THE POSSIBILITY OF LITHOPHILE ELEMENTS IN EARTH’S CORE: THE HIGH PRESSURE ELECTRONIC TRANSITIONS OF RUBIDIUM AND POTASSIUM

A Thesis

Presented in Partial Fulfillment of the Requirements for the Degree Master of Science in the Graduate School of The Ohio State University

By

Sabrina A.R.A. Whitaker, B.S.

*****

The Ohio State University
2009

Master’s Exam Committee:

Professor Wendy Panero, Adviser

Professor Fengyuan Yang

Approved By:

______________________________
Adviser
The School of Earth Sciences Graduate Program
Copyright
Sabrina A.R.A. Whitaker
2009
ABSTRACT

Long-lived radionuclides such as potassium, uranium, and thorium are sources of heat generation in the interior of the Earth. $^{40}\text{K}$ decays to $^{40}\text{Ca}$ and $^{40}\text{Ar}$ with a half-life of about 1.25 Gy, responsible for ~ 10% of the Earth’s current heat production. While not a major component of heat production, $^{87}\text{Rb}$ decays to $^{87}\text{Sr}$ with a half-life of 48 Gy, and the $^{87}\text{Sr}^{86}\text{Sr}$ ratio is taken as a tracer for geochemical reservoirs throughout Earth history. Previous experiments on potassium solubility in iron at high pressures show varying results as to the possible concentration of potassium in the core. While there have not been any previous studies on rubidium, it often substitutes for potassium in minerals due to its similar ionic charge and radius and therefore similar results are expected.

This study evaluates the effect of sample preparation on the effect of solubility of Rb or K in iron. All samples after quench showed ~ 2% expansion of the iron lattice when analyzed by X-ray diffraction, for a distribution coefficient of 0.03 at 2500 K. Samples loaded with powder in air varied more than those loaded in a nitrogen environment or with foil. TEM and nano – SEM studies found the amount of Rb alloyed with iron to be below the detection limit (3000 ppm), placing an upper bound on the distribution coefficient of 0.012, broadly consistent with the results from XRD.

Therefore, the upper bound for K and Rb in the core is inferred to be 8 ppm and 17 ppb, respectively. This implies an upper bound of $5 \times 10^{10}$ W for the power in the core due to radioactive decay of K. The possibility of Rb in the core could impact the
cycling and distribution of Rb with respect to Sr, affecting the interpretation of 
$\text{Sr}^{87}/\text{Sr}^{86}$ with respect to mantle geochemical processes.
Dedicated to Gigi
ACKNOWLEDGEMENTS

I would like to express my gratitude to my adviser Dr. Wendy R. Panero for the opportunity to study materials at extreme conditions, as well as for her guidance and support. I would like to also thank my committee members Dr. Gunter Faure and Dr. Fengyuan Yang for their discussions and comments as this work progressed.

Thank you to Henry Scott for contributions in programming, Elizabeth Cottrell for SEM imaging contributions, and CDAC for financial support. In addition, I would like to thank Dr. Jingzhu Hu, Dr. Sanjit Ghose, and Dr. Zhiqiang Chen at Brookhaven National Laboratory at beamline X17C; Dr. Yue Meng at beamline HPCAT at Argonne National Laboratory; and Daniel Huber and Dr. Hendrik Colijn at The Ohio State University Campus Electron Optics Facility for technical assistance. I graciously thank Matthew Whitaker for helpful discussions.

Furthermore, I thank Daniel Reaman, Jason Kabbes, Jeffrey Pigott, and Eugenia Hyung for their help in preparing samples and collecting data. And finally, a heartfelt thank you to my family and friends for the support and time they extended to me as I invested my interests in researching the high pressure reactions of potassium and rubidium with iron.
VITA

August 29, 1985………………………………………Born – Tinker Airforce Base, OK

2007…………………………………………………..B.S. Physics, Indiana University, South Bend, IN

2007 – Present………………………………………..Graduate Research and Teaching Associate, The Ohio State University

PUBLICATIONS

* Published under maiden name S. Huggins


FIELDS OF STUDY

Major Field: Earth Sciences
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>ii</td>
</tr>
<tr>
<td>Dedication</td>
<td>iv</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>v</td>
</tr>
<tr>
<td>Vita</td>
<td>vi</td>
</tr>
<tr>
<td>List of Tables</td>
<td>viii</td>
</tr>
<tr>
<td>List of Figures</td>
<td>ix</td>
</tr>
</tbody>
</table>

## Chapters:

1. Introduction ......................................................... 1
2. Sample Preparation .................................................. 5
   2.1 Introduction ..................................................... 5
   2.2 Experimental Methods and Data Analysis ....................... 6
      Sample Loading ...................................................... 8
      Laser Heating ...................................................... 9
   2.3 Results and Discussion ......................................... 13
3. Rubidium and Potassium ................................. 16
   3.1 Experimental Methods and Analysis ......................... 16
   3.2 Results ........................................................ 16
   3.3 Modeling Rubidium in the Deep Earth ...................... 18
   3.4 Results and Discussion ....................................... 19

References .......................................................... 24

Appendix A: Tables and Figures ................................. 26

Appendix B: Glove-box Notes and Plans ......................... 46
LIST OF TABLES

Table

1  Results from Previously Published Experiments...........................................28
2  Sample Conditions.........................................................................................29
3  Partition Coefficients.....................................................................................30
4  High Pressure Volumes and Lattice Expansion for Iron Wire.........................31
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Amount of Oxidation of Powder Vs Foil</td>
<td>32</td>
</tr>
<tr>
<td>2</td>
<td>Vegard’s Law</td>
<td>33</td>
</tr>
<tr>
<td>3</td>
<td>Etching Iron Foil in HCl</td>
<td>34</td>
</tr>
<tr>
<td>4</td>
<td>Loading in the Glove-box</td>
<td>35</td>
</tr>
<tr>
<td>5</td>
<td>Synchrotron X-ray Diffraction Schematic</td>
<td>36</td>
</tr>
<tr>
<td>6</td>
<td>X-ray Diffraction Profiles</td>
<td>37</td>
</tr>
<tr>
<td>7</td>
<td>The Percent Difference from Pure Iron For All Sample Conditions</td>
<td>38</td>
</tr>
<tr>
<td>8</td>
<td>A Trench Dug to Create a Thin Foil by FIB</td>
<td>39</td>
</tr>
<tr>
<td>9</td>
<td>Percent Difference from Pure Iron For Rb</td>
<td>40</td>
</tr>
<tr>
<td>10</td>
<td>Percent Difference from Pure Iron For K</td>
<td>41</td>
</tr>
<tr>
<td>11</td>
<td>A Foil from Iron Foil and Rb at 64 GPa examined by nano-SEM</td>
<td>42</td>
</tr>
<tr>
<td>12</td>
<td>A Foil from Iron Foil and Rb at 20 GPa examined by TEM</td>
<td>43</td>
</tr>
<tr>
<td>13</td>
<td>Model of Crust and Mantle Compared to Bulk Silicate Earth</td>
<td>44</td>
</tr>
<tr>
<td>14</td>
<td>Model of Core with Experimentally Determined Distribution Coefficient</td>
<td>45</td>
</tr>
<tr>
<td>15</td>
<td>Range of Distribution Coefficients that Change $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in Model</td>
<td>46</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

