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BOSTON UNIVERSITY

GRADUATE SCHOOL OF ARTS AND SCIENCES

Dissertation

EXPERIMENTAL INVESTIGATION OF OLIVINE AND OLIVINE-RICH ROCKS AT HIGH PRESSURE AND HIGH TEMPERATURE

by

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Submitted in partial fulfillment of the

requirements for the degree of

Doctor of Philosophy

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DEDICATION

To my beloved parents, wife, and daughter. To the loving memory of my grandparents.

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EXPERIMENTAL INVESTIGATION OF OLIVINE AND OLIVINE-RICH ROCKS AT HIGH PRESSURE AND HIGH TEMPERATURE

(Order No.

)

SHANGSHANG MU

Boston University Graduate School of Arts and Sciences, 2015

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ABSTRACT

Olivine is the most abundant mineral in Earth's upper mantle and is one of the major minerals discovered in extraterrestrial objects. Its physical properties govern the dynamics of the upper mantle. The most dynamic regions of the upper mantle are sites where melting and melt segregation occurs. These regions are also the most variable in terms of their oxygen fugacity. We therefore conducted piston cylinder experiments to determine the intergranular melt distribution, and explore a range of oxygen buffers. We annealed olivine aggregates in metallic and graphite capsules to determine the oxygen fugacities are below their corresponding metal-oxide buffers. The oxygen fugacity in nickel₈₀-iron₂₀ and graphite capsules most closely represents the intrinsic oxygen fugacity of Fo90 olivine, while iron capsules are too reducing perhaps explaining the formation of "dusty" olivine in chondrites.

We annealed olivine-basalt aggregates in order to determine the melt distribution. The results show that the length of olivine grain boundaries wetted by melt (grain boundary wetness) increases with increasing melt content to values well above those predicted by a simplified model which is commonly applied to this system. At fixed melt content the grain boundary wetness increases with increasing grain size. These observations emphasize that the dihedral angle of the simplified system is not adequate to characterize the melt distribution in partially molten rocks. Our observations indicate that at upper mantle grain sizes the shear viscosity of partially molten rocks is one order of magnitude lower than predicted by the simplified model.

Naturally partially molten rocks exist in the form of olivine-rich troctolites or plagioclase dunites, but the conditions for their formation are not entirely clear. We therefore conducted step-cooling experiments that indicate that slow cooling of samples with a steady-state microstructure reproduces the interstitial geometry observed in natural samples. The grain boundary wetness determined from the interstitial phases is somewhat reduced during slow cooling relative to samples quenched from high temperature. The microstructural similarity of experimental and natural samples suggests that mush zones identified beneath mid-ocean ridges may have lower melt contents than previously envisioned.

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CHAPTER I

INTRODUCTION

1. Olivine – the Most Abundant Mineral in the Upper Mantle

Olivine is a magnesium iron silicate with the formula (Mg,Fe)₂SiO₄. The ratio of magnesium and iron ranges between the two end members of the solid solution series: forsterite (Mg₂SiO₄) and fayalite (Fe₂SiO₄). Commonly compositions of olivine are expressed as molar percentages of forsterite (Fo). Olivine is typically found in mafic rocks such as basalt, gabbro, and is the primary mineral in ultramafic rocks such as dunite and peridotite. Since the upper part of the Earth's mantle is composed of ultramafic rocks, olivine is therefore the most abundant mineral in the Earth's upper mantle. Its physical properties govern behaviors of upper mantle rocks, and hence the dynamics of the upper mantle.

Olivine and its high-pressure polymorphs are also major minerals discovered in extraterrestrial objects. Although no samples of the moon mantle have been found, seismic studies show that at least the middle mantle of the moon is composed of an olivine-bearing pyroxenite (e.g. Kuskov et al., 1995); Spectral reflectance data indicates that exposures of olivine on the moon surface are believed to be mantle origin (Yamamoto et al., 2010). Similar to the upper mantle of the Earth, the upper mantle of the Mars consists of perodotite that is primarily of mineral olivine (Longhi et al., 1992). Moreover, Most chondrites are rich in olivine.

Since olivine is so abundant in Earth's upper mantle and on other terrestrial planets, investigating olivine and olivine-rich rocks promotes understanding properties and

dynamics of not only the Earth's upper mantle but also potentially formation and evolution of other planets.

2. The Redox State of the Mantle

The redox state of the Earth's mantle has long been studied by various geological disciplines. It has broad impacts on C-O fluids equilibria (Blundy et al., 1991), partial melting behaviors, such as degassing of volatile components (Kasting et al., 1993) and magma generation (Holloway 1998), and physical properties of olivine, such as electrical conductivity (Dai and Karato 2014) and rheology (Ryerson et al., 1989).

Oxygen fugacity is a key parameter in describing the redox state in the interior of the Earth. By definition it is simply the partial pressure of oxygen in a gas phase, representing the chemical potential of oxygen (Carmichael, 1991). Oxygen fugacity controls the redox conditions at which a rock forms and exists. It affects physical properties of rocks and minerals including diffusion, deformation, phase equilibrium and electrical conductivity, etc. Laterally, the most dynamic regions of the upper mantle such as mid-ocean ridges, plumes (hot-spots) and subduction zones are sites where melting and melt segregation occurs. These regions are also the most variable in terms of their oxygen fugacity. Longitudinally, oxygen fugacity has a wide impact not only on the near surface evolution of the earth, but also on the processes associated with the core formation. When describing oxygen fugacity, we usually refer the value to a redox buffer. A redox buffer is formed by a chemical reaction involving an assemblage of minerals or compounds that constrains oxygen fugacity as a function of temperature at a given pressure. The most common buffer used to describe oxygen fugacity in the upper mantle is fayalite- magnetite-quartz (FMQ) buffer, which refers to the reaction 3 Fe₂SiO₄ + O₂ = $2 \text{ Fe}_3\text{O}_4 + 3\text{SiO}_2$. Most of upper mantle oxygen fugacity data measured from mantle xenoliths is reported corresponding to FMQ buffer. Other common buffers include magnetite-hematite (MH) buffer, indicating very oxidizing chemical environment that is approximately 5 log units above FMQ buffer. It is constrained by the reaction $4\text{Fe}_3\text{O}_4 + O_2 = 6\text{Fe}_2\text{O}_3$. In contrast, iron-wustite (IW) buffer represents very reducing redox state that is approximately 5 log units below FMQ buffer. The corresponding reaction is $2\text{Fe} + O_2 = \text{FeO}$.

In the Earth's upper mantle, oxygen fugacity has a large influence on the magma, determining the abundance and composition of minerals, fluid-melt partitioning and the physical properties of the melt (Behrens and Gillard, 2006). Oxygen fugacity is different among various tectonic settings of the upper mantle, and constrained by a range of fluid and melt phases associated with volatiles phase. Water plays an important role in shaping the oxygen fugacity of the upper mantle. Based on experimental results of Matveev et al. (1997), high-density silicates and normally anhydrous upper mantle minerals still dissolve an amount of water. This process alters the composition of free fluid phase and therefore affects the oxygen fugacity. Furthermore, the mantle convection process brings high-density hydrous silicates and constitutional water in anhydrous mantle minerals to the uppermost mantle. The dehydration process at subduction zones brings water to the free fluid phase and changes the upper mantle oxygen fugacity.

The most dynamic regions of the upper mantle such as mid-ocean ridges, plumes and subduction zones are the most variable in terms of their oxygen fugacity. The general trend and constraint of oxygen fugacity among these different tectonic settings are

1) Subduction zone has the highest oxygen fugacity

The high oxygen fugacity is related to the rehydration and carbonation processes in subduction zones. The downgoing slabs bring a large amount of oxides (recycling of hydrous fluids) to the upper mantle, In this subduction process, mantle fluid system is replenished by free fluid H₂O and CO₂, and dehydration and decomposition of carbonate, bringing up the oxygen fugacity (Ringwood, 1994). As a result, arc magmas have more oxidized environments in general. Lee et al. (2010) investigated the redox state of arc mantle using Zn/Fe systematics and imply oxygen fugacity is between FMQ -1 and FMQ +1 log unit.

2) Mid-ocean ridges have lower oxygen fugacity than continental mantle.

The oxygen fugacity of most of the Earth's mid-ocean ridge systems are revealed by either analyzing the Fe3⁺ to total Fe ratios in quenched MORB glasses, or oxygen thermobarometry measurements of abyssal spinel peridoties. Oxygen fugacity of mid-ocean-ridges is up to 4 log units below FMQ (Bryndzia et al., 1989) to at FMQ (Cottrell and Kelly, 2011). Oxygen fugacities of continental mantle are estimated by geobarometry methods. These analyses indicate oxygen fugacity is from slightly above FMQ to 2 log units below the FMQ (Wood et al. 1990, Frost and McCammon 2008). The less oxygen fugacity of oceanic mantle may associate with the fact that more partial melting takes place in oceanic region.

3) Melt-free area has higher oxygen fugacity than partial melting area In partial melting process, a large amount of H₂O and CO₂ dissolve in melt and this process decreases the oxygen fugacity of mantle. At the oxygen fugacity of primary mantle melts genesis that is around FMQ, oxidation of small amounts of sulfide to sulfate buffers the melt and prevents the ferric/ferrous ratio of the residual mantle from increasing (Cottrell and Kelly, 2011). Thus increasing in fraction of partial melting area will decrease the oxygen fugacity unless a processed exists to reintroduce oxygen to the mantle.

4. Mantle plumes have lower oxygen fugacities than mantles at the same depth. The mechanism may be similar to partial melting. Higher temperature of plumes than that of surrounding mantle makes less oxygen stays in plume phase. Compared to our knowledge of oxygen fugacity of the upper mantle, much less data is available to constrain oxygen fugacity in the lower mantle. Rock and mineral samples from the lower mantle are lacked to measure intrinsic oxygen fugacity. O'Neill and Wall (1987) have used nickel precipitation curve to constrain the minimum oxygen fugacity of the upper mantle. Since Ni-rich metallic phase is not observed in most peridotite, they conclude that the minimum oxygen fugacity of the upper mantle is above the nickel precipitation curve, which is almost coincident with the IW buffer. Given Earth is composed of a metallic Ni-Fe core, oxygen fugacity of the lower mantle is below the IW buffer.

The stability of olivine is limited by the redox state of iron. Control of redox conditions in experiments is therefore of importance. The experimental study described in Chapter II explores the responses of mineral olivine to different redox conditions. The various oxygen fugacities are set by using different capsule materials to form redox couples with olivine crystals. The change in olivine composition as a function of oxygen fugacity is investigated.

3. Partial Melting in the Upper Mantle

Partial melting plays a key role for shaping the continued evolution not only in the solid Earth but also the Earth's surface. In Earth's upper mantle, olivine in peridotite never melts due to its high melting temperature. Partial melting is triggered when the geotherm is higher than the solidus of some minerals with lower melting points in peridotite, such as clinopyroxene and garnet (basaltic ingredients). These minerals melt to form basaltic magma distributed in olivine matrix. The magma may further migrate to leave the olivine matrix at certain conditions. The most dynamic regions of the upper mantle such as mid-ocean ridges, plumes and subduction zones are sites where melting and melt segregation occurs. Furthermore, potentially the asthenosphere is partially molten at small degrees.

Partial melting in the mantle cannot be observed directly, but are commonly inferred from geophysical observations. The low seismic velocity and high attenuation zones and numerous zones of high electrical conductivity anomaly are associated with presence of melt. These indirect methods indicate that the most dynamic regions of the upper mantle such as mid-ocean ridges, subduction zones and hot spots are partially molten at different degrees. Analysis of seismic low velocity zone in the mantle wedge of northeastern Japan infers that subduction zones contain 0.04 - 6% melt (Nakajima et al., 2005). Electrical conductivity measurements at East pacific Rise indicate that mid-ocean ridges contain 1-4% melt (Baba et al. 2006) and seismic structure of Iceland suggests that hotspots have 1-5% melt (Li and Detrick 2006). Furthermore, in the asthenosphere away from these dynamic regions associated with magma ascending, partial melting may still occur. Seismic study by Gutenberg (1948) shows that the low velocity zone in the asthenosphere at a depth between 70 and 80 km may be explained by the presence of a small amount of melt. Anderson and Sammis (1970) suggest that the low velocity zones cannot be interpreted by high temperature gradients along. A small amount of partial melting is consistent with the decrease in seismic velocity. Melt content in the sub-oceanic asthenosphere interpreted from electrical conductivity data is approximately 0.45-9%(Drury, 1978). A recent electrical conductivity study of the lithosphere-asthenosphere boundary confines the melt content to 1-2.1% for a mantle containing moderate H₂O (Naif et al., 2013).

Melt contents in the upper mantle deduced from seismic or electrical conductivity models require and are very sensitive to specific melt geometry. At a constant degree of seismic attenuation or electrical conductivity anomaly, the derived melt content changes with using different melt distribution models. This emphasizes the importance of determining actual melt geometry in the upper mantle. The first melt distribution model applied to rocks is adapted from the discipline of materials science and assumes that melt forms an interconnected network of tubes along grain edges (Bulau and Waff, 1977, Waff and Bulau, 1979, Bulau et al., 1979). Subsequent melt distribution models are from observations of laboratory produced partially molten rock samples using either natural or synthetic upper mantle minerals and melt powder. Early experimental studies indicate that the melt not only forms triple junctions, but also larger pockets surrounded by four or more grains (Waff and Faul, 1992; Faul et al., 1994; Faul, 1997). These melt inclusions (melt pockets) cause greater seismic wave velocity reduction (Hammond and Humphreys, 2000). Recent high-resolution imaging of experimental samples improves

the model by confirming that melt also wets some two-grain boundaries of olivine grains (Garapić et al., 2013), which will have a significant influence on melt contents determined from previous seismic and electrical conductivity studies.

Determining actual melt geometry reconciles the discrepancies in melt retention and melt segregation derived from geochemical and seismic models. Geochemical models of partial melting at mid-ocean ridges suggest that melt segregates from the source region at porosities of order 0.1% (e.g. Spiegelman and Elliott, 1993; Richardson and McKenzie, 1994; Salters and Longhi, 1999; Lundstrom, 1999) and upwells rapidly (Richardson and McKenzie, 1994; Salters and Longhi, 1999). However, seismic data obtained by the mantle electromagnetic and tomography (MELT) experiment (The MELT Seismic Team, 1998) differs with the geochemical models, predicting a seismic low velocity zone consisting of 1-2% basaltic melt based on the geometry of thin, elongated inclusions (Faul et al., 1994). A permeability model using the same melt geometry (Faul, 2001) implies that a deep, volatile-rich melt with low viscosity and density is mobile at 0.1% porosity, which is consistent with the geochemical models, but basaltic melt is able to migrate only at a porosity over 1%. This permeability model also requires melt retention in a broad zone, consistent with the seismic data.

The mechanical properties of partially molten upper mantle rocks are very sensitive to the melt geometry. Rocks deformation studies (Jackson et al., 2004;Faul et al., 2004) using the melt geometry of thin, elongate inclusions (Faul et al., 1994) predict that melt affects

seismic velocities and attenuation by elastically accommodated grain boundary sliding. However, the existence of individual melt layers on two-grain boundaries excludes the grain boundary sliding mechanism and suggests the melt squirt theory (Garapić et al., 2013) that the flow of melt between adjacent melt inclusions squirt from one crack to another with respect to the stress (Mavko and Nur, 1975).

The experimental study described in Chapter III simulates the melt distribution in a kind of olivine-rich upper mantle rock named dunite at pressure and temperature conditions beneath mid-ocean ridges. The quantified melt distribution at micro scales is extrapolated to upper mantle's grain size to infer the physical state of the region beneath mid-ocean ridges where magma generates and the seismic low velocity zone in the asthenosphere where partial melting may occur.

4. Olivine-rich Troctolites: a Window into Partial Melting in the Mantle

Mid-ocean ridges are the most productive source of magma. Partial melting occurs within the ascending upper mantle beneath mid-ocean ridges as a result of decompression melting. The upwelling magma cools before approaching the surface to form gabbro and quenches at the surface to produce mid-ocean ridge basalt (MORB), making up the oceanic crust from surface to depth. At shallow depth of mid-ocean ridges, the ascending melt towards the surface passes through a partially crystallized mush zone (Sinton and Detrick, 1992) and accumulates on top of it to form a shallow crustal magma chamber (melt lens) in the oceanic crust. Olivine-rich troctolites form in gabbroic sequences of the mush zone, and are found by deep drilling at mid-ocean ridges (e.g. Suhr et al., 2008; Drouin et al., 2010) and in ophiolites from the surface (e.g. Faul et al., 2014; Renna and Tribuzio, 2011; Sanfilippo et al, 2013). This kind of rock is characterized by high volume proportion of olivine with interstitial plagioclase and clinopyroxene, relatively rare in terms of composition and texture. Preliminary observations suggest that the formation of interstitial texture is due to crystallization of clinopyroxene and plagioclase from basaltic melt in rocks of mantle origin. It is believed that the interstitial geometry preserved in olivine-rich troctolites may reveal the basaltic melt distribution in the upper mantle, which is observed only in experiments. Therefore, natural olivine-rich troctolites serve as an important link between experiments, direct observations in the field and indirect observations such as seismic and electromagnetic imaging and of partially molten regions.

The experiments stated in Chapter IV tests the hypothesis that the formation of olivinerich troctolites is a result of melt impregnation of former mantle rocks and following crystallization. These processes are simulated by evenly mixing basaltic melt into olivine grains, and lowering the temperature to allow crystallization of pyroxene and plagioclase from the melt. The experimental analogues are compared with naturally olivine-rich troctolites to explore the similarities in texture. The comparisons between experimental and natural samples help apply experimental results at micro scales at upper mantle's conditions to larger scales in space and time of natural partially molten regions, leading to a better understand the process of melt genesis and migration.

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CHAPTER II

OXYGEN FUGACITY SET BY DIFFERENT CAPSULE MATERIALS IN PISTON CYLINDER EXPERIMENTS

Abstract

The stability of olivine is limited by oxidation/reduction of iron. Control of redox conditions in experiments is therefore of importance. Samples of anhydrous Fo90 olivine aggregates were annealed in iron, nickel, nickel₈₀-iron₂₀ and graphite capsules in direct contact with capsule materials at a range of temperatures and a pressure of 1 GPa in a piston cylinder apparatus for 168 hours to determine the oxygen fugacities set by the capsule materials. A few olivine samples were annealed with added metal-oxides at different duration or with platinum oxygen fugacity sensors. Post-run samples were imaged and analyzed compositionally. Oxygen fugacities of olivine aggregates in these capsules were determined from compositional and thermodynamic data. The results show that oxygen fugacities are below their corresponding metal/metal-oxide buffers but keep relative order. Specifically, oxygen fugacities in nickel capsules are in between CCO and IW buffers (2-3 log units below NNO buffer); in nickel₈₀-iron₂₀ and graphite capsules are at or 1 log unit below IW buffer, most closely representing the intrinsic oxygen fugacity of anhydrous melt-free Fo90 olivine; while in iron capsules are 2 log units below IW buffer, which are too reducing that relate to redox conditions of core formation and on other terrestrial planets and planetesimals perhaps explaining the formation of "dusty" olivine in chondrites. For those experiments with added metal-oxides in iron and nickel capsules, no metal-oxides were preserved in post-run samples, indicating that metal/metal-oxide buffers cannot maintain oxygen fugacities at their corresponding buffers for relatively long duration in piston cylinder experiments. Heterogeneity of oxygen fugacity observed in experiments with platinum oxygen fugacity sensors

emphasizes that it is important to minimize their volume while using platinum as external oxygen fugacity sensors.

1. Introduction

Oxygen fugacity is specifically defined as the partial pressure of oxygen in a gas phase, which takes into account the chemical potential of oxygen (Carmichael, 1991). It is the measure of the availability of oxygen to participate in chemical reactions in a system. Oxygen fugacity controls the redox conditions at which a mineral or rock forms and exists. It affects physical properties of rocks and minerals including diffusion, deformation, phase equilibrium and electrical conductivity, etc. The oxygen fugacity of the mantle various in different tectonic settings and is described by common redox buffers like MH, FMQ and IW in order of decreasing oxygen fugacity.

