable increase in REE concentration. If P_2O_5 was replacing carbonate (as in a low temperature alteration process (Knudsen and Gunter, 2002 and references therein), it might not have the capacity to incorporate REE into the structure. The decrease in REE might also reflect a decrease in the REE solubility relative to P_2O_5 in the ground water that produced the alteration. Another possibility is that the excess phosphates are actually phosphorites produced by microorganisms. Phosphorites are dramatically reduced in REE relative to magmatic phosphates (Weckwerth and Schidlowski, 1995). Regardless of the mechanism for producing or mobilizing low-temperature phosphates, if the phosphates have been affected by secondary processes, the REEs have likely been affected more heavily than the major igneous phases where REE are less susceptible to alteration (Bouvier et al., 2005).

In the above scenarios, the assumption is that because the increase in P_2O_5 is correlated with an increase in the LREE, that the secondary phosphates remelted in the experiments were the source of the REE. Alteration products in nakhlite NWA 817 were

shown to be LREE enriched relative to their olivine neighbors (Gillet et al., 2002).

Crozaz et al. (2003) have also shown that LREE enrichment and Ce anomalies in pyroxene and olivines can be attributed to terrestrial weathering. Therefore, if weathered pyroxene or olivine was inadvertently incorporated into the melt inclusions, this might also explain the increase in the LREE. As the high P_2O_5 -bearing melts were all found in olivine hosts, it is reasonable to assume that the same secondary process that increased the P_2O_5 concentration could also have altered the olivine. Regardless of the source or the P_2O_5 and REE changes, the addition of REE with a different signature may explain why a comparison of P and La produce confusing information on the compatibility of these elements in shergottites (Treiman, 2003). In addition, Blichert –Toft et al. (1999) have shown that U-Pb ratios are correlated to P_2O_5 concentrations. As we have shown that the LREE elements are correlated with P_2O_5 concentrations and as many of the radiometric age dating systems are contained in the phosphates, this may affect the apparent age of the meteorite (Bouvier et al., 2005; Bouvier et al., 2008).

Implications of high P_2O_5 concentrations in ALH 77005

As the bulk rock REE signatures for some shergottites are consistent with one of the magmatic phosphate end members used in this study, this suggests that the sedimentary component is a localized phenomenon. However, the P_2O_5 concentration of the non-contaminated melt can be used as a guide to understanding the ALH 77005 magma and its source region. The relatively high P_2O_5 concentrations found in martian meteorites have several implications. First, P competes with Si for other cations (like Ca) thereby increasing the Si-O-Si bonds in the melt and moving the boundary curve between

olivine and low-Ca pyroxene such that low-Ca pyroxene crystallization is favored (Ryerson, 1985; Hess, 1995). P_2O_5 can have two other important effects on SNC magmas. First, P_2O_5 increases the likelihood of immiscible liquids forming within a magma (Longhi, 1990). Second by increasing the Si-O-Si bonds in a melt, pyroxene crystallization is favored over olivine and the available SiO_2 in the system will go down thereby increasing the likelihood that an SNC magma would evolve away from a quartz-rich system. Thus high concentrations of P_2O_5 in a melt combined with a high-saturation point for phosphates can combine to change the apparent mineralogy of a rock.

In addition, the high P_2O_5 concentration in the melt has implications for the source region. It is commonly assumed that the major REE sink in the martian mantle is garnet or majorite. However almost all martian materials including those found at the surface have higher P_2O_5 concentrations than their terrestrial counterparts. In order to get 1 wt % phosphorous in the early magma of ALH 77005, the source region must have contained a phosphate phase that was completely melted. Because the REE signature that is representative of the phosphates is also the REE signature of the melt found trapped in early crystallizing crystals, the REE signature of the melt is really the REE signature of the phosphates melted from its source. This implies that garnet and majorite were less important in controlling the REE chemistry of the shergottites than phosphates.

Conclusions

1. P_2O_5 concentration for ALH 77005's parent magma at phosphate saturation drops off quickly with decreasing temperature, decreasing MgO concentrations of the melt, and increasing crystallinity.

2. P_2O_5 concentrations found in olivine-hosted melt inclusions at low-MgO concentrations are slightly lower than the best-fit curve for phosphate saturation within the melt. These likely reflect the differences between saturation of Cl-apatite (in the inclusions) and merrillite (in the experiments).
3. REE concentrations in the MREE and HREE were unaffected by increases in P_2O_5 . In addition, P_2O_5 is not correlated with TiO_2 or Al_2O_3 in a way that suggests the P_2O_5 concentrations in high- P_2O_5 bearing melt inclusions could be the result of a diffusion-related process at the boundary of the melt inclusion. In addition, the P_2O_5 concentrations in melt inclusions in the first crystallizing phase, chromite, and the second crystallizing phase, olivine, are not consistent with P_2O_5 concentrations increasing due to magmatic differentiation.
4. Enrichment of phosphate phases along fractures in ALH 77005 suggests that at least some of the phosphates present in ALH 77005 may have been remobilized during impact and/or are secondary weathering products. In addition, P_2O_5 is correlated with Cl. Cl concentrations are higher in some olivines than could be explained through magmatic differentiation and suggest Cl contamination in some inclusions. Thus the high- P_2O_5 concentrations are thought to be the result of secondary processes.
5. REE concentrations in the MREE and HREE were unaffected by increases in P_2O_5 however the LREE show slight increases with increased P_2O_5 . Crozaz and Wadhwa (2001) and Crozaz et al. (2003) have shown that LREE can be enriched during terrestrial alteration; this supports the hypothesis of secondary processes effecting the P_2O_5 concentration in melt inclusions. The impact of remobilized or

secondary phosphates must be considered when calculating REE melt compositions and in attempts to model the source region based on REE trends in the melts.

6. The contribution of secondary phosphates to the shergottites could explain the decoupling of La and P observed by Treiman (2003).

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Figure Captions

Figure 1. P_2O_5 contents in partially to completely rehomogenized olivine-hosted melt inclusion as a function of MgO. Two lines have been added to show the possible best fit curve for the data. The solid line is a best fit curve for chromite- and olivine-hosted melt inclusions, excluding inclusions with greater than 3 wt % P_2O_5 . Due to the small size of many of the melt inclusions, data is based on as few as one analytical point within a given melt inclusion (Calvin and Rutherford, 2008). Analytical error bars are approximately the size of the circles.

Figure 2. The appearance of mineral phases at different temperatures. Experiments were all run anhydrous at ~35 MPa.

Figure 3. A. P_2O_5 concentration vs. MgO where decreasing MgO represents increasing crystallization. B. P_2O_5 concentration vs. temperature of the experiment.

Figure 4. Backscatter image of two saturation experiments. A. Experiment PS7 showing merrillite and chromite. B. Experiment PS10 showing low-Ca pyroxene, plagioclase, phosphate, ilmenite, and a high- SiO_2 phase. Phos: phosphate; Plag: plagioclase; pyx: pyroxene; ilm: ilmenite.

Figure 5. MgO vs. P_2O_5 for olivine- (circles), chromite- (triangles), and low-Ca pyroxene-hosted (diamonds) melt inclusion are shown against the phosphate saturation curve (squares) determined from the experiments in this study. Lines are fit to olivine-hosted melt inclusions (top) and phosphate-saturated experimental melts (bottom).

Figure 6. Cl concentrations for olivine-hosted melt inclusions (circles), low-Ca pyroxene-hosted inclusions (diamonds), chromite-hosted inclusions (triangles), and high- P_2O_5 bearing olivine-hosted melt inclusions (squares). A. MgO concentration vs. Cl concentration. B. P_2O_5 concentration vs. Cl concentration.

Figure 7. P_2O_5 concentrations for chromite- and olivine-hosted inclusions are plotted with renormalized major element values for high- P_2O_5 bearing melt inclusions. The renormalized melt inclusions are the high- P_2O_5 bearing inclusions adjusted to assume that 3 wt% P_2O_5 was the actual value. CaO was removed assuming a 1:1 molar ratio. A. P_2O_5 vs. CaO and B. P_2O_5 vs. TiO_2 are used as indicators of magmatic processes. TiO_2 being a +4 cation should diffuse slowly. If P_2O_5 enrichment was the result of a boundary layer, TiO_2 should also be increased. C. P_2O_5 vs. Cl. Cl has been shown to be enriched in some melt inclusions above what would be possible through magmatic fractionation. The high- P_2O_5 bearing inclusions show a trend of increasing Cl with increased P_2O_5 . D. P_2O_5 vs. S are used as indicators of weathering processes. While melt inclusions enriched in P_2O_5 have high sulfur there is not a correlation between high- P_2O_5 and sulfur.

Figure 8. A. Backscatter image and B. X-ray map of olivine and a melt inclusion in ALH 77005. Bright areas are phosphate rich. In addition to phosphates filling the fractures and appearing in the olivine-hosted inclusions, the olivine-host also shows P_2O_5 zoning.

Figure 9. A. REE patterns for melts found in reheated inclusions and melt pockets of ALH 77005. B. REE patterns for melts found in reheated inclusions normalized to the bulk rock value. Grey stars are whole rock value from Ma et al. (1992). Black circles, red stars, and green circles are melt inclusions containing 0.58, 1.72, and 8.08 wt % P_2O_5 respectively. Grey squares are interstitial melts that contain 3.90 wt % P_2O_5 .