Carbonaceous chondrites are considered to contain remnants of the early solar system from which the Earth formed, and therefore are a starting point in determining the chemical makeup of the Earth [McDonough and Sun, 1995]. However, there is ~30-50% less potassium and rubidium found in the silicate mantle and crust, or Bulk Silicate Earth (BSE), than would be expected based on meteorite compositions, even when allowing for the volatility of these elements [Bukowinski, 1976; McDonough and Sun, 1995]. The amount of K and Rb that is actually depleted in the BSE is highly dependent on the models used to get the absolute values for these elements. Also, there is a debate as to the K/U ratio which is used to determine the absolute value for K in the BSE. For the purposes of this study the values are from McDonough and Sun [1995] for the BSE are 240 ppm K and 0.6 ppm Rb, which is very different from the chondritic meteorite values of 560 ppm K and 2.3 ppm Rb. The discrepancy between chondritic meteorites and the BSE lends itself to the possibility that potassium and rubidium as alkali metals could be located in the Earth’s core, requiring that they be able to form solutions with iron. However, at low pressures, the low electronegativity of the alkalis cause these elements to dominantly bond ionically, forming oxides, halides, and silicates, and therefore making it more likely to find these elements in silicate material instead of alloying with metals,
including iron. The effect of pressure, however, is for rubidium and potassium to undergo \( ns^1 \) to \((n-1)d^1 \) electronic transitions, where \( n \) is the primary quantum number of the outer electron shell [Bukowinski, 1976; Parker et al., 1996; Takemura and Syassen, 1983]. This transition changes the chemical behavior of the alkali metal to a transition metal-like behavior, allowing for the formation of intermetallic alloys. The electronic transition occurs over a broad pressure range at room temperature as the energy states of the s-shell electrons overlaps with the d-shell electrons, for rubidium the transition is at approximately 40 gigapascals (GPa) and for potassium it is \(~25 \) GPa. This makes it possible for potassium and rubidium to be incorporated into the Earth’s core at high pressures.

Long-lived radionuclides such as potassium, rubidium, uranium, and thorium are sources of heat generation and geochemical tracers in the interior of the Earth. Without radiogenic heat sources, the age of the inner core is approximately 2 Ga [Stacey and Loper, 2007]. However, there is evidence from rocks that a geomagnetic field existed at least 3.5 billion years ago and therefore an outer core existed about that time and an inner core must have formed before that time [Labrosse et al., 2001]. In order to help balance Earth’s heat budget, radiogenic isotopes must help make up the balance. If the age of the inner core is approximately the same as the age of the Earth, 4.6 billion years old, than about 4 TW must be from radiogenic sources in the outer core [Labrosse et al., 2001]. As one radiogenic heat source, \(^{40}\text{K} \) decays to \(^{40}\text{Ca} \) and \(^{40}\text{Ar} \) with a half-life of about 1.25 Gy, responsible for as much as 10 TW of the Earth’s current heat production of
approximately 41 GPa, and K is responsible for approximately 10% of Earth’s heat loss \cite{Bouhifd et al., 2007; Rollinson, 2007}.

While not a contributor to heat generation in the Earth, $^{87}$Rb decays to $^{87}$Sr with a half-life of 48 Gy, and $^{87}$Sr/$^{86}$Sr ratios are used as tracers for geochemical reservoirs throughout Earth’s history \cite{Faure, 2005}. The large electronic radius of Rb is relatively more incompatible than Sr in a solid silicate, and therefore melts are assumed to have an initially higher Rb/Sr ratio than the source rock. The $^{87}$Sr/$^{86}$Sr ratio is then taken as tracer for the formation of the mantle and crust. With the initial $^{87}$Sr/$^{86}$Sr of 0.699 a model for the Bulk Silicate Earth (BSE) based on the radiogenic decay of $^{87}$Sr gives today’s $^{87}$Sr/$^{86}$Sr as 0.705 and a Rb/Sr of 0.03. However, values for Mid Ocean Ridge Basalts (MORBs), which give experimentally determined present day $^{87}$Sr/$^{86}$Sr, have a much lower range for the $^{87}$Sr/$^{86}$Sr ratio of ~ 0.7022-0.703 \cite{O’Nions et al., 1979}. Instead a two layer model of extraction of the crust from the top half of the mantle for the last two billion years creates a model that provides an $^{87}$Sr/$^{86}$Sr ratio that agrees more with observed data. However, if the effect of pressure is to alter the behavior of Rb in the Earth’s interior, the implicit assumption of relative partitioning of Sr and Rb behavior is no longer valid, altering the interpretation of $^{87}$Sr/$^{86}$Sr ratios and inferences of deep-planetary processes.

By incorporating such radiogenic isotopes as rubidium and potassium into the core, Earth’s heat budget and its geochemical history might be better understood. Because the dynamics of Earth’s interior are largely controlled by Earth’s heat budget, a
better limit on the heat budget will allow for improved understanding of the magnetic field, the size and properties of the inner core, and the convection of the outer core. Better understanding of Earth’s geochemical history will allow for a better constraint on the age and the conditions at which the core was formed.