1.1. Oxygen Fugacity Control in Piston Cylinder Experiments

End-loaded piston cylinder apparatus is widely used in high-pressure and hightemperature studies. This instrument allows relatively long experimental duration at upper mantle's high pressure and high temperature conditions to form equilibrium texture. The oxygen fugacity control in the experimental sample is very crucial and complicated. Unlike pressure and temperature can be directly adjusted once the instrument is well calibrated, normally oxygen fugacity is imposed to the rock/mineral sample by the invariant reaction in the surrounding metal/metal-oxide redox buffer during the course of the run. To simplify the sample assembly, a large number of experimental studies used a metallic sample container and the corresponding metal-oxide powder of the metallic sample container to form a redox buffer. The corresponding metal-oxide powder is placed at top and/or bottom of the silicate sample (Figure 1). A redox buffer can also consist of a metal piece and the corresponding metaloxide inside the capsule if the sample container is made up of another metal or nonmetallic material. When the chemical reaction of the metal/metal-oxide buffer reaches its equilibrium, composition of the silicate sample changes to accommodate the imposed oxygen fugacity. Simply speaking, if the chemical environment is too oxidizing, excess oxygen will oxidize the metal to form metal-oxide. In contrast, metal-oxide will be reduced to release oxygen if the chemical environment is too reduced. In either way the oxygen fugacity is constrained to a constant value by this redox buffer. The oxygen fugacity can be determined from the compositions of all chemical components participating this reaction and thermodynamic data of this reaction. (see appendix I for detail of this part). When using a metal/metal-oxide buffer, it is assumed that the buffer imposed its oxygen fugacity to the assembly, so the oxygen fugacity of this system is determined by thermodynamic data of the metal/metal oxide reaction itself. It is also assumed that the fO2 of the specimen rapidly reaches its equilibrium value (Raterron et al.1998).

There are three common used metal/metal-oxide buffers in experimental studies: NNO, IW and CCO. Oxygen fugacity of NNO buffer is constrained by the reaction $2Ni + O_2 =$ 2NiO. This buffer is close to the natural fayalite-iron-quartz (FMQ) buffer, representing a relatively oxidizing condition at the earth's uppermost mantle. Whereas IW buffer is around 4 log-bar units below the NNO buffer. At oxygen fugacity slightly below the IW buffer, NiO in olivine will be reduced to form nickel-rich metal and reduced iron metal will also partition into the Ni to form alloy (O'Neill and Wall, 1987) relating to the redox condition of core formation, so IW buffer represents a very reducing redox state in lower mantle. The oxygen fugacity buffered by CCO is relatively neural comparing to NNO and IW (figure 2). CCO buffer is confined by chemical reactions that carbon reacts with oxygen to produce carbon oxides.

Oxygen fugacity of the experimental sample can not only be imposed by the surrounding redox buffer as mentioned above, but can also be constrained by the capsule and the housed sample itself. In the latter case, the silicate sample is directly in contact with the metallic capsule and the silicate/metallic capsule couple serves as an oxygen fugacity buffer. The oxygen fugacity is controlled by the reaction between the capsule material and the silicate sample. In previous high-pressure and high-temperature studies, iron, nickel, nickel-iron alloy and graphite were used as capsule materials. These studies are summarized in the following four paragraphs.

Iron capsules have been used by several Fe-Me interdiffusion studies to control oxygen fugacity (Bertran-Alvarez et al., 1992; Bejina et al., 1997,1999; Raterron et al., 1998). They report that olivine and iron maintain oxygen fugacity at known value within the stability field of olivine (Nitsan 1974). This technique does not require extra metal-oxide to buffer the oxygen fugacity, which simplifies the sample assembly. The ductile behavior of iron also protects olivine samples from deformation. This behavior is more

important when housing single crystal olivine (Bertran-Alvarez et al. 1992 and Bejina et al. 1999). Pure iron has also been used by Jackson et al. (2004) to house melt-bearing olivine aggregates to perform mechanical testing.

Nickel capsules (jackets) were used in deformation studies of olivine aggregates in the diffusion creep regime. Hirth and Kohlstedt (1995) housed olivine +enstatite +/- melt aggregates in nickel jacket to conduct deformation experiments from 1100-1300 °C at 300 MPa for 5 hours. S. Zhang et al. (2000) tested simple shear stress of olivine aggregates by jacketing the sample into a nickel sleeve and deforming it at 1200-1300 °C and up to 300 MPa. They claimed that the oxygen fugacity was likely controlled by the NNO buffer. Since no nickel oxide was added to the sample assembly, a possible explanation is that presumably a nickel oxide layer was formed on the surface of nickel sleeve at high temperature and the metal and metal-oxide together buffered the oxygen fugacity.

Nickel-iron alloy capsules were also used in varied deformation studies of olivine aggregates. Iron and nickel loss from olivine and alloy with the adjacent metallic capsule is a common problem in high-pressure and high-temperature experimental studies. Ironnickel alloy capsules overcome this problem by pre-equilibrium the composition of the nickel-iron alloy with the olivine. This technique has been used by Jackson et al. (2002), Jackson et al. (2004), Faul and Jackson (2007), Jackson and Faul (2010), and Farla et al. (2010) in deformation experiments of olivine aggregates. The olivine specimens were surrounded by Ni₇₀Fe₃₀ foil in experiments reported by above studies. The variation in composition of nickel-iron alloy can also impose different oxygen fugacity to the olivine sample. If the alloy that contains more iron than the equilibrium composition, metallic iron will be oxidized and released to the silicate as FeO until the equilibrium alloy composition is reached. This reaction consumes oxygen and the Fe-bearing samples gain extra iron from the metallic capsule. If the alloy contains less iron than the equilibrium composition, FeO in iron-bearing silicates will be reduced and alloy with the nickel capsule. This reaction releases oxygen to the sample. If the alloy is pre-equilibrium with the olivine, the oxygen fugacity in the capsule will be somewhat neutral.

Graphite capsules were first used by Ito and Kennedy (1967) in melting experiments to overcome the iron loss problem, and have became widely used in high-pressure and hightemperature experiments of anhydrous Fe-bearing samples especially for partially molten samples. The oxygen fugacity is limited by the presence of graphite at or below CCO (Taylor and Green 1989, Ulmer and Luth 1991).

1.2. Motivation of This Study

Oxygen fugacity imposed by iron, nickel, and nickel-iron alloy at high-pressure and hightemperature conditions for a relatively long duration is uncertain and needs to be studied systematically. Published estimates of oxygen fugacity in different capsules were predominately from diffusion and deformation experiments, which do not require relatively long experimental duration. In addition, these estimates are hard to compare because they did not provide compositional information of their sensors or used different thermodynamic models to estimate oxygen fugacity. This study annealed olivine aggregates from the same batch in iron, nickel, nickel-iron alloy and graphite capsules at 1 GPa and a range of temperature for relatively long duration of 168 hours. All the experimental parameters except oxygen fugacity were under controlled conditions. Therefore the changes in oxygen fugacity only reflect the influences of different capsule materials. A few experiments with added metallic oxides were performed to explore the efficiency of metal-oxide buffer at relatively long duration. Some short duration experiments were conducted to study the change of oxygen fugacity with experimental duration.

2. Methods

2.1. Experimental Setup

All runs were carried out in a 1/2" diameter end-loaded piston cylinder apparatus at a pressure of 1 GPa and temperatures from 1200 °C to 1400 °C for 24 to 168 hours (Table 1). The furnace assembly consisted of an outer NaCl sleeve, Pyrex sleeve, graphite heater and MgO inner spacers. San Carlos or sol-gel Fo90 olivine powder was placed in high purity graphite, pure iron, pure nickel and iron-nickel alloy capsules. Selected capsules contained nickel oxide/iron oxide or single crystal orthopyroxene as oxygen fugacity buffer materials or platinum wire/foil/powder as oxygen fugacity sensors. An alumina

disk was placed between the thermocouple and the capsule to prevent penetration of the thermocouple into the sample, as well as for insulation of the capsule. All furnace components were kept in a drying oven at 105 °C for at least 24 hours before use to ensure anhydrous condition. Temperature and run duration were controlled by a Eurotherm controller by using a type B (Pt-Rh) thermocouple. The power was manually increased until the temperature reached 400 °C. Then the temperature was increased at a rate of 50 °C/ minute until reached the target temperature. When the runs were finished, samples were quenched to room temperature in less than a minute by turning off the power to the furnace, followed by pressure release.

2.2. Post-run Sample Preparation, Image Capturing and Compositional Analysis The post-run samples were sectioned through the long axis, vacuum-impregnated in epoxy and polished with diamond paste, then alumina suspension and finally with colloidal silica to produce surfaces free of damage for image capturing.

High-resolution secondary electron images were obtained on a Zeiss Supra 55 VP field emission scanning electron microscope (SEM) at 5-15 kV acceleration voltage and 4.5 mm working distance, with an aperture of 30 or 60 μ m. Compositional Analysis was processed by using an EDAX energy dispersive spectroscopy (EDS) detector integrated with the microscope. Compositions of olivine and orthopyroxene were calibrated by standard mineral samples from Department of Mineral Sciences, Smithsonian Institution, Washington, D.C. (Jarosewich et al. 1980; Jarosewich 2002).

3. Experimental Results

- 3.1. Description of Post-run Samples
- 3.1.1. Overview

High-pressure and high-temperature annealing changed the dimension of capsules and texture of olivine grains. Metallic capsules show good mechanical integrity and the initial aspect ratios were somewhat preserved. No wide cracks crossing through entire samples were observed in those olivine aggregates annealed in metallic capsules (Figure 3a to 3c). Olivine samples housed in graphite capsules shrank along vertical axis and expanded along horizontal axis. Wide cracks go all the way through the entire sample vertically (Figure 3d). These observations indicate graphite capsules were deformed during cold pressing. Olivine aggregates have experienced grain growth and the post-run grain sizes are multiple times coarser than the starting grain size (Figure 4a to 4d).

Figure 3 shows the entire post-run olivine aggregates in pure iron, pure nickel, nickeliron alloy and graphite capsules. These samples were annealed at 1 GPa and 1400 °C for 168 hours, representing typical experimental conditions of this study. Figure 3a shows cross-section of olivine aggregate housed in Fe capsule. A large number of metallic blebs visible at this low magnification are distributed throughout the entire olivine sample. Slightly more metallic blebs are at the top and bottom. Olivine aggregate annealed in Ni capsule is shown in Figure 3b. Relatively big metallic blebs in olivine aggregate are aligned along olivine-capsule contact. A few big metallic blebs are in the center of the olivine aggregate (indicated by white arrows). Olivine aggregate annealed in Ni-Fe capsule (Figure 3c) has a large number of olivine grains plucked out during polishing. The plucking indicates that the strength of chemical bonding at grain boundaries were reduced and grain boundaries mobility was enhanced. Similar to Figure 3b, metallic blebs in olivine grains are aligned along olivine-capsule contact (indicated by black arrows), but show smaller sizes. No metallic blebs in the center can be resolved at this magnification. Figure 3d shows an intact area of olivine aggregate annealed in graphite capsule. As mentioned above, this post-run sample deformed when cold pressing due to relatively low density of the capsule material graphite. No metal particles can be detected at this magnification.

Figure 4 shows higher magnification SEM images of olivine grains in the center of the above four capsules. In iron capsule (Figure 4a), cracks formed from quenching distribute across olivine grains. Large metallic blebs with average diameter of 10 μ m are along olivine grain boundaries and at triple junctions. Intermediate metallic blebs with average diameter of 3 μ m are along cracks inside olivine grains. Much smaller metallic blebs (0.5-2 μ m in diameter) appear in the interior of olivine grains. In nickel capsule (Figure 4b), pattern of cracks is similar to that formed in iron capsule. Metallic blebs with 0.5-2

µm diameters appear in the interior of olivine grains. The small holes in the interior of olivine grains are presumably produced by loss of metallic blebs during polishing. Meltlike phase formed at a few triple junctions and some of them penetrate further through olivine grain boundaries, even connect adjacent triple junctions of relatively finer grains. A melt-like pocket is surrounded by eight olivine grains. Relatively large metallic blebs (diameter around 5 µm) include in melt-like pockets and triple junctions. In nickel-iron capsule (Figure 4c), a few tiny holes are in olivine interiors. The total numbers are much less than that in olivine grains in nickel capsule. A few number of these holes are filled with metallic blebs with 0.5-2 µm diameters. A portion of olivine grain boundaries is separated by gaps. Some of the grains were already plucked off during polishing. Olivine grains in graphite capsule (Figure 4d) also have tiny holes in the interior and along grain boundaries filled with metallic blebs with 0.5-1 µm diameters. A large number of opx grains (grain sizes are much smaller than olivine) present along olivine grain boundaries and in the interior of olivine grains. Cracks formed during quenching are across olivine grains.

3.1.2. Orthopyroxene Rinds at Sample-capsule Contacts

Orthopyroxene rinds were observed at capsule-crystal contacts in all runs housed in metal capsules. Texturally they were revealed by relatively darker color and lower topography than olivine grains in SEM images (Figure 5). Compositionally, they were identified by roughly 50% less Si atoms than that in olivine grains. Figure 6 shows an EDS line scan of

major elements concentrations from capsule towards olivine grains. The orthopyroxene rind is distinguished from olivine by the plateau in Silicon concentration line and corresponding the step in Magnesium concentration line.

3.1.3. Post-run Metal Oxides

For those runs with metal/metal-oxide buffers (CAP6, CAP7 and CAP8), no metal-oxides were detected from SEM images or EDS analysis. Figure 7a shows a very rough boundary between iron capsule and silicate grains (CAP7). A large number of metallic clots are within olivine grains and partially connected with the iron capsule. A few finegrained olivine crystals are enclosed in the iron capsule near the contact. These observations indicate that a portion of the iron oxide has been reduced and alloyed with the original iron capsule to form a new rough contact and the rest metallic iron reduced from iron oxide are distributed in olivine grains close to the contact. Olivine grains housed in nickel capsule with added nickel oxide for 168 hours (CAP6) does not show any difference with those samples without nickel oxide annealed at the same condition (Figure 7b). Although the run duration of the other nickel/nickel-oxide experiment at same pressure and temperature condition (CAP8, Figure 7c) was only 24 hours, no oxide was left in the post run sample. The rough contact between metallic nickel and crystals indicate that reduced nickel from nickel oxide was alloyed with the nickel capsule. Olivine grains close to the contact are brighter then those towards the center, indicating they have higher metal concentration.

3.2. Olivine Composition

Forsterite numbers (Fo#) of olivine aggregate housed in the same capsule material increased with increasing temperature at constant run duration (Figure 8). Olivine samples housed in Ni capsules have the highest Fo#, which implies relatively more iron loss. At 1200 °C, relative great gradient of Fo exists between olivine grains in the center and at edge. Olivine grains in the center slightly lost iron, whereas grain at edge lost much more iron. The gradient decreases with increasing temperature. At 1400 °C, almost all Fe diffused out from olivine grains in the entire capsule and the gradient does not exist. Fo# of olivine grains housed in the center of iron capsules increase from Fo90 at 1300 °C to Fo93 at 1400 °C. Olivine grains at edge systematically have lower Fo number than those in the center. At 1300 °C, the starting composition of olivine grains in the center has been preserved. Olivine grains at edge gained iron from the iron capsule, showing a lower Fo# of 88. At 1350 °C with added iron oxide, the starting composition of olivine grains in center was somewhat preserved, with slightly iron loss. Fo# of olivine grains at edges are 5 units lower than those in center. At 1400 °C, olivine grains experienced iron loss, resulting in a higher Fo# of 93. Grains at edge has a little bit lower Fo# than those in the center. Fo# of olivine housed in graphite and Fe-Ni capsules were approximately 90, indicating no iron was diffused out from olivine and the starting olivine composition was preserved.

Figure 9 shows Fo# of olivine grains in the center of nickel capsule versus run duration. For those samples without nickel oxide added, fayalite concentration decreases with increasing run duration for both series of samples annealed at 1200 °C and 1300 °C. For the 24-hour run with added nickel oxide, the starting fayalite concentration was somewhat preserved. The starting fayalite concentration of the 240-hour run with added nickel oxide was not preserved but is significantly higher than those without nickel oxide.

3.3. Oxygen Fugacity

Figure 10 shows all oxygen fugacities determined from available EDS data as a function of temperature (data is from Table 8-11 in Appendix I). Four different methods were employed to calculate the values, depending on availability of phases. The first method (termed FePt) used olivine-opx-metal equilibria, indicated by the following two equations:

 $Fe_2SiO_4 = 2 Fe + SiO_2 + O_2 \quad [1]$

 $Mg_2SiO_4 + SiO_2 = Mg_2Si_2O_6 \quad [2]$

Olivine orthopyroxene

Since platinum foils/particles were inserted into the sample prior to the runs, iron reduced from olivine crystals alloyed with the platinum oxygen fugacity sensors. Reaction [2] represents the formation of opx rind at edge of samples. This reaction buffered silica activity in reaction [1]. The oxygen fugacity determined from this equilibria is (full derivation available in Appendix I)

$$logfO_{2} = logK - 2loga_{Fe}^{me} - loga_{SiO2} + loga_{Fa}^{ol} + logfO_{2}^{0}$$
$$= \frac{-\Delta G^{0}}{2.303RT} + \frac{\Delta V(P-1)}{2.303RT} - 2\log(\gamma_{Fe}^{met}, X_{Fe}^{met}) - loga_{SiO2} + \log(\gamma_{Fa}^{ol}, X_{Fa}^{ol})$$

 X_{Fe}^{met} in the above equation represents mole concentration of iron in iron-platinum alloys, and X_{Fa}^{ol} stands for mole concentration of fayalite (Fe₂SiO₄) in olivine adjacent to the iron-platinum alloy. These two values were determined by EDS measurement. The other thermodynamic parameters are available from literature (see Appendix I). The second method (termed FeNi) followed the same equations above but measured mole fractions of iron alloyed with nickel blebs or nickel capsules and fayalite concentration in olivine grains adjacent to the metal alloy, and used their corresponding thermodynamic data (see Appendix I).

The third method (termed NiFe) is suitable for natural San Carlos olivine. The minor amount of Ni₂SiO₄ contained in this natural olivine was reduced to form metallic nickel, silica and oxygen:

 $Ni_2SiO_4 = 2 Ni + SiO_2 + O_2$ [3]

This reaction taked place with reaction [1] at the same time during annealing. Compositional data for using this method to calculate oxygen fugacity was mole concentrations of nickel in nickel-iron alloy and Ni_2SiO_4 in olivine adjacent to the metal alloy. The equation for oxygen fugacity calculation is similar to the one for FePt method but iron and fayalite are substituted with nickel and Ni_2SiO_4 , respectively.

$$\begin{split} logfO_{2} &= logK - 2loga_{Ni}^{met} - loga_{SiO2} + loga_{Ni2SiO4}^{ol} + logfO_{2}^{0} \\ &= \frac{-\Delta G^{0}}{2.303RT} + \frac{\Delta V(P-1)}{2.303RT} - 2\log(\gamma_{Ni}^{met}.X_{Ni}^{met}) - loga_{SiO2} \\ &+ \log(\gamma_{Ni2SiO4}^{ol}.X_{Ni2SiO4}^{ol}) \end{split}$$

The associated thermodynamic data is summarized in Appendix I.

The last method (termed opx) refers to the equilibria between iron, silica, oxygen and opx rind:

 $Fe + SiO_2 + 0.5O_2 = FeSiO_3[4]$

The oxygen fugacity equation for this equilibria is (full derivation in Appendix I)

$$logfO2 = -2logK + 2logX_{Fs} + 2logY_{Fs} - 2logX_{Fe} - 2logY_{Fe} - 2logA_{SiO2}$$

Mole concentrations of iron in iron-nickel alloy and Ferrosilite (FeSiO₃) in

orthopyroxene were measured by EDS. Other parameters are indicated in Appendix I.

CAP1, CAP3, CAP4, CAP6, CAP7, CAP9, CAP11, CAP12 and CAP18 were determined by using multiple methods mentioned above. The differences between these methods from the same sample were within 1 log unit, and most of them were within 0.5 log unit, showing good data agreement. This figure emphasizes that oxygen fugacities of runs in different capsules were lower than their corresponding buffers, but preserve relative orders. Oxygen fugacity of runs in the same capsule material increases with increasing temperature, which is consistent with the trend of the corresponding buffer.