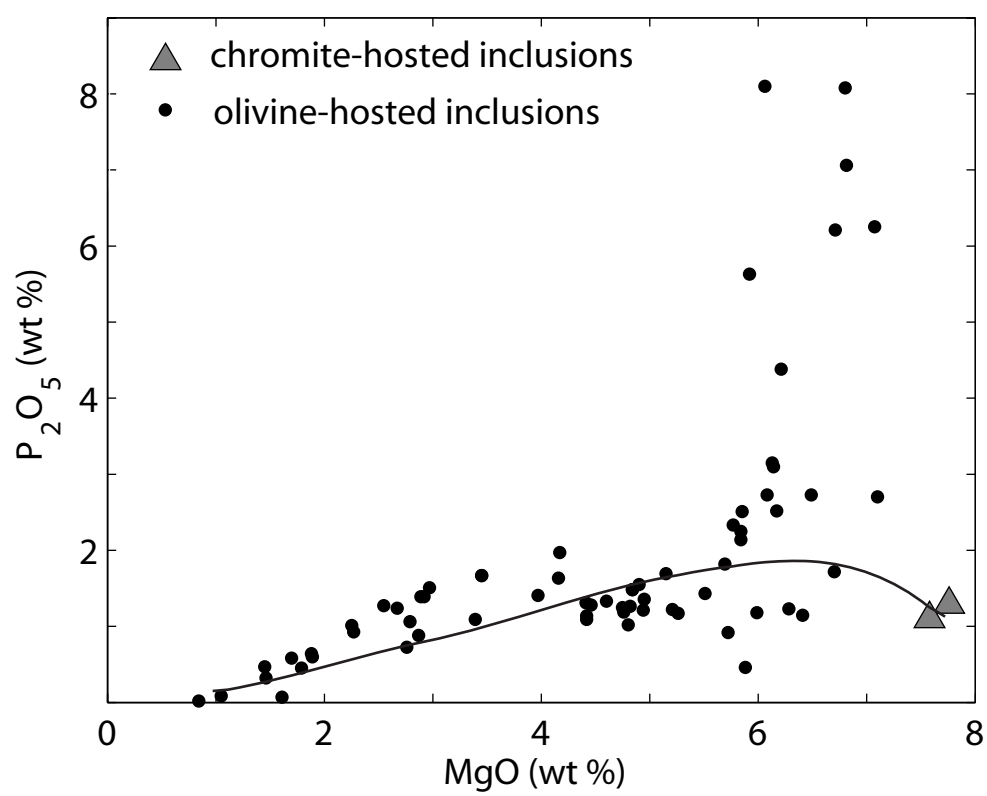


Figure 1

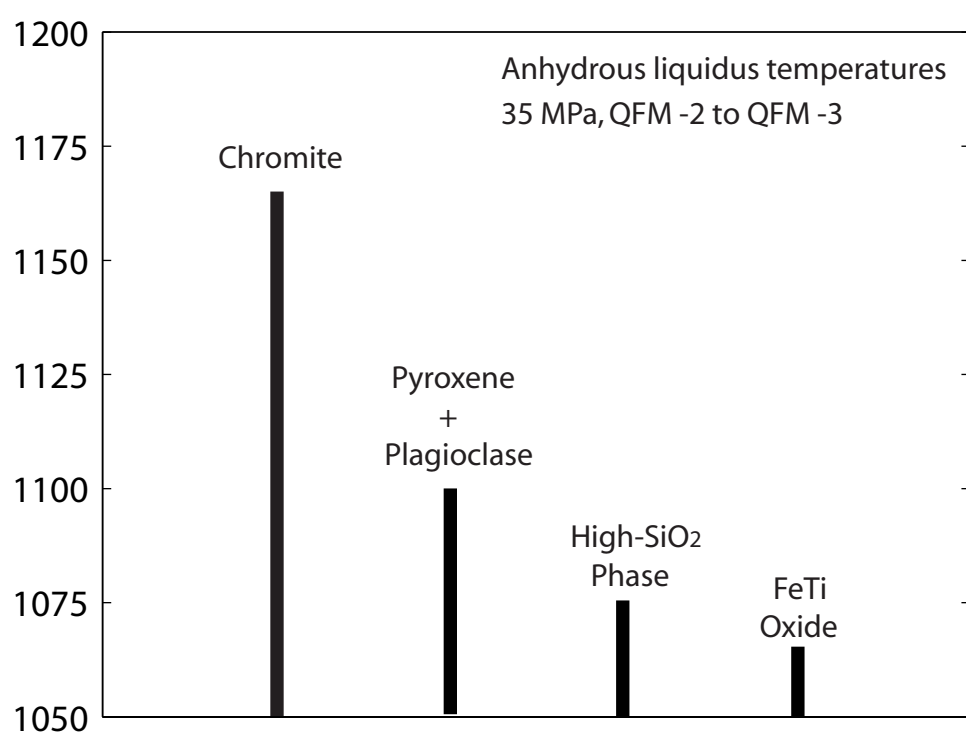


Figure 2

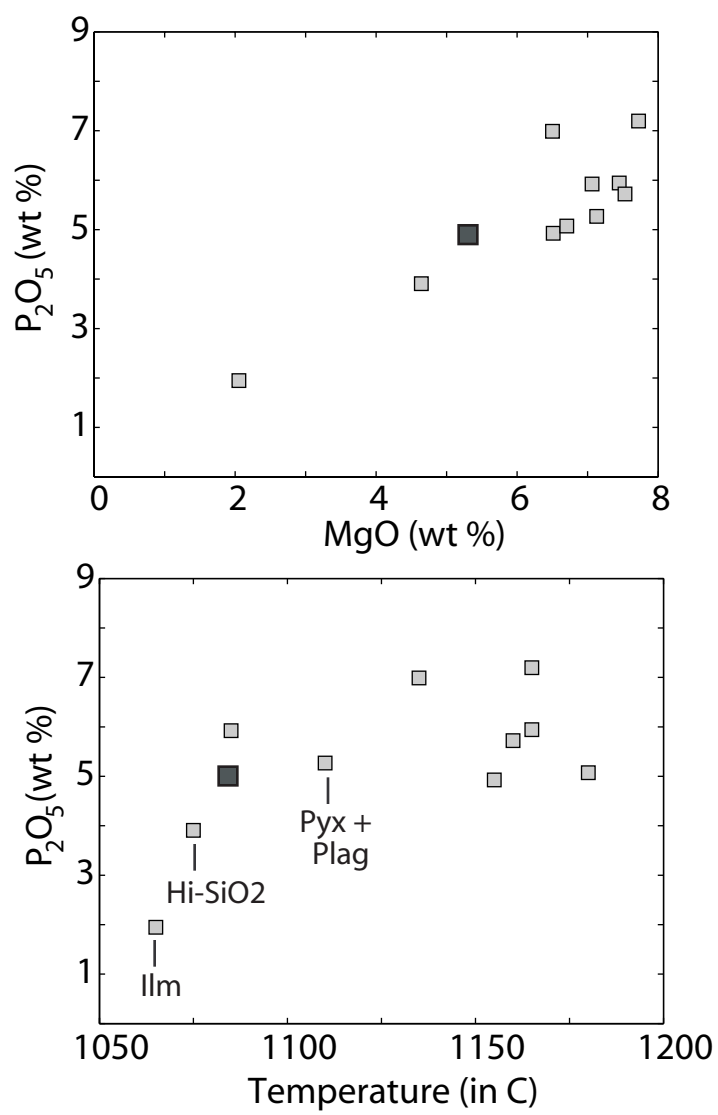


Figure 3

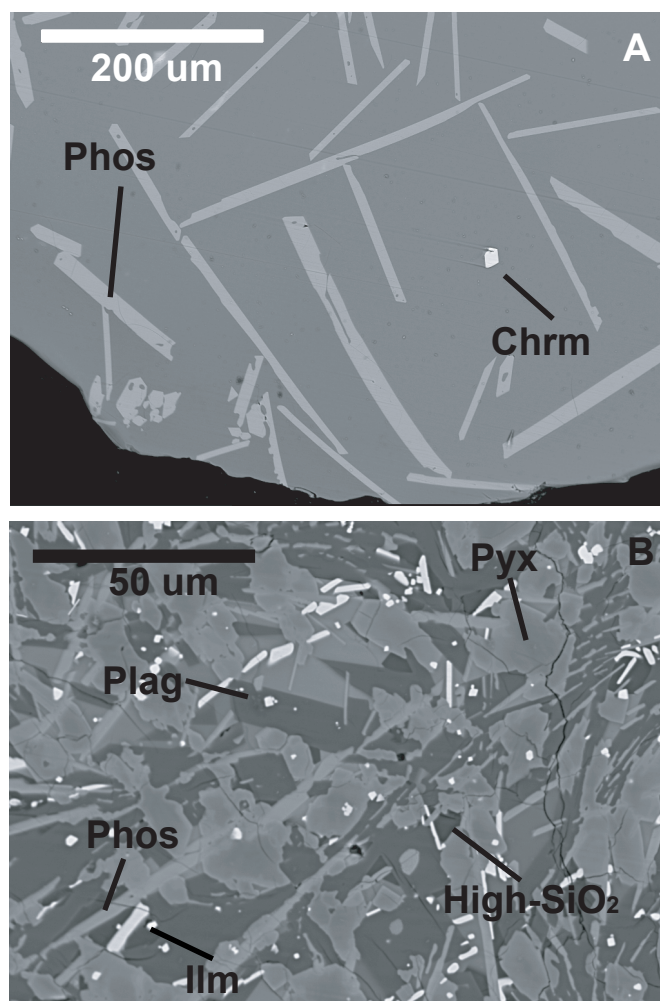


Figure 4

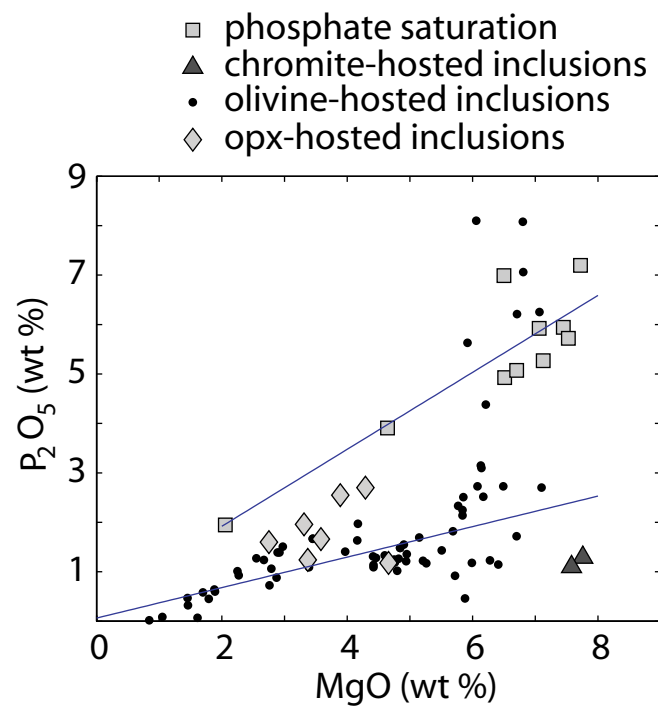


Figure 5

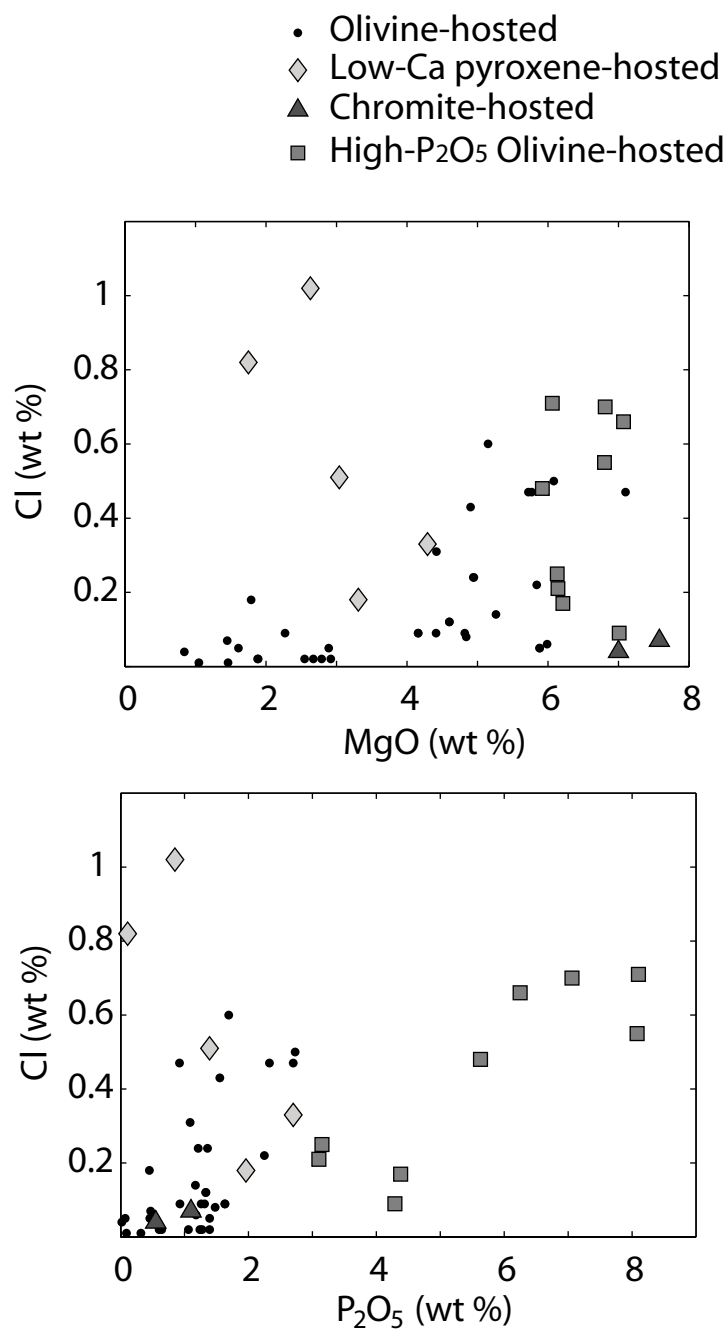


Figure 6

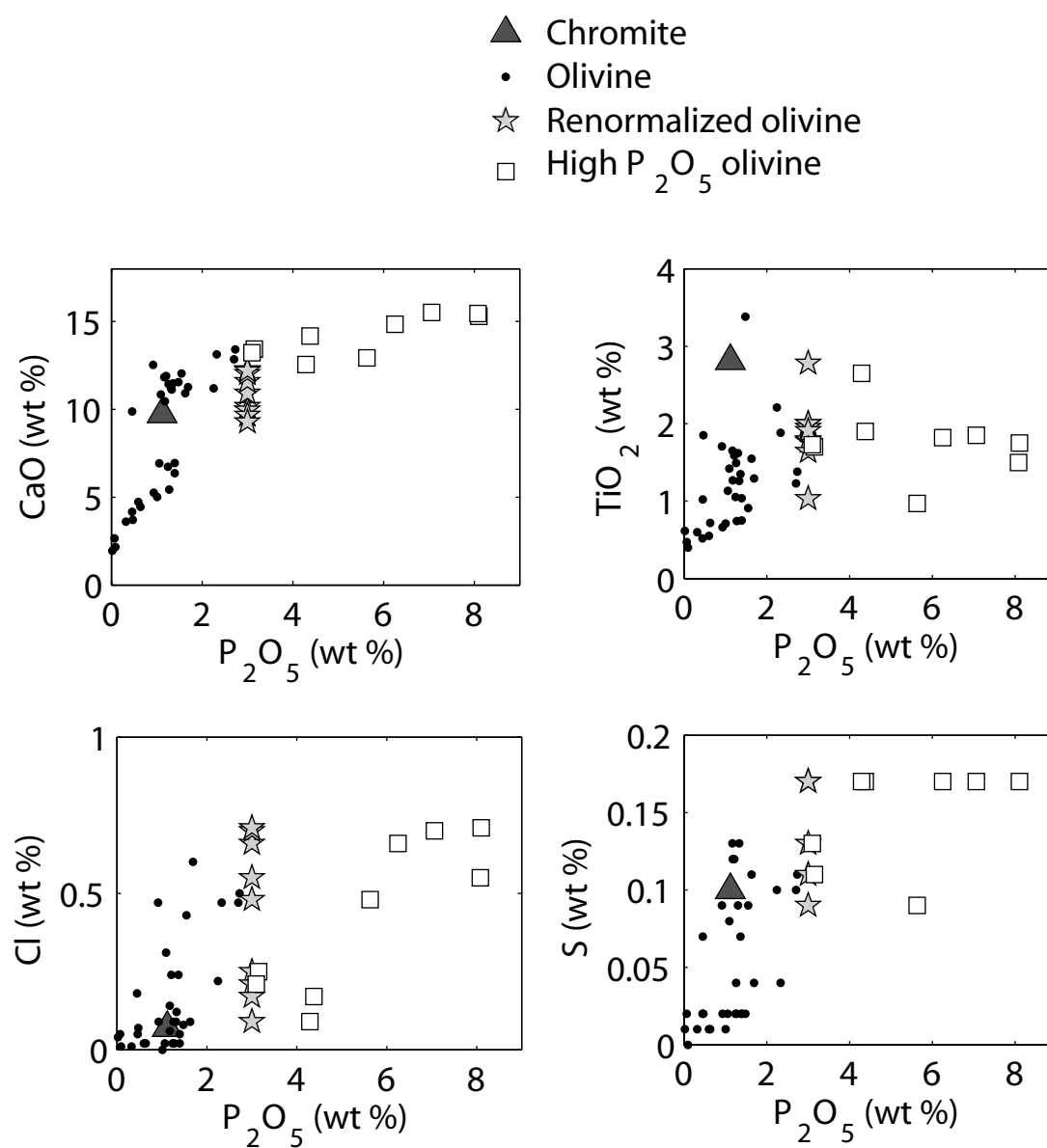


Figure 7

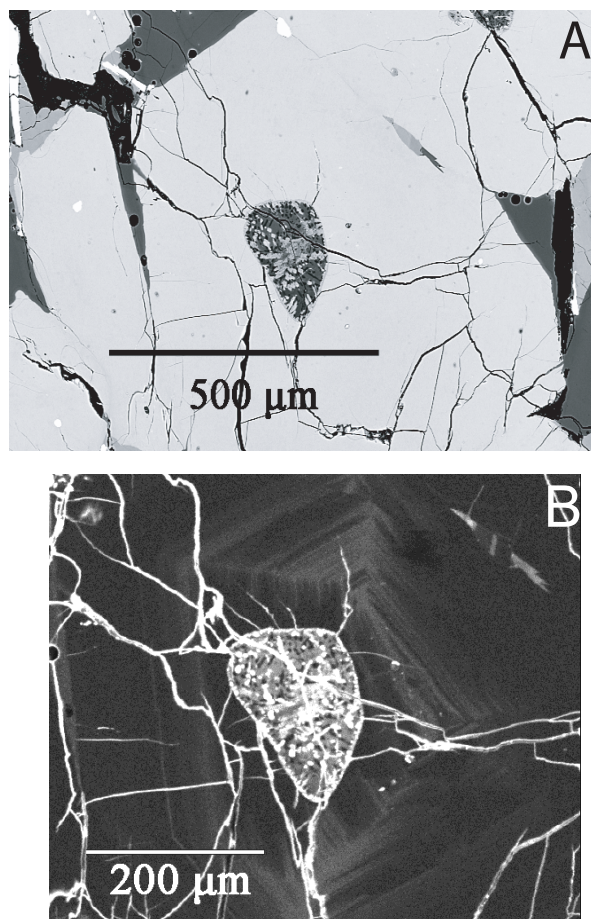


Figure 8

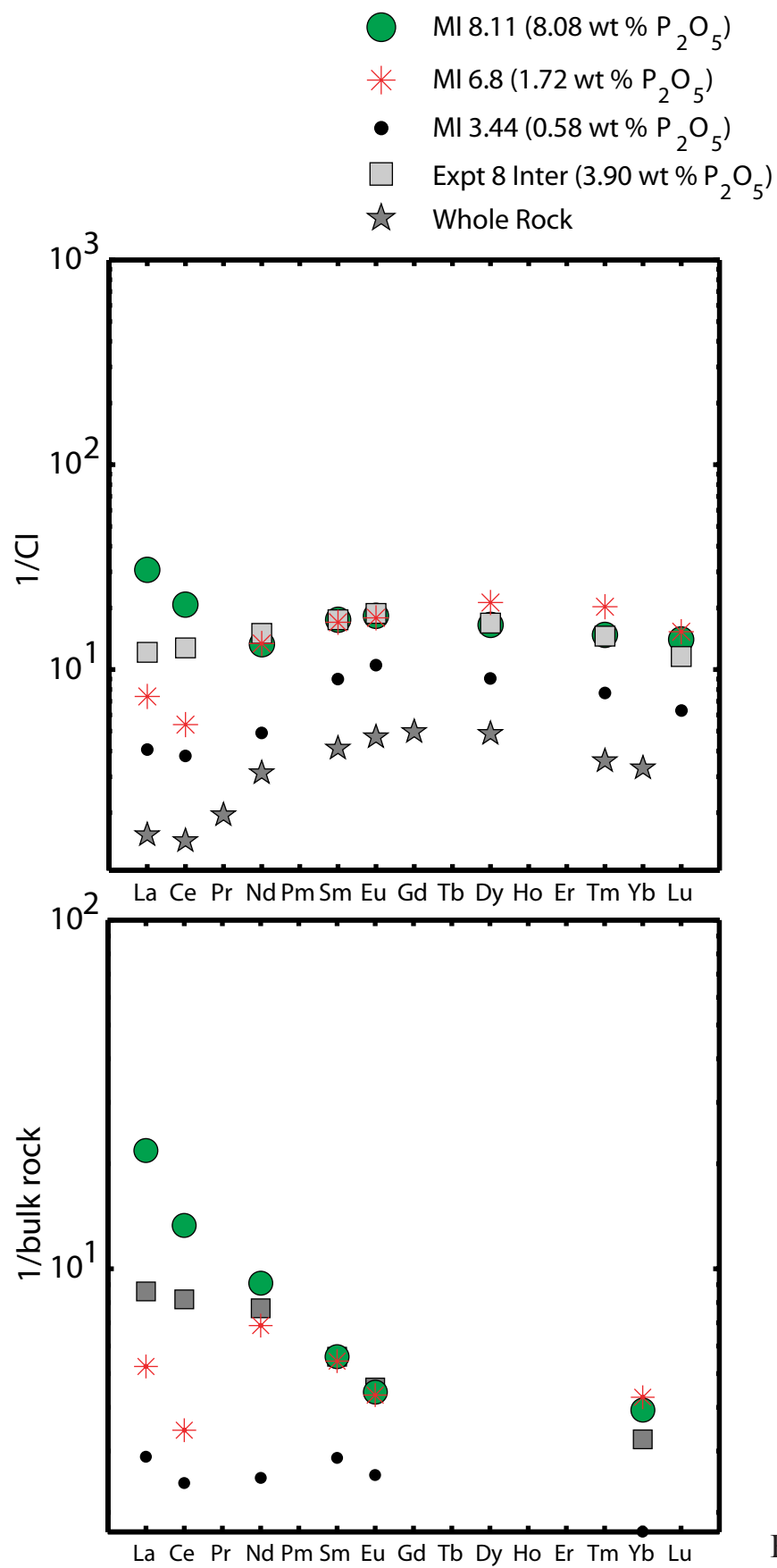


Figure 9

Table 1. Run conditions for phosphate saturation experiments.

Expt #	Temp (in C)	Press (in MPa)	Duration (in hours)	Oxidation	Mineral Assemblage*
PS2	1165	35	71	QFM – 3.7	Chrm
PS1	1165	35	28.5	QFM – 3.7	Chrm
PS5	1160	35	48	QFM – 3.7	Chrm
PS4	1155	37	48	QFM – 3.7	Chrm
PS8	1135	35	44	QFM – 3.5	Chrm
PS9	1110	35	71	QFM – 3.3	Chrm, High-Ca pyx, Plag
PS13	1085	35	72	QFM – 3.1	Chrm, Pyx, Plag
PS14	1080	35	72	QFM – 3.0	Chrm, Pyx, Plag
PS12	1075	35	72	QFM – 3.0	Chrm, Pyx, Plag, High-SiO ₂ phase
PS10	1065	35	72	QFM – 2.9	Chrm, Pyx, Plag, High-SiO ₂ phase, FeTi oxide
PS19 [†]	1080	35	75	QFM – 3.0	Chrm, Pyx, Plag

* All experiments contained phosphate crystals in addition to the minerals listed.

[†] Reversal experiment.

Table 2: Composition of accessory phases found in crystallization experiments.
Phosphate analyses from experimental samples and the Wilbeorce Apatite standard.

Experiment	PS13	PS19	Apatite standard		FeTi oxide
Na ₂ O	0.24	0.22	0.26	MgO	4.32
MgO	3.97	3.72	0.00	Al ₂ O ₃	0.24
P ₂ O ₅	46.39	46.08	41.42	TiO ₂	50.18
CaO	46.51	46.57	54.44	Cr ₂ O ₃	1.99
FeO	2.03	2.49	0.02	FeO	38.72
Other	---	---	2.00	MnO	0.61
Total	99.14	99.08	98.14	Total	96.05
Ca/P ₂ O ₅ (in moles)	2.54	2.56	3.33	FeO+MgO/TiO ₂	1.01

Table 3. Glass compositions in equilibrium with a phosphate saturated melt compared with melt compositions found in rehomogenized melt inclusions from ALH 77005 (Calvin and Rutherford, 2008).

Expt #	PS1	PS2	PS4	PS13	PS19	08-8	08-11	14-3
Temp	1165	1165	1155	1085	1080			
Press	35	35	37	35	35			
SiO ₂	46.06	49.32	47.41	46.36	48.13	44.26	39.49	46.58
TiO ₂	4.31	2.07	4.24	3.32	4.47	0.97	1.5	2.65
Al ₂ O ₃	11.3	11.98	11.18	9.98	10.34	10.41	7.87	10.78
FeO	6.8	7.85	9.09	11.54	13.14	15.98	17.54	13.00
MnO	0.03	0	0.11	0.23	0.28	0.45	0.41	0.47
MgO	7.72	7.45	6.51	7.06	5.25	5.92	6.8	7.01
CaO	14.31	13.19	12.62	12.38	11.34	12.93	15.46	12.55
Na ₂ O	1.64	1.93	1.87	1.83	1.76	1.84	1.38	1.89
P ₂ O ₅	7.2	5.94	4.93	5.92	4.90	5.63	8.08	4.29
K ₂ O	0.09	0.14	0.14	0.15	0.20	0.64	0.31	0.12
