IMPROVEMENTS TO ARGON-ARGON DATING OF EXTRATERRESTRIAL MATERIALS

by

John Randolph Weirich

A Dissertation Submitted to the Faculty of the
DEPARTMENT OF PLANETARY SCIENCES
In Partial Fulfillment of the Requirements
For the Degree of

DOCTOR OF PHILOSOPHY

In the Graduate College

THE UNIVERSITY OF ARIZONA

2011
THE UNIVERSITY OF ARIZONA
GRADUATE COLLEGE

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I hereby certify that I have read this dissertation prepared under my direction and recommend that it be accepted as fulfilling the dissertation requirement.

________________________________________________ Date: 2/21/11
Dissertation Director: Timothy Swindle
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SIGNED: John Weirich
ACKNOWLEDGEMENTS

Tim Swindle, you’ve been an excellent advisor these past five years, I really don’t think there is any way for things to have gone smoother. Not only am I a better scientist, my writing skills have also greatly improved, though I still have much to learn. Clark Isachsen, without you running Tim’s mass spectrometer, I would have been lost. Despite a perfect storm of equipment failures, you were able to get it back up and running. Additionally, any time I needed a contraption to make my work easier, you were always able to build it out of broken laboratory equipment. Ken Domanik, you always