Studies on potassium solubility in iron at high pressures 26 GPa – 128 GPa [Hirao et al., 2008; Lee and Jeanloz, 2003] show varying results as to the possible concentration of potassium in the core. Two basic ways have been employed to study the effects of pressure on potassium and iron. One is a result of concentrations that are derived through secondary means assuming that Vegard’s law applies to the mixture of iron with potassium or potassium enriched minerals. In these experiments, the solution between iron and potassium is assumed to be ideal, such that lattice expansion of the iron is assumed to be a linear relationship between the iron and potassium volume at a given pressure. In experiments that explore the amount of K that alloys with iron, two nearly identical experiments show variations between a few tens of ppm of potassium to as much as 7000 ppm could be found alloyed with iron at high pressure [Gillet et al., 2006; Lee and Jeanloz, 2003]. The other method for evaluating these high-pressure results is to implement the use of the scanning Transmission Electron Microscope (TEM). By using the TEM, the reaction of K-silicate and Fe can be quenched to room temperature with as much as 0.8 wt% K in the metal phase [Hirao et al., 2006].
CHAPTER 2

SAMPLE PREPARATION

2.1 Introduction

Previous experiments used either pure potassium metal and pure iron foil [Gillet et al., 2006], pure potassium metal and pure iron powder [Lee and Jeanloz, 2003] or a K-silicate and iron powder as starting materials [Gessmann and Wood, 2002; Hirao et al., 2006; Ito et al., 1993]. These experiments explored pressures from ~26 GPa to 134 GPa and temperatures of ~2500K – 3500K (Table 1). The experiment conducted using the iron foil resulted in ~100 ppm K alloying with the Fe- metal, while the experiments using iron powder found that ~2000-7000 ppm K could alloy with the iron – metal at high pressures and temperatures [Hirao et al., 2006; Lee and Jeanloz, 2003]. Higher concentrations of K were found in experiments starting with micron-sized iron powder, and lower concentrations in iron foil.

The surface of iron oxidizes quickly in air, forming an oxidized layer ~10-100 nm thick in less than 5 minutes [Reaman et al., 2007]. The approximate 10-100 nm iron oxide layer corresponds to a volume fraction of .5%-5% on a 4 micron thick foil, and a volume fraction of 3%-33% on a 1 μm powder (Figure 1). The oxidizing potential of the experiments with iron powder is significantly greater than for foils because of the considerable increase in surface area of iron powder relative to the foil. The presence of
oxygen in the iron has been shown to be a dominant control of the partitioning of potassium between iron and silicate [Corgne et al., 2007].

In order to determine if the difference in the amount of K entering the iron lattice was due to the oxidation of the iron, a glove-box suitable for loading samples in an oxygen-free environment was designed and tested (see Appendix for plans). Samples of iron foil that were well-stripped of oxidation or powder that was never exposed to air were loaded into a Diamond Anvil Cell (DAC) and then compared to samples of both foil and powder that were loaded in air.

2.2 Experimental Methods and Data Analysis

Vegard’s law [Vegard, 1921] states that at constant temperature a linear relationship exists between the crystal lattice constant of an alloy and the concentrations of the constituent end-members (Figure 2). In order to use Vegard’s law, it is necessary to obtain the lattice constant and unit cell volume of the alloy in question. X-ray diffraction can be used to determine the lattice constants of a material under various conditions, which in turn can be used to determine the unit cell volume. X-ray diffraction is also used in the identification of new phases. In these experiments, powder X-ray diffraction was used to determine lattice constants for the ε-phase of iron at high pressures and the α-phase of iron after quenching to ambient pressure. Diffraction patterns were also used to search for the presence of any new phases that could have formed between iron and the K or Rb-silicate used in these experiments in order to determine whether Vegard’s law was valid for iron and these alkali metals under these experimental conditions.
Diamond anvil cells (DAC) were used to generate high pressures in these experiments. DAC experiments rely on the following principle:

\[ P \equiv F/A \]  

(1)

This relationship simply states that pressure, \( P \), is directly proportional to force, \( F \), and inversely related to area, \( A \). In DAC experiments, the working faces of the diamonds are in the range of hundreds of microns in diameter. The small area allows for very high pressures to be generated by moderate forces. Normally, this amount of force is provided by screws that are tightened by hand when bringing the pistons of the cell together.

A DAC consists of a piston and cylinder in which diamond anvils are mounted; in these experiments, diamonds with culet diameters of 200 - 500 \( \mu m \) were used. A gasket made of a thin metal foil is used to contain the sample between the opposing diamonds during compression. This gasket is pre-indentated by placing the gasket between the diamonds and hand-tightening the screws of the DAC that apply the pressure. Once indented, a hole is then electrically drilled in the center of the indentation using an electrical discharge machine (EDM), thereby forming the sample chamber. The gaskets used in these experiments were stainless steel or rhenium discs indented to a thickness of \( \sim 40 \mu m \), and the sample chambers ranged from 90 - 260 \( \mu m \) in diameter. After the gasket was indented and drilled, it was placed on top of the diamond and held in place with modeling clay at the edges. The gasket was then aligned, and the sample was loaded as described in the following section.
Sample Loading

Samples have been prepared in a manner that reproduces previous experimental studies. We used four starting materials: (1) a sample of natural high purity orthoclase (actual composition $K_{0.915}Na_{0.067}Al_{1.06}Si_{2.96}O_8$, referred to as KAlSi$_3$O$_8$ in this study)[Foland, 1974] (2) synthetic rubicline (actual composition $Rb_{0.97}Na_{0.01}K_{0.02}Al_{1.01}Si_{2.99}O_8$, referred to as RbAlSi$_3$O$_8$ in this study) [Hovis, 2007] (3) 4 µm thick iron foil from Alfa Aesar (99.8% pure); (4) 99.98% pure iron powder from Alfa Aesar, packed under argon by the manufacturer, with an average grain size of ~1 µm. KAlSi$_3$O$_8$ and RbSi$_3$O$_8$ were used instead of pure potassium or rubidium metal because it is unlikely that K and Rb existed in the pure metallic form during core formation. Additionally, pure K and Rb both oxidize quickly in air and are very flammable outside of an oxygen-free, low moisture environment, making it difficult to test the effect of loading the sample in air.

Layers of KAlSi$_3$O$_8$ or RbAlSi$_3$O$_8$ were loaded into DACs in contact with iron powder or iron foil with the KAlSi$_3$O$_8$ acting as the pressure transmitting medium in each experiment. One additional sample was loaded with 99.998% pure iron wire that was compressed between two diamonds in order to create a foil and KAlSi$_3$O$_8$.

Eight samples consisted of a thin iron foil sandwiched between two layers of potassium feldspar which was both part of the experimental sample and acted as a pressure-transmitting medium during the experiment. In three of these samples, inside the oxygen-free glove-box the iron foil was cleaned with a 6 Molar solution of HCl and
loaded into the DAC in order to ensure that the foil was cleaned of any oxidation and to prevent exposure to air before loading (Figure 3). Five samples consisted of iron foil sandwiched between rubicline layers; three of these samples were prepared in the glove box as above (Figure 4). One additional sample was made by compressing a thin iron wire (99.998% pure from Alpha Aesar) between two diamonds to make a foil; this sample was then loaded with potassium feldspar. In order to measure the pressure on the sample, a few grains of ruby (Al₂O₃) were added to the sample chamber during loading. Pressure was then measured using the ruby fluorescence technique [Mao et al., 1978]. Samples were compressed to pressures between 12 and 82 gigapascals (GPa).