3.3.1. Oxygen Fugacity in Different Capsules

Figure 11 shows oxygen fugacities of samples annealed in nickel capsules as a function of temperature. This figure emphasizes that oxygen fugacity of olivine in nickel capsules fall in the area between CCO buffer and IW buffer. Differences between determined oxygen fugacities from the same sample vary from 0.1 to 0.9 log unit. At 1200 °C and 1400 °C, determined oxygen fugacities match each other very well. The sample annealed for 50 hours has slightly higher oxygen fugacity than that annealed for 168 hours. At 1300 °C, 10 data points from 3 samples annealed at 168 hours distribute across 1.2 log units.

Oxygen fugacities for olivine grains housed in iron capsule were 2 log units below IW buffer (Figure 12). Oxygen fugacity of the run annealed at 1350 °C for 168 hours with added Fe₂O₃ does not show higher value than those without oxide added. For the two samples annealed at the same run condition, oxygen fugacity of CAP1 determined from nickel concentration in olivine and iron capsule and that of CAP14 determined from iron concentration in olivine and platinum are highly matched with each other.

Oxygen fugacities for olivine housed in graphite and nickel₈₀-iron₂₀ capsule for 168 hours were within 1 log unit and approximately 2.5 log unit below CCO buffer (Figure 13). The sample annealed in graphite capsule for 50 hours had oxygen fugacity slightly lower than CCO buffer. Differences for oxygen fugacities of same sample determined from different methods were within 0.5 log units.

3.3.2. Oxygen Fugacity versus Run Duration

Varies samples annealed in nickel capsules for a range of duration indicate that oxygen fugacities remain constant with increasing time. Figure 14 shows oxygen fugacities of olivine aggregates annealed in nickel capsules determined from iron concentration in nickel. From 94 to 240 hours run duration, oxygen fugacity kept at approximately -9 log units. The sample with added nickel oxide annealed for 240 hours did not show a significant higher oxygen fugacity than that in other samples without nickel oxide. EDS analysis did not indicate any nickel oxide left, either. Oxygen fugacity in the sample with added nickel oxide added at top and bottom of the capsule were consumed after 24 hours; olivine grains adjacent to capsule at top and bottom have higher nickel concentration.

4. Discussion

This experimental study systematically investigated oxygen fugacities of olivine aggregates annealed in iron, nickel, nickel₈₀-iron₂₀ and graphite for relatively long experimental duration. In general, these metallic/graphite only capsule techniques cannot maintain the oxygen fugacity of anhydrous melt-free olivine aggregates at their

corresponding metal/metal-oxide buffers for run duration over 24 hours. In other words, metal oxide coatings do not form at metal-crystal interface at the reported pressure and temperature condition to buffer the oxygen fugacity with the capsule materials. However, metallic/graphite only capsule techniques are able to control the oxygen fugacity of olivine grains over the course of run at values lower than their corresponding metal/metal-oxide buffers. Their relative orders are kept and remains unchanged throughout the course of the run.

Post-run olivine aggregates are still within the stability field of olivine (Nitsan 1974). Although olivine grains annealed in these capsules have varies degree of iron loss, EDS analysis shows that their compositions are still stoichiometric (except those adjacent to metallic capsule turned to orthopyroxene).

4.1. Graphite and Ni₈₀Fe₂₀ Capsules

The identical oxygen fugacity determined from olivine aggregates in graphite and $Ni_{80}Fe_{20}$ capsules represent the intrinsic oxygen fugacity of olivine samples. It suggests that the intrinsic oxygen fugacity of anhydrous melt-free Fo90 olivine is at or 1 log unit below IW buffer. The preserved starting composition of entire olivine aggregates in both types of capsules indicates that these grains were neither oxidized nor reduced. It is consistent with the observations of SEM images that these samples do not show metallic

blebs along grain boundaries and cracks. Nickel and iron concentrations of the post-run Ni₈₀Fe₂₀ remained unchanged, indicating that this alloy is pre-equilibrium with the olivine aggregates and will not release or consume oxygen at the experimental pressure and temperature conditions.

Olivine grains annealed in $Ni_{80}Fe_{20}$ capsules were easy to pluck off during polishing, indicating bonds between olivine grains are relatively weaker than those annealed in other capsules.

4.2. Nickel Capsules

Nickel is the most studied capsule material in this experimental study. The oxygen fugacity determined in nickel capsule is 2-3 log units below NNO buffer. It is the highest oxygen fugacity among that of all capsule materials investigated in this study. All olivine grains in nickel capsules have experienced different degrees of iron loss. Due to the iron concentration gradient at crystal-capsule contact, olivine grains adjacent to nickel capsules have more severe iron loss than those in the center. This process is similar to the observations of iron loss to noble-metal capsules being reported by various experimental studies as early as 1962 (Yoder and Tilley noticed iron loss from basalt to platinum container). At high temperature and relatively low oxygen fugacity, high activity of metallic iron leads to the reduction of iron oxide from olivine grains. The metallic iron is readily to diffuse into the metallic capsule and alloy with nickel.

The use of nickel oxide cannot increase oxygen fugacity for experiments longer than 24 hours, but only reduces the rate of iron loss to the nickel capsule. This study implies that although oxygen fugacity is very stable in nickel capsules during long duration experiments, this technique is not suitable for studying upper mantle olivine due to the iron loss problem.

4.3. Iron Capsules

The oxygen fugacity determined in iron capsule is 2 log units below IW buffer, which represents a strong reducing condition. This study shows that olivine grains have iron loss problem at 1400 $^{\circ}$ C in iron capsules, but this problem can be fixed by lowering the temperature to 1350 $^{\circ}$ C or 1300 $^{\circ}$ C and combining with add Fe₂O₃.

Previous high-pressure and high-temperature studies of iron-bearing samples in iron capsules had much higher pressures and much shorter durations than those in this study. These studies were mainly diffusion studies at pressures ranging from 4.6-9 GPa and run duration from 15 minutes to several hours. Bertran-Alvarez et al. (1992) report an oxygen fugacity of -0.5 log units below IW buffer from a 6-hour diffusion experiment of a single crystal San Carlos Fo90 olivine at 900 °C and 7 GPa. Raterron et al.1998 determined that the oxygen fugacity was 1-2 log units above IW buffer by following the experiments described by Bertran-Alvarez et al. (1992) with much shorter run duration of only half an

hour. Other diffusion studies of single crystal olivine by Jaoul et al. (1995) and Bejina et al. (1999), and a deformation study of single crystal garnet by Cordier et al. (1996) estimated the oxygen fugacities following Bertran-Alvarez et al. (1992) and claimed that their experiments were conducted under known oxygen fugacity conditions established by placing crystals in direct contact with iron capsules. The determined oxygen fugacities from the 30-min experiment by Bertran-Alvarez et al. (1992), 6-hour experiment by Raterron et al. (1998) and 168-hour experiments from this study imply that the oxygen fugacity of capsuling olivine in iron capsules is 1-2 log units above IW buffer at the beginning, then quickly drops to IW buffer after 6 hours, and keeps decreasing until reaches 2 log units below IW buffer and remains unchanged for up to 168 hours. This observation suggests that iron capsules are not suitable for housing olivine aggregates at oxygen fugacity above IW buffer in high-pressure and high-temperature experiments that require relatively long duration (i.e. partial melting experiments requiring steady state grain growth).

A notable feature for olivine grains annealed in iron capsule is the significant amount of metallic blebs. Relatively larger metallic blebs are close to the iron capsules and along grain boundaries and cracks. Small metallic blebs are mainly inside olivine grains. EDS analysis shows composition of these metallic blebs are iron alloyed with small amount of nickel. In reducing chemical environment, iron oxide in olivine quickly reduced to metallic iron. The concentration gradient between metallic iron capsule and olivine leads to the metallic iron to be oxidized and diffuse into olivine crystal lattice to compensate

reduced FeO. This process keeps iron diffusion from capsule to the center of olivine aggregates, causing a large number of big metallic blebs throughout olivine grain boundaries and cracks. Since grain boundaries and cracks provide paths for iron diffusion, larger metallic blebs are nucleated along grain boundaries and cracks. At this extremely oxygen fugacity, nickel oxide in olivine grains are also reduced to metallic nickel and are readily to alloy with metallic iron. This observation further suggests that iron capsule is not suitable for annealing olivine samples at upper mantle's pressure and temperature for relatively long time. The low oxygen fugacity imposed by the equilibrium between the capsule material and olivine sample itself leads to nucleation of metallic phase in olivine, which is not observed in natural samples from the upper mantle.

These iron-nickel blebs are similar to the "dusty" olivine grains in different kinds of chondrites, which are characterized by the presence of Fe-Ni metallic particles throughout the interior of olivine grains. The texture of "dusty" olivine has been experimentally reproduced by researches using low-pressure furnaces. Boland and Duba (1981) heated single crystal Fo92 olivine to temperatures in the range of 950-1500 °C for several hours under controlled oxygen fugacity by mixing of gas and observed that half of the iron in olivine has been reduced to metallic phase. Fe inclusions are also observed in olivine single crystal over a few microns from the Fe capsule after 35 minutes at 6.4 GPa and 1490-1595 °C (Raterron et al.1998). Recently, Cohen and Hewins (2004) used vertical muffle tube furnaces to heat powder of chondritic meteorite composition at 1 atm and 1580 °C for 1-18 hours under controlled oxygen fugacity of -11.8, which was 3.7 log

unites below the IW buffer. They observe metallic iron both as melt droplets and inclusions in olivine, similar to those found in chondrules. Oxygen fugacities of iron-capsules experiments in my study at higher pressure of 1 GPa and similar temperature from 1300-1400 °C were approximately 2 log unites below the IW buffer, which is consistent with the low-pressure furnace studies. The small amount of nickel in the metallic phase reported in these studies indicate that the oxygen fugacity is below the nickel precipitation curve (approximately at IW buffer, refer to O'Neill and Wall 1987), which matches oxygen fugacities determined in my study.

Although iron capsules have some problems to house olivine grains at upper mantle's pressure and temperature conditions for long duration, they are ideal for studying physical properties of iron-bearing rocks under redox conditions relates to core formation and on other terrestrial planets and planetesimals. As mentioned above, IW buffer is close to the nickel precipitation curve, which is associated with the redox condition of core formation (O'Neill and Wall 1987). Based on mineralogical and geochemical studies of meteorites and lunar samples, oxygen fugacity of small asteroidal bodies ranges from IW-5 to IW+1; lunar samples yield IW-2 to slightly above IW, and the basaltic shergottites on Mars are from close to or slightly below IW to IW+2 (summarized by Wadhwa 2008).

4.4. Size of Platinum Sensors

The size of platinum sensor affects the texture and composition of olivine grains surrounding the sensors. For the sample with added micron size platinum powder as oxygen fugacity sensor, no textural and compositional changes were observed from olivine grains around platinum powder. For the olivine aggregate in iron capsule with relatively big platinum foil, a metallic bleb-free halo around the foil is very obviously observed (Figure 15). In contrast, olivine grains outside the halo show a large number of metallic blebs along grain boundaries and in the interior of olivine grains. This observation outside the halo is very similar to that of CAP1. These two samples had the exactly same run condition, but CAP1 is without platinum foil.

Relatively large size of platinum sensors may cause oxygen fugacity heterogeneity. In CAP14, iron in adjacent olivine grains incorporated into the metallic Pt phase until an alloy with the equilibrium composition is produced. Oxygen was released during this process and the produced oxygen tended to oxide olivine grains surrounding the Pt foil. This oxygen fugacity heterogeneity is indicated in the image by the much less metallic blebs inside the halo than the outside. Although the oxygen fugacity outside the halo in CAP14 cannot be determined from nickel concentration in olivine and metallic iron (solgel olivine does not contain nickel oxide), it should be close to the oxygen fugacity determined from CAP1 due to the same experimental conditions. Based on the oxygen fugacity determined from CAP1 and that determined from the iron concentration in the Pt-Fe alloy, the oxygen fugacities outside and inside the halo are -12 and -11 log units, respectively. This difference implies that although the iron capsule imposed an extremely reduced chemical environment to the entire sample, locally this low oxygen fugacity is somewhat relieved by released oxygen due to iron incorporation to platinum foil.

This study emphasizes the importance of minimizing the oxygen fugacity imposed by the platinum sensor. This problem has been noticed by grove (1981), who used PtFe alloy that is in equilibrium with basaltic melt as oxygen fugacity sensor to eliminate releasing oxygen. The method used in this study provides an alternative way to solve this problem and has advantages in three aspects. Firstly, the micron size platinum particles will quickly equilibrate with the iron-bearing experimental samples and excessed oxygen is negligible. In contrast, EDS data shows that the platinum foil in CAP14 was still not equilibrated with iron after 168 hours indicating release of oxygen was throughout the entire experiment duration. Secondly, using this method does not require calculations of the equilibrium composition of PtFe alloy. Lastly, the post-run composition of PtFe particles is measureable from multiple points evenly distributed throughout the entire sample, ensuring the accuracy of determined oxygen fugacity.

5. Conclusions

This study systematically investigated oxygen fugaciteis set by iron, nickel, nickel₈₀iron₂₀ and graphite capsules at relatively long experimental duration. The results show that these capsule materials effectively control oxygen fugacity between slightly below CCO buffer to 2 log units below IW buffer. Oxygen fugacities in nickel capsules are in between CCO and IW buffers (2-3 log units below NNO buffer); in nickel₈₀-iron₂₀ and graphite capsules are at or 1 log unit below IW buffer, most closely representing intrinsic oxygen fugacity of anhydrous melt-free Fo90 olivine; and in iron capsules are 2 log units below IW buffer, representing a strong reducing condition that relates to core formation and on other terrestrial planets and planetesimals perhaps explaining the formation of "dusty" olivine in chondrites. For those experiments with added metal-oxides in iron and nickel capsules, no metal-oxides were preserved in post-run samples, indicating that metal/metal-oxide buffers cannot maintain oxygen fugacities at their corresponding buffers for relatively long duration in piston cylinder experiments. Heterogeneity of oxygen fugacity observed in experiments with platinum oxygen fugacity sensors emphasizes that it is important to minimize their volume while using platinum as external oxygen fugacity sensors.

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Tables

Run #	Capsule Material	Temperature (°C)	Pressure (Gpa)	Duration (hours)	Sensors
CAP1	Pure Iron	1400	1	168	
CAP2	Pure Nickel	1400	1	168	
CAP3	Ni-Fe Alloy	1400	1	168	
CAP4	Pure Nickel	1300	1	168	
CAP5	Pure Nickel	1300	1	80	NiO
CAP6	Pure Nickel	1300	1	240	NiO
CAP7	Pure Iron	1350	1	168	Fe ₂ O ₃
CAP8	Pure Nickel	1300	1	24	NiO
CAP9	Graphite	1400	1	168	
CAP10	Ni-Fe Alloy	1400	1	168	
CAP11	Pure Nickel	1300	1	168	
CAP12	Pure Nickel	1200	1	168	Pt wires
CAP13	Pure Iron	1300	1	168	Pt wires
CAP14	Pure Iron	1400	1	168	Pt foil
CAP15	Graphite	1400	1	48	Pt foil
CAP16	Pure Iron	1300	1	108	Pt foil
CAP17	Pure Nickel	1200	1	50	Pt powder
CAP18	Pure Nickel	1300	1	94	Pt powder

 Table 1. Summary of experimental conditions

Figures



Figure 1. Metal/metal oxide buffer assembly. Metal/Metal Oixde buffer assembly used in this study. This assembly is commonly used by other researchers. Metal oxide is added at top and bottom of the olivine sample.



Figure 2. Oxygen fugacities of metal/metal-oxide buffers at pressure (1 GPa) and temperature conditions of this study.








Figure 3. SEM images of sectioned experimental capsules. Same San Carlos olivine powder was annealed in 4 different capsules for 168 hours at 1400 oC and 1 GPa. (a) Olivine aggregate in Fe capsule (CAP1). Metal particles visible at low magnification are distributed throughout the entire cross section of olivine aggregate. Slightly more metal particles are at the top and bottom. Compared to CAP2 and CAP3, CAP1 has much more metal particles presented. (b) olivine aggregate in Ni capsule (CAP2). Visible metal particles at low magnification are distributed in olivine grains along olivine-capsule contact. Multiple metal particles are in the center of the cross section of olivine aggregate (indicated by white arrows). (c) olivine aggregate in Ni-Fe capsule (CAP3). A large

number of olivine grains were plucked out when polishing. The plucking indicates that the strength of chemical bonding at grain boundaries were reduced and grain boundaries mobility was enhanced. (high resolution image show cracks along grain boudnaries). At this magnification, metal particles are only detected in olivine grains along olivinecapsule contact (indicated by black arrows). (d) olivine aggregate in graphite capsule (CAP9). This post-run sample was shrank along vertical axis and expanded along horizontal axis due to relatively low density of the capsule material graphite. No metal particles can be detected at this magnification.





Figure 4. High magnification SEM images showing center of olivine aggregates annealed at 1400 °C and 1 GPa for 168 hours in different capsules. (a) CAP1 iron capsule. (b) CAP2 nickel capsule. (c) CAP3 iron-nickel capsule. (d) CAP9 graphite capsule.



Figure 5. Orthopyroxene rinds formed in different metal-crystal contacts. Compared to olivine, opx rind shows lower topography and darker color. (a) in Ni₈₀-Fe₂₀ capsule (CAP10). (b) in iron capsule (CAP1). (c) in nickel capsule with added NiO powder (CAP6). (d) in nickel capsule (CAP11).



Figure 6. Orthopyroxene rinds indicated by EDS line scan. Orthopyroxene rinds are distinguished from olivine by the plateau in Silicon concentration line and correspondingly the step in Magnesium concentration line.



Figure 7. capsule-crystal contacts where metal-oxides were added. (a) Rough boundary between iron capsule and silicate grains (CAP7). A large number of metallic clots are within olivine grains and partially connected with the iron capsule. A few fine-grained olivine crystals are enclosed in the iron capsule near the contact. (b) Olivine grains housed in nickel capsule with added nickel oxide for 168 hours (CAP6) does not show any difference with those samples without nickel oxide annealed at the same condition. (c) Although the run duration of the other nickel/nickel-oxide experiment at same pressure and temperature condition (CAP8) was only 24 hours, no oxide was left in the post run sample. The rough contact between metallic nickel and crystals indicate that reduced nickel from nickel oxide was alloyed with the nickel capsule. Olivine grains close to the contact are brighter then those towards the center, indicating they have higher metal concentration.



Figure 8. Summary of Fo# of post-run samples. The red line indicates the Fo# of pre-run olivine. Each symbol represents the average Fo# of multiple points from the same sample, with error bar indicating the standard deviation. For those symbols without error bars, the error bar is smaller than the symbol itself. Symbols with solid fill represent Fo# of olivine grains in the center of samples, whereas symbols without solid fill represent Fo# of olivine grins adjacent to the capsules. The five diamond symbols connected by straight lines at top show Fo# of samples annealed in nickel capsules for 168 hours from 1200 °C to 1400 °C. The three delta symbols connected by straight lines show Fo# of samples for 168 hours from 1300 °C to 1400 °C. They imply that Fo# of olivine aggregate housed in the same capsule material increase with increasing temperature at constant run duration.



Figure 9. Fo# of olivine grains in the center of nickel capsule versus run duration. For those samples without nickel oxide added, fayalite concentration decreases with increasing run duration for both series of samples annealed at 1200 °C and 1300 °C. For the 24-hour run with added nickel oxide, the starting fayalite concentration was somewhat preserved. The starting fayalite concentration of the 240-hour run with added nickel oxide is significantly higher than those without nickel oxide.



Figure 10. All oxygen fugacities determined from available EDS data as a function of temperature. This figure emphasizes that oxygen fugacities of runs in different capsules were lower than their corresponding buffers, but preserve relative orders. Oxygen fugacity of runs in the same capsule material increases with increasing temperature, which is consistent with the trend of the corresponding buffer.



Figure 11. Oxygen fugacities of samples annealed in nickel capsules as a function of temperature. Samples are distinguished by symbols. Colors indicate different methods to calculate oxygen fugacities.



Figure 12. Oxygen fugacities of samples annealed in iron capsules as a function of temperature. Samples are distinguished by symbols. Colors indicate different methods to calculate oxygen fugacities.



Figure 13. Oxygen fugacities of samples annealed in nickel₈₀-iron₂₀ and graphite capsules as a function of temperature. Samples are distinguished by symbols. Graphite capsules are indicated by delta and squares. Colors indicate different methods to calculate oxygen fugacities.



Figure 14. Oxygen fugacities of olivine aggregates annealed in nickel capsules versus experiment duration. This figure emphasizes that oxygen fugacities remain constant with increasing time.