Total	99.46	99.87	98.09	98.77	99.95	99.04	98.95	99.54

Mineral	N/A	N/A	N/A	Pyx	Plag	Pyx	Plag	Olivine	Olivine	Olivine
SiO ₂				52.55	55.59	52.70	55.80	38.12	38.12	
FeO				12.46	0.42	16.21	0.51	22.42	22.42	
MgO				25.00	---	22.94	---	38.31	38.31	
Al ₂ O ₃				2.25	27.27	1.53	27.11	0.15	0.15	
Na ₂ O				0.09	4.71	0.08	4.66	0.01	0.01	
MnO				0.34	---	0.38	---	0.57	0.57	
TiO ₂				0.60	---	0.67	---	0.05	0.05	
Cr ₂ O ₃				0.80	---	0.60	---	0.16	0.16	
CaO				4.19	10.83	3.33	11.55	0.48	0.48	
K ₂ O				0.00	0.05	0.02	0.09	---	---	
Mg_Nu m										
Total				98.28	98.87	98.46	99.72	100.26	100.26	

* N/A = Experiments that did not have major mineral phases to analyze.

Table 4: Major, volatile, and REE compositions of melt for 3 melt inclusions (3.44, 6.8, and 8.11) and one interstitial melt (8.interstitial) in partially reheated chips of ALH 77005.

	3.44	6.8	8.Inter	8.11
SiO₂	65.98	48.34	46.24	39.49
TiO₂	0.71	1.52	2.45	1.50
Al₂O₃	16.35	10.10	11.40	7.87
Cr₂O₃	0.00	0.22	0.15	0.10
FeO	4.20	16.21	12.71	17.54
MnO	0.06	0.46	0.38	0.41
MgO	1.70	6.70	7.28	6.80
CaO	3.82	11.51	12.00	15.46
Na₂O	3.47	1.79	2.00	1.38
P₂O₅	0.58	1.72	3.90	8.08
K₂O	2.29	0.18	0.45	0.31
total	99.17	98.74	98.96	98.94
H₂O(wt%)	0.039	0.029	0.034	0.369
F (ppm)	957	165	280	580
S (ppm)	82	1330	1148	*
Cl (ppm)	157	3608	3712	5319
La	4.07	7.39	12.13	30.74
Ce	3.79	5.38	12.76	20.77
Nd	4.90	13.40	15.02	13.27
Sm	8.99	17.03	17.51	17.51
Eu	10.54	17.88	18.79	18.25
Dy	9.04	21.27	16.85	16.56
Er	7.69	20.25	14.57	14.76
Yb	6.29	15.30	11.59	14.06

* Sulfur was above the detectability range.

Appendix 1. Glass compositions for saturation experiments.

Experiment	PS4	PS13	PS14	PS12	PS7	PS2	PS1	PS5	PS8	PS9	PS10
Pressure	370	370	370	370	355	350	350	350	350	350	350
Temperature	1155	1085	1080	1075	1112	1165	1165	1160	1135	1110	1065
SiO ₂	47.41	46.36	48.06	50.24	52.31	49.32	46.06	49.31	45.46	48.73	57.12
TiO ₂	4.24	3.32	3.13	5.28	3.19	2.07	4.31	2.92	2.27	2.80	3.26
Al ₂ O ₃	11.18	9.98	11.31	10.44	12.52	11.98	11.30	11.57	10.88	11.83	13.10
FeO	9.09	11.54	10.22	11.95	3.40	7.85	6.80	6.32	11.38	9.55	10.66
MnO	0.11	0.23	0.26	0.37	0.00	0.00	0.03	0.27	0.00	0.36	0.24
MgO	6.51	7.06	6.70	4.64	8.31	7.45	7.72	7.53	6.50	7.13	2.05
CaO	12.62	12.38	12.13	10.43	12.62	13.19	14.31	13.47	13.95	12.76	8.28
Na ₂ O	1.87	1.83	1.87	1.74	1.96	1.93	1.64	2.22	1.82	2.22	2.38
K ₂ O	0.14	0.15	0.13	0.25	0.13	0.14	0.09	0.12	0.13	0.12	0.73
P ₂ O ₅	4.93	5.92	5.07	3.91	4.91	5.94	7.20	5.72	6.99	5.27	1.95

Appendix 2. Mineral compositions for saturation experiments.