Samples using iron powder instead of foil were also prepared. Iron powder from a previously unopened bottle that was packed under argon was ground together with potassium-feldspar, sandwiched between two layers of potassium-feldspar and loaded into the DAC in the glove-box, which provided an oxygen-free environment in order to prevent the powder from ever being exposed to air. This same sample preparation process was repeated for an additional sample that was loaded in air. These two samples were taken to pressures of ~26-28 GPa.

Laser Heating

After compression, all samples were laser heated in five-minute spot increments in order to melt the iron (>2500 K) and to allow for equilibration, after which the laser was moved to a new spot and the process repeated. Three different laser systems were utilized in this study. Those samples studied at Sector 16 of the Advanced Photon Source
(APS) at Argonne National Laboratory (ANL) made use of two YLF: Nd lasers and implemented the double sided heating technique with a wavelength, $\lambda = 1053$ nm [Meng et al., 2006]. One sample at ~80 GPa was heated using a 50 W cw Yb-doped fiber laser, also set up for double sided laser heating, with a $\lambda = 1064$ nm in Dr. Andrew Campbell’s laboratory at The University of Maryland. All other samples were laser-heated at The Ohio State University (OSU) in Dr. Wendy Panero’s high pressure mineral physics laboratory with a diode pumped YLF laser, $\lambda = 1053$ nm. This laser system is only designed for single sided heating, but samples were turned over in order to heat equally on both sides. Experimental Methods

These samples were then used in synchrotron-based X-ray powder diffraction experiments. These experiments were conducted at beamlines X17C of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL) in Upton, NY or at HPCAT (High Pressure Collaborative Access Team) in Sector 16 of APS in Argonne, Illinois. Samples were analyzed with monochromatic X-ray diffraction, with wavelengths as noted in Table 2. Data were collected at room $T$ both at high pressure after heating and again after decompression.

The incident X-ray beam enters the sample chamber through one diamond, diffracts off of the sample materials, and the diffracted X-rays are then collected by an image plate detector in the form of Bragg rings. The positions of these rings allow us to determine the structure of material through Bragg’s equation (Figure 5):

$$\lambda = 2d \sin \theta$$

(2)
where $\lambda$ is wavelength (Å), $d$ is d-spacing (Å), and $\theta$ is the angle between the diffracting plane and the detector in degrees.

The first step in analyzing the data from these experiments is to integrate the two dimensional digital image of the X-ray pattern that was collected on the image plate into a one dimensional graph of two-theta versus intensity using a program called Fit2D. Previously published X-ray diffraction data can be used to index the peaks present in the 1-D pattern with specific Miller indices corresponding to specific planes of atoms within the crystal structure and identify phases present in the sample. Each of these planes within the crystal repeats after a certain distance, and this distance is the d-spacing value associated with each of the diffraction peaks. Previously published data (e.g. Hirao, 2008 for the phase existing between 12-22 GPa, the hollandite II phase of K-spar) indexed diffraction data at a specific set of pressure and temperature conditions, and it is possible to calculate the expected position of the peaks at other pressures for the phases expected in the samples (Figure 6).

Several different phases were expected to be present in these experiments. The hollandite phase of the K- and Rb-feldspar was expected to exist after laser heating at pressures between ~10 and 22 GPa, above which the hollandite-II phase was expected for the potassium feldspar. Hollandite II was assumed to exist for Rb-microcline somewhere above ~22 GPa because of the similarity between K-hollandite and Rb-hollandite, and the similar ionic radius and charge between the two elements. Ruby peaks were expected from the ruby added for in-situ pressure measurements. In samples at pressures greater
than ~15 GPa, ε-iron was indexed, while the α-iron phase was indexed below this pressure.

Since θ and λ are known parameters, Bragg’s equation can be used to determine the d-spacings of the indexed peaks. These indexed peaks and d-spacings can then be used to determine the unit cell volume of the material. In the simple case of α-iron, which is a cubic material in which the six faces are arranged in three parallel pairs, all sides are of an equal length, and the angles between the axes are all 90°, the volume can be represented as:

\[ V = a^3 \]  

(3)

However, ε-iron is not cubic, but rather hexagonal, and its volume is represented by:

\[ V = \sqrt{\frac{3}{2}} a^2 c \]  

(4)

Therefore, it is necessary to use the hexagonal crystal equation in order to find \( a \) and \( c \) from the d-spacings and hkl's:

\[ \frac{1}{d} = \frac{4}{3a^2} (h^2 + hk + k^2) + \frac{1}{c^2} l^2 \]  

(5)

From here the lattice parameter, \( a \), of α-iron, and the lattice parameters, \( a \) and \( c \), of ε-iron can be used to determine the composition of the resulting alloy.

Volumes can be determined from the lattice parameters as shown above, and the % difference from the volume of pure α-iron at ambient pressure (23.554 Å³)
[Wyckoff, 1974] can be calculated. The difference in the volume of the recovered iron compared to pure iron can then be plotted as a function of synthesis pressure (Figure 7).

In order to gain more quantitative results on the composition of the iron, the lattice expansion used to quantify the amount of potassium or rubidium that was incorporated into the iron was verified by using other techniques. Focused Ion Beam (FIB) Milling (Figure 8) was used to extract cross sections of the recovered samples with approximate electron transparency for analysis in a transmission electron microscope (TEM) using energy dispersive X-ray spectroscopy (EDS) at The Ohio State University’s Campus Electron Optics Facility. Measurements were also conducted using a nano-scanning electron microscope (SEM) in EDS mode by Elizabeth Cottrell at the Smithsonian Institute.

2.3 Results and Discussion

In these experiments, several phases were observed. KAlSi$_3$O$_8$-hollandite or RbAlSi$_3$O$_8$, was observed after compression above ~10 GPa and after laser heating above ~2500K until the phase transition to hollandite II at ~22 GPa. Hollandite II was assumed to exist for Rb-microcline after compression and laser heating somewhere above ~22 GPa because of the similar ionic charge to K. Rb-Hollandite II was indeed observed at 34 GPa; however the exact pressure for this phase transition still needs to be resolved because there are not pressures between 20 and 34 GPa, and therefore the transition could exist anywhere between these two pressures. Ruby, Al$_2$O$_3$, was observed in some samples due to the ruby added for in-situ pressure measurements. Above ~15 GPa after
temperature quench ε-iron was observed, and the α-iron phase was observed below this pressure or after temperature and pressure quench. However, enough miller indices of ε-iron to obtain the lattice parameters were seen only when using an iron wire that was compressed between two diamonds at APS. This is most likely due to the form the iron was in and because in other samples the peaks of ε-iron also overlapped with peaks of ruby and it was unclear which material was being identified. However, the ε – iron phase was clearly observed in several foil samples although only one or two diffraction peaks were seen and at least three were needed in order to determine the lattice parameters.