Figure 15. Metallic bleb-free halo around Platinum foil in sample housed in iron capsule (indicated by yellow dash line).

CHAPTER III

GRAIN BOUNDARY WETNESS OF PARTIALLY MOLTEN DUNITES

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Abstract

Samples of Fo₉₀ olivine and basaltic melt were annealed at a range of temperatures and a pressure of 1 GPa in a piston cylinder apparatus from 1 to 336 hours. Post-run samples have melt contents from 0.03% to 6.8% and mean grain sizes from 4.3 to 84.5 µm. The grain boundary wetness, a measure of the intergranular melt distribution, was determined by analyzing high-resolution SEM images. The results show that grain boundary wetness increases with increasing melt content to values well above those predicted by the idealized isotropic equilibrium model for a finite dihedral angle. Additionally, at fixed melt content grain boundary wetness increases with increasing grain size. Samples annealed at a range of temperatures and constant melt content show that grain boundary wetness does not depend on temperature. These observations emphasize that the dihedral angle alone is not adequate to characterize the melt distribution in partially molten rocks. Including the grain size sensitivity of the grain boundary wetness, diffusion creep viscosities at upper mantle grain sizes are significantly lower compared to predictions from the idealized model, suggesting that diffusion creep may be the dominant deformation mechanism for partially molten regions of the upper mantle.

1. Introduction

The grain scale distribution of melt plays a key role for physical properties of partially molten regions in Earth's upper mantle (Shankland and Waff, 1977; Hirth and Kohlstedt, 1995; Faul 2001; ten Grotenhuis, 2005, Yoshino et al., 2009). The physical principle governing the grain scale melt distribution in partially molten rocks is the surface energy between solid grains and melt (Waff and Bulau, 1979, Bulau et al., 1979). This was originally expresses as a balance of surface tensions, establishing a fixed dihedral angle between two crystalline grains and the melt. For a dihedral angle greater than 0° and up to 60°, grain boundaries are melt free and the melt forms an interconnected network along three-grain edges (triple junctions) at all melt fractions. For dihedral angles greater than 60°, a threshold melt fraction is needed to form an interconnected network. A dihedral angle of 0° implies complete wetting of all grain boundaries. A model developed for the three-dimensional melt distribution based on surface tension equilibrium assumes grains of a fixed size with space filling geometry and isotropic surface energy. The predicted melt geometry has constant interfacial curvature and is self-similar, i.e. independent of grain size and melt fraction (von Bargen and Waff, 1986).

Experimental observations indicate that the melt geometry of partially molten rocks is not adequately described by this idealized isotropic equilibrium model (Waff and Faul, 1992; Faul et al, 1994; Faul 1997). Observations from post-run samples show that melt not only forms triple junctions with constant interfacial curvature, but also larger pockets surrounded by four or more grains with faceted crystal-melt interfaces. Faceting is due to anisotropic surface energy of olivine, first noted by Cooper and Kohlstedt (1982). The faceted crystal-melt interfaces are slow growing and tend to stabilize the melt pockets (Waff and Faul, 1992). High-resolution imaging shows that triple junctions include smoothly curved as well as faceted interfaces (Cmíral et al., 1998). Importantly melt also wets some, but not all, two-grain boundaries (Faul 1997, Garapić et al., 2013).

A key aspect not considered in the idealized model is that surface energy reduction also drives grain growth. Theories for normal grain growth predict that polycrystalline aggregates have a stationary normalized grain size distribution, with grains below a critical size shrinking, while grains above the critical size grow (Atkinson 1988). In particular, at sites where grains shrink and disappear, neighboring grains not previously in contact have to adjust their grain boundary plane orientations to the new environment. Consequently, the interstitial melt geometry is not static as assumed in the idealized model, but a dynamic, continuously evolving distribution. In analogue experiments where the growth process could be directly observed with a microscope Walte et al. (2003) showed that this process produces transiently wetted two-grain boundaries even in near isotropic systems with a dihedral angle that is larger than that of the olivine-basalt system.

Experimental observations coupled with grain growth models therefore imply that the melt geometry in partially molten systems cannot be characterized by the dihedral angle alone. A parameter is needed that better accounts for the variability of the melt geometry

observed in partially molten rocks. Dividing the melt geometry into different geometrical categories (Faul, 1997, Cmíral et al., 1998) incurs the problem that the division is necessarily somewhat arbitrary, as a continuous range of geometries is observed. A relatively straight forward parameter that is model-independent and includes measurement of the total interfacial area is the grain boundary wetness ψ (Takei, 1998, 2002). It is defined as the ratio of the length of solid-liquid boundaries (L_{sl}) divided by the total grain boundary length (solid-liquid + solid-solid) (Yoshino et al, 2005):

$$\psi = \frac{L_{sl}}{L_{sl} + 2L_{ss}}$$

Since grain growth is an important aspect of the melt geometry the wetness needs to be determined for a range of grain sizes. The measurements need to be made over a sufficiently large area to be representative of the melt distribution, and at sufficiently high resolution to include melt cusps deeply penetrating between two grains, as well as fully wetted two-grain boundaries with a thickness to 100 nm (Cmíral et al., 1998, Garapić et al., 2013).

2. Methods

2.1. Experimental Setup

The starting material for the experiments consisted of solution-gelation derived Fo90 olivine powder with a mean grain size of 1 μ m. For details of the preparation of the

powder see Jackson et al. (2002). The olivine powder was mixed with basaltic glass powder by grinding in an agate mortar (see Table 2 of Faul et al. 2004 for the composition of the oxide-derived basalt). All experiments were carried out in a 1/2" diameter end-loaded piston cylinder apparatus at a pressure of 1 GPa and temperatures from 1250 °C to 1450°C for 1 to 336 hours (Table 2). Only anhydrous components were used for the furnace assembly consisting of an outer NaCl sleeve, Pyrex sleeve, graphite heater and MgO inner spacers. The sample material was encapsulated in high purity graphite capsules. A small number of experiments were conducted in graphite-Pt double capsules and NiFe capsules. No discernable differences were observed between the different capsule materials. For all assemblies the capsule was separated from the graphite heater by a thin alumina sleeve. The fully dense alumina sleeve also ensured the mechanical integrity of the capsule during initial compression. An alumina disk was placed between the thermocouple and the capsule to prevent penetration of the thermocouple into the capsule, as well as for insulation of the capsule. All furnace components were kept in a drying oven at 105 °C for at least 24 hours before use. Starting materials for 1-hour runs were annealed at 450 °C in a muffle oven overnight.

Temperature and run duration were controlled with a Eurotherm controller using a type B (Pt-Rh) thermocouple. The power was manually increased until the temperature reached 400 °C. The temperature was then ramped up by the controller at a rate of 50 °C/ minute until reached the target temperature. At the end of an experiment the samples were quenched by turning off the power to the furnace, followed by pressure release.

The capsule was placed at the center of the hot zone of the furnace in order to avoid melt segregation due to thermal gradients (Lesher and Walker, 1988). To determine the hot zone axial temperature profiles were mapped by conducting a number of temperature calibration experiments following the method of Watson et al. (2002). This method uses the fact that Al₂O₃ reacts with MgO at high pressures and temperatures to form a spinel layer. The width of the spinel layer is a function of temperature (T, in K), pressure (P, in GPa) and time (t, in s): $\Delta X = [8.58 \times 10^{11} \cdot \exp(-48865/T - 2.08 \cdot P^{0.5}) \cdot t]^{0.5}$ (Watson et al., 2002). The upper part of the calibration assemblies consisted of an Al₂O₃ thermocouple sleeve inside a MgO sleeve, with the thermocouple at the position of the bottom of the capsule in the actual experiments. The lower part of the graphite furnace consisted of an MgO spacer with empty Al₂O₃ thermocouple sleeve along axis. After each calibration experiment the whole assembly was sectioned longitudionally in order to measure the spinel layer width every 0.5 mm. The axial temperature distribution for each experiment was constructed by using the equation above. The results show that the temperature along the length of sample location varies by less than 10 °C and temperatures measured by the thermocouple do not need to be corrected (Figure 16).

2.2. Post-run Sample Preparation and Image Processing

The post-run samples were sectioned through the long axis, vacuum-impregnated in epoxy and polished with diamond paste, then alumina suspension and finally with colloidal silica to produce surfaces free of damage for imaging.

High-resolution secondary electron images were obtained on a Zeiss Supra 55 VP SEM at 5-15 kV acceleration voltage and 4.5 mm working distance, with an aperture of 30 μ m. Each image consists of 2048 x 1536 pixels with a resolution of 0.014 to 0.029 μ m/pixel (depending on magnification). For each sample, we made mosaics of 6 x 6 or 8 x 8 overlapping images to obtain a representative area (Table 1).

The public domain software ImageJ was used for digital imaging processing. Melt-solid boundaries were traced on screen for conversion to binary images. Grain boundaries were traced by orientation contrast of neighboring grains and connecting triple junctions to obtain solid-solid boundaries. The mean grain diameter was calculated from the average circle-equivalent grain area in an image and multiplied by 4/pi to correct for sectioning effects of a sphere (Faul and Scott, 2006). Dihedral angles for select samples were measured on the same maps.

3. Results

3.1. Description of the Melt Geometry

As outlined above, the melt geometry needs to be determined for steady state grain growth conditions. The smallest mean grain size of this study is approximately four times the starting grain size so that considerable microstructural evolution has taken place from the initial powders. Normalized grain size distributions confirm that steady state grain growth conditions were achieved even at the shortest run durations (Figure 17). Normalized grain size distributions are independent of the mean grain size (see e.g. Faul and Scott, 2006).

While the melt distribution in the isotropic model is independent of melt fraction, experimental observations show a change of the melt geometry with increasing melt content at constant grain size. At 0.5% most of the melt resides in triple junctions of varied size and shape (Figure 18a). At 1.7% melt penetrates further onto grain boundaries (Figure 18b). A number of adjacent triple junctions are connected by melt layers, implying fully wetted grain boundaries and a dihedral angle of 0°. Larger melt pockets occur at four or more grain corners. At higher melt contents and particularly at coarse grain sizes, the majority of the grain boundaries tend to be wetted by melt (Figure 18c, d). While crystal-melt interfaces of coarse-grained aggregates are frequently rounded, faceted crystal-melt interfaces dominate at small grain sizes (Figure 18e). Wetted-two grain boundaries occur only infrequently at the fine grain sizes. In addition to changes with melt fraction the melt geometry also changes with grain size at constant melt content (Figure 19). In the fine-grained sample with a mean grain size of 8.6 μ m (Figure 19a) the melt resides predominantly in triple junctions and larger melt pockets of varied sizes and shapes. In contrast, at a mean grain size of 40.5 μ m (Figure 19b), wetted two-grain boundaries are common and connect melt pockets. A few small triple junctions are surrounded by relatively small grains. The images illustrate that the melt distribution of coarser-grained samples includes more wetted two-grain boundaries compared to fine-grained samples at the same melt content.

3.2. Grain Boundary Wetness

For a more quantitative assessment of the melt distribution we measured the grain boundary wetness ψ of 18 samples with grain sizes from 4 to 84 µm and melt contents from below 0.1 to 6.8% (Table 1, Figure 20). For reference, grain boundary wetness was also calculated with the idealized isotropic equilibrium model for a rhombic dodecahedral grain shape for dihedral angles of 10° and 30° (Takei, 2002). The grain boundary wetness of experimental samples with a mean grain size smaller than 10 µm falls on the contour predicted by the idealized model for a dihedral angle of 30° up to a melt content of 3%. The wetness of samples with grain sizes from 20 – 30 µm falls near the contour for a dihedral angle of 10° to about 2% melt. Coarse-grained samples (mean grain size > 40 μ m) with melt contents near 2% and higher have values for the wetness well above those predicted by the idealized model.

The relationship between grain boundary wetness and grain size is shown in Figure 21. Two subsets of the data from Figure 20 with similar melt contents show that at near constant melt content wetness increases with grain size. The increase at the coarsest grain size at 2% melt reflects the increase in wetness seen in Figure 20 at this melt content. The melt content at which this increase occurs may depend on grain size, such that the increase occurs below 2% for coarser grain sizes.

In order to evaluate a possible dependence of wetness on temperature experiments were conducted at (near) constant melt content and a range of temperatures (Figure 22). At a melt content of 2% two samples with very similar grain size near 13 µm yield the same grain boundary wetness, even though their experimental temperature differed by 200°C. The most coarse-grained sample in this Figure has the highest grain boundary wetness, despite a temperature that is 100°C lower than that of a more fine-grained sample, emphasizing that it is grain size that determines the wetness rather than temperature.

Additionally, dihedral angles were measured for the same samples to evaluate a possible dependence of wetness on temperature. Zero dihedral angles indicating wetted two-grain boundaries, were included in the measurements. At constant melt content and grain size the dihedral angle is independent of temperature for two experiments differing by 200°C

(Figure 22). The Figure shows that dihedral angle does not depend on temperature but is sensitive to grain size, similar to the wetness.

4. Discussion

The principal difference between the assumptions of the isotropic equilibrium model and real systems is that polycrystalline aggregates at elevated temperatures do not have a static microstructure, but rather one that evolves due to surface energy driven grain growth (Walte et al., 2003). This results in a broadening of the grain size distribution (the size difference between the smallest and the largest grains increases with mean grain size), in contrast to the assumption of grains of a single size and uniform shape. Establishment of slow growing, facetted crystal-melt interfaces further stabilizes larger melt pockets (Waff and Faul, 1992).

The most important observations of this study are the grain size dependence of the wetness at constant melt content and the increase in wetness at melt contents of about 2% above the predictions of the idealized model. This increase in wetness takes place at a similar melt content where Faul (1997) inferred interconnection (overlap) of melt pockets approximated as ellipsoidal inclusions. Since the wetness is grain size dependent (Figure 21), this transition likely occurs at lower melt contents at larger grain sizes.

4.1. Limitations of the Present Study

Grain growth and microstructural maturation require relatively long duration experiments at high temperature (up to 1400°C). The graphite in the furnaces used in our study was relatively fine-grained and stronger than the surrounding materials, leading to the development of cracks in the furnaces during pressurization. At high temperatures glass infiltrated the cracks, increasing the furnace resistance over time to levels where temperature could no longer be maintained and the experiment had to be terminated. Additionally the resultant relatively small radial variations in temperature can cause inhomogeneity of the melt distribution, with melt accumulating at higher temperatures patches. We therefore limited the experimental durations to two weeks. As grain growth rates correlate with melt content we were not able to obtain relatively coarse-grained samples (> 40 μ m) at low melt contents (< 2%). Clinopyroxene begins to crystallize from the basalt composition used in our study at temperatures below 1250°.

The coincidence of the wetness predicted by the isotropic model and the measured wetness at small grain sizes (Figure 20) illustrates the limitation of using wetness as a parameter to characterise the melt distribution. At small grain sizes the melt resides in relatively isometric pockets bounded by faceted crystal-melt interfaces. The surface to volume ratio of this melt geometry is similar to that calculated for melt residing in a triple junction network with constant interfacial curvature. Measuring the wetness can not discern these differences in the melt geometry. Grain size dependence and melt fraction dependence also create a non-uniqueness so that both parameters need to be given along with the wetness. However, including all interfaces in a given area into a measure of the melt distribution is preferable over essentially point measurements at selected locations (dihedral angles) for characterization of the melt geometry. Wetted grain boundaries (i.e. dihedral angles of zero degrees) are typically not included in distributions of measured dihedral angles.

4.2. Comparison with Previous Studies

The importance of resolution for observation of the melt geometry has been pointed out previously. Cmíral et al. (1998) showed from high resolution transmission electron microscope images that true dihedral angles (where the grain boundary was tilted parallel to the electron beam) between olivine and basaltic melt have values of 10° or below. By contrast earlier studies using light micrographs to measure dihedral angles reported much larger values for the same system (Waff and Bulau, 1979, von Bargen and Waff, 1986). Garapić et al. (2013) demonstrated with high resolution SEM imaging and serial sectioning that the thin layers on two-grain boundaries observed earlier (Faul et al., 1994, Faul 1997) as well as in this study are indeed wetted two-grain boundaries.

Similarly, grain boundary wetness will be underestimated at insufficient resolution, particularly if layers on two-grain boundaries with a width of 100 nm are not resolved. For example Yoshino et al. (2005) imaged their samples with resolutions ranging from 0.06 to 0.3 μ m/pixel, while Zhu et al. (2011) in their synchrotron study had a resolution

of 0.7 μ m/voxel. Thin layers on two-grain boundaries, contributing disproportionally to wetness but little to area (volume) of melt, could not be resolved in these studies, while larger triple junctions and pockets were imaged. These authors concluded therefore that the isotropic model provides a sufficient description of the melt geometry.

A dependence of the melt geometry on melt fraction was noted in previous studies. Hirth and Kohlstedt (1995) observed an increase in wetness in with increasing melt content in their samples with mean grain sizes ranging from 10 to 18 µm. They observed a large number of wetted two-grain boundaries at a melt content greater than 5% with a decrease of the dihedral angle from 38 ° to close to 0°. A change of the melt distribution as a function of melt content was also noted by Yoshino et al. (2005), who described an increasing number of wetted two grain boundaries at melt contents above 2%.

4.3. Temperature Sensitivity of Dihedral Angle and Grain Boundary Wetness Yoshino et al. (2009) reanalyzed the 1 GPa experiments with a lherzolite composition of Yoshino et al. (2005) and conducted additional experiments at higher pressures to examine the melt distribution. Based on their observations they concluded that the dihedral angle decreases with increasing temperature to values near zero at the highest temperatures in their study (1500 - 1720°C). However, in contrast to the starting composition of the present experiments with olivine and a fixed amount of basaltic melt, Yoshino et al. (2009) examined the melt distribution as a function of temperature of a lherzolite composition. For a lherzolite at fixed pressure the melt content will increase with increasing temperature as the pyroxene mode decreases (e.g. Baker and Stolper, 1994, Walter, 1998). As is shown in Yoshino et al. (2005, Table 1, KLB1 composition) as temperature increases the melt content increases from 2.4% at 1200°C to 30% at 1350°C with a concomitant increase in grain size from 13 to above 50 µm. As the results presented here show, the apparent decrease in dihedral angle at this temperature range is related to the increase in melt fraction and grain size in their experiments. Additionally the cumulative frequency diagrams of dihedral angles in Figure 2 of Yoshino et al. (2009) do not include angles with a value of zero.

We did not observe a temperature dependence of wetness or dihedral angle (Figure 22), consistent with measurements at high resolution at a temperature range from 1200 to 1450°C by Cmíral et al (1998) and Faul and Scott (2006). In the present study samples with a mean grain size below 10 µm have larger dihedral angles due to the larger number of junctions formed by facetted crystal-melt interfaces. Overall no temperature dependence of wetness or dihedral angle is observed at temperatures up to 1450°C when grain size and melt fraction are accounted for.

5. Implication on Viscosity of the Upper Mantle

Diffusion creep experiments are carried out with fine-grained aggregates in order to avoid the transition to dislocation creep at experimentally accessible stresses and strain rates.
Grain sizes in the experiments of Hirth and Kohlstedt (1995) and Mei et al. (2002) that deformed in diffusion creep were < 15 μ m, with melt geometries dominated by facetted crystal-melt interfaces (Figure 3 of Hirth and Kohlstedt, 1995, Figure 5 of Mei et al., 2005), similar to the fine-grained samples of this study (Figures 18e, 19a). At low melt contents (1 – 5%) the enhancement of creep rates due to melt is therefore moderate. Figure 19 illustrates how the melt geometry changes as a function of grain size. The increased number of wetted grain boundaries at grain sizes of tens of μ m should enhance creep rates for these aggregates, but this is difficult to verify experimentally.

Takei (1998) examined the relationship between macroscopic mechanical properties and microscopic geometry of solid-liquid composites. She concluded that the grain boundary contiguity φ ($\varphi = 1 - \psi$, i.e. 1 - wetness) is the primary factor that determines the macroscopic properties of granular composites. The melt content affects the properties only indirectly through the grain boundary contiguity. Takei and Holtzman (2009a) develop this model further to derive constitutive relations of partially molten rocks deforming by grain boundary diffusion creep (termed compositional model). When finite liquid diffusivity and reaction rates are included at low melt fractions, they predict a decrease in viscosity from melt-free conditions to a melt content of 1% by one order of magnitude (Takei and Holtzman 2009a,b). This prediction is consistent with experimental observations that show a substantial increase in strain rates in the diffusion creep regime for the first percent of melt (Faul and Jackson, 2007).