Experiment	PS13			PS9			PS10			PS19		
Pressure	370			350			350					
Temperature	1085			1110			1065					
	Hpx	Plg	Lpx	Hpx	Plg	Lpx	Hpx	Plg	Lpx	Hpx	Plg	
SiO ₂	51.08	55.59	54.90	50.71	54.76	52.33	49.05	56.11	52.70	51.00	55.83	
TiO ₂	1.2		0.35	1.27		0.93	1.96		0.67	1.32		
Al ₂ O ₃	2.84	27.27	0.70	2.46	28.23	1.22	4.29	27.34	1.53	2.87	27.83	
FeO	9.53	0.42	11.93	6.36	0.48	18.16	7.67	0.63	16.21	8.68	0.45	
MnO	0.29		0.38	0.26		0.59	0.28		0.38	0.32		
MgO	19.63		25.98	17.80		21.04	16.89		22.94	17.37		
CaO	12.94	10.83	4.91	17.33	11.80	4.95	15.66	10.71	3.33	15.94	10.97	
Na ₂ O	0.28	4.71	0.04	0.35	4.06	0.05	0.3	4.46	0.08	0.34	4.47	
K ₂ O	0.01	0.05	0.00	0.00	0.04	0.01	0	0.12	0.02	0.00	0.06	

Chapter 4: Shergottite formation

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Abstract

Shergottite EETA 79001 is unique among the martian meteorites in that it contains two basaltic lithologies (lithologies A and B) separated by a planar contact. Lithology A contains megacrysts of an olivine-pyroxene mafic cumulate. This study reports the results of crystallization experiments on the Eg composition, the parental melt of EETA 79001 lithology A, and partial melting experiments on chips of lithology A. Crystallization of the Eg composition produces olivine and low-Ca pyroxene that is consistent with the composition of those phases in the megacrysts. Further crystallization produces plagioclase and high-Ca pyroxene consistent with the basaltic groundmass of lithology A. The residual melt composition is consistent with the melts produced through reheating lithology A. The primitive shergottite Yamato 980459 is much higher in MgO concentration than the Eg composition used for these experiments, however models assuming olivine crystallization from the Y98 bulk rock produce a liquid composition very similar to Eg. Moreover, the bulk rock compositions for lithology B and the evolved basaltic shergottite QUE94201 also fall along this liquid line of descent suggesting it is valid for all shergottites whose bulk rock composition is representative of the liquid from which it formed. When this liquid line of descent is compared with Gusev crater rocks, it is determined that the shergottite liquid line of descent is higher in SiO₂ and CaO but lower in all other major elements. This suggests that either the Gusev crater rocks are not representative of the magma from which they form or they did not form from a shergottite-like magma.

Introduction

Based on age, mineralogy, and isotopes, martian meteorites have been divided into 4 groups: shergottites, nakhlites, chassignites, and the single meteorite ALH 84001 (McSween and Treiman, 1998 and references therein). Of these four groups, the shergottites have the youngest crystallization ages and comprise the largest group of martian meteorites with approximately 23 unique members. The shergottites are further subdivided into basaltic, olivine-phyric, and lherzolitic end members (Goodrich, 2003). With the advent of analyses from the martian rovers, Spirit and Opportunity, many researches have drawn analogies between the rocks at the surface of Mars with the bulk rock chemistry and mineralogy found in the shergottites (McSween et al., 2006). Thus understanding the magmatic composition of the shergottites and their petrogenetic evolution could potentially shed light on large-scale processes on Mars.

EETA 79001 (EETA) is unique among the martian meteorites in that it has a planar contact that separates two lithologies (McSween and Jarosewich, 1983). Lithology A (lith A) is a vesicular basalt containing crystals of plagioclase and pyroxene. In contrast, Lithology B (lith B) is coarser grained and composed primarily of phenocrysts of pigeonite, augite, and maskelynite. Based on the mineralogy and grain sizes, lith A is grouped with the olivine-phyric shergottites while lith B is grouped with the basaltic shergottites. In addition, lith A contains megacrysts (lith X) of olivine, orthopyroxene, and chromite that are petrologically similar to lherzolitic shergottites such as ALH 77005 (ALH) and LEW 88516 (LEW) (Treiman, 1993). Thus EETA has examples of all three types of shergottites within a single sample. Because the three distinct textures and lithologies are physically linked, understanding how these magmas

evolved will allow constraints to be placed not only on the relationships between the three lithologies in EETA but also the three classes of shergottites.

This study examines the melt compositions of EETA in three ways. First, crystallization experiments are performed on the Eg composition (Longhi and Pan, 1989), which is a best estimate of the parental melt of lith A based on analyses of the mineral phases in that samples. The crystallization experiments, performed at 1 atm and QFM, produce a liquid line of descent and the associated mineral assemblages to be compared with the apparent mineralogy of EETA. Second, partial melting experiments are performed on chips of EETA lith A. The reheating experiments produce a near equilibrium between a liquid ground mass and the associated mineral assemblages. This allows a comparison between the mineral-melt assemblages created in the crystallization experiments with those found in the natural sample. Finally, these two melt assemblages are compared with the liquid line of descent and mineral-melt equilibrium assemblages determined for the lherzolitic shergottites in Calvin and Rutherford (2008) and Calvin and Rutherford (Chapter 2). The addition of these recent studies of the lherzolitic shergottites allows the comparison of lith X with lith A and their relationship to each other during the petrogenesis of this rock.

Methods

Partial Melting experiments. Reheating experiments were performed on chips of EETA 79001 lithology A, following the procedure in Calvin and Rutherford (2008). Chips were surrounded in graphite and sealed in platinum tubing. The graphite fixes the oxidation state of the experiments between QFM -2.5 and -3.0 depending on the pressure

of the experiment as the graphite reacts with oxidized (terrestrial) elements with in the sample. The temperature of the experiments varied between 1145 and 1165°C. Run conditions can be found in Table 1. After the initial experiments, it was determined that experiments run for 24+ hours closely approached Fe and Mg exchange equilibrium between the olivine host and the melt inclusion. Samples were quenched by immersing the pressure vessel in H₂O and thick sections were made. Chips from the experiments were polished until a melt pocket was exposed. Once exposed, the melts were analyzed for major, minor, and some trace elements. The associated minerals were also analyzed for the same suite of major and minor elements.

Minerals and associated melts were analyzed for major and minor elements using a Cameca SX-100 electron microprobe at Brown University. An accelerating voltage of 15 kV and a focused beam (1-2 μm) were used for all analyses. Glasses were analyzed with a 10 nA beam while minerals were analyzed with a 15 nA beam. Complete microprobe run conditions are as those found in Calvin and Rutherford (2008). Two polished thin sections of EETA 79001 were also used in this study: 445 and 447 from NASA Johnson Space Center in Houston, TX.

Crystallization experiments. Crystallization experiments were performed on the Eg composition determined from point-counting statistics of EETA lith A (Longhi and Pan, 1989). The experiments were run in a 1 atmosphere, gas mixing furnace at an $f\text{O}_2$ of QFM with final temperatures ranging between 1350 and 1100°C. The charge was taken 50°C above the liquidus for 24 hours to saturate the Pt loop with Fe. The temperature was then dropped to the final temperature and the charge allowed to equilibrate for at

least 48 hours. In addition, one complete fractionation was done. Eg3 was synthesized from the residual glass found in Eg crystallization experiments. These crystallization experiments were done in the same manner as those from the Eg compositions. Run conditions can be found in Table 1. Microprobe analyses on the glass and minerals were performed at the Johnson Space Center on the Cameca Cambax microprobe. Because the sample used to saturate the platinum wire was not discarded prior to running the experiments, there is potential that the Fe concentrations in some experiments are lower and/or higher than is appropriate.

Results

Partial melting experiments. Reheating experiments produced interstitial melts with two different types of associated mineral assemblages: olivine with low-Ca pyroxene and chromite (Figure 1a) and high-Ca pyroxene with plagioclase (Figure 1b). The first assemblage contained olivine of Fo_{62} and a low-Ca pyroxene ranging between $\text{En}_{61}\text{Fs}_{26}\text{Wo}_{13}$ and $\text{En}_{57}\text{Fs}_{24}\text{Wo}_{19}$. Chromites have Cr/Al ratios of around 5. The second assemblage contained high-Ca pyroxene of $\text{En}_{45}\text{Fs}_{21}\text{Wo}_{35}$ and plagioclase ranging between $\text{An}_{60}\text{Ab}_{39}\text{Or}_1$ and $\text{An}_{65}\text{Ab}_{34}\text{Or}_0$. Analyses of glasses produced during partial melting experiments along with the minerals in equilibrium with the melts can be found in Table 2. In Figure 2, the melts are shown to be tightly constrained based on the mineral assemblage, however the two mineral assemblages differ significantly in all major elements with the exception of CaO. In a given experiment the mineral assemblage in equilibrium with melt sometimes varied. However regardless of the mineral phases present, the melt composition within a given experiment tends to be homogenous.

Crystallization experiments. In the 1 atm Eg crystallization experiments, olivine was the first phase to appear on the liquidus, followed by low-Ca pyroxene. The temperature at which these phases began crystallizing is shown in Figure 3. The olivine crystallizing at high temperatures (1250-1278 °C) has an Mg # of 78 while at low temperatures (1100 °C) olivine rims have an Mg# of 47. Low-Ca pyroxene began crystallization at 1260 with CaO concentrations of 1.8 wt % ($\text{En}_{73}\text{Fs}_{20}\text{Wo}_7$). At low temperatures (1100 °C), pyroxenes have CaO concentrations (7.7 wt %) consistent with pigeonite ($\text{En}_{45}\text{Fs}_{32}\text{Wo}_{23}$). Analyses of glasses in the crystallization experiments along with the minerals in equilibrium with them are given in Table 3. As shown in Figure 2, the MgO concentration in the glass decreases with increasing crystallization of olivine and low-Ca pyroxene while Al_2O_3 , CaO, and all minor elements increase.

Crystallization experiments starting from the Eg3 compositions show different ranges in mineral assemblages and compositions. Eg3 produced olivine, low-Ca pyroxene, and plagioclase with decreasing temperature. Olivine ranged between Fo_{65} and Fo_{48} with the higher Mg # corresponding to higher crystallization temperatures. CaO concentrations in the pyroxenes of the Eg3 experiments ranged between 6.0 and 9.3 wt % ($\text{En}_{53}\text{Fs}_{29}\text{Wo}_{19}$ to $\text{En}_{39}\text{Fs}_{34}\text{Wo}_{27}$). Eg3 experiments were the only experiments to produce plagioclase. Plagioclase came on the liquidus at 1100°C with a composition of $\text{An}_{72}\text{Ab}_{28}\text{Or}_0$ at high temperatures and $\text{An}_{64}\text{Ab}_{36}\text{Or}_0$ at low temperatures. The residual melt compositions in these experiments are shown in Figure 4. As mentioned in the methods section, the sample was not discarded after being used to saturate the platinum

wire. Therefore, the Fe concentrations in some runs may not be appropriate with respect to the other major and minor elements.

Experimental conditions and shergottite petrogenesis.

The major factors governing the appearance and composition of minerals present in the shergottites are considered to be pressure, oxygen fugacity, and water content for any given temperature. Pressure was shown to be a very important factor in determining the crystallization of the lherzolitic shergottites in that experiments run at high pressure failed to produce olivine and instead formed a reaction relationship with low-Ca pyroxene (Calvin and Rutherford, 2008). Lithology A of EETA 79001 contains megacrysts similar in mineralogy and composition to the lherzolitic shergottites (McSween and Jarosewich, 1983). As both the megacrysts and the lherzolitic shergottites contain abundant olivine, all experiments were run at pressures of less than 38 MPa. Oxygen fugacities ranging from QFM – 4 to QFM (e.g. Ghosal et al., 1998; Hale et al., 1999; Wadhwa, 2001; Herd et al., 2002; McCanta et al., 2004) have been suggested for the shergottites. All experiments in this study are within the range defined by these previous studies and as will be shown in the next section, variations in fO_2 over this range did not effect the partitioning of Fe into Fe-bearing phases such as olivine and low-Ca pyroxene. Finally, if water is present in significant amounts, it can have a significant effect on the crystallization and liquid line of descent of a mafic magma (Wasserburg, 1957; Kushiro, 1969; Kushiro, 1975). Since there is still no evidence of significant H_2O having been present in the ALH 77005 and EETA 79001 magmas (e.g. no hydrous phases have been reported), no H_2O was added to these experiments.

Discussion

Petrogenetic relationships of EETA lithologies

Determining the parental melts of the SNC meteorites is a crucial step towards understanding the interior of Mars and the processes by which the martian rocks crystallized. The crystallization experiments in this study were performed on the Eg composition (Longhi and Pan, 1989), which was determined to be the parental melt of EETA lith A through point counting of mineral phases within the lithology which texturally appear to be cumulus crystals. There are some potential areas of danger when using point counting methods such as under or overestimating rim material, non-representative samples, etc. (Herd et al., 2002). However, if the Eg composition represents the parental melt, crystallizing this magmatic composition under the right conditions (ie., pressure, oxygen fugacity, water content, etc.) should reproduce the mineralogy of EETA lith A.

By comparing the melt and mineral assemblages found in the crystallization experiments with those found in the melting experiments, it is possible to assess whether the crystallization of Eg could have produced a rock similar to lith A including the megacrysts within it. Lithology A is a vesicular basalt containing crystals of plagioclase and pyroxene (McSween and Jarosewich, 1983). In addition, lith A contains megacrysts (lith X) of olivine, orthopyroxene, and chromite that are petrologically similar to ilherzolithic shergottites (Treiman, 1993). However the megacryst minerals are zoned and sometimes contain halos at the crystal margin, suggesting that they were out of

equilibrium with the magma that formed the surrounding lithology (McSween and Jarosewich, 1983).