Experiments involving foil varied at similar pressures under different sample preparation techniques. In some cases, samples loaded in nitrogen had a larger volume than those loaded in air, while in other samples the reverse was true. However, both powders loaded in air and loaded in a nitrogen environment had a lower percentage of lattice expansion than that loaded with iron foil and K at similar pressures. The expansion of the iron lattice was on average 0.34% greater in the foil than powder loaded in nitrogen and on average 0.88% greater for a powder loaded in air. However, EDS analysis on iron powder loaded in air indicated that ~1.15 wt% K was found in the iron, although most of it was found on the outer edge of the powder grains and almost no iron was found in the very center of the iron grain. This indicates that the iron powder may have been too thick of a sample and should have been thinned further, especially because X-ray diffraction indicates that only 0.08wt% K should have alloyed with the iron in this sample.
Because all peaks from X-ray diffraction could be identified, it clearly shows that no new phase was created between K atoms and Fe atoms or between KAlSi$_3$O$_8$ and Fe. Therefore, Vegard’s law should hold true that any expansion of the iron lattice is due to an alloy between one of the constituents of the feldspar, with K or Rb being most likely.

EDS analysis on any Rb foils found the amount of rubidium to be below detection limits. Although the lattice expansion determined by X-ray diffraction is inconclusive on the effect of loading powdered samples in air, EDS analysis indicates that there may be some effect, and because the amount of potassium and rubidium that can theoretically be alloyed with iron is so small, it is necessary to minimize sample reaction with air.

Therefore, samples should either be loaded with an iron foil or with iron powder to avoid exposure to air.
CHAPTER 3

POTASSIUM AND RUBIDIUM

3.1 Experimental Methods and Analysis

A series of experiments was performed to examine the s-to-d transition in K and Rb by using synchrotron X-ray diffraction to examine the amount of expansion of the iron lattice as described in the previous section.

3.2 Results

The experimental parameters including synthesis pressures and volumes are listed in Tables 2 and 4. Figures 9 and 10 show the expansion of the iron lattice after pressure and temperature quench. There appears to be a 1 – 2% iron expansion of the iron lattice from that of pure iron above the electronic transition of K and Rb shown in samples after T quench and after both T and P quench, and the amount of alkali metal in the iron appears to increase as synthesis pressure increases based on pressure quenched samples. There are not enough high pressure samples to determine whether this also occurs at high pressure.

Quantitative analysis of the chemical compositions of metallic iron and Rb in samples recovered from 64 GPa (Run 1007Rb2) (Figure 11) and 20 GPa (Run 308Rb4) (Figure 12), both above ~2500 K were examined using EDS mode in TEM or nano-SEM. These analyses show that any incorporation of rubidium into the iron lattice in either
sample is below the detection limit, about 3000 ppm. However, TEM and nano-SEM clearly show that the silicate is interacting with the iron foil. There are clear structures that show iron diffusing into the silicate and what appears to be RbAlSi$_3$O$_8$ becoming more enriched in one part of the sample compared to another (Figure 11 and 12). Also, the sample at 64 GPa analyzed by nano-SEM in EDS mode determined 13.17 +/- 0.47 wt% O, 7.69 +/- 0.30 wt% Al, and 6 +/- 0.22 wt% Si in the iron region.

In order to directly compare these results to previous experiments the partition coefficient was determined for all samples with a positive change in volume (Table 2). The partition coefficient describes the ratio of concentrations of a compound in the two phases of a mixture of two immiscible materials at a particular temperature. The partition coefficient is defined in these experiments as:

$$D_{silicate} = \frac{[K]_{K/Rb in\ metallic\ iron}}{[K]_{K/Rb in\ silicate}}$$

Where [K] is concentration in weight percent.

And, from thermodynamics:

$$D_{silicate} = \exp \left( \frac{\Delta G - \Delta G^0}{RT} \right)$$

The partition coefficient of potassium between metallic iron and K-silicate is determined to be $D_K$ (distribution coefficient with respect to K) = 0.0252 at 25.4 GPa and $D_K = 0.0328$ at 72 GPa both at ~2500 K. The $D_{Rb}$ (distribution coefficient with respect to Rb) above the electronic transition for Rb is 0.0282 at 64.4 GPa, which corresponds to a concentration of 17 ppb in the core of the Earth.
The highest $D_K$ at 72 GPa with iron foil and KAlSi$_3$O$_8$ corresponds to a concentration of nearly 8 ppm in the core assuming:

$$[K]_{core} = ([K]_{silicate})([K]_{BSE})$$  \hfill (8)

Where $[K]$ is the concentration in weight \% and $[K]_{BSE}$ for potassium is 240 ppm while for rubidium it is 0.6 ppm [McDonough and Sun, 1995].

3.3 Modeling Rubidium in the deep Earth

A model was created in order to determine whether the concentration of Rb that is possible in Earth’s core is enough to change the $^{87}$Sr/$^{86}$Sr ratio from the Bulk Silicate Earth model to more closely match observed present day ratios in Mid Ocean Ridge Basalts (MORBs). In order to do this, the model for the crust and mantle (Figure 13) that was illustrated in Turcotte and Schubert, [2002] was applied to the core. The distribution coefficient of 0.03 that was obtained in these experiments at pressures above the electronic transition of 40 GPa was used. From here, it was assumed that the relationship for the fractionation coefficient, $f_c$, held true and that it could be scaled from given information for the mantle, knowing that the distribution coefficient for a mantle rock containing Rb is 0.01 and the fractionation factor of -0.78 [Blatt et al., 2006; Turcotte and Schubert, 2002].

Then, the following equation was used:

$$f_{cc} = \frac{D_{sj}}{D_{si}} - 1$$  \hfill (9)
From here the ratio of the enrichment factor of the daughter to the enrichment factor of the parent, or $D_{sj}/D_{si}$, was determined. Then, the bulk composition of the core was determined by:

$$\mu_{cc} = \mu_0 \left( \frac{D_{sf}}{D_{si}} \right)$$  \hspace{1cm} (10)

The bulk composition of the core, $\mu_{cc}$ was found assuming an initial bulk composition equal to the current bulk composition of 0.0892. Once this was determined, an assumption was made that a similar equation for the core would exist similarly to those for mantle and crust for the equation:

$$\alpha_{cc} = a_0 + \lambda(\tau_e - \tau_{cc})\mu_0 + \lambda(\tau_{cc} - \tau)\mu_{cc}$$  \hspace{1cm} (11)

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, $\alpha_{cc}$ was determined from the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and the decay constant $\lambda = 1.42 \times 10^{-11}$ yr, the initial bulk composition, $\mu_0$ from above, the bulk composition for the core, $\mu_{cc}$, as determined above, the age of the Earth, $\tau_e = 4.6$ Gyr and the age of the core, $\tau_{cc} = 3.5$ Gyr [Brodholt and Nimmo, 2002]. And,

$$\tau \equiv \tau_e - t$$  \hspace{1cm} (12)

This model showed that the small amount of distribution of Rb in the core would correspond to very little change in the present day $^{87}\text{Sr}/^{86}\text{Sr}$ ratio as shown in Figure 14.