The resistance to diffusion, γ , in the Takei and Holtzman (2009a, b) model is determined by the ratio of the total cross-sectional area of grain boundaries to that of the liquid. This ratio decreases with increasing grain size. The model viscosity is linked to the melt fraction by the melt fraction-dependent grain boundary wetness. The latter is calculated with the idealized isotropic model for a dihedral angle of 30°. Since this model is self similar, the wetness itself is independent of grain size. The significantly weaker dependence on melt content above 1% melt is due to the fact that at higher melt contents the viscosity is mainly controlled by diffusion through the liquid.

Figure 23 shows a comparison of experimental parameters (wetness, grain size and melt fraction) with calculations of the resistance to diffusion based on the idealized model (Takei and Holtzman (2009a,b). When the experimental data are superimposed on contours of grain size at their measured wetness one can see that the resistance to diffusion in the experiments decreases more rapidly with increasing melt content relative to the idealized model. This is due to the more rapid increase of the experimentally determined wetness relative to the prediction of the idealized model (Figure 20), combined with the grain size dependence of wetness (Figure 21).

Figure 24 shows the normalized shear viscosity calculated with the Takei-Holtzman (2009a, b) model. At melt contents above 1% the grain size sensitivity is minor for grain

sizes above 50 µm. Below 1 % the viscosity decrease at the onset of melting becomes increasingly a step-like drop for grain sizes approaching 1 mm. Since the measured wetness increases more quickly with melt content than predicted by the idealized model the viscosity decreases more quickly as well above 1% melt. The difference to the isotropic model reaches 30% for melt contents between 1.5 and 2% and 60% for melt contents of 4%. A remaining question is at what melt content the wetness increases above the predictions of the idealized model for mantle grain sizes. The decreased resistance to diffusion also implies that the melt geometry remains surface energy controlled, as fast diffusion alleviates stress heterogeneities.

6. Conclusions

This experimental study of partially molten dunite shows that grain boundary wetness increases with increasing melt content to values well above those predicted by the idealized isotropic equilibrium model. At constant melt content, grain boundary wetness increases with increasing grain size, in contrast to the assumption of a self-similar melt distribution in the idealized model. No temperature sensitivity of the melt geometry is observed when grain size and melt fraction as factors influencing the melt distribution are accounted for. The experimental observations indicate that wetness increases more quickly as a function of melt content at mm to cm grain sizes inferred for the upper mantle. With the experimentally measured wetness the resistance for diffusion through the liquid phase in the solid-liquid composite model of Takei and Holtzman (2009a, b)

decreases more quickly than predicted by the idealized model. Correspondingly the shear viscosity decreases more quickly, enhancing diffusion creep at small melt fractions. Diffusion creep may therefore dominate in partially molten regions of the upper mantle.

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Tables

Sample	$T (^{\circ}C)$	t	Wetness	Melt	Grain size	# of grains
	(°C)	(hour)	(ψ)	fraction (ϕ)	(µm)	
MELT4	1350	120	0.69	0.041	40.5	109
MELT5	1350	27	0.38	0.022	25.3	136
MELT10	1350	81	0.19	0.004	30.9	120
MELT13	1350	336	0.52	0.019	49.8	137
MELT18	1350	288	0.16	0.004	15.3	170
MELT19	1350	1	0.1	0.003	8.9	180
MELT20	1350	1	0.38	0.03	8.6	340
MELT21	1350	1	0.23	0.012	8.7	135
MELT22	1350	336	0.21	0.005	32.5	104
MELT23	1400	336	0.76	0.068	84.5	122
MELT24	1350	1	0.21	0.011	7.8	166
MELT25	1400	130	0.43	0.017	43	108
MELT27	1250	1	0.19	0.01	4.3	327
MELT28	1450	1	0.34	0.021	13.5	122
MELT29	1250	72	0.27	0.019	8.6	269
MELT30	1250	140	0.34	0.019	12.9	147
MELT31	1250	361	0.21	0.009	12.6	249
MELT33	1350	304	0.27	0.015	17.5	167

 Table 2. Summary of run conditions and image analysis

The pressure was 1GPa for all experiments.

Figures



Figure 16. Temperature distribution along the long axis of the furnace assembly determined from the width of a spinel layer of a calibration experiment at 1400 °C and 1 GPa after one week. 0 mm on the x axis indicates the top of the designed capsule location. The positive and negative numbers represent the distances from the top of capsule towards the bottom and top of the furnace, respectively. The temperature is within 10 °C from top to bottom of the designed capsule location (0 to 4 mm) at the peak of the temperature distribution. The thermocouple is located within this broad peak, therefore no correction to the sample temperature is applied.



Figure 17. Histograms of grain size distributions. Grain sizes are normalized by the mean. (a) A fine-grained sample with a mean grain size of 8.7 μ m (MELT20). (b) A coarse-grained sample with similar melt content (MELT32). Both histograms show lognormal distributions indicating that steady state grain growth conditions were established at the shortest run duration.











Figure 18. SEM images of experimental samples at 1 GPa, The images represent parts of the larger maps from which wetness and grain sizes were measured. (a) to (c), show the influence of increasing melt content at near constant grain size (approximately 40 μm). The predominant melt geometry changes from triple junctions (a) to wetted two-grain boundaries and melt pockets (c). (a) 0.5% melt (MELT22). (b) 1.7% melt (MELT25). (c) 4.1% melt (MELT4). (d) shows the experiment with the coarsest mean grain size and highest melt content in this study (84.5μm and 6.8% melt, MELT23). Only few solid-solid grain boundaries are present in this image (arrows), most of the grain boundaries are wetted by melt. (e) Melt distribution in a fine-grained sample (8.6 μm, 3%, MELT 20). Comparison with (b) at similar melt content but significantly larger grain size illustrates

the changes in melt distribution with increasing grain size towards increasing wetness (Table 1).



Figure 19. Influence of mean grain size on the melt distribution. (a) Binary image of a portion of MELT20 with a melt content of 3.8% and a mean grain size of 8.6 μm. The original SEM image has a resolution of 0.014μm /pixel. (b) Binary image of MELT4

with 4.1% melt and 40.5 μ m mean grain size. The original SEM image has a resolution of 0.029 μ m/pixel. These two images show that coarser grained samples have more wetted two-grain boundaries at a similar melt content, and consequently higher grain boundary wetness.



Figure 20. Grain boundary wetness as a function of melt fraction for all samples of this study. The lines indicate grain boundary wetness calculated with the ideal isotropic model for dihedral angles of 10° and 30°. Labels show the mean grain size of each sample. Relatively fine grained samples (yellow triangles) follow the line predicted for a 30° dihedral angle (purple line) up to a melt fractions of 0.03. Medium grained samples (orange squares with 30.9, 32.5 and 25.2µm mean grain sizes) follow the contour line predicted for 10° dihedral angle up to a melt fraction of 0.02 (blue line). Coarse grained samples (red dots and the three orange squares over 38µm) have wetness values well above those predicted by the ideal isotropic model at melt fraction above about 0.016.



Figure 21. Grain boundary wetness as a function of mean grain size. Dots show experiments with melt contents of approximately 2%, diamonds 0.3-0.5%. The data indicate that grain boundary wetness increases with increasing mean grain size for constant melt content. Comparison with Figure 20 indicates that the higher wetness of the most coarse-grained sample is suggestive of a steeper increase at this grain size and melt fraction.



Figure 22. Effect of temperature on wetness and dihedral angle at a melt content of 2%. The mean grain size (in μ m) and dihedral angle of each experiment is indicated by the numbers on and adjacent to the symbols, respectively. Two experiments with nearly identical grain size (12.9 and 13.5 μ m) have the same grain boundary wetness and dihedral angle (within the error of measurement), although there is a temperature difference of 200 °C. Wetness and dihedral angle therefore do not depend on temperature for fixed grain size and melt fraction.



Figure 23. Resistance to diffusion through the liquid phase in a solid-liquid composite calculated from wetness and contoured by grain size (eq. 37 Takei and Holtzman 2009b). The contours show that at a fixed grain size the resistance decreases steeply initially and then more moderately with increasing wetness. The melt content shown at the top of the figure is used to calculate the grain boundary wetness from the idealized isotropic equilibrium model for a dihedral angle of 30°. For this idealized model at fixed melt content the resistance deceases with increasing grain size. The squares show the wetness measured in the experiments at the corresponding grain sizes and their calculated resistance to diffusion. The measured melt contents are shown next to each data point. Comparison of the experimentally determined melt contents with the melt contents of the

idealized model (top horizontal axis) at a given wetness (bottom horizontal axis) show that the resistance to diffusion decreases more quickly with melt content than predicted by the idealized model.



Figure 24. Shear viscosity normalized by the viscosity of a melt-free aggregate calculated as a function of grain boundary wetness and grain size with the model of Takei and Holtzman (2009b). Symbols represent experimental wetness and grain size measurements with melt contents indicated next to the symbols. As for Figure 23, melt contents corresponding to the wetness on the bottom axis for the idealized model are shown at the top axis. Similar to the resistance to diffusion the viscosity calculated from the experimental parameters decreases more quickly with increasing melt content compared to the predictions of the idealized model.

CHAPTER IV

EXPERIMENTAL STUDY OF OLIVINE-RICH TROCTOLITES

Abstract

Naturally partially molten rocks exist in the form of olivine-rich troctolites or plagioclase dunites, but the conditions for their formation are not entirely clear. The primary purpose of this study is to investigate the effects of cooling process on the geometry of the interstitial phases. We therefore conducted experiments where olivine-basalt aggregates were annealed at 1350 °C and 0.7 GPa for 5 to 7 days to produce a steady state microstructure. At this temperature only olivine and minor orthopyroxene are present as crystalline phases. We then cooled the samples over one week below their solidus temperature, following different protocols. The post-run samples were sectioned, polished, imaged at high resolution and analyzed by using a field emission scanning electron microscope. The geometry of the interstitial phases was quantified by determining the grain boundary wetness, in this case the ratio of the length of polyphase to single phase (olivine-olivine) boundaries. Observations show that at 1200 °C clinopyroxene nucleates distributed throughout the aggregate at many sites, forming relatively small, rounded to near euhedral grains. During slow cooling below 1200 °C few clinopyroxene grains nucleate and grow with a poikilitic shape, partially or fully enclosing olivine grains, as is observed in natural samples. The experiments indicate that slow cooling of samples with a steady-state microstructure reproduces the interstitial geometry of plagioclase and clinopyroxene observed in natural samples. The grain boundary wetness determined from the interstitial phases is somewhat reduced during

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slow cooling relative to samples quenched from high temperature. Crystallization of interstitial solid phases reduces grain boundary wetness more at lower melt content. The microstructural similarity of experimental and natural samples suggests that the grain boundary wetness of olivine-rich troctolite layer in the mush zone is somewhat lower than that in the region of partially-molten dunite at constant melt content. Furthermore, the shear velocity in troctolite layer may be higher than that in the region of partially molten dunite.

1. Introduction

The earth's upper mantle is partially molten in varies tectonic settings including midocean ridges, subduction zones and hotspots. Due to mantle rising beneath mid-ocean ridges, shallow crustal magma chamber (melt lens) is formed beneath many fast- and intermediate-spreading centers (Detrick et al., 1987). Seismic studies have detected a network composed of crystallized rock and melt under the melt lens, which is termed the mush zone (Sinton and Detrick, 1992). The fitting of seismic data indicates the mush zone consists of 2.5-18% melt (Crawford et al., 1999). Olivine-rich troctolite intervals are found from gabbroic sequences of the mush zone by deep drilling program at mid-ocean ridges (e.g. Suhr et al., 2008; Drouin et al., 2010), and in ophiolites (e.g. Faul et al., 2014; Renna and Tribuzio, 2011; Sanfilippo et al, 2013). These sill-like lenses are generally tens of meters thick and hundred of meters long (Detrick et al., 1987). The olivine-rich troctolites are characterized by high volume proportion of olivine with interstitial plagioclase and clinopyroxene. Typically the clinopyroxene occurs in the form of few large, poikilitic grains.

Whether olivine-rich troctolites are formed from melt impregnation of former mantle rocks or a cumulate derivation of primitive melt (fractional melting) is still in debate. Reasons supporting a cumulate nature include cumulus-intercumulus appearance at a first glance, located at the bottom of a magma chamber, and compositionally the Fo# of olivine in olivine-rich troctolites is in between that of olivine in gabbros and that of mantle olivine (summarized by Suhr et al. 2008). Lissenberg and Dick (2008) favors that

the formation of olivine-rich troctolites is from reaction between migrating melt and olivine matrix crystallized from primitive cumulates. They state that troctolites and olivine gabbros from Kane gabbro suite contain cumulus assemblages of olivine with anhedral to euhedral shapes and plagioclase. Suhr et al. (2008), Renna and Tribuzio (2011) and Sanfilippo et al. (2013) suggest that olivine-rich troctolites are derived from partial dissolution of replacive mantle dunite and later the olivine-rich matrix is impregnated by MORB-type melt. Renna and Tribuzio (2011) studied olivine-rich troctolites from Ligurian ophiolites and observed that the relatively coarse-grained and mainly subhedral olivine and spinel are included in clinopyroxene occurring as large poikilitic grains. The high Mg# and Cr contents of poikilitic clinopyroxene indicates their formation through reaction between an olivine-spinel matrix and an infiltrating MORB type melt. Suhr et al. (2008) studied olivine-rich troctolites samples from Atlantis Massif. Compositionally, the high Ni in olivine for a given Mg# and high Cr in cpx suggest they are more mantle origin. Textually, although the olivine grains are relatively small resembling cumulus feature, the optical extinction across adjacent grains indicates that these grains were formerly larger but became dissected by dissolution. They suggest that the 50 m thick olivine-rich troctolite layer was originated from a former hartburgite or lherzolite mantle trapped between two intrusive units. Then the rock body was converted to a coarse-grained crust-mantle transition zone dunite, a precursor to the olivine-rich troctolites. Followed by melt percolation, the coarse-grained dunite body was lowered in Mg# and became fine-grained. At the final stage, clinopyroxene and plagioclase were crystalized from the interstitial melt. Similar texturally and compositional evidence were

found in samples from the Parece Vela Basin, supporting a melt-rock reaction between a MORB-like melt and dunite (Sanfilippo et al. 2013).

As indicated by the paragraph above, Suhr et al. (2008), Renna and Tribuzio (2011) and Sanfilippo et al. (2013) suggest replacive features of the host olivine-rich rocks, but whether the host olivine-rich rocks shows replacive feature is also debatable. Cann et al. 1999 states that dunites are derived from fractures filled with olivine precipitated from migrating melt. These dunites are replacive features, formed by dissolution of pyroxene and precipitation of olivine in migrating MORB magma at the same time (Kelemen et al. 1995a, b). Faul et al. (2014) and Faul and Garapić (2014) studied Krivaja-Konjuh massif and found evidence of impregnation by melt from the abundant patches of plagioclase in the spinel lherzolites. The trapped melt started off at larger depth and was silica undersaturated when it reached the plagioclase stability field. This melt dissolved pyroxene and locally converted the peridotites to massive olivine-rich troctolites. The high Ni content and euhedral texture of olivine grains indicate they are mantle origin and remained texturally equilibrated with the presumably MORB-type melt. Faul and Garapić (2014) observed progressive misorientation across individual grains due to previous deformation, further indicating mantle origin of olivine grains. In contrast, they did not observe signs of deformation in the interstitial clinopyrxoene and plagioclase, showing that the interstitial phases were crystallized from the melt. Similarly, Drouin et al. (2010) studied olivine-rich troctolites from the Atlantis Massif and reported that the

misorientations of olivine grains are consistent with deformation of mantle peridoties. These grains are embedded in large, undeformed pyroxene and plagioclase poikiloblasts.

This experimental study aims to complement filed observations of olivine-rich troctolites in ophiolites and from mid-ocean ridges. The compositions of starting materials were controlled so that the olivine grains remained and texturally equilibrated with the melt, simulating original mantle olivine. The primary purpose of this study is to investigate the effects of cooling process on the geometry of interstitial clinopyroxene and plagioclase.

2. Experimental Setup and Image Processing

All runs were carried out in a 1/2" diameter end-loaded piston cylinder apparatus. The starting material was prepared by mixing sol-gel Fo90 olivine with a mean grain size of 1 μ m and approximately 10 wt% of synthetic basaltic glass powder together in an agate mortar. The olivine-basalt aggregates were housed in graphite capsules. The furnace assembly was similar to those described in chapter II and all furnace components were kept in a drying oven at 105 °C for at least 24 hours before starting the experiments.

Initially, the olivine-basalt aggregates were annealed at 1350 °C and 0.7 GPa for 5 to 7 days to produce a steady state microstructure. At this temperature only melt and olivine exists. The samples were then cooled over one week below their solidus temperature, following different protocols. During cooling orthopyroxene crystalizes first, then clinopyroxene and finally plagioclase. Experiments were ended by quenching the

samples to room temperature in less than one minute. Temperature-time paths for each experiment are show in Figure 25. After quenching, the experimental capsules were unloaded, mounted in epoxy and sectioned longitudinally. The sections were polished on diamond pastes, followed by alumina suspension and silica suspension to produce surfaces free of damage. Finally the samples were carbon coated for imaging and EDS analysis.

The polished samples were imaged at high resolution and analyzed by using a Zeiss Supra 55 field emission SEM. The public domain software ImageJ was used for digital image processing. Each sample has a mosaic of 6 x 6 to 8 x 8 overlapping images, and each image has a size of 2048 x 1536 pixels and resolution of 0.014 to 0.029 μ m/pixel depending on grain size. At least 200 olivine grains were covered in the imaging areas. Determination of grain boundary wetness is similar to the processes described in chapter 2. For the digitization of interstitial phases, boundaries of former melt and pyroxene were traced separately (Figure 26).

3. Results

3.1. Overview

Both quenched samples and step-cooled samples show steady-state grain growth of olivine. The melt distribution in the samples quenched from 1350 °C is homogeneous.

The interstitial phases in the samples XTAL2 to XTAL8 experienced step-cooling are homogenous. In XTAL1 there is a melt layer accumulated at the top of olivine aggregate. Some melt pockets are vertically aligned. More clinopyroxene is crystalized at the bottom of the aggregate. These observations indicate a temperature gradient during the course of the run and the bottom of the aggregate was colder than the top. Mean grain sizes of olivine in samples annealed at 1350 °C for 1 week and those followed by step-cooling for another week are almost identical, indicating that grain growth rate is very temperature sensitive and the growth rate at 1350 °C is significantly faster than that below 1250 °C.

The two samples quenched from 1350 °C show that only olivine is presented as solid phase and melt is presented as liquid phase at this annealing temperature. These observations indicate that all phases other than these two are products of step-cooling at lower temperatures. In order to find out proper cooling protocols, MELTS modeling (Ghiorso and Sack, 1995; Asimow and Ghiorso, 1998) was conducted to predict solid phases crystalized from the MORB basalt from 1350 °C to 1100 °C. The result shows that plagioclase crystalizes at temperature below 1230 °C at 0.7 GPa (Figure 27). In addition, equilibrium crystallization experiments of basalt at 0.7 GPa reported by Villiger et al. (2007) shows that orthopyroxene, clinopyroxene and plagioclase crystalized below 1210 °C and are stable phases between 1210 °C and 1150 °C. Hence, the fist step of cooling protocols was to drop the temperature from 1350 °C to 1250 °C at a fairly fast rate (in 24

hours), then the rate was decreased to allow crystalize of plagioclase and clinopyroxene, following different temperature-time paths.

Whether interstitial pyroxene phases crystalize depends on cooling time and rate at or below 1200 °C. The results show that interstitial orthopyroxene and clinopyroxene are able to crystalize at 1200 °C for a week. Alternatively, the cooling time needs to be below 1175 °C for at least 5 days. In contrast, the sample annealed at 1175 °C for 4 days did not crystalize clinopyroxene, and the sample cooled from 1200 °C to 1150 °C for 2 days does not show interstitial clinopyroxene or orthopyroxene.

3.2. Major Element Compositions of Minerals

3.2.1. Olivine

The starting compositions of olivine grains have been preserved (Table 4). This is expressed by an average Fo number between 89.9 to 90.5. Olivine grains do not show compositional gradient in samples without thermal gradient. Anhedral and rounded olivine grains enclosed in interstitial to poikilitic clinopyroxene have slightly lower Fo number of 89.9. Fo numbers of olivine grains in the matrix are in between 90.1 and 90.5. Olivine grains do not show compositional variations with cooling history.