Despite plagioclase and pyroxene being the dominant mineral phases in EETA's lith A, olivine was the first phase on the liquidus during the crystallization experiments from the Eg composition. Olivines range from Mg# of 78 to 52 with the higher numbers corresponding to higher temperature experiments. Olivine cores in megacrysts of lithology A have Mg# of 76 while the rims are Mg # 55 (Herd et al., 2002) and therefore olivine cores of the megacrysts are consistent with olivines found in the high temperature range of the crystallization experiments while the olivine rims are consistent with the olivine rims. Pyroxene follows olivine on the liquidus in the crystallization experiments and ranges in composition from 1.69 wt % to 8.68 wt % CaO, again depending on the temperature. Mg/Fe ratios of the pyroxene range between $\text{En}_{73}\text{Fs}_{20}$ and $\text{En}_{45}\text{Fs}_{32}$. In EETA's lith A, the CaO concentration of the pyroxene ranges from 3.03 to 14.5 wt % with Mg/Fe ratios producing pyroxene between $\text{En}_{53}\text{Fs}_{29}$ to $\text{En}_{39}\text{Fs}_{34}$ (McSween and Jarosewich, 1983). The range of pyroxene and olivine compositions are shown in Figure 5 along with the compositions of those phases in the crystallization experiments. The range of pyroxene in lith X is consistent with the range of pyroxene in the Eg crystallization experiments.

Plagioclase in the form of maskelynite is zoned from $\text{An}_{63}\text{Ab}_{36}$ in the core to $\text{An}_{56}\text{Ab}_{43}$ on the rim (McSween and Jarosewich, 1983). Plagioclase did not appear in the Eg crystallization experiments. Crystallization experiments of Eg3, which represents a residual melt from the Eg crystallization experiments, did produce plagioclase. These crystals ranged from $\text{An}_{72}\text{Ab}_{28}$ at high temperatures (1100°C) to $\text{An}_{64}\text{Ab}_{35}$ (1075°C) at

low temperatures. Thus the crystallization experiments were able to reproduce the core compositions of the pyroxenes and plagioclases in the lith A matrix as well as the olivines and pyroxenes found in lherzolitic aggregates found in lithology A. This suggests that a) the Eg composition is a good parent melt composition for EETA lith A and b) that the lherzolitic component (lith X) can be derived from the same melt as lith A. The disequilibrium textures which amount to zoning features in the megacrysts are consistent with the composition of olivine and pyroxene that formed late in the Eg and Eg3 crystallization. This suggests that the megacrysts may be cognate xenoliths that formed early in the EETA crystallization, settled out of the magma and were subsequently redistributed during the crystallization of lith A.

Equilibrium melts in EETA79001 and the Eg liquid line of descent.

The crystallization experiments also allow melts in equilibrium with various mineral phases to be compared with each other. Because EETA's ground mass is microcrystalline, the residual melts are compared with melts formed in reheating experiments on lith A. To better compare the crystallization and partial reheating experiments, the EETA melts have been subdivided in Figure 2 according to the associated mineral assemblages. This is important as many of the melts found in the crystallization experiments were in equilibrium with olivine and low-Ca pyroxene only, while melting experiments formed melts in equilibrium with Cr-spinels, high-Ca pyroxene and plagioclase in addition or instead of low-Ca pyroxene and olivine. The EETA 79001 partial melting experiments found in equilibrium with low-Ca pyroxene and olivine effectively match both the magmatic and mineral compositions of the Eg liquid

line of descent suggesting that these olivine rich regions could have formed through dry crystallization of the Eg composition. The melts in equilibrium with high-Ca pyroxene and plagioclase-rich reheating experiments show a significantly lower FeO concentration than either the olivine- and pyroxene-rich partial melting experiments or the crystallization experiments run from Eg.

Lithology X is petrologically similar to lherzolitic shergottites ALH 77005 and LEW 88516 (Treiman, 1993). Thus a comparison can be made to the crystallization experiments performed on ALH 77005 parental melt by Calvin and Rutherford (Chapter 2). ALH 77005 contains two lithologies (McSween et al., 1979): one lithology composed chiefly of euhedral chromite and olivine (Fo_{75}), poikilitically enclosed by low-Ca pyroxene ($\text{En}_{74}\text{Fs}_{20}\text{Wo}_6$ to $\text{En}_{53}\text{Fs}_{22}\text{Wo}_{25}$) with interstitial maskelynite and high-Ca pyroxene and a second lithology that contains subhedral olivine, low-Ca pyroxene with interstitial maskelynite, Ti-rich chromite, ilmenite, troilite, and merrillite.

Compositionally, the megacryst minerals in EETA 79001 are similar to ALH 77005 (Figure 5) except that they are normally zoned and sometimes contain halos at the crystal margin; these observations suggests the minerals were out of equilibrium with the magma that formed the surrounding lithology (McSween and Jarosewich, 1983) at the conditions prevailing in the magma.

Because of the mineralogical similarities between ALH and lith X, the residual melt composition from anhydrous crystallization experiments on ALH parental melt (Calvin and Rutherford, 2008) can be compared with the melt composition from Eg crystallization experiments. This liquid line of descent is shown on Figure 6. As is shown, the starting melt composition for the ALH 77005 melt plots on the Eg liquid line

of descent for SiO_2 and CaO concentrations but is slightly lower in FeO and higher in Al_2O_3 . The major element compositions in the olivine and low-Ca pyroxene at this stage of crystallization are consistent between the experiments so this can not explain the differences in the FeO and Al_2O_3 . There are several possible explanations for the discrepancy in FeO and Al_2O_3 . The first depends on oxygen fugacity. The Eg crystallization experiments were performed at QFM while the ALH crystallization experiments were performed at QFM – 1.7 to – 3.7. Herd et al. (2002) noted that crystallization experiments on the Eg composition produced olivine only at higher oxidation states. Therefore the ratio of olivine to low-Ca pyroxene in experiments run at QFM would be higher than those run at QFM – 2 and olivine would be nonexistent at IW. As Fe partitions into olivine and low-Ca pyroxene differently, the change in oxidation state between the experiments might explain the differences in the FeO concentration. A second possibility is that the ALH 77005 parental melt contains three elements not included in the Eg synthesis used for this study: K_2O , P_2O_5 , and Cr_2O_3 . As K_2O would only be incorporated in late stages of crystallization, it probably does not effect the crystallization of this rock. P_2O_5 however is in high abundance in many martian rocks and can move the boundary between olivine and low-Ca pyroxene such that low-Ca pyroxene crystallization is favored, thereby changing the ratio of low-Ca pyroxene and olivine in the rock. In addition, chromite is the first phase on the liquidus in ALH and presumably in the megacrysts of EETA. Chromite would incorporate small amounts of MgO , FeO , and Al_2O_3 . While the effect on the liquid line of descent would be minimal, the absence of P_2O_5 and Cr_2O_3 , could explain the discrepancy in the FeO and Al_2O_3 values between ALH and Eg liquid lines of descent. It should also be noted that the ALH

parental melt is from a chromite-hosted melt inclusion that may have formed prior to olivine and/or low-Ca pyroxene crystallization. There is no evidence that this melt was in equilibrium with olivine and low-Ca pyroxene at the time of crystallization and this could also result in the discrepancy.

What is significant about the liquid lines of descent is that the CaO, Al₂O₃, and FeO all merge. The path of Al₂O₃ would change with decreasing temperature and would likely meet the ALH crystallization experiments as Al₂O₃ should begin to turn down with the onset of plagioclase crystallization. In fact, two complete separations of the Eg magma were done from the liquid line of descent and both of these separates show the decrease in Al₂O₃ and are more consistent with the ALH liquid line of descent (Figure 6). The implication of this overlap is that both lith X and lith A could have been formed from the same parental melt composition. Lith X could be a cognate xenocryst that was formed early in the magmatic evolution of the parent melt and then redistributed later in the magmas life. This is consistent with Wadhwa et al. (1994) who suggested a similar scenario and would explain why the overgrowths on olivine and pyroxene in the megacrysts are consistent with the olivine and pyroxene compositions in the late stage of the Eg crystallization experiments.

Petrogenesis of Shergottites

The shergottites have been grouped together based on their young ages and composition (McSween and Treiman, 1998). The shergottite class has been further subdivided into basaltic shergottites that contain pyroxene and plagioclase, olivine-phyric shergottites that are basaltic in nature but contain higher amounts of olivine, and

hercynitic shergottites that contain large olivine and low-Ca pyroxene grains interspersed with high-Ca pyroxene and plagioclase and appear to be cumulates (Goodrich, 2003).

The major differences between the shergottites are in the mineralogy and the size of the mineral grains, although some shergottites such as EETA also have different trace element and radiogenic element signatures as well as different crystallization and ejection ages (McSween and Treiman, 1998). This suggests that while similar in many respects, the shergottites are not necessarily related as if formed from a single magma body. Nevertheless, given their mineralogical and geochemical similarities, it is reasonable to assume that under similar pressure, temperature, oxygen fugacity and water concentrations, these melts would have evolved similarly. Therefore, this study considers the major element evolution of the shergottite parent melts in an effort to understand how the shergottites could have evolved under different conditions and how the shergottites could relate to one another through a similar parent source.

The most primitive shergottite, Yamato 980459 (Y98), is an olivine-rich shergottite. The meteorite is thought to be a quenched magma that contained no cumulus crystals and therefore the bulk rock is interpreted as the magmatic composition (Dalton et al., 2005). Estimates of the MgO concentrations for this rock range between 18.10 and 19.64 wt %. As shown in Figure 7, the Y98 magma is considerably more primitive (high MgO) than either the ALH or Eg parent melt compositions. However, based on the phase diagram developed for the shergottites by Calvin and Rutherford (Chapter 2), a molten Y98 would be solidly within the olivine field at low pressures (<500 bars) (Figure 8). Crystallization of olivine would bring the Y98 residual melt close to the parental melt of ALH and the liquid line of descent for EETA lith A (Figure 7). Experiments were

conducted on the ALH parent melt and it was determined that this melt sits along the boundary curve that separate olivine from low-Ca pyroxene at low-pressures (Calvin and Rutherford, Chapter 2). At the point that Y98 intersected the EETA liquid line of descent it would proceed to follow the liquid line of descent defined by EETA and crystallize low-Ca pyroxene. Based on the reasoning above, the composition of the residual glass during Y98 crystallization would eventually meet the composition of the ALH parental melt, if equilibrium crystallization is assumed. Therefore the phase diagram developed for the lherzolitic shergottites would still be applicable for Y98 after crystallization brings it to MgO concentrations of 10 wt % or lower.

For comparison, the bulk rock composition of QUE94201 (QUE), an evolved basaltic shergottite, has also been plotted on Figure 7. McSween et al. (1996) have argued that the bulk rock composition of QUE is likely a true representative of a shergottite magma because the rock does not contain cumulus pyroxene. QUE plots close to the liquid line of descent defined by the Eg crystallization experiments except in SiO₂ where it is almost 2 wt % lower than the Eg crystallization experiments. QUE plots closer to the composition of EETA partial melts in equilibrium with plagioclase and high-Ca pyroxene which is also consistent with the mineralogy of QUE. Thus the bulk rock of this basaltic shergottite plots where it would be expected for a plagioclase and pyroxene-bearing shergottite. Again we note that the Eg crystallization experiments do not include the minor elements Cr₂O₃, P₂O₅, and K₂O which were present in QUE; the addition of these elements might explain slight discrepancy in the overall major element composition.

As discussed in Calvin and Rutherford (Chapter 2) and shown in Figure 8, the ALH parental melt is very close to the boundary curve that separates olivine from low-Ca pyroxene. Therefore, small changes in pressure would change the ratio of olivine to low-Ca pyroxene. In fact, despite ALH being an olivine-rich meteorite, crystallization at pressures greater than 50 MPa would produce a rock completely devoid of olivine. If we apply this to basaltic shergottites and olivine-phyric shergottites, the presence or absence of olivine can be explained through intrusions at different depths. Deep intrusions (> 35 MPa) or melts that had begun crystallizing at depth would fail to produce any olivine and instead produce low-Ca pyroxene, followed by high-Ca pyroxene, and eventually plagioclase. Shallower intrusions (< 50 MPa) could produce large olivines as observed in the olivine-phyric shergottites.

Implications for Gusev Crater Rocks

Spirit rover explored the basaltic rocks of Gusev crater and through rapping the surface of the rocks, it was possible to take numerous bulk rock measurements of these rocks (McSween et al., 2006). McSween et al. (2006) have shown that on the surface the Gusev basalts are similar in their mineralogical composition to the olivine-phyric shergottites in that they contain olivine that may range in composition from Fo₈₁₋₅₅. Although they also pointed out that the Na₂O and Al₂O₃ concentrations of the Gusev crater basalts are higher than those in the Shergottites, which they interpret as the absent or minimal amount of plagioclase in the olivine-phyric shergottites. Having defined the liquid line of descent and the relationships of the shergottites, if we assume that the rover bulk rock analyses are representative of the magmatic composition, it is now possible to

look at the Gusev crater rocks in comparison with the shergottites. This is shown in Figure 7 where the Gusev bulk rocks are placed along side the liquid lines of descent for Y98, EETA, and ALH. While the Gusev crater rocks show a reasonable differentiation trend in these plots, suggesting they may represent a liquid line of descent for the Gusev region magmas, they do not overlap the liquid line of descent for Y98 assuming olivine crystallization, nor do they intersect the experimentally determined liquid lines of descent for EETA and ALH (Chapter 2). This leaves two possibilities: the bulk rock measurements of the Gusev crater rocks do not represent the magmatic composition from which they form or the Gusev crater rocks represent a significantly lower in SiO_2 , FeO , and CaO and higher in Al_2O_3 , Na_2O , and K_2O . The fact that the melt is higher in alkalis while still being lower in SiO_2 suggests that this is not a good magmatic match to the shergottite melts.