3.4 Discussion and Conclusion

Rb samples that were analyzed by EDS analysis should represent both rubidium and potassium experiments because of their similar ionic charge and further evidenced by
the similarity in the Rb-silicate and K-silicate phase transitions from hollandite to hollandite II as discussed previously.

The Rb sample loaded in a nitrogen environment at 20 GPa showed that there was no detectable rubidium in the iron by either X-ray diffraction analysis or by EDS analysis, which is not surprising since the electronic transition for Rb is at approximately 40 GPa. However, based on the expansion of the iron in Run 1007Rb02 at ~64 GPa, by Vegard’s law approximately 7000 ppm of Rb should have been detected by EDS if only Rb was alloying with iron at high pressures. This amount of rubidium is well above the detection limit; however, it may be that the observed iron lattice expansion is not solely caused by the incorporation of Rb or K into the iron lattice. Because of the observed reaction between the RbAlSi$_3$O$_8$ and the iron foil, the apparent enrichment of one part of RbAlSi$_3$O$_8$ compared to another section of the sample and the EDS analysis of the iron foil after quenching from 64 GPa that showed Al, Si, and O, these elements may be causing the expansion of the iron lattice. In addition, the sample examined by TEM found SiO$_2$ inclusions within the iron, showing that the SiO$_2$ does dissociate from the Rb and Al. These may only be artifacts of the sample conditions since it is known that the distribution coefficient varies greatly with temperature, and perhaps this played a part as to why so little Rb was found in the iron. Otherwise, it may be that Al, Si, and O alloy with iron more readily than Rb. This indicates that Vegard’s law is less reliable when using a sample of mixed composition. It may be best to use Vegard’s law when only two components of a system will alloy with each other.
However, from the model created for the decay of rubidium in the core, it is shown that even if the greatest amount of Rb from these experiments was incorporated into the core at 17 ppb and a distribution coefficient of 0.03, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio would not change from the BSE (Figure 14). In fact, in order to make any noticeable change a $D_{\text{Rb}}$ of at least 1.67 is needed. The concentration of Rb in the core for this distribution coefficient corresponds to ~ 1ppm (Figure 15).

The experiments to determine the distribution coefficient for potassium experiments determined that even though the distribution coefficients were roughly equal, much more K than Rb may be present in the core of the Earth due to lower concentration of Rb in the BSE. For K, The $D_{\text{K}}$ value at 25 GPa and 2500 K of $2.5 \times 10^{-2}$ is comparable to previously published data at 26 GPa and 2600 K of $3.8 \times 10^{-2}$ [Ito et al., 1993]. At the lowest pressure obtained in this experiment the $D_{\text{K}} = 0.0014$ at 12 GPa. This $D_{\text{K}}$ is not surprising because 12 GPa is well below the electronic transition for K. The reaction between molten iron and K-silicate gives a higher value of $D_{\text{K}}$ at 72 GPa than that at 25 GPa. This suggests that pressure may significantly affect the solubility of potassium in metallic iron melt above the electronic transition for potassium at high pressure. This is most likely caused by pressure changing the relative volumes of K and Rb with respect to iron. However, the distribution coefficient is affected greatly by temperature and this is the only metal foil that was melted with a double sided laser. Therefore, it is possible that instead of pressure being the cause of the increased solubility, this sample could have
been heated more consistently at a higher T that increased the solubility of the K into the iron.

These X-ray diffraction experiments show that up to 8 ppm of K can be incorporated into the core of the Earth. 8 ppm of potassium in Earth’s core provides 5 x $10^{10}$ W for the present day heat production based on

$$Q_{\text{core}} = H_K M_{\text{core}}$$  (13)

Where $H_K$ is $3.48 \times 10^{-9}$ W kg$^{-1}$ and the mass of the core is taken to be $1.85 \times 10^{24}$ kg, and Q is an upperbound because the mass of the core includes both the inner and outer core and it is unlikely that any K will be found in the inner core [Turcotte and Schubert, 2002]. Based on the current heat flux of 2-10 TW this would correspond to ~0.5% - 2.5% of the total current heat flux across the core mantle boundary (CMB) [Buffet, 2002]. While this is not enough to completely power the geodynamo, it helps to provide some power while not taking into consideration other radiogenic sources, and it is possible that even more K could be present in the core due to the presence of sulfur or oxygen in the core [Corgne et al., 2007; Gessmann and Wood, 2002].

The K and Rb that could be found in the core does help to explain the difference between chondritic meteorites and values that have been determined for the BSE, especially if even higher concentrations of K and Rb are found at core pressures similar to compositions determined by other experiments of ~35 ppm [Hirao et al., 2008]. The value of 8 ppm in the core changes K in the BSE when normalized to CI chondrites and Mg to 0.187 from 0.184, and for the 17 ppb value of Rb the ratio normalized to
chondrites changes from 0.110 to 0.112 [McDonough and Sun, 1995]. Both of these follow the volatility trend for the moderately-volatile lithophile elements as described in McDonough and Sun [1995].

These experiments provided many challenges that needed to be identified and overcome. Some of these experimental difficulties include sample loading in the glove box. The glove-box should be updated to make sample loading easier and more straightforward. Other problems include the amount of oxygen that is in feldspar, which makes the amount of effect of oxidation of the iron arguable. To correct this problem, these experiments might be repeated with pure rubidium loaded in the glove-box in order to prevent combustion, and iron foil and powder both exposed to air and not. This way, the true effect instead of the relative effect of oxygen on these experiments might be better understood.
REFERENCES


Bouhifd, M. A., et al. (2007), Potassium partitioning into molten iron alloys at high-pressure: Implications for Earth's core, Phys. Earth Planet. Inter., 160(1), 22-33.


Hirao, N., et al. (2008), Hollandite II phase in KAISi3O8 as a potential host mineral of potassium in the Earth's lower mantle, Phys. Earth Planet. Inter., 166(1-2), 97-104.