3.2.2. Clinopyroxene

Table 5 shows major element clinopyroxene compositions. Most major element concentrations in interstitial clinopyroxene show correlations with cooling history. The sample step-cooled until 1100 °C (XTAL4) has most concentration variations comparing to other samples. Concentrations of TiO₂, Al₂O₃, CaO, and K₂O show negative correlations with Mg# of clinopyroxene. (Figure 28 to 31) CaO concentrations distribute from 13.6 to 17.8, decreasing with increasing Mg# of clinopyroxene. In general, the longer duration the sample annealed at lower temperature, the higher the CaO concentration. Majority of the samples have average TiO₂ concentrations from 1.12 to 1.78. Average TiO₂ concentration of XTAL4 is 4.64, which is a bit higher than other samples. Average Al₂O₃ concentration of XTAL4 is 16.1, which is significantly higher than that of other samples ranging from 4.6 to 5.6. Average Na₂O concentration is confined from 0.6 to 0.7, not showing variation with cooling history.

3.2.3. Orthopyroxene

Orthopyroxene grains are depleted in those oxides not included in starting basaltic glass powder, and enriched in FeO and MgO, which are major oxides in olivine (Table 6). Concentrations of major oxides are constrained in narrow ranges. Mg# of orthopyroxene is between 90 and 91. Orthopyroxene grains do not contain Na₂O, TiO₂ and K₂O. Concentrations of SiO₂ and Al₂O₃ show correlations with final temperatures. Average SiO₂ concentrations drop with decreasing final temperatures, from 56.4 (XTAL5) to 55.6 (XTAL6) to 55 (XTAL4 and XTAL8). Average Al_2O_3 concentrations increase with decreasing quenching temperatures, from 1.5 (XTAL5), to 2.3 (XTAL6) and to 4.2 (XTAL4). Average CaO concentrations range from 1.21-1.38 except XTAL6 that is 4. No compositional difference between interstitial orthopyroxene and orthopyroxene enclosed in poikilitic clinopyroxene.

3.2.4. Plagioclase

Major element plagioclase compositions are shown in Table 7. The anorthite content in plagioclase (An#) ranges from 0.4 to 0.62 and positively correlates with increasing Mg# of interstitial clinopyroxene (Figure 32). Both An# and Mg# decrease with lowering final temperatures. Compared to starting composition of the basaltic powder, plagioclase crystalized from the melt is enriched in Al₂O₃ and Na₂O; decreased in FeO, MgO and CaO; concentrations of TiO₂ and K₂O are slightly increased. In general, these trends mentioned above are more obviously reflected by plagioclase crystalized at lower temperatures.

3.3. Description of the Interstitial Phase Geometry

SEM images show that interstitial phases and their geometries change with cooling temperature. For the sample cooled from 1350 °C to 1200 °C over four days (XTAL5, Figure 33a, also Figure 34a), cpx grains nucleate adjacent to former melt pockets,

sometimes forming relatively small, rounded to near euhedral grains. A few large opx grains occur, surrounding olivine grains. Fewer grain boundaries are wetted by melt. The sample experienced fast cooling from 1350 °C to 1250 °C in a day, and then slow cooling from there to 1150 °C (XTAL8, Figure 33b, also Figure 34b) exhibit different interstitial phase geometry. During slow cooling below 1200 °C, cpx occurs distributed throughout the aggregate with poikilitic shape, partially or fully enclosing olivine grains. In contrast to the olivine grains not enclosed in clinopyroxene, the olivine chadacrysts are more rounded and smaller. Some large opx grains are formed adjacent to poikilitic cpx grains. The sample quenched from 1125 °C has higher pyroxene vol.% that that cooled from 1200. Plagioclase phase has geometry similar to that quenched from 1350 °C. For example, the triple junctions and pockets have low dihedral angles. A few olivine grains are separated by former melt thin layers. In contrast, interstitial pyroxene phase is usually rounded at corners, yielding greater dihedral angles.

Cooling rate also affects interstitial phase geometry. The cooling rate of both XTAL5 and XTAL8 were relatively slow, showing smooth boundaries of interstitial phases. These boundaries are clearly indicated by the EDS mapping of silicon concentration (Figure 34a and 34b). The interior of pyroxene phase is smooth, not showing holes or former melt pockets in the interiors. Although XTAL2 and XTAL8 were quenched from similar temperature, the fast cooling rate of XTAL2 makes it exhibits very different interstitial phase geometry (Figure 34c). The clinopyroxene phase in XTAL2 has very rough edges and includes tiny former melt pockets and orthopyroxene grains. The
clinopyroxene grains are poikilitic, partially or fully enclosing olivine grains, which is similar to the texture in XTAL8.

3.4. Grain Boundary Wetness and Corresponding Melt Geometry

Grain boundary wetness was determined from step-cooling samples, and compared with samples quenched from 1350 °C with similar melt contents. Results from two groups of experiments demonstrate that the difference in grain boundary wetness between quenched sample and step-cooled sample varies with melt content. Comparison between the quenched sample with 43 µm grain size (MELT35) and step-cooled sample with 39 µm grain size (XTAL2) at approximately 9% melt content indicates that the grain boundary wetness decreases from 0.9 to 0.6. SEM image shows that at this melt content only basaltic melt is present as interstitial phase in the quenched sample. Almost all olivine grain boundaries are wetted by basaltic melt (Figure 35a). In contrast sample, SEM image of the step-cooled sample (Figure 35b) shows that interstitial phases retreated from olivine grain boundaries. The dihedral angles between olivine and interstitial phases are increased from those in the quenched sample overall. The rounded dihedral angles formed between olivine grains and pyroxene phase are much greater than those relatively sharp dihedral angles between olivine grains and plagioclase phase. Plagioclase best preserves the interstitial melt geometry. At 12% melt content and 47 μ m grain size, grain boundary wetness of the step-cooled sample (XTAL8) is 0.65, which is only slightly lower than that of the quenched sample (MELT40) of 0.71. SEM image of the quenched

sample (Figure 36a) shows that at this melt content majority of the melt forms very big pockets fully or partially enclosing olivine grains. Some of these olivine grains show euhedral crystal shape. Unlike most olivine grain boundaries are separated by melt at 9% melt content, at 12 % melt content the flat grain boundaries of these euhedral olivine grains partially form olivine-olivine grain boundaries with adjacent olivine grains. SEM image of the step-cooled sample (Figure 36b) shows that pyroxene phases crystalized from the very big melt pockets existed at 1350 °C. The dihedral angles between olivine and interstitial phases are somewhat greater than those shown in the quenched sample. This observation is more obviously demonstrated by the dihedral angles between olivine and pyroxene phases.

4. Discussion

4.1 Reduction of Grain Boundary Wetness

The comparisons between quenched samples and step-cooled samples at different melt contents suggest that crystallization of interstitial solid phases reduces grain boundary wetness more at lower melt content. This observation is mainly due to the different melt geometry of quenched samples (partially molten dunite) at different melt contents. At relatively lower melt content of 9%, a large portion of the olivine grain boundaries are wetted by melt (Figure 35a). During cooling, the retreat of interstitially crystallizing solid phases from olivine boundaries results in decreased grain boundary wetness. The rounded dihedral angles between olivine and pyroxene phases shown in Figure 35b emphasize that pyroxene appears to retreat from grain boundaries relatively quickly. At 12% melt content, there are much more free spaces filled by basaltic melt around olivine grains (Figure 36a) than those at 9% melt content in the quenched sample. These spaces indicate that a large number of olivine grains are able to grow freely without constraining by their neighboring grains and therefore these unconstrained grain boundaries have low surface energy. As a result, olivine-basalt aggregate at this high melt content has much less locally transient, high-energy configurations to form wetted two-grain boundaries (Walte et al. 2003) than those in the sample at lower melt content. Although the dihedral angles between olivine and interstitial phases are somewhat increased (Figure 36b), indicating retreat from olivine grain boundaries, this retreat does not cause significant decrease in grain boundary wetness due to less wetted two-grain boundaries at this high melt content.

4.2. Comparison with Other Experimental Studies

4.2.1. Geometry of Clinopyroxene

Comparison of my experiments with the experiments reported by Saper and Liang (2014) and Tursack and Liang (2012) shows that the geometry of poikilitic clinopyroxene crystalized from melt depends on the CaO concentration in the melt, cooling rate and final temperature. Saper and Liang conducted reactive dissolution and crystallization experiments (2014) to test whether the formation of plagioclase-bearing peridotites results from impregnation of basalt into residual peridotites. The reaction couple consisted of spinel lherzolite + 12% MORB mixture and MORB basaltic powder. The sample PDLS-6 was annealed at 1300 °C and 1 GPa for 24 hours, then cooled to 1050 °C as pressure dropped to 0.7 GPa and guenched after 72 hours. A control experiment annealed the melt-impregnated lherzolite at 1300 °C for 24 hours show that all minerals except olivine were completely incorporated into the melt. Hence in fact the crystallization experiment started from a partially molten dunite at the side far from the melt-rock reaction boundary, which is similar to the experimental condition of my study. Their SEM image of the area far from the melt-rock reaction boundary shows interstitial plagioclase and relatively large poikilitic clinopyroxene grains with smaller, rounded olivine chadacrysts. The geometry of plagioclase from their study shows high similarity to that in sample XTAL8 from my study. Both clinopyroxene phases from their sample and my samples are poikilitic, but their poikilitic clinopyroxene grains are much larger than those in my experimental samples. Presumably this discrepancy comes from the higher CaO concentration in their MORB basalt (12.5 vs. 10.7). More importantly, their melt composition when crystallization began incorporated with 13% dissolved clinopyroxene from lherzolite. In addition, their final temperature was 1050 °C, which was 100 to 150 °C lower than my final temperatures. Although their sample had much less cooling time, but the high concentration of clinopyroxene ingredient enriched in the melt with decreasing temperature and lower final temperature mainly contributed to the crystallization of large poikilitic clinopyroxene grains. The experiment PDET 1 reported by Tursack and Liang (2012) used a reaction couple formed by lherzolite and basaltic

powder. The composition of the basaltic powder is similar to that used in my study in terms of SiO2 and CaO concentrations. The sample was annealed at 1300 °C for 24 hours and fast-cooled to 1200 °C in one hour. Similar as PDLS 6, the lehrzolite turned to partially molten dunite after annealing at 1300 °C for 24 hours and the crystallization started from this condition. SEM images show that the region far from dunite-melt interface is composed of small, near euhedral clinopyroxene grains and occasionally relatively small poikilitic clinopyroxene, which is similar to the geometry of clinopyroxene shown in one of my samples cooled until 1200 °C (XTAL5, Figure 34a). Grain edges of clinopyroxene in PDST 1 are rough, which is similar to that in my fastcooled sample XTAL2 (Figure 34c).

4.2.2. Formation of Orthopyroxene

Comparison of orthopyroxene in my experimental samples to that in samples reported by Tursack and Liang (2012) and Saper and Liang (2014) suggests that the formation of poikilitic orthopyroxene requires pre-existing orthopyroxene at relatively high temperature. Orthopyroxene is shown in their crystallization experiments after annealing at 1300 °C for only 1 hour reported. These grains are poikilitic with inclusions of olivine and/or clinopyroxene. Some of orthopyroxene grains are adjacent to poikilitic clinopyroxene grains. The sample cooled for longer duration shows relatively larger poikilitic grains. These observations are similar to the geometry of orthopyroxene from my experimental samples. They attributed the formation of poikilitic orthopyroxene to short duration that helps preserve a higher SiO2 concentration and orthopyroxene crystallized around undissolved orthopyroxene. Although the starting materials of my experiments do not contain orthopyroxene, the basaltic glass powder used in my experiments is silica oversaturated and could react with olivine grains. This high abundance of silica is consistent with the observation that my olivine-basalt aggregates annealed at 1350 °C with relatively low melt contents exhibit minor amount of rounded orthopyroxene grains and more orthopyroxene grains are presented in those samples annealed at 1250 °C (described in Chapter II). These rounded orthopyroxene grains played the similar role to those undissolved orthopyroxene described in Tursack and Liang (2012) and Saper and Liang (2014). Upon cooling, orthopyroxene crystallized around pre-existing orthopyroxene to from poikilitic texture.

4.3. Comparison with Field Observations

Figure 37 is an EBSD map of an olivine-rich troctolite from Krivaja-Konjuh (geological settings described in Faul et al., 2014). In this EBSD map green represents olivine grains, red is cpx, light blue is plagioclase, dark blue and pink are spinel. Black is not indexed but is predominantly altered interstitial plagioclase. This map indicates that cpx is more resistant to alteration and preserves the interstitial geometry better. Although plagioclase is mostly altered but the texture still shows interstitial geometry. Comparison between experimental and natural samples show that upon slow cooling of samples equilibrated at

high temperatures reproduces similar interstitial geometry of plagioclase and cpx observed in olivine-rich troctolties from field samples.

As indicated by other field studies (e.g. Suhr et al. 2008; Renna and Tribuzio 2011; Sanfilippo et al. 2013), plagioclase is interstitial to olivine, euhedral to subhedral within poikilitic clinopyroxene, or subhedral to poikilitic clinopyroxene in natural olivine-rich troctolites. Plagioclase in my experimental samples shows similar interstitial geometry distributed in olivine-rich matrix. A few small former melt pockets composed of plagioclase with faceted edges are enclosed in poikilitic clinopyroxene (Figure 34c). These plagioclase grains in former melt pockets may resemble euhedral to subhedral plagioclase within poikilitic clinopyroxene observed in field samples. But individual plagioclase grains are too fine-grained to be resolved by SEM. A TEM study by Faul et al. (2004) shows that individual plagioclase grains in a sample after staged cooling are down to nanometer range. Such nanocrystalline plagioclase excesses the resolution of SEM. The discrepancy in grain size between natural and experimental plagioclase is due to the very different cooling time. Intrusive igneous rocks usually require millions of years to cool. Compared to such a geologic time scale, the cooling time for the formation of plagioclase in lab is way too short to grow relatively big enhedral to subhedral grains. Clinopyroxene in olivine-rich troctolites from field samples shapes from granular to interstitial to poikilitic. All these features have been observed in my experimental samples with different cooling history. Rounded to near euhedral clinopyroxene is shown in the sample cooled at 1200 °C (Figure 34a). Interstitial to poikilitic clinopyroxene has

been observed in the samples cooled below 1200 °C (Figure 34b and 34c). Overall, my experimental samples serve as analogues to the olivine-rich troctolties from ophiolites and mid-ocean ridges. The interstitial textures of plagioclase and clinopyroxene can be reproduced upon slow cooling. The difference in grain size is due to different cooling time.

5. Implications

5.1. Melt Content and Shear Velocity in Mush Zone

This study provides better constrains on the melt content estimated from shear viscosities in the mush zone beneath mid-ocean ridges. Crawford et al. calculated the shear viscosity in mush zone beneath east pacific rise and estimated a range of melt content from 2-18% (1999). The wide range is introduced by using two seismic models assuming different melt geometry. One melt geometry that needs a large volume of melt causes equivalent shear wave attenuation to another melt geometry that requires less melt and therefore is more efficient at reducing seismic velocities (Mavko, 1980). Specifically, the lower bound is estimated from a model assuming a thin film or sphere melt geometry (Goetze, 1977; Mavko et al. 1979) with strong anelastic effects while the upper bound is based on a tube geometry without anelastic effects. The tube geometry is similar to the ideal isotropic model suggested by Bulau and Waff (1977), Waff and Bulau (1979) and Bulau et al. (1979). According to the results of quenched and step-cooled samples of olivinebasalt aggregates, the melt geometry of olivine-basalt aggregate is neither pure film nor pure tube. For a combined melt geometry of thin films and tubes, the melt content in the mush zone is higher than the previously estimated lower bound and lower than the upper bound. Measurement of grain boundary wetness suggests that a large portion of the olivine grain boundaries are wetted by melt and the degree of wetting is somewhat decreased during cooling. It indicates that the grain boundary wetness of olivine-rich troctolite layer in the mush zone is somewhat lower than that in the region of partiallymolten dunite at constant melt content. Furthermore, the shear velocity in troctolite layer may be higher than that in the region of partially-molten dunite.

6. Conclusions

To better understand the formation of olivine-rich troctolites found in ophiolites and midocean ridges, step-cooled experiments of olivine-basalt aggregates were conducted. The results show that slow cooling of samples equilibrated at high temperature reproduces interstitial geometry of plagioclase and clinopyroxene observed in field olivine-rich troctolites. For those samples cooled until 1200 °C, tnterstitial phases and their geometries change with cooling temperature. Clinopyroxene grains form relatively small, rounded to near euhedral grains. During slow cooling below 1200 oC, clinopyroxene occurs distributed throughout the aggreagate with poikilitic shape, partially or fully enclosing olivines. Some large orthopyroxene grains are formed adjacent to poikilitic clinopyroxene grains. Clinopyroxene at slow cooling history shows smooth boundaries, while rapid cooling results in rough edges and includes tiny plagioclase pockets and orthpyroxene grains.

During cooling retreat of interstitially crystallizing solid phases from olivine boundaries results in decreased grain boundary wetness. Plagioclase best preserves the interstitial melt geometry, while orthopyroxene appears to retreat from grain boundaries relatively quickly. The comparisons between quenched samples and step-cooled samples at different melt contents indicate that crystallization of interstitial solid phases reduces grain boundary wetness more at lower melt content. The microstructural similarity of experimental and natural samples suggest that the grain boundary wetness of olivine-rich troctolite layer in the mush zone is somewhat lower than that in the region of partially-molten dunite at constant melt content. Furthermore, the shear velocity in troctolite layer may be higher than that in the region of partially-molten dunite.

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Tables

	Final cooing strategies at/below 1200 °C	Phases
XTAL1	at 1200 °C for 7 days	ol opx cpx plag
XTAL2	at 1150 °C for 7 days	ol opx cpx plag
XTAL3	1200 °C to 1150 °C at 25 °C/day	ol plag
XTAL4	1200 °C to 1100 °C at 20 °C/day	ol opx cpx plag
XTAL5	at 1200 °C for 7 days	ol opx cpx plag
XTAL6	at 1175 °C for 4 days	ol opx plag
XTAL7	1200 °C to 1150 °C at 10 °C/day	ol opx cpx plag
XTAL8	1200 °C to 1130 °C at 14 °C/day	ol opx cpx plag

 Table 3. Conditions of step-cooling experiments.

The final pressure of all experiments was 0.7 GPa.