Conclusion

1. Dry crystallization of the Eg parental melt composition produces a liquid line of descent on Harker diagrams that intersects the melts found in reheating experiments of EETA lith A. This observation supports the possibility that one liquid line of descent links the lith A parent melt to the observed rock.
2. Crystallization of the Eg parental melt composition defines trends which includes the parental melt composition of lherzolitic shergottite, ALH suggesting that dry crystallization of the lith A parental melt can produce the composition of the lherzolitic shergottites at least where major elements are concerned. Because the megacrysts of olivine and low-Ca pyroxene found in lith A, closely match the

mineralogy and composition of the lherzolithic shergottites (ALH), the Eg composition could have produced the megacrysts early in crystallization.

3. Olivine fractionation operating on the bulk rock compositions of the primitive shergottite Y98 yields a residual melt composition equivalent to the Eg composition, suggesting that a Y98-type magma could be a parental melt for the Eg composition.
4. The bulk rock composition of the evolved shergottite QUE, which is suggested to be the melt composition, falls near the liquid line of descent defined by the Eg and ALH crystallization experiments. Combining the QUE and Y98 results suggests that the magmatic composition of all shergottites can be modeled from this study.
5. The bulk rock composition of the Gusev crater basalts do not fall on the liquid line of descent for the shergottites as defined by this study. This suggests that either the bulk rock composition of the Gusev crater rocks is not consistent with the magmatic composition or that the Gusev crater rocks are not petrogenically related to the shergottite composition.

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Figure Captions

Figure 1. Backscatter images of partial melting experiments. A. Olivine, low-Ca pyroxene, and chromite with associate melt. B. Plagioclase and high-Ca pyroxene with residual melt.

Figure 2. Harker diagrams showing the residual melt composition from the Eg crystallization experiments along with the melt produced in partial melting experiments of EETA chips. Dark circles represent Eg crystallization experiments in equilibrium with with cpx and/or plag. Light circles represent Eg crystallization experiments in equilibrium with olivine and/or low-Ca pyroxene. Dark diamonds represent EETA melts in equilibrium with with cpx and/or plag. Light diamonds represent EETA melts in equilibrium with olivine and low-Ca pyroxene.

Figure 3. The liquidus temperatures for the different phases formed during the Eg and Eg3 crystallization experiments are shown.

Figure 4. Harker diagrams showing the relationship of ALH 77005 parental melt (triangle), EETA 79001 lith A interstitial melts (diamonds) and Eg crystallization experiments (circles) with a complete fractionation of the Eg liquid line of descent (Eg3 - stars).

Figure 5. Pyroxene and olivine compositions found megacrysts in EETA79001 (circles), Eg crystallization experiments (squares), and ALH 77005 (diamonds).

Figure 6. Harker diagrams showing the residual melt from dry crystallization experiments of the ALH 77005 parental melt (light diamonds) vs. the crystallization experiments from the Eg composition (circles).

Figure 7. Harker diagrams showing the relationship of Y98 and the residual melt composition assuming olivine crystallization (square) with ALH 77005 parental melt (triangle), EETA 79001 lith A interstitial melts (diamonds), the Eg crystallization experiments (circles), QUE bulk rock (stars) and Gusev crater bulk rock compositions (dark circles).

Figure 8. Phase diagram showing the relationship of the Y98 (diamond), Eg composition (small circle), ALH 77005 parental melt (triangle), and EETA 79001 melt in equilibrium with olivine and low-Ca pyroxene (large circle).