Mao, H. K., et al. (1978), Specific Volume Measurements of Cu, Mo, Pd, and Ag and Calibration of Ruby R1 Fluorescence Pressure Gauge From 0.06 to 1 Mbar, J. Appl. Phys., 49(6), 3276-3283.


Reaman, D., et al. (2007), Synthesis and analysis of controlled geometry samples in the laser-heated diamond anvil cell, in *COMPRES* edited, Lake Morey, VT.


Appendix A:
Tables and Figures
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Form of Iron</th>
<th>Phase of iron</th>
<th>Form of K</th>
<th>P (GPa)</th>
<th>T (K)</th>
<th>Amount of K alloyed with Fe (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gillet, 2006</td>
<td>Foil</td>
<td>?</td>
<td>pure K</td>
<td>42</td>
<td>3000</td>
<td>~100</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>metal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>pure K</td>
<td></td>
<td>&gt;250</td>
<td></td>
</tr>
<tr>
<td>Lee, 2003</td>
<td>powder</td>
<td>ε - iron</td>
<td>metal</td>
<td>57.5</td>
<td>0</td>
<td>7000</td>
</tr>
<tr>
<td>Ito, 1993</td>
<td>powder</td>
<td>α - iron</td>
<td>silicate</td>
<td>26</td>
<td>2873</td>
<td>2000</td>
</tr>
<tr>
<td>Hirao, 2005</td>
<td>powder</td>
<td>ε - iron</td>
<td>silicate</td>
<td>104</td>
<td>3350</td>
<td>2000</td>
</tr>
<tr>
<td>Hirao, 2005</td>
<td>powder</td>
<td>ε - iron</td>
<td>silicate</td>
<td>134</td>
<td>3500</td>
<td>8000</td>
</tr>
</tbody>
</table>

Table 1: Results from previous experiment results of Fe and K/K-silicate experiments
<table>
<thead>
<tr>
<th>Run</th>
<th>synthesis P</th>
<th>Conditions</th>
<th>Material</th>
<th>Wavelength</th>
<th>Zero Pressure Volume (Å³)</th>
<th>% difference from Pure Iron</th>
</tr>
</thead>
<tbody>
<tr>
<td>1007K1</td>
<td>13.67</td>
<td>air</td>
<td>foil/KAISi₃O₈</td>
<td>0.4066</td>
<td>23.45</td>
<td>-0.44</td>
</tr>
<tr>
<td>1007K2</td>
<td>18.9</td>
<td>air</td>
<td>foil/KAISi₃O₈</td>
<td>0.4066</td>
<td>23.79</td>
<td>1.00</td>
</tr>
<tr>
<td>1007K3</td>
<td>25.42</td>
<td>air</td>
<td>foil/KAISi₃O₈</td>
<td>0.4066</td>
<td>23.82</td>
<td>1.14</td>
</tr>
<tr>
<td>308K4</td>
<td>12</td>
<td>nitrogen</td>
<td>foil/KAISi₃O₈</td>
<td>0.4066</td>
<td>23.56</td>
<td>0.04</td>
</tr>
<tr>
<td>308K5</td>
<td>41</td>
<td>nitrogen</td>
<td>foil/KAISi₃O₈</td>
<td>0.4066</td>
<td>23.66</td>
<td>0.46</td>
</tr>
<tr>
<td>308K6</td>
<td>72</td>
<td>nitrogen</td>
<td>foil/KAISi₃O₈</td>
<td>0.4066</td>
<td>23.905</td>
<td>1.488</td>
</tr>
<tr>
<td>1007Rb1</td>
<td>34.74</td>
<td>air</td>
<td>foil/RbAlSi₃O₈</td>
<td>0.4066</td>
<td>23.74</td>
<td>0.80</td>
</tr>
<tr>
<td>1007Rb2</td>
<td>64.37</td>
<td>air</td>
<td>foil/RbAlSi₃O₈</td>
<td>0.4066</td>
<td>23.87</td>
<td>1.33</td>
</tr>
<tr>
<td>308Rb3</td>
<td>10-13.5</td>
<td>nitrogen</td>
<td>foil/RbAlSi₃O₈</td>
<td>0.4066</td>
<td>23.61</td>
<td>0.22</td>
</tr>
<tr>
<td>308Rb4</td>
<td>20</td>
<td>nitrogen</td>
<td>foil/RbAlSi₃O₈</td>
<td>0.4066</td>
<td>23.45</td>
<td>-0.46</td>
</tr>
<tr>
<td>308Rb5</td>
<td>35</td>
<td>nitrogen</td>
<td>foil/RbAlSi₃O₈</td>
<td>0.4066</td>
<td>23.50</td>
<td>-0.25</td>
</tr>
<tr>
<td>1108K7</td>
<td>26</td>
<td>nitrogen</td>
<td>powder/KAISi₃O₈</td>
<td>0.4066</td>
<td>23.742</td>
<td>0.796</td>
</tr>
<tr>
<td>309K8</td>
<td>28.9</td>
<td>air</td>
<td>powder/KAISi₃O₈</td>
<td>0.412515</td>
<td>23.62</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Below ns¹ transition

<table>
<thead>
<tr>
<th>air K foil</th>
<th>Air Rb foil</th>
<th>N₂ K foil</th>
<th>N₂ Rb foil</th>
<th>air K powder</th>
<th>N₂ K powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.57</td>
<td>0.80</td>
<td>0.04</td>
<td>-0.16</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