	SiO_2	FeO	MgO	Fo#
XTAL1	40.6	9.79	49.59	90
XTAL2	40.37	9.36	50.28	90.5
XTAL3	43.94	9.08	47.00	90.16
XTAL4	40.74	9.6	49.66	90.2
XTAL5	40.34	9.7	49.96	90.18
XTAL6	40.48	9.54	49.99	90.3
XTAL7	40.26	9.6	50.14	90.3
XTAL8	41.06	9.63	49.32	90.13

 Table 4. Major element olivine compositions (average values, wt %)

	SiO ₂	TiO ₂	Al_2O_3	FeO	MgO	CaO	Na ₂ O	K ₂ O	Total	Mg#
XTAL1	48.55	2.73	10.98	3.55	16.23	16.95	0.78	0	99.95	89
XTAL2	52.16	1.78	5.6	3.96	20.1	15.64	0.7	0	99.94	90
XTAL4	43.7	4.64	16.13	3.57	13.55	17.76	0.61	0	99.96	87
XTAL5	52.86	1.81	5.12	4.33	21.29	14.58	0.62	0	100	89.8
XTAL6	53.12	1.14	4.59	4.68	22.27	13.56	0.64	0	100	89.5
XTAL7	53.04	1.12	4.7	4.34	21.83	14.41	0.575	0	100	90
XTAL8	52.65	1.14	5.56	4.12	20.44	15.6	0.48	0	100	90

 Table 5. Major element clinopyroxene compositions (average values, wt %)

	SiO ₂	TiO ₂	Al_2O_3	FeO	MgO	CaO	Na ₂ O	K ₂ O	Total	Mg#
XTAL1	54.9	0.5	3.93	6.17	32.67	1.8	0	0	100.1	90.4
XTAL4	54.97	0	4.19	6.22	33.05	1.38	0	0	100	90.4
XTAL5	56.38	0	1.48	6.02	34.73	1.22	0.37	0	100	91.1
XTAL6	55.56	0.64	2.32	6.58	31.19	4.04	0	0	100	89.4
XTAL8	55.09	0.68	2.33	6.66	30.4	4.5	0.36	0	100	89.0

 Table 6. Major element orthopyroxene compositions (average values, wt %)

	SiO ₂	TiO ₂	Al_2O_3	FeO	MgO	CaO	Na ₂ O	K ₂ O	Total	An#
Initial ^a	47.90	2.40	13.90	10.70	11.60	10.70	2.20	0.50	99.90	
XTAL1	49.81	2.24	23.67	4.39	6.07	7.91	5.09	0.76	99.94	46
XTAL2	50.99	3.10	20.86	5.01	6.73	8.21	4.60	0.56	100.06	50
XTAL3	49.03	1.84	18.63	7.28	11.18	8.01	3.60	0.40	99.95	55
XTAL4	52.41	3.06	24.39	3.69	4.17	6.13	5.09	1.07	100.00	40
XTAL5	52.40	2.91	19.63	5.41	6.81	8.43	4.13	0.43	100.01	53
XTAL6	52.82	3.03	17.89	5.82	6.86	9.39	3.71	0.50	100.00	58
XTAL7	50.81	3.50	19.97	5.77	7.49	8.81	3.01	0.65	100.00	62
XTAL8	51.41	2.90	20.23	5.50	7.21	8.16	4.02	0.60	100.00	61

 Table 7. Major element plagioclase compositions (average values, wt %)

a. Starting composition of basaltic powder

Figures



Figure 25. Summary of typical run conditions. Initially, all samples were annealed at 1350°C and 0.7 GPa for 5 to 7 days to produce a steady state microstructure. At this temperature only melt and olivine exists. MELT 35 and MELT 40 were quenched directly from this temperature. The other XTAL samples were cooled over approximately one week below their solidus temperature, following different protocols as indicated by lines of different colors. During cooling orthopyroxene crystalizes first, then clinopyroxene and finally plagioclase. Experiments were ended by quenching to room temperature in less than one minute.



Figure 26. Example of image processing. (a) A portion from a high resolution mosaic. The original mosaic has a resolution of 0.014 μ m/pixel. (b) Triple junctions, melt pockets and wetted-two grain boundaries formed by basaltic melt in Figure a were carefully traced on screen to convert to binary image (in red); Interstitial crystals in Figure a were traced on screen to convert to binary image (in black); Olivine-olivine grain boundaries in Figure a were traced on screen by orientation contrast and connecting triple junctions to create binary images of solid-solid boundaries (in blue).



Figure 27. MELT modeling (Ghiorso and Sack, 1995; Asimow and Ghiorso, 1998) of the starting melt composition from 1350 °C to 1100 °C at 0.7 GPa. The x-axis indicates temperatures in °C x 1000.



Figure 28. TiO₂ content versus Mg# in clinopyroxene. Generally, TiO₂ content decreases with increasing Mg#.



Figure 29. Al_2O_3 content versus Mg# in clinopyroxene. As indicated by this figure, Al_2O_3 content decreases with increasing Mg# in general.



Figure 30. CaO content versus Mg# in clinopyroxene. Although data scatters at Mg# of 90, it still shows a trend that when the Mg# increases from 87 to 90, CaO content keeps decreasing.



Figure 31. K₂O content versus with Mg# in clinopyroxene. The trend is clear that with increasing Mg#, K₂O content decreases.



Figure 32. Anorthite content (an#) in plagioclase versus Mg # of interstitial clinopyroxene. Generally, an# in plagioclase shows positive correlation with Mg# in clinopyroxene.





Figure 33. SEM images of sections of samples with different cooling history. (a) XTAL5 quenched from 1200 °C. At this temperature, cpx grains nucleate adjacent to former melt pockets, sometimes forming relatively small, rounded to near euhedral grains. A few large opx grains occur. Compared to samples quenched from 1350 °C, fewer olivine grain boundaries are wetted. (b) XTAL8 cooled below 1200 °C. Cpx occurs distributed throughout the aggregate with poikilitic shape, partially or fully enclosing olivine grains. Some large opx grains are formed adjacent to poikilitic cpx grains.













Figure 34. SEM images and EDS mapping of major element concentrations of samples with different cooling protocols. (a) XTAL5. (b) XTAL8. (c) XTAL2. cpx at slow cooling history shows smooth boundaries (XTAL5 and XTAL 8)., while rapid cooling results in rough edges and includes tiny plagioclase pockets and opx grains (XTAL2).



Figure 35. Comparison between quenched and step-cooled sampls at 9% melt content and similar grain size. (a) quenched sample with 43 μ m grain size (MELT35). At this melt content only basaltic melt is present as interstitial phase in the quenched sample. Almost all olivine grain boundaries are wetted by basaltic melt. (b) step-cooled sample with 39 μ m grain size (XTAL2). Interstitial orthopyroxene retreated from olivine grain boundaries. The dihedral angles between olivine and interstitial phases are greater than

those in the quenched sample (MELT35) overall. Plagioclase best preserves the interstitial melt geometry.


Figure 36. Comparison of quenched and step-cooled samples at 12% melt content and 47 μ m grain size. (a) The quenched sample (MELT40) at this melt content majority of the melt forms very big pockets fully or partially enclosing olivine grains. Some of these unconstrained olivine grains show euhedral crystal shape. These unconstrained grain

boundaries are low energy and partially or fully connected with adjacent grain boundaries (indicated by arrows). (b) The step-cooled sample (XTAL8) shows that pyroxene phases crystalized from the very big melt pockets existed at 1350 °C. The dihedral angles between olivine and interstitial phases are somewhat greater than those shown in the quenched sample (MELT40). This observation is more obviously demonstrated by the dihedral angles between olivine and pyroxene phases.



Figure 37. EBSD map of an olivine-rich troctolite from Krivaja-Konjuh (geological settings described in Faul et al., 2014). Green represents olivine grains, red is cpx, light blue is plagioclase, dark blue and pink are spinel. Black is not indexed but is predominantly altered interstitial plagioclase. This map indicates that cpx is more resistant to alteration and preserves the interstitial geometry better. Although plagioclase is mostly altered but the texture still shows interstitial geometry.

APPENDICES

Appendix I: Thermodynamic Background and Calculation of Oxygen Fugacity

Definition of Terms

Standard state the standard state for an ideal gas is defined as P=1 bar, T.

Species In chemistry, a species can be defined as an ensemble of chemical identical molecular entities that can explore the same set of molecular energy levels on a characteristic or delineated time scale (from IUPAC).
 Phase A physically distinctive form of matter, such as solid, liquid, gas or plasma. A phase of matter is characterized by having relatively uniform chemical and physical properties (e.g. a gas mixture of O₂ and H₂ has one phase (gas) and two species (O₂ and H₂)).

List of Symbols

P pressure

T temperature

f_i fugacity of species I, which is the partial pressure of species I in the gas phase.
 It is closely related to the thermodynamic activity.

a_i activity of species i. It represents the concentration of species I in the system.

 X_i mole fraction of species I, which equals weight percent of species I divided by its atomic/molecular weight.

 Υ_i activity coefficient of species i. It is defined as the ratio of the activity of speciesi to its mole fraction

K equilibrium constant of a chemical reaction

G Gibbs free energy, is a thermodynamic potential that measures the useful work obtainable from a thermodynamic system at a constant temperature and pressure (isothermal, isobaric).

 ΔG change in Gibbs free energy

 ΔV volume change

R gas constant, which is 8.314 J/mol K

1. Full Derivation of Oxygen Fugacity Equations

1.1. Relationship Between Chemical Equilibrium and Concentration of ReactantsConsider a general chemical reaction,

$$dD + eE = gG + hH$$

where D, E, G and H are chemical species and d, e, g and h are the stoichiometric coefficients (e.g., $2H_2 + O_2 = 2H_2O$). At given pressure and temperature, the equilibrium constant K is

$$K = \frac{[a_G]^g [a_H]^h}{[a_D]^d [a_E]^e}$$

The above equation is also called law of mass action. It states that the equilibrium constant is a function of activities of chemical species. Activity is a measure of the effective concentration of a species in a mixture and it relates to its chemical potential. For condensed species, the activities relate to their mole fraction, and this relationship is described by activity coefficient

activity coefficient
$$\gamma_i = \frac{a_i}{X_i} = \frac{activity of i}{mole fraction of i}$$

In an ideal solution, a=X, then activity coefficient =1. A nonideal solution is one in which the activities of the species are not equal to their mole fractions. If >1, then the species i is said to exhibit a positive deviation from ideal behavior, and if <1, then the species I is said to exhibit a negative deviation.

For a gas, the activity is simply the fugacity divided by a reference pressure to give a

dimensionless quantity. This reference pressure is called the standard state and normally chosen as 1 atmosphere or 1 bar. For example, the activity of oxygen in gas phase is

$$a_{02} = \frac{f_{02}}{f_{02}^0} = f_{02}$$

So in geochemical systems, when both solutions and gases present in a chemical reaction, the chemical potentials of solutions (liquid and solid) are represented by activities, and the chemical potentials of gases are represented by fugacities. Thus, at standard state (P=1,T), the equilibrium constant K of a gas participated reaction $dD + eE = gG + O_2$ is

$$K = \frac{[a_G]^g[f_{O2}]}{[a_D]^d[a_E]^e} \qquad (1)$$

Taking log at both sides and substituting activities with mole fractions and activity coefficients, we get

$$\log K = \log \left(\frac{a_G^g}{a_D^d a_E^e} fO2 \right) = \log \left(\frac{[X_G \ G]^g}{[X_D \gamma_D]^d [X_E \gamma_E]^e} fO2 \right)$$

Rearranging parameters, the equation becomes

$$logK = logf_{O2} + glogX_G + glog\gamma_G - dlogX_D - dlog\gamma_D - elogX_E - elog\gamma_E$$
(2)

1.2. Relationship Between Equilibrium Constant and Gibbs Free Energy

The Gibbs free energy of a system at any moment in time is defined as the enthalpy of the system minus the product of the temperature times the entropy of the system.

$$G = H - TS$$

The Gibbs free energy of the system is a state function because it is defined in terms of thermodynamic properties that are state functions. The change in the Gibbs free energy of the system that occurs during a reaction is therefore equal to the change in the enthalpy of the system minus the change in the product of the temperature times the entropy of the system.

$$\Delta G = \Delta H - \Delta (TS)$$

The standard Gibbs free energy change for a reaction is ΔG^0 . At chemical equilibrium $\Delta G=0$, Neither the forward nor the reverse, the reaction becomes $\Delta G^0 = -RT \ln K^0$ (3)

This is a very important equation. It relates the standard Gibbs free energy change of a reaction to the experimentally determinable equilibrium constant. Based on Raoult's law derived from gas mixtures, the vapor pressure of an ideal solution is dependent on the vapor pressure of each chemical species and the mole fraction of the species present in the solution. According to the equilibrium constant equation, equilibrium constant is a function of partial pressure. The ideal gas law PV = nRT, relates pressure, volume and mole fraction to temperature and gas constant. Combining all these equations together, equation (3) is derived (the full derivation is very long). Now this equation has been applied to general chemical equations. For example, in geochemistry, the equation for calculating metal-oxide buffers (will be discussed later) is derived from equation (3). In this case, it considered condensed metal and metal oxide exist as vapor species in

the gas phase. It is also widely used in calculating oxygen fugacity in gas mixtures, minerals and melts.

The next step is applying this equation at standard state to general pressure and temperature conditions. At constant temperature, the partial derivative of equation (3) to pressure gives

$$\left(\frac{\partial \Delta G^{0}}{\partial P}\right)_{T} = -\left(\frac{\partial RTlnK}{\partial P}\right)_{T}$$

The variation of the molar Gibbs free energy of a closed system of fixed composition, with pressure at constant temperature, is given by the fundamental equation

$$dG = VdP$$

So the change in volume is

$$\Delta V = \left(\frac{\partial \Delta G^0}{\partial P}\right)_T,$$

Substituting the partial derivative of ΔG^0 with ΔV , and moving ∂P from right side to left side, we get

$$\Delta V dP = -RT dlnK$$

Integrating this equation from 1 bar (standard state) to given pressure gives

$$\int_{1}^{P} \Delta V dP = \int_{1}^{P} -RT dlnk$$

$$\Delta V \Delta (P-1) = [-RTlnK]_1^P = RTlnK - RTlnK^0$$

Where K is the equilibrium constant at given P, T, and K^0 is equilibrium constant at standard state. Since at standard sate,

$$\Delta G^0 = -RT ln K^0$$

Substituting $-RTlnK^0$ with ΔG^0 , we get

$$\Delta V(P-1) = \Delta G^0 + RT lnK$$

Therefore equilibrium constant at given P and T is

$$lnK = -\frac{\Delta G^0}{RT} + \frac{\Delta V(P-1)}{RT}$$

Because $\log 10/\ln = 2.303$,

$$logK = -\frac{\Delta G^0}{2.303RT} + \frac{\Delta V(P-1)}{2.303RT}$$
(4)

Plugging in equation (2), then equation (4) becomes

$$logf_{O2} + glogX_G + glog\gamma_G - dlogX_D - dlog\gamma_D - elogX_E - elog\gamma_E$$
$$= -\frac{\Delta G^0}{2.303RT} + \frac{\Delta V(P-1)}{2.303RT}$$

Moving parameters other than oxygen fugacity to the right side of the above equation, we get

$$log f_{02} = -g log X_G - g log \gamma_G + d log X_D + d log \gamma_D + e log X_E + e log \gamma_E - \frac{\Delta G^0}{2.303 RT} + \frac{\Delta V(P-1)}{2.303 RT}$$
(5)

The standard Gibbs free energy changes ΔG^0 at given P and T for a chemical reaction can be represented by the form ((*Gaskell*, 2003)

$$\Delta G^0 = a + bT \ln T + cT (J) \tag{6}$$

Coefficients a and b can be checked from thermodynamic data, and lists the range of temperature in which the expression is valid. Similar as ΔG^0 , values of volume changes and activity coefficients can be found from published thermodynamic data. Mole fraction of each species can be measured by analytical techniques. Thus, if the mole fraction of species can be measured, and activity coefficients, standard Gibbs free energy change and volume change are literature values, the oxygen fugacity of this system can be calculated.

1.3. Oxygen Fugacity Equation for Metal/Metal-oxide Buffers

In high pressure high temperature experiments reported by literatures, oxygen fugacity during the course of experiment is controlled by metal/metal-oxide buffers. Some common buffers are

 $2Ni + O_2 = 2NiO$ (NNO)

 $2Fe + O_2 = 2FeO$ (IW)

 $C + O_2 = CO/CO_2$ (CCO)

When using such a method, it is always assumed that the buffer imposes its oxygen fugacity to the assembly, and the oxygen fugacity is often calculated without taking into account the silicate specimen. It is also assumed that the oxygen fugacity of the specimen rapidly reaches its equilibrium value, which is assumed to be that of the calculated buffer oxygen fugacity at given pressure, temperature (Raterron et al., 1998). Such a chemical reaction involves a gas species and two condense species and can be represented by the following equation

 $M + 0.5O_2 = MO$

Similar to equation (1), the equilibrium constant of the above equation is a function of activities of species, and the activity of gas species can be represented by fugacity. Thus, the chemical equilibrium at standard state is

$$K = \frac{[MO]}{[M] \ [f_{O2}]^{0.5}}$$

The activity of pure substances in condensed phases (solid or liquids) is normally taken as unity (the number 1), which means pure liquids and solids do not contribute to the chemical equilibrium. In this case, when both metal and metal oxide phase exist, the activities of these two phases are set to 1 (Medard et al. 2008, Nicholis et al. 1971 and O'Neill 1987a) and So the above equation becomes

$$K = f_{02}^{-0.5}$$

Take log at both sides

$$logK = -0.5logf_{02}$$

Plug in equation (4) to get oxygen fugacity at given T, P

$$-0.5log f_{O2} = -\frac{\Delta G^0}{RT} + \frac{\Delta V(P-1)}{RT}$$

Plug in equation (6)

$$log f_{O2} = -\frac{a}{RT} - \frac{bT}{RT} - \frac{cTlnT}{T} + \frac{\Delta V(P-1)}{RT}$$

Now we can set -a/R=A, -b/R=B, -c/R=D, and $\Delta V/R=C$. Rewriting the above

equation, finally we get the equation for calculating metal/metal oxide buffer

$$logf_{O2} = \frac{A}{T} + B + C(P-1)/T + DlnT$$

Coefficients for A, B, C and D of common buffers are summarized in Table 7 of Hirschmann et al., 2008.

2. Applications in Geochemical Thermodynamic Calculations

2.1. Oxygen Fugacity Calculation for Olivine-Opx-Metal Equilibria

Experiments of olivine housed by Fe, Ni, Ni-Fe and graphite capsules show five phases coexist in the olivine-capsule systems: oxygen, silica, olivine, opx rind formed at olivine-capsule contact, metallic iron (or nickel) alloyed with metal blebs or metallic capsules. The chemical reactions for iron reduction is

 $Fe_2SiO_4 = 2 Fe + SiO_2 + O_2 \quad [1]$

Olivine iron silica oyxgen

The chemical equation for the formation of opx rind is

 $Mg_2SiO_4 + SiO_2 = Mg_2Si_2O_6$ [2]

Olivine silica Orthopyroxene

Where Fe_2SiO_4 is the Fe-rich end member of olivine (Fayalite) and is represented by symbol Fa. Mg_2SiO_4 is the Mg-rich end member of olivine (Forsterite), which is the majority composition of San Carlos olivine. In this system, silica activity in reaction [1] is buffered by reaction [2], as long as opx rind, olivine and iron coexist in the capsule, the oxygen fugacity is buffered by this olivine-opx-metal equilibria. The following three methods are basically based on this equilibria.

2.1.1. Using Fe Concentration in FePt Alloy

The Fe reduced from olivine also alloys with Pt. Since the activity-composition relation of Fe-Pt alloy is known (earlier literature usually use activity coefficient from Heald 1967, this study uses a recent calibration from Fonseca et al.,2009), the redox state of this system can be determined by inserting a Pt wire into olivine grains and calculating the oxygen fugacity based on thermodynamic properties of the Pt-Fe system (Jamieson et al. 1991, Woodland and O'Neill 1997, Kessel et al. 2001). In the system with Pt sensor, reaction [1] takes place between Pt wire and adjacent olivine grains. The chemical equilibrium constant of this reaction is

$$K = \frac{a_{Fe}^{met^2} . a_{SiO2}}{a_{Fa}^{ol}} . a_{O2} = \frac{a_{Fe}^{met^2} . a_{SiO2}}{a_{Fa}^{ol}} . fO2$$

In above equation, a_{Fe}^{met} is activity of Fe in Fe-Pt alloy, a_{Fa}^{ol} is activity of Fa in olivine. a_{sio2} is the activity of Silica, which is buffered by the presence of opx rind through reaction [2] (Rubie et al. 1993).

Rewriting equation (5) we get oxygen fugacity equation for calculating olivine-opx-metal equilibria

$$logf O_{2} = log K - 2log a_{Fe}^{me} - log a_{SiO2} + log a_{Fa}^{ol} + log f O_{2}^{0}$$
$$= \frac{-\Delta G^{0}[1]}{2.303RT} + \frac{\Delta V(P-1)}{2.303RT} - 2\log(\gamma_{Fe}^{met}.X_{Fe}^{met}) - log a_{SiO2} + \log(\gamma_{Fa}^{ol}.X_{Fa}^{ol})$$

In the above equation, mole fractions of Fe in alloy (X_{Fe}^{met}) and Fa in olivine (X_{Fa}^{ol}) can be measured by EDS. Values of other parameters can be checked from literature mentioned in the following text.

Summary of Thermodynamic data

Standard Gibbs Free Energy of Reactions [1]

Equation is obtained by using electrochemical technique (O'Neill, 1987a).