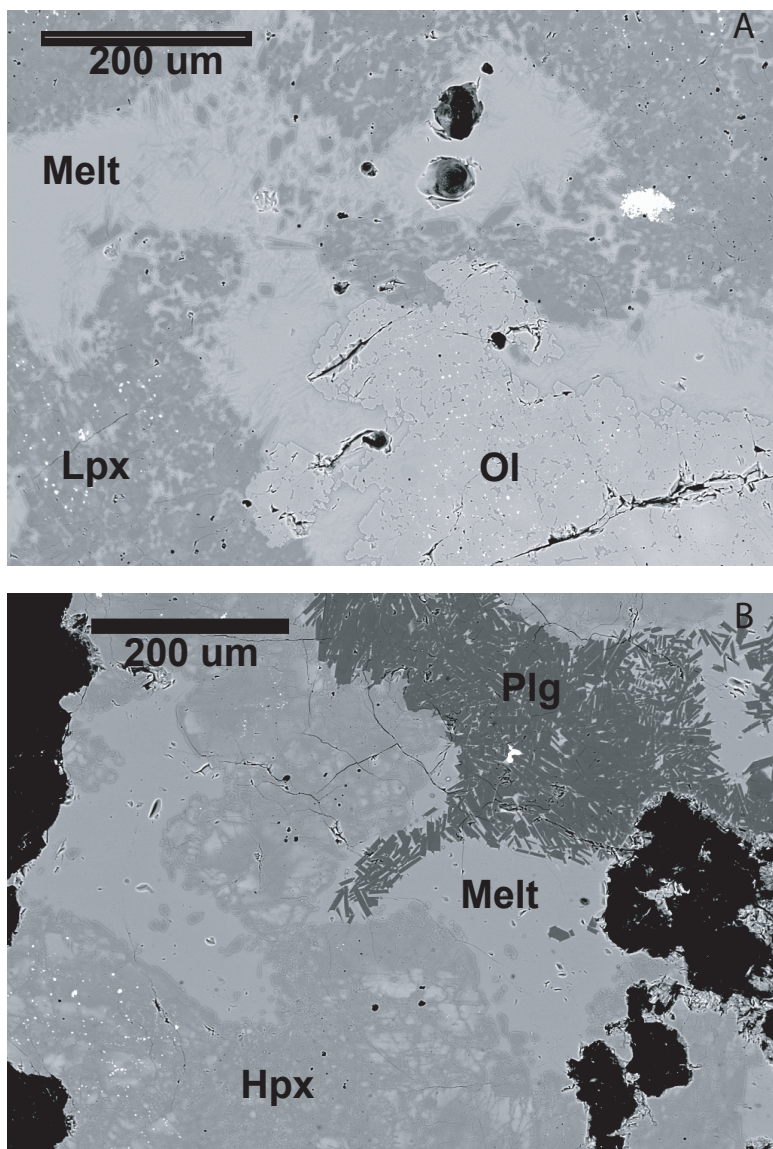


Figure 1

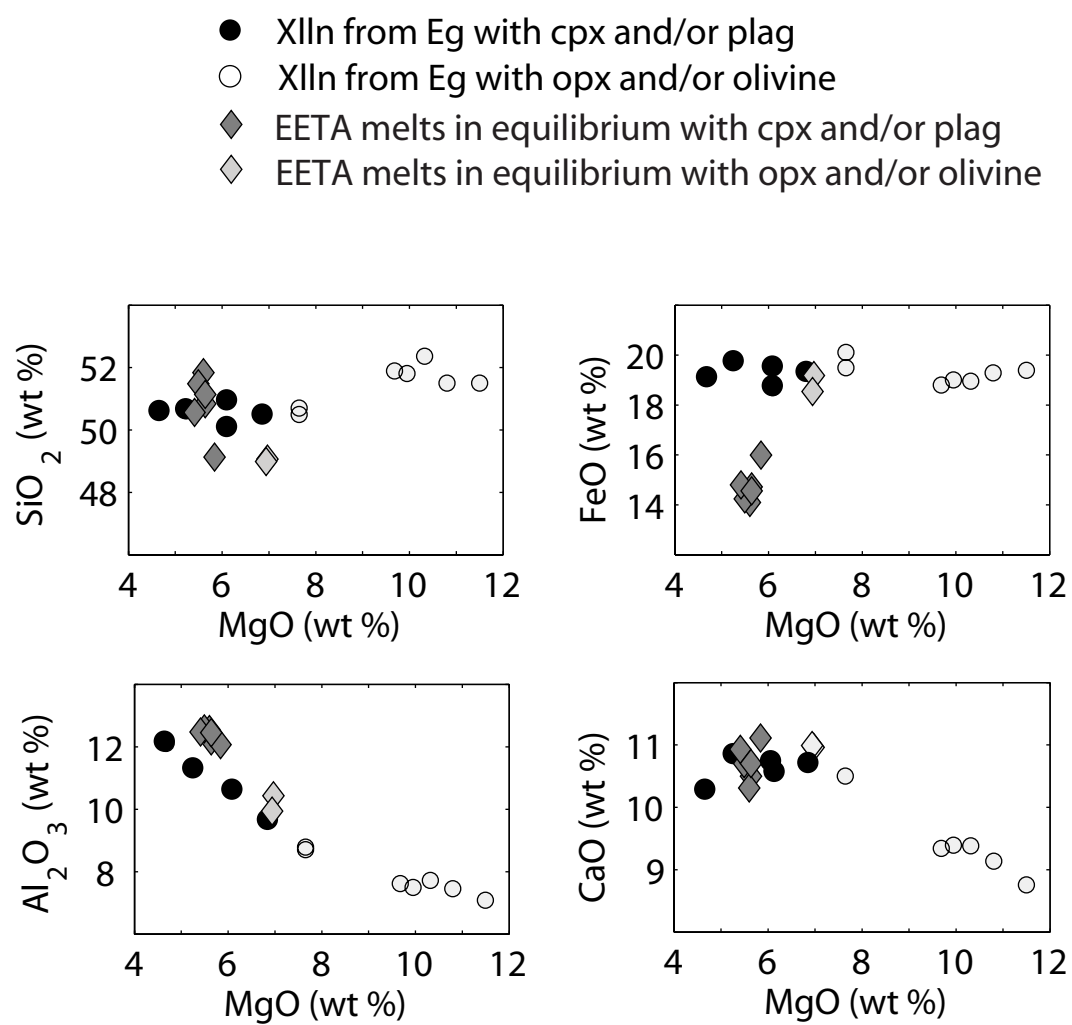


Figure 2

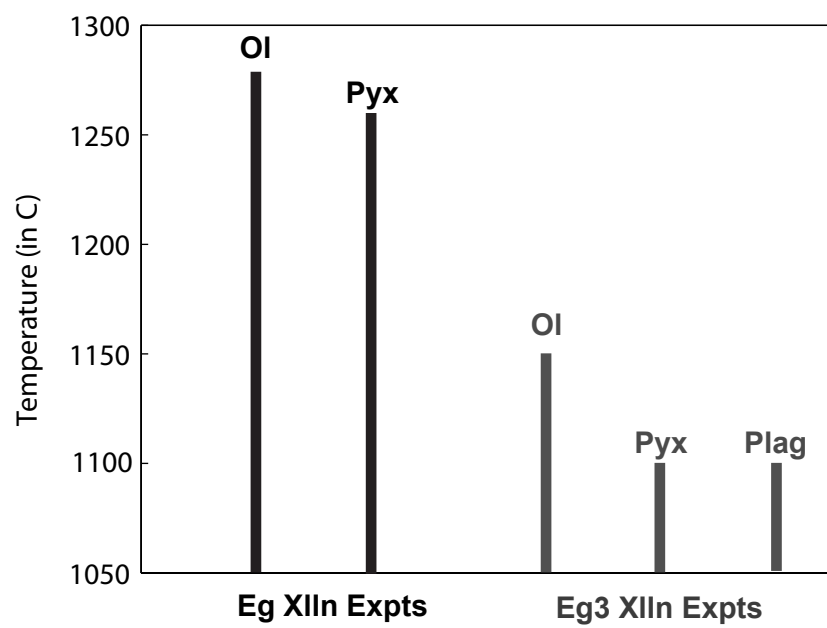


Figure 3

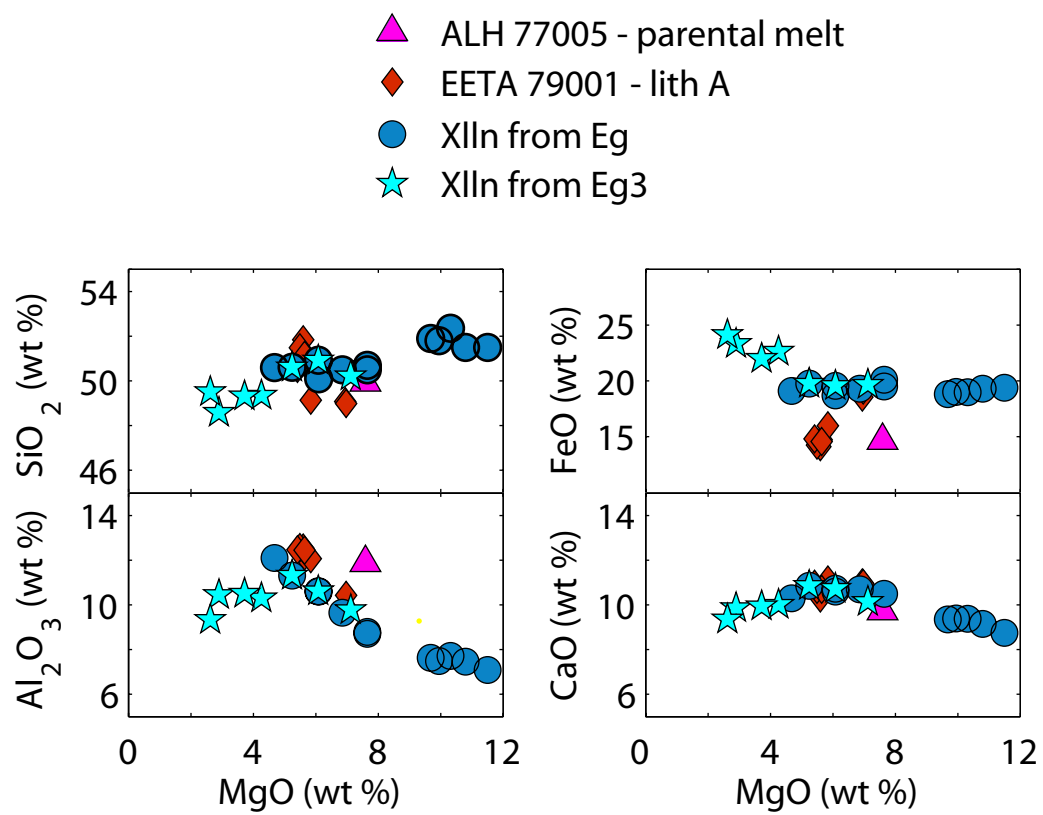


Figure 4

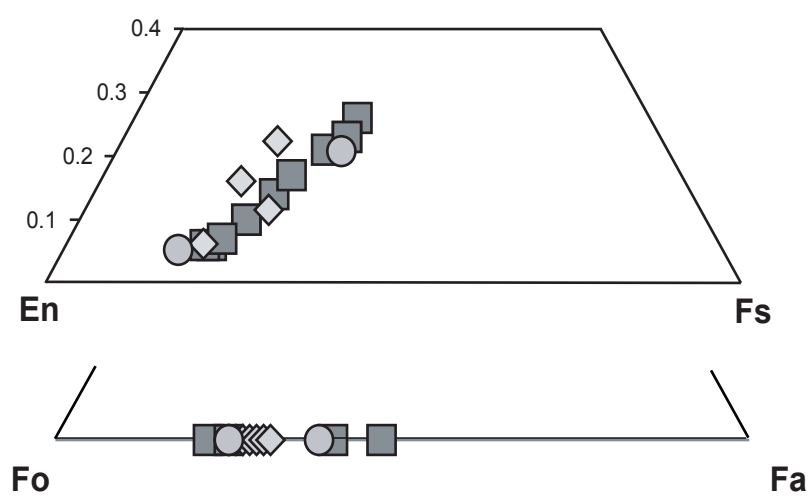


Figure 5

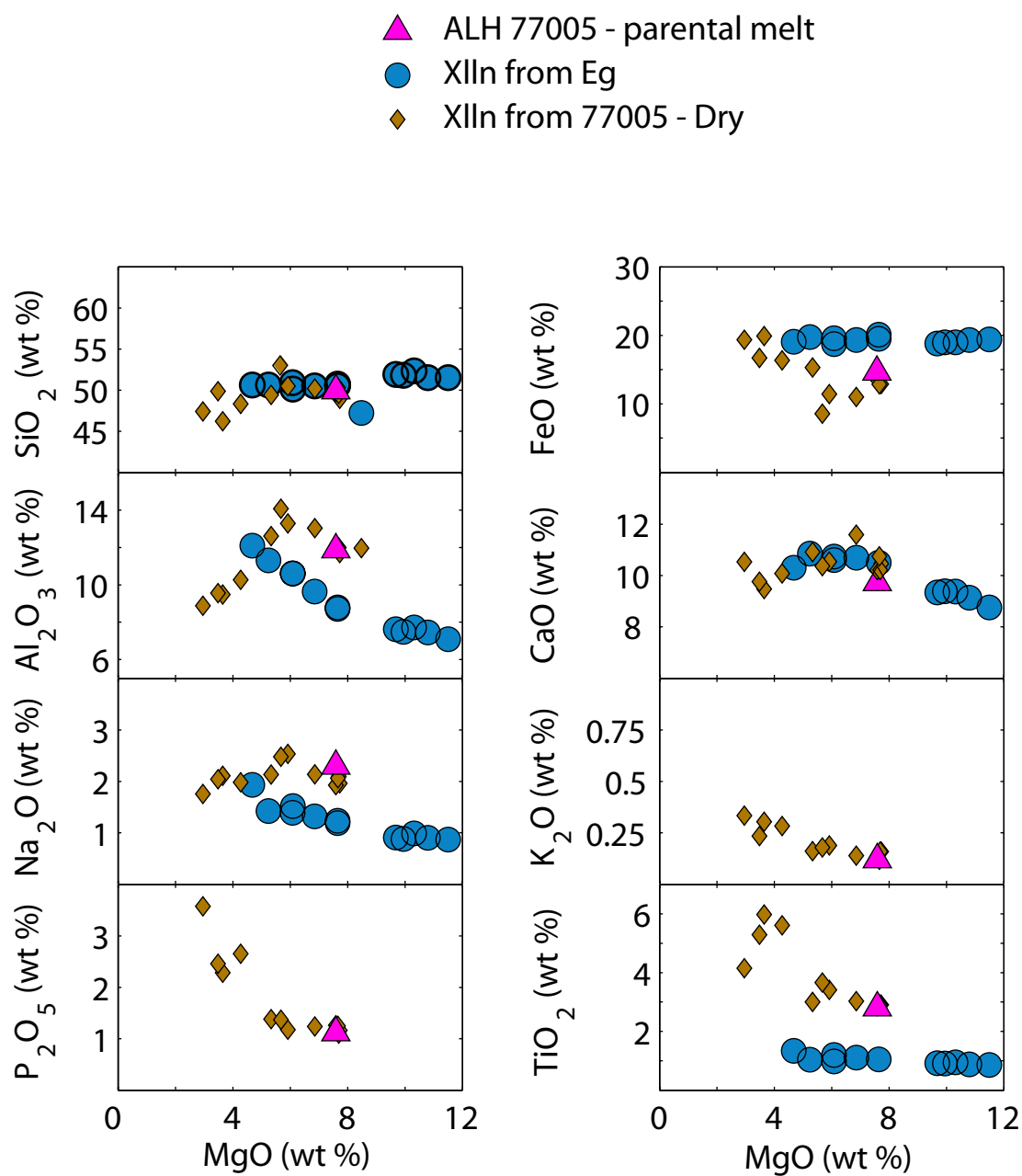


Figure 6

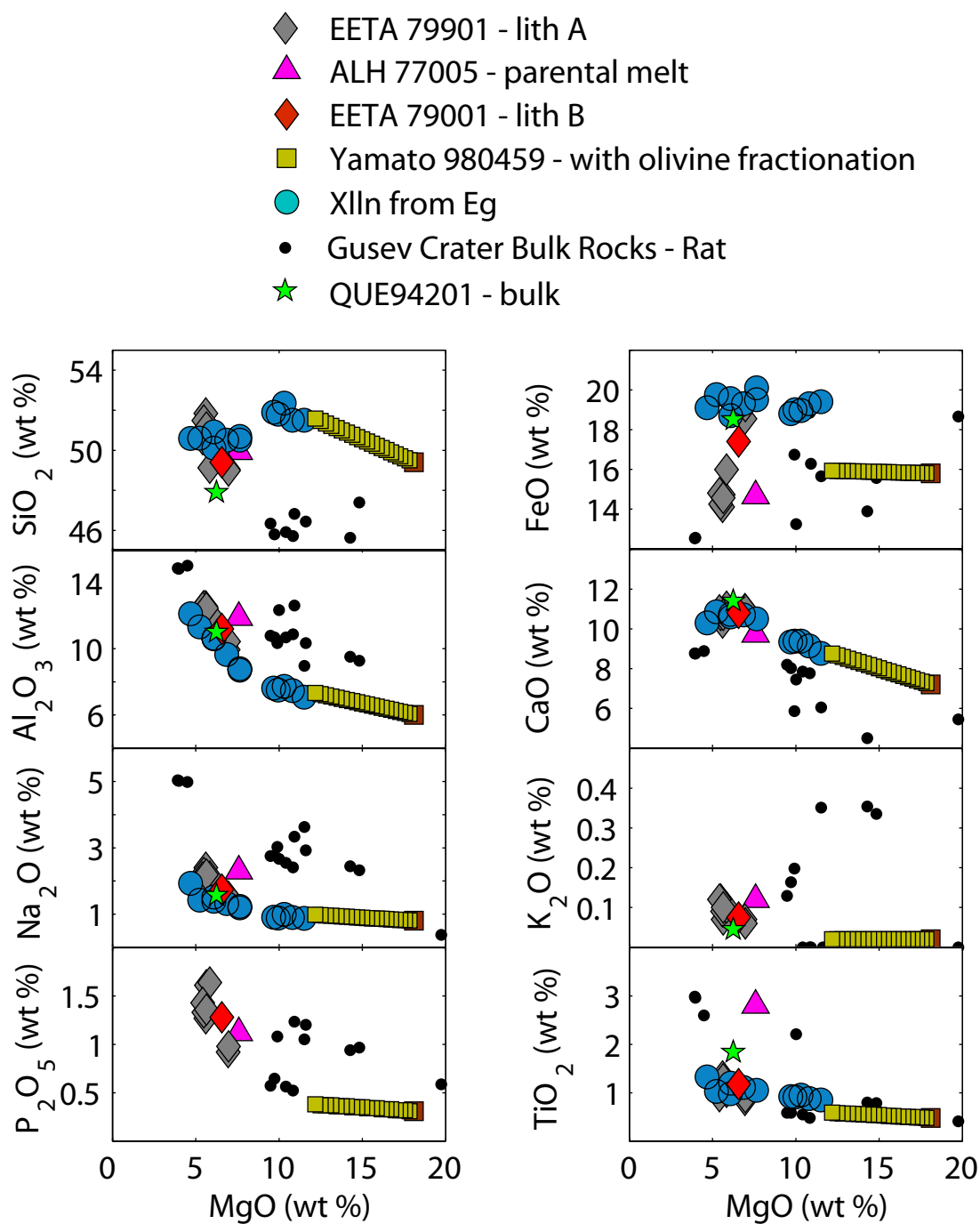


Figure 7

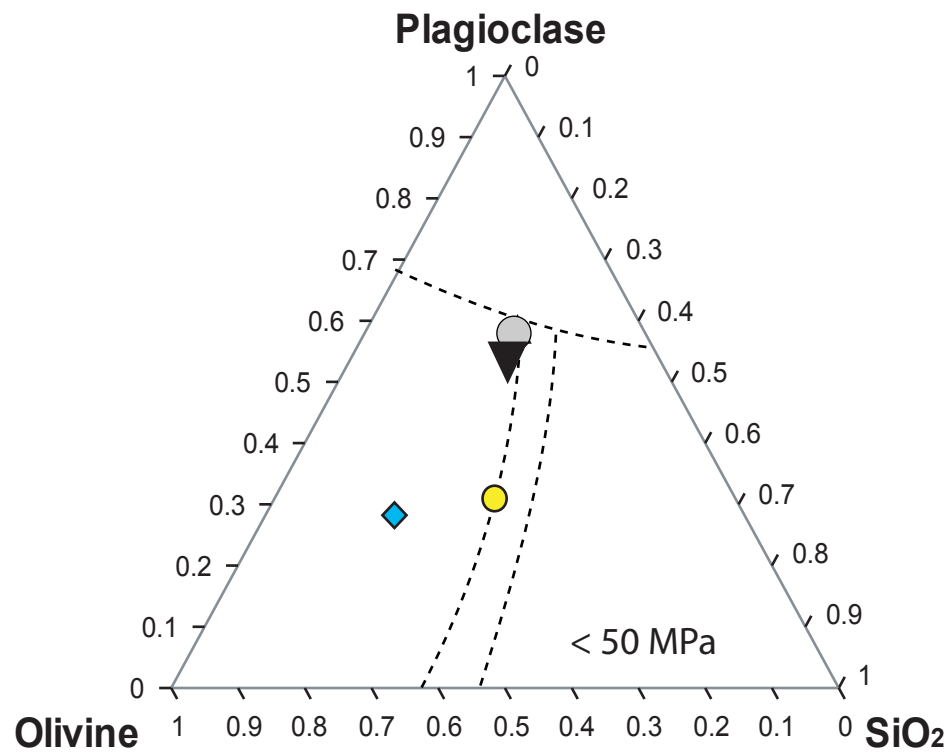


Figure 8

Table 1. Run conditions for remelting experiments performed on chips of EETA79001, 199.

Experiment	Temp (in °C)	Pressure (in bars)	Duration	Oxidation	Mineral Phases
E79-1	1165	1000			
E79-5	1155	800	48	QFM -2.5	lpyx
E79-3	1155	800	71	QFM -2.5	plag, hpyx
E79-4	1150	800	61	QFM -2.5	plag, lpyx
E79-6	1145	800	56	QFM -2.5	lpyx
Eg1-000	1350	1	72	QFM	
Eg1-001	1300	1	72	QFM	
Eg1-005	1278	1	72	QFM	ol
Eg1-013	1260	1	72	QFM	ol, lpyx
Eg1-030	1255	1	72	QFM	ol
Eg1-002	1250	1	72	QFM	ol, lpyx
Eg1-008	1250	1	72	QFM	ol, lpyx
Eg1-003	1200	1	72	QFM	ol, lpyx
Eg1-010	1200	1	72	QFM	ol, lpyx
Eg1-012	1175	1	72	QFM	ol, lpyx
Eg1-004	1150	1	72	QFM	ol, lpyx
Eg1-009	1150	1	72	QFM	lpyx
Eg1-015	1125	1	72	QFM	ol, lpyx
Eg1-011	1100	1	72	QFM	
Eg1-016	1100	1	72	QFM	ol, lpyx

Mineral phases represent the minerals found in equilibrium with the reported melts.
 Ol = olivine, chrm = chromite, plag = plagioclase, lpyx = low-Ca pyroxene, hpyx =
 high-Ca pyroxene

Table 2. Glass compositions for experimentally generated melts in EETA 79001 lithology A.