Above (n-1)d¹ transition

| 0.04       | 1.33        | 0.98      | NA         | 0.26         | 0.796        |

Table 2: Sample conditions and resulting volumes and % difference from pure iron for all quenched samples. Average % difference from pure iron for all experimental conditions listed in bottom table.
<table>
<thead>
<tr>
<th>Run</th>
<th>Composition from mole fraction</th>
<th>Concentration (wt%)</th>
<th>Distribution coefficient</th>
<th>Concentration in core (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1007K2</td>
<td>Fe0.996K0.004</td>
<td>0.2881</td>
<td>0.0223</td>
<td>5.4</td>
</tr>
<tr>
<td>1007K3</td>
<td>Fe0.995K0.005</td>
<td>0.3256</td>
<td>0.0252</td>
<td>6.1</td>
</tr>
<tr>
<td>308K4</td>
<td>FeK0.003</td>
<td>0.0184</td>
<td>0.0014</td>
<td>0.3</td>
</tr>
<tr>
<td>308K5</td>
<td>Fe0.998K0.002</td>
<td>0.1364</td>
<td>0.0106</td>
<td>2.5</td>
</tr>
<tr>
<td>308K6</td>
<td>Fe0.994K0.006</td>
<td>0.4234</td>
<td>0.0328</td>
<td>7.9</td>
</tr>
<tr>
<td>1007Rb1</td>
<td>Fe0.998Rb0.002</td>
<td>0.4404</td>
<td>0.0172</td>
<td>1.0E-02</td>
</tr>
<tr>
<td>1007Rb2</td>
<td>Fe0.995Rb0.005</td>
<td>0.7238</td>
<td>0.0282</td>
<td>1.7E-02</td>
</tr>
<tr>
<td>308Rb3</td>
<td>Fe0.999Rb0.00084</td>
<td>0.1302</td>
<td>0.0051</td>
<td>3.0E-03</td>
</tr>
<tr>
<td>1108K7</td>
<td>Fe0.997K0.003</td>
<td>0.2299</td>
<td>0.0178</td>
<td>4.3</td>
</tr>
<tr>
<td>309K8</td>
<td>Fe0.999K0.001</td>
<td>0.0806</td>
<td>0.0062</td>
<td>1.5</td>
</tr>
<tr>
<td>Detection limit of EDS</td>
<td>0.3000</td>
<td>0.0117</td>
<td>7.02E-03</td>
<td></td>
</tr>
</tbody>
</table>

Table 3: The concentration (wt%), distribution coefficient, and the corresponding concentration in the core.
<table>
<thead>
<tr>
<th>Run</th>
<th>Pressure (GPa)</th>
<th>Conditions</th>
<th>Material</th>
<th>Volume at P (Å³)</th>
<th>% difference from Pure Iron at P</th>
<th>Wavelength (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0309K9</td>
<td>33</td>
<td>air</td>
<td>Iron wire/K-feldspar</td>
<td>15.82</td>
<td>1.40</td>
<td>0.412515</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Iron wire/K-feldspar</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0309K9</td>
<td>47</td>
<td>air</td>
<td>Iron wire/K-feldspar</td>
<td>15.11</td>
<td>1.30</td>
<td>0.412515</td>
</tr>
</tbody>
</table>

Table 4: Volume change of iron at pressure. These percent difference correspond to ~1.05wt% K alloyed in the iron.
Figure 1: The amount of oxidation that occurs on an iron powder versus an iron foil
Figure 2: Vegard’s law dependence of the lattice parameter of the cubic solid solution of bcc-K and bcc-Fe. The green and blue dot represents the approximate molar fraction the alkali metal takes up in the bcc-iron lattice.
Figure 3: Iron etching in 6 Molar solution of HCl.
Figure 4: Sample loading in oxygen free glove-box
Figure 5: Synchrotron X-ray diffraction and Bragg equations.
Figure 6: X-Ray diffraction of quenched samples, with increasing synthesis pressure. Synthesis pressures are labeled. Samples with KAlSi$_3$O$_8$ (blue) and those loaded with RbAlSi$_3$O$_8$ (green). Quenched samples show iron (black) and high pressure KAlSi$_3$O$_8$/RbSi$_3$O$_8$ (Hollandite, red). Un-labeled peaks are either ruby or unconverted feldspar.
Figure 7: Volume % difference of recovered iron compared to pure iron as a function of synthesis pressure. Generally, the expansion of iron tends to increase as the synthesis pressure increases. The percent difference is highest at 80 GPa with an approximate 1.5% increase. Vertical bars indicate the ~P of the K (blue) and Rb (green) electronic transition.
Figure 8: Trench created by the Focused Ion Beam (FIB) to prepare for TEM
Figure 9: Volume % difference of recovered iron from a sample loaded with Rb compared to pure iron as a function of synthesis pressure. Generally, the expansion of iron tends to increase as the synthesis pressure increases. The percent difference is highest at 64 GPa with an approximate 1.4% increase. The vertical bar indicates the pressure of the Rb electronic transition.
Figure 10: Volume % difference of recovered iron from a sample loaded with K compared to pure iron as a function of synthesis pressure. Generally, the expansion of iron tends to increase as the synthesis pressure increases. The percent difference is highest at 72 GPa with an approximate 2% increase. Vertical bar indicates the pressure of the K electronic transition.
Figure 11: Nano-SEM image of recovered RbAlSi$_3$O$_8$ and iron foil sample. Synthesized at 64 GPa and above melting T of iron. Rb in iron foil was below detection limits by EDS analysis.
Figure 12: TEM image of recovered $\text{RbAlSi}_3\text{O}_8$ and iron foil sample loaded in nitrogen environment. Synthesized at 20 GPa and above melting T of iron. Rb in iron foil was below EDSX detection limit.
Figure 13: The change in $^{87}\text{Sr}/^{86}\text{Sr}$ for the mantle and crust when a crust differentiates from the mantle 2 billion years ago. After [Turcotte and Schubert, 2002]
Figure 14: Model based on [Turcotte and Schubert, 2002]. A distribution coefficient of 0.03 was used with no apparent difference from the Bulk Silicate Earth.
Figure 15: How the $^{87}\text{Sr}/^{86}\text{Sr}$ changes in the core with time from the BSE. It takes a large change in distribution coefficient to make an apparent change in the amount of $^{87}\text{Sr}/^{86}\text{Sr}$ today.
Appendix B:

Glove-box Notes and Plans
Notes:

• These plans are slightly modified original plans in order to better accommodate microscope lights and gas hose.

• In order to fit the top of the glove-box to the microscope, it is necessary to take the plans and the microscope to the machine shop. They must cut two pieces that fit on either side of the head of the microscope and slide together to meet in the middle.

• After the plans are taken to the machine shop and latex pieces are received, dry fit the pieces together to make sure there wasn’t a mistake, and then use Weld-On #3 from McMaster-Carr to glue together. A paper towel or brush works best. Seal all seams, inside and out with latex caulk.

• If the pressure from the gas is too great, it will break the glove-box; make sure a reliable regulator for the gas is used.

• This box is not designed for liquid argon loading at this time.

• An oxygen sensor was added to the box in order to verify that 0.0% oxygen is in the glove-box at the time of loading.

• Packing tape and clear plastic (found at hardware store as a painting tarp), are used to seal any leaks around microscope and gloves.

• Latex gloves taped into plastic are used in the appropriate openings.

• This box uses a modified Bausch and Laumb microscope (the height is increased by approximately 4 inches) in order to accommodate the lab jack in the box. For a better design, discard of the lab jack and adjust plans to better accommodate a regular height microscope.

• A better design would also allow for shelves or a place that is meant for keeping items in order.

• A box of Kimwipes, a bottle of acetone, a bottle of deionized water, and a small beaker are generally kept in the glove-box
Door

Approx. 1/5 scale