 $\Delta G^{0}[1] = -564800 + 144.4T (J/mol)$

Silica Activity

In equation [2], a_{SiO2} is given by (O'Neill 1987)

$$loga_{SiO2} = \frac{\Delta G^{0}}{2.303RT} + loga_{Mg2Si2O6}^{opx} - loga_{Mg2SiO4}^{ol}$$

Since both Mg_2SiO_4 and Mg_2Si2O_6 are the major components of San Carols olivine and opx, their activity coefficients are close to 1. $loga_{SiO2}$ is

$$loga_{SiO2} = \frac{\Delta G^0}{2.303RT}$$

Thus the calculation only depends on the accuracy of Gibbs free energy change of this equation (Holland and Powell, 1998).

$$\Delta G^{0} = -14540 + 71.44T - 8.9 \text{ Tln}(T) - 0.375 \text{ P}(\text{in kb})\text{J/mol}$$

$$loga_{Si02} = (-14540 + 72.44T - 8.9\ln(T) - 0.375P)/(2.303RT)$$

Activity Coefficient of Fe in Fe-Pt ALloy

Equation for activity of Fe in Fe-Pt alloy is from equations 4-7 in Fonseca et al. (2009):

$$log\gamma_{Fe}^{met} = (1 - X_{Fe}^{met})^2 [0.0062T - 12.302 + (0.0017T - 2.565)(4X_{Fe}^{met} - 1)]$$

Activity Coefficient of Fa in olivine

Equation for activity of Fa in olivine is from O'Neill et al. (2003):

$$log\gamma_{Fa}^{ol} = (1 - X_{Fa}^{ol})^2 [(2600 + 108P)/(2.303RT)]$$

Change in volume

$$\Delta V^{\circ} = 0.866 \text{ (J/bar)}$$

Data for oxygen fugacity calculation using this method is in Table 8.

2.1.2. Using Fe Concentration in Ni-Fe Alloy

If there are Ni-Fe alloys enclosed in the capsule with the presence of a opx rind, the oxygen fugacity can be calculated using the same method and equations described in section 2.1.1 but with activity-composition relation of iron in Ni-Fe alloy.

$$logf O_{2} = log K - 2log a_{Fe}^{met} - log a_{SiO2} + log a_{Fa}^{ol} + log f O_{2}^{0}$$
$$= \frac{-\Delta G^{0}}{2.303 RT} + \frac{\Delta V (P-1)}{2.303 RT} - 2\log(\gamma_{Fe}^{met} \cdot X_{Fe}^{met}) - log a_{SiO2} + \log(\gamma_{Fa}^{ol} \cdot X_{Fa}^{ol})$$

Mole concentrations of iron in Ni-Fe alloy (X_{Fe}^{met}) and fayalite in olivine (X_{Fa}^{ol}) are measureable. Required thermodynamic data are summarized below.

Summary of thermodynamic data

Standard Gibbs Free Energy of Reactions [1]

Same as the one in section 2.1.1

Silica Activity

Same as the one in section 2.1.1

Activity Coefficients of Fe in Fe-Ni Alloy

 γ_{Fe}^{met} at a range of mole fractions of Fe in Fe-Ni alloy are summarized in Talbe III of Conard et al.,1978. *Activity Coefficient of Fa in Olivine* Same as the one in section 2.1.1

Change in Volume

$$\Delta V^{\circ} = 0.866 \text{ (J/bar)}$$

Data for oxygen fugacity calculation using this method is in Table 9.

2.1.3. Using Ni Concentration in Ni-Fe Alloy

Natural San Carlos olivine contains minor amount of Ni₂SiO₄. The following reaction takes place with reaction [1] at the same time,

 $Ni_2SiO_4 = 2 Ni + SiO_2 + O_2$ [3]

If nickel concentration in Ni-Fe alloy and Ni_2SiO_4 concentration in olivine are detectable, the oxygen fugacity can be calculated using an equation similar to that in section 2.1.2, but iron and fayalite are replaced by nickel and Ni_2SiO_4 , respectively.

$$logf O_{2} = log K - 2log a_{Ni}^{met} - log a_{SiO2} + log a_{Ni2SiO4}^{ol} + log f O_{2}^{0}$$
$$= \frac{-\Delta G^{0}}{2.303RT} + \frac{\Delta V(P-1)}{2.303RT} - 2\log(\gamma_{Ni}^{met}.X_{Ni}^{met}) - log a_{SiO2}$$
$$+ \log(\gamma_{Ni2SiO4}^{ol}.X_{Ni2SiO4}^{ol})$$

Standard Gibbs Free Energy of Reactions [3]

 $\Delta G^{\circ} = -485700 + 179.2T (J/mol)$

Silica Activity

Same as the one in section 2.1.1

Activity coefficient of Ni2SiO4 in olivine

Approximately 1.

Activity Coefficients of Ni in Ni-Fe Alloy

Available from the table in section 2.1.2 (Conard et al., 1978).

Change in volume

$$\Delta V=0.67 (J/bar)$$

Data for oxygen fugacity calculation using this method is in Table 10.

2.2. Oxygen Fugacity Calculation for Metal-Silica-Opx Equilibria

With the presence of opx rind, oxygen fugacity is also buffered by the following equilibria:

 $Fe + SiO_2 + 0.5O_2 = FeSiO_3[4]$

Ferrosilite

The equilibrium constant of this reaction can be expressed as

$$logK = \log\left(\frac{a_{fs}}{a_{Fe}a_{SiO2}f_{O2}^{0.5}}\right)$$

Then oxygen fugacity is

 $logfO2 = -2logK + 2loga_{Fs} - 2loga_{Fe} - 2loga_{SiO2}$

 $= -2\log K + 2\log X_{Fs} + 2\log \gamma_{Fs} - 2\log X_{Fe} - 2\log \gamma_{Fe} - 2\log a_{SiO2}$

Mole concentrations of Ferrosilite in opx and iron in iron-nickel alloy are available from EDS data.

Summary of Thermodynamic Data

Equilibrium Constant

 $\log K = 12776/T - 2.45 + 0.0079(P - 1)/T$ (Williams 1971)

Silica Activity

Same as the one in section 2.1.1

Activity coefficient of iron in nickel

Available from the table in section 2.1.2 (Conard et al., 1978).

Activity coefficient of ferrosilite in opx

 $\log \gamma_{\rm fs} = 0.22(1-X_{\rm fs})^2$ (Williams 1971))

Data for oxygen fugacity calculation using this method is in Table 11.

Tables

Table 8. Data for oxygen fugacity calculation using Fe concentration in FePt alloy

Run#	Cap	Т	X_{Fe}^{met}	X_{Fa}^{ol}	$\frac{\Delta G^{0}}{2.3RT}$	$2log rac{X_{Fa}^{ol}}{X_{Fe}^{met}}$	2logγ ^{ol} a	$2log\gamma_{Fe}^{met}$	logSi	$\frac{\Delta V}{2.3RT}$	logfO2
CAP11	Ni	1573	0.23	0.02	-11.21	-2.35	0.17	-3.08	-0.17	0.29	-9.85
CAP18	Ni	1573	0.22	0.06	-11.21	-1.16	0.16	-3.12	-0.17	0.29	-8.63
CAP17	Ni	1473	0.26	0.07	-12.48	-1.15	0.17	-3.44	-0.18	0.31	-9.55
CAP15	С	1673	0.09	0.01	-10.09	-2.23	0.17	-3.53	-0.17	0.27	-8.19
CAP14	Fe	1673	0.33	0.01	-10.09	-3.23	0.17	-1.65	-0.17	0.27	-11.06

Pressure = 1 Gpa

					ΔG^{0}	X_{Fa}^{ol}				ΔV	
Run#	Cap	Т	X_{Fe}^{met}	X_{Fa}^{ol}	2.3 <i>RT</i>	$2109 \overline{X_{Fe}^{met}}$	2logγ ^{ol} Fa	$2log\gamma_{Fe}^{met}$	logSi	2.3 <i>RT</i>	logfO2
CAP1	Fe	1673	0.92	0.07	-10.09	-2.3	0.15	0	-0.17	0.27	-11.79
CAP7	Fe	1623	0.75	0.11	-10.63	-1.66	0.14	-0.02	-0.17	0.28	-11.68
CAP3	NiFe	1673	0.19	0.09	-10.09	-0.69	0.14	-0.58	-0.17	0.27	-9.61
CAP2	Ni	1673	0.02	0.02	-10.09	0.03	0.16	-1.3	-0.17	0.27	-8.15
CAP4	Ni	1573	0.04	0.04	-11.21	-0.67	0.17	-1.2	-0.17	0.29	-9.72
CAP6	Ni	1573	0.02	0.03	-11.21	0.25	0.17	-1.32	-0.17	0.29	-9.00
CAP8	Ni	1573	0.02	0.04	-11.21	0.81	0.17	-1.34	-0.17	0.29	-8.43
CAP11	Ni	1573	0.01	0.02	-11.21	0.12	0.17	-1.36	-0.17	0.29	-9.10
CAP18	Ni	1573	0.02	0.02	-11.21	0.11	0.17	-1.31	-0.17	0.29	-9.16
CAP9	С	1673	0.28	0.10	-10.09	-0.93	0.14	-0.35	-0.17	0.27	-10.08

Table 9. Data for oxygen fugacity calculation using Fe concentration in FeNi alloy

Pressure = 1 Gpa

Run#	Cap	Т	X_{Ni}^{met}	X_{Ni}^{ol}	$\frac{\Delta G^0}{2.3RT}$	$2log rac{X_{Ni}^{ol}}{X_{Ni}^{met}}$	2logγ ^{ol}	2logy ^{met}	logSi	$\frac{\Delta V}{2.3RT}$	logfO2
CAP7	Fe	1623	0252	1e-4	-10.09	-2.3	0.15	0	-0.17	0.27	-11.79
CAP3	NiFe	1673	0.81	0.01	-5.80	-4.22	0	-0.08	-0.17	0.21	-9.56
CAP2	Ni	1673	0.99	0.03	-5.80	-3.12	0	6e-4	-0.17	0.21	-8.54
CAP4	Ni	1573	0.97	0.01	-6.77	-3.81	0	3e-3	-0.17	0.22	-10.18
CAP6	Ni	1573	0.99	0.02	-6.77	-3.47	0	-0.001	-0.17	0.22	-9.84
CAP8	Ni	1573	0.985	0.13	-6.77	-1.79	0	-0.001	-0.17	0.22	-8.16
CAP11	Ni	1573	0.99	0.03	-6.77	-3.10	0	9e-4	-0.17	0.22	-9.47

Table 10. Data for oxygen fugacity calculation using Ni concentration in NiFe alloy

Pressure = 1 Gpa

Run#	Cap	Т	X_{Fe}^{met}	X_{Fs}^{opx}	2logSi	2K	$2log\gamma_{Fs}^{opx}$	$2log\gamma_{Fe}^{met}$	logfO2
CAP1	Fe	1673	1	0.07	-0.35	10.47	0.38	0.00	-12.11
CAP3	NiFe	1673	0.19	0.07	-0.35	10.47	0.38	-0.58	-10.09
CAP2	Ni	1673	0.01	0.01	-0.35	10.47	0.43	-1.37	-8.43
CAP4	Ni	1573	0.02	0.02	-0.35	11.44	0.42	-1.32	-9.29
CAP6	Ni	1573	0.01	0.01	-0.35	11.44	0.43	-1.37	-9.29
CAP11	Ni	1573	0.02	0.02	-0.35	11.44	0.42	-1.34	-9.13
CAP12	Ni	1473	0.02	0.05	-0.35	12.55	0.40	-1.25	-9.85
CAP18	Ni	1573	0.02	0.02	-0.35	11.44	0.42	-1.26	-9.34
CAP9	С	1673	0.28	0.09	-0.35	10.47	0.37	-0.37	-10.41

Table 11. Data for oxygen fugacity calculation using Ferrosilite concentration in Orthopyroxene

Pressure = 1GPa

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Appendix II: Temperature Calibration of Piston Cylinder Apparatus

1. Introduction

Temperature measurements of piston cylinder experiments are achieved by inserting a Pt-Rh thermocouple into the graphite furnace to measure the temperature right above the experimental sample (Figure 38). The temperature measured by the Pt-Rh thermocouple may need to be corrected to reflect the actual temperature at the measurement point. Furthermore, the experimental sample is required to be placed at the hottest part of the furnace (hot zone) to avoid axial thermal gradient across the sample. Thermal gradients across the partially molten samples are severe problems that may cause inhomogeneous melt distribution/melt segregation (Lesher and Walker, 1988) and abnormal grain growth. Axial thermal gradients lead the melt to migrate along vertical channels (Figure 39a) and form a melt layer at the hotter end of the olivine aggregate (Figure 39b). Since grain growth rate of olivine is proportional to temperature, a thermal gradient can cause an axial grain size distribution with coarse-grained olivine grains towards the hotter end. In order to locate the hot zone of the furnace, the axial temperature distribution of the furnace needs to be mapped. This appendix describes temperature calibration experiments that I have conducted to correct potential measurement errors of the thermocouple and map the hot zone axial temperature profiles following the method of Watson et al. (2002).

2. Methods and Experimental Setup

This method uses the fact that Al₂O₃ reacts with MgO at high pressures and temperatures to form a spinel rim. The width of the spinel rim is a function of temperature (T, in K), pressure (P, in GPa) and time (t, in s): $\Delta X = [8.58 \times 10^{11} \cdot \exp(-48865/T - 2.08 \cdot P^{0.5}) \cdot t]^{0.5}$ (Watson et al., 2002). The upper part of the calibration assemblies consisted of an Al_2O_3 thermocouple sleeve inside a MgO sleeve, with the thermocouple junction at the position of the bottom of the capsule in the actual experiments. The lower part of the graphite furnace consisted of an MgO spacer with empty Al₂O₃ thermocouple sleeve along axis. For the experiments conducted at 2 GPa, the two Al_2O_3 thermocouple sleeves covered entire axial length of the furnace, with direct contact at the thermocouple junction. For the experiments conducted at 1 GPa, the upper and lower Al_2O_3 thermocouple sleeves were separated by a thin Al₂O₃ disk. The lower sleeve did not go through the very bottom of the MgO spacer (Figure 40). The calibration experiments were conducted at 1400 °C and at 1 or 2 GPa for 168 hours. The whole post-run furnaces were sectioned along the axis, mounted in epoxy, and polished using the methods described in main chapters. The measurement was taken under a Zeiss Supra 55 field emission scanning electron microscope. The spinel rim is well defined by the layer sandwiching between coarsegrained polycrystalline MgO and fine-grained polycrystalline Al₂O₃ under scanning electron microscope (Figure 41). The spinel layer width of each calibration experiment was measured every 0.5 mm on both sides of the cross section on screen. The axial temperature distributions were constructed by using the equation mentioned above.

3. Results

A total of 10 experiments have been conducted. The first 6 experiments were used to address an issue of the proportional-integral-derivative (PID) controller issue of the piston cylinder apparatus and test calibration sample assemblies to allow the sample to maintain the designated pressure and temperature throughout the course of the run. The sample assemblies used in the last four experiments have yielded good results.

Figure 42 shows axial temperature profiles for experiments at 1400 °C and 1 GPa and 2 GPa for 168 hours. The profiles cover 15mm to 25 mm of the central portions of the furnace, given a total furnace length of 30 mm. Each point represent the average temperature measured from spinel layers at both sides. Temperature gradients at the center of the furnace are gentle and become steeper towards the two ends. Temperature distributions along the top of the furnace (measured from the top Al₂O₃ sleeve) do not show abrupt temperature change. In contrast, three of the four runs show abnormal temperature distributions at the bottom of the furnace.

The axial temperature profiles at hot zone have reached the requirements for conducting real experiments. The temperatures measured from the width of spinel layer are identical to those measured by the thermocouple, indicating the thermocouple does not need to be corrected. Temperature variations along the length of actual sample location are within 10 °C. CAL9 shows the best temperature profile that the temperature gradient along the location of the actual sample is less than 5 °C.

4. Discussion

The axial temperature profiles at hot zone were acquired at relatively extreme conditions, ensuring that the acquired calibration results can be applied to the real experiments. In other words, the results emphasize that the hot zone of the furnace is able to keep itself intact under the high pressure, high temperature and long duration conditions. The calibration temperature 1400 °C is almost the highest temperature in real experiments (only a partial-molten sample described in Chapter II was annealed at 1450 °C). The calibration pressure 2 GPa is much higher than that in the real experiments that conducted at or below 1 GPa. Although the duration of a large portion of the real experiments was longer than that of the calibration experiments, the lower pressure and temperature conditions in these real experiments could compensate the longer duration.

The temperature distribution anomaly at the bottom is due to deformation of the furnace. The furnace assembly needs to be pressurized at room temperature so that each furnace part is in good contact with adjacent parts to ensure good electric conductivity. This cold-press may cause deformations along the graphite furnace. With increasing pressure and temperature, the cracks caused by deformation will be enlarged by injected molten glass from the pyrex sleeve and local hotspots will develop at these cracks. Post-run furnaces show more cracks at the bottom of the furnace than those at the rest portion. More deformation features were observed from calibration samples annealed at higher pressure of 2 GPa. These observations are consistent with the temperature distribution anomaly at the bottom and more serious anomaly shown in calibration samples annealed at 2 GPa.

Although the deformation at the bottom of furnace does not affect the axial temperature profile of the hot zone, it indicates potential furnace failure and needs to be paid close attention. The results show that the deformation at bottom can be reduced by gently pressurizing the furnace to 0.4 GPa at room temperature, and then increasing the pressure to target pressure after the temperature reaches 400 °C. This method ensures that all furnace parts are compacted together but the moderate pressure avoids large deformation. When the temperature is above 400 °C, the furnace parts start to become softer as the plastic deformation is reduced. CAL9 followed this step pressurizing strategy and shows a very nice axial temperature profile from top to bottom of the furnace. Furthermore, the temperature variation along the length of the actual sample is less than 5 °C, indicating that this pressurizing strategy does benefit the accuracy of the real experiments.

5. Conclusions

In conclusion, the temperature calibration experiments indicates that

- 1. The temperature measured by the thermocouple reflects the actual temperature at the measurement point. Hence no temperature correction was needed.
- 2. The temperature variation along the length of the actual sample is within 10 °C and can be further reduced to 5 °C by using a step pressurizing strategy. This small temperature variation is able to maintain homogeneous melt distribution and normal grain growth.

 Step pressurizing strategy can be used to reduce deformation of the furnace and further minimizes temperature variation along the length of the actual experimental sample.

Overall, all the experiments described in the main chapters were conducted under carefully calibrated temperature conditions and therefore the data reliability were ensured.

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Tables

 Table 12. Summary of temperature calibration experiments

Experiment #	Duration (hr)	Temperature (°C)	Pressure (Gpa)
CAL7	168	1400	2
CAL8	168	1400	2
CAL9	168	1400	1
CAL10	168	1400	1

Figures



Figure 38. Cross-section of pressure vessel with graphite furnace inserted. The thermocouple only measures temperature at the point right above the actual experimental sample, but the axial temperature profile needs to be mapped in order to find out the hot zone of the furnace.



Figure 39. Melt migration caused by thermal gradients. (a) The arrows indicating an axial melt channel that caused by melt migration from bottom to top due to thermal gradient. In samples with homogeneous melt distribution, melt pockets are not aligned in one direction but shows various orientations. (2) The arrows indicating a melt layer
formed in between the capsule and olivine aggregate. The melt was driven by thermal gradient to migrate through various vertical channels and finally accumulated at the top.



Figure 40. Cross-section of furnace assemblies used in temperature calibration experiments. The assembly on the left was used in calibration experiments at 2 GPa. The two Al_2O_3 sleeves are in direct contact at the thermocouple junction. The lower Al2O3 sleeve reaches the bottom graphite disk. The assembly on the right was used in calibration experiments at 1 GPa. The two Al_2O_3 sleeves are separated by a thin Al_2O_3 disk right below the thermocouple junction. The lower Al_2O_3 sleeve does not reach the bottom graphite disk.



Figure 41. SEM image of spinel rims formed near the thermocouple junction. The spinel rims are indicated by the arrows. They are in between coarse-grained polycrystalline MgO spacer (to the two sides) and fine-grained polycrystalline Al₂O₃ thermocouple sleeve (adjacent to the thermocouple).



Figure 42. Axial temperature profiles of calibration experiments at 1400 °C and 1 GPa and 2 GPa for 168 hours. The length of the actual experimental sample is indicated by the section between the two red lines. The temperature variations in this section are within 10 °C. Temperatures measured at the thermocouple junction (0 mm) from spinel width are exactly the target temperature 1400 °C. Temperature distribution abnormally is shown at the bottom of the furnace for experiments conducted at 2 GPa and one experiment conducted at 1 GPa. The experiment conducted at 1 GPa with step pressurizing (CAL9) shows normal temperature distribution throughout the entire furnace.

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