Expt #	E79-1	E79-1	E79-5	E79-4	E79-4	E79-6	E79-6
Temp (in C)	1165	1165	1155	1150	1150	1145	1145
Press (in bars)	1000	1000	800	800	800	800	800
Time (in hours)	19	19	48	61	61	56	56
SiO ₂	48.99	49.07	55.34	50.84	51.84	49.92	51.15
TiO ₂	0.91	0.85	1.16	1.29	1.34	1.08	0.95
Al ₂ O ₃	10.43	9.94	13.20	12.19	12.55	12.20	12.65
Cr ₂ O ₃	0.24	0.26	0.16	0.16	0.14	0.17	0.17
FeO	19.18	18.54	9.44	14.72	14.40	14.78	14.85
MnO	0.52	0.56	0.46	0.50	0.53	0.46	0.39
MgO	6.97	6.94	5.81	5.64	5.60	6.01	5.73
CaO	10.96	10.99	11.15	10.50	10.31	11.24	10.65
Na ₂ O	1.51	1.53	2.06	2.25	2.40	1.94	2.11
P ₂ O ₅	0.98	0.92	1.23	1.61	1.27	1.73	1.12
K ₂ O	0.06	0.07	0.12	0.07	0.09	0.99	0.11
Sulfur	0.20	0.07	(not meas)	0.13	0.13	(not meas)	0.04
Chlorine	0.04	0.03	(not meas)	0.02	0.03	(not meas)	0.03
Mg #	39	40	52	41	41	42	41
Total	100.74	99.67	100.12	99.76	100.49	100.51	99.87
Mineral Assemblage	lpyx (> 3.7%)	ol, lpyx (>1 to 4%, chrm)	lpyx (4-6%)	hpyx	hpyx, plag	hpyx, plag	hpyx, plag

Minerals: ol = Olivine, lpyx = low-Ca pyroxene, hpyx = high-Ca pyx, chrm = chromite, plag = plagioclase. The number following lpx denotes the wt % CaO in the pyroxenes.

Table 3. Representative glass compositions for crystallization experiments from the Eg composition.

Experiment	Eg1-000*	Eg1-002	Eg1-008	Eg1-003	Eg1-010	Eg1-009
Temp (in C)	1350	1250	1250	1200	1200	1150
SiO ₂	50.5	51.9	51.8	50.5	50.7	50.1
TiO ₂	0.85	0.92	0.91	1.05	1.05	1.2
Al ₂ O ₃	6.97	7.62	7.49	8.71	8.79	10.6
FeO	18.8	18.8	19	20.1	19.5	18.7
MnO	0.47	0.52	0.51	0.5	0.49	0.44
MgO	11.9	9.68	9.95	7.65	7.65	6.09
CaO	8.59	9.34	9.39	10.5	10.5	10.6
Na ₂ O	0.95	0.91	0.88	1.23	1.19	1.52
Mg#	53.07	47.91	48.34	40.48	41.21	36.78
Total	99.03	99.69	99.93	100.24	99.87	99.25
Minerals	none	ol, lpyx	ol, lpyx	ol, lpyx	ol, lpyx	ol, lpyx

* Starting Composition.

Mineral phases: ol = olivine; lpyx = low-Ca pyroxene

Appendix 1. Glass and mineral compositions from

Experiment	E79-1	E79-5	E79-4	E79-6
Pressure (in MPa)	100	80	80	80
Temperature (in C)	1165	1155	1150	1145
SiO ₂	49.07	55.34	50.84	51.15
Al ₂ O ₃	9.94	13.20	12.19	12.65
TiO ₂	0.85	1.16	1.29	0.95
FeO	18.54	9.44	14.72	14.85
MnO	0.56	0.46	0.50	0.39
MgO	6.94	5.81	5.64	5.73
CaO	10.99	11.15	10.50	10.65
Na ₂ O	1.53	2.06	2.25	2.11
K ₂ O	0.07	0.12	0.07	0.11
P ₂ O ₅	0.92	1.23	1.61	1.12

	Ol	Lpyx	Lpyx	Lpyx	Plag	Hpyx	Lpyx	Plag
SiO ₂	35.84	53.31	52.67	52.35	52.05	51.18	52.76	53.38
Al ₂ O ₃	0.05	0.64	1.07	3.47	29.84	1.86	1.14	29.03
TiO ₂	0.02	0.11	0.24	0.13		0.28	0.19	
FeO	34.00	16.74	18.10	15.75	0.63	13.73	15.98	0.25
MnO	0.77	0.62	0.69	0.65		0.52	0.61	
MgO	27.62	22.88	20.08	21.06		17.21	21.72	
CaO	0.37	3.70	5.40	5.22	13.20	13.26	5.96	11.99
K ₂ O	0.03	0.02	0.02	0.00	0.04	0.00	0.03	0.21
Na ₂ O			0.08	0.09	3.83	0.11	0.14	4.34
Cr ₂ O ₃	0.09	0.48	0.46	0.34		0.70	0.50	

* Mineral abbreviations. Ol:olivine, Lpyx: low-Ca pyroxene, Plag: plagioclase, Hpyx: high-Ca pyroxene.

Appendix 2. Glass compositions from Eg crystallization experiments.

Analysis	Temp	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO
Eg1-000	1350	50.5	0.85	6.97	18.8	0.47	11.9	8.59
Eg3-022	1350	50.21	0.9	9.77	19.66	0.43	7.12	10.14
Eg4-035	1350	52.68	0.86	6.9	18.13	0.5	10.66	8.86
Eg1-001	1300	51.5	0.85	7.08	19.4	0.5	11.5	8.76
Eg1-005	1278	51.5	0.88	7.46	19.3	0.49	10.8	9.14
Eg1-013*	1260	51.6	0.9	7.58	18.8	0.5	10.3	9.35
Eg1-029	1260	48.72	0.89	7.88	18.5	0.5	10.37	9.45
Eg1-030	1255	52.36	0.95	7.72	18.96	0.52	10.32	9.38
Eg1-002	1250	51.9	0.92	7.62	18.8	0.52	9.68	9.34
Eg1-008	1250	51.8	0.91	7.49	19	0.51	9.95	9.39
Eg4-036	1250	52.93	0.93	7.31	18.94	0.5	9.74	9.53
Eg1-003	1200	50.5	1.05	8.71	20.1	0.5	7.65	10.5
Eg1-010	1200	50.7	1.05	8.79	19.5	0.49	7.65	10.5
Eg1-012	1175	50.5	1.11	9.65	19.3	0.47	6.86	10.7
Eg1-004	1150	49.5	1.37	11.2	21.4	0.43	3.7	10.7
Eg1-009	1150	50.1	1.2	10.6	18.7	0.44	6.09	10.6
Eg3-023	1150	50.92	0.98	10.62	19.56	0.44	6.08	10.73
Eg3-024	1130	50.61	1.03	11.31	19.77	0.43	5.24	10.86
Eg1-015	1125	50.6	1.33	12.1	19.1	0.42	4.68	10.3
Eg1-006	1100							
Eg1-011	1100	50.7	2.6	10.89	20.21	0.38	3.69	9.6
Eg1-016	1100	49.9	2.26	10.8	21.2	0.44	3.94	9.88
Eg3-025	1100	49.34	1.43	10.3	22.62	0.45	4.26	10.01
Eg3-027*	1100	48.58	2.03	10.45	23.32	0.45	2.9	9.86
Eg3-028	1100	49.31	1.79	10.51	21.99	0.44	3.72	9.94
Eg3-026	1075	49.5	2.33	9.33	24.11	0.46	2.62	9.35
Eg1-032	1290-1250	52.12	0.93	7.58	18.47	0.48	10.12	9.26
Eg1-033	1290-1250	52.95	0.81	7.81	18.53	0.5	9.96	9.47
Eg1-034	1290-1250	52.25	0.91	7.7	18	0.49	9.77	9.22
Eg4-037	1250-1200	51.23	1.08	8.64	19.83	0.47	6.27	10.98
Eg4-038	1250-1200	52.31	1.03	8.38	18.78	0.46	7.32	10.5
Eg4-039	1250-1150	52.57	0.9	9.5	19.57	0.48	5.87	11.25
Eg4-040	1250-1150	52.48	0.94	9.06	19.94	0.47	5.55	11.28

Appendix 3. Olivine compositions for Eg crystallization experiments

Analysis	Temp	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	
Eg1-005	1278	38.1	0	0	21	0.41	40.9	0.27	
Eg1-013*	1260	38.4	0	0	22.5	0.51	39.7	0.3	
Eg1-029	1260	37.2	0.01	0.05	22.02	0.55	38.79	0.29	
Eg1-030	1255	38.86	0.01	0.02	22.76	0.52	39.46	0.28	
Eg1-002	1250	38.2	0	0	22	0.51	39.2	0.28	
Eg1-008	1250	38.3	0	0	23.3	0.52	38.8	0.3	
Eg1-003	1200	38.3	0	0	26.5	0.58	36	0.4	
Eg1-010	1200	37.5	0	0	27.1	0.58	35.4	0.38	
Eg1-012	1175	37.2	0	0	29.1	0.6	33.7	0.4	
Eg1-004	1150	36.4	0	0	31.7	0.58	31.1	0.41	
Eg3-023	1150	35.89	0.02	0.03	30.99	0.6	32.02	0.37	
Eg3-024	1130	35.21	0.03	0.03	34.89	0.64	28.86	0.43	
Eg1-015	1125	35.8	0	0	36.1	0.66	27.8	0.44	
Eg1-006	1100	38.4	0	0	21.7	0.47	39.6	0.29	
Eg1-016	1100	35.2	0	0	39.9	0.67	24.9	0.46	
Eg3-025	1100	33.69	0.08	0.12	42.29	0.77	20.67	0.62	
Eg3-028	1100	33.99	0.04	0.04	42.23	0.67	21.78	0.5	
Eg1-032	1290- Core	1250	38.29	0.02	0.02	21.18	0.47	39.33	0.24
Eg1-032	Rim		37.99	0	0	22.16	0.49	38.61	0.32
Eg1-033	1290- Core	1250	39.09	0.02	0.01	21.38	0.43	40.97	0.26
Eg1-033	Rim		38.74	0	0	23.14	0.54	39.24	0.31
Eg1-034	1290- Core	1250	38.59	0.02	0.01	20.36	0.47	40.11	0.26
Eg1-034	Rim		38.34	0.01	0.01	22.13	0.5	38.8	0.29

Appendix 4. Pyroxene composition for Eg crystallization experiments.

Analysis	Temp	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O
Eg1-013*	1260	55.7	0.1	0.68	14	0.48	28.58	1.82	0
Eg1-002	1250	55.9	0.09	0.5	13.37	0.49	28.38	1.69	0
Eg1-008	1250	55.2	0.08	0.34	14.52	0.48	27.78	1.91	0
Eg4-036	1250	55.32	0.09	0.31	14.97	0.49	27.54	1.89	0.01
Eg1-003	1200	54.9	0.09	0.47	16.15	0.56	26.32	2.81	0
Eg1-010	1200	54.7	0.09	0.51	16.23	0.56	25.72	2.82	0
Eg1-012	1175	53.7	0.16	0.94	17.2	0.59	23.7	4.1	0
Eg1-004	1150	53.5	0.18	1.13	18.15	0.58	21.97	5.13	0
Eg1-009	1150	52.8	0.22	1.28	17.64	0.61	22.18	5.18	0
Eg3-024	1130	52.63	0.13	0.88	19.6	0.55	20.6	5.94	0.04
Eg1-015	1125	52.8	0.28	1.9	19.6	0.58	18.6	6.47	0
Eg1-006	1100	51	0.51	2.06	21.13	0.61	16.23	8.68	0
Eg1-016	1100	51.18	0.34	1.4	21.28	0.57	17.5	7.68	0
Eg3-025	1100	50.73	0.36	2.41	22.06	0.59	14.88	9.3	0.18
Eg3-027*	1100	50.59	0.38	1.92	22.96	0.59	16.2	7.9	0.09
Eg3-028	1100	51.9	0.3	1.62	20.3	0.58	18.52	7.04	0.04
Eg3-026	1075	50	0.28	1.2	28.2	0.69	13.4	6.76	0.07
Eg4-037	1250-								
Core	1200	54.39	0.11	0.5	17.23	0.52	25.06	2.8	0.02
Eg4-037 Rim		54.11	0.13	0.48	17.5	0.55	24.42	3.01	0.02
Eg4-039	1250-								
Core	1150	55.18	0.11	0.48	16.85	0.55	26.11	2.44	0.01
Eg4-039 Rim		54.28	0.09	0.52	17.97	0.63	24.38	3.12	0.03

Appendix 5. Plagioclase compositions for Eg crystallization experiments.

Analysis	Temp	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O
Eg3-025	1100	50.08	0.05	29.42	1.99	0.02	0.35	14.34	3.08
Eg3-027*	1100	53.44	0.09	28	2.88	0.05	0.5	12.7	3.8
Eg3-028	1100	52.59	0.06	29.6	1.68	0.05	0.3	13.24	3.65
Eg3-026	1075	54.74	0.17	26.42	3.78	0.09	1.25	12.2	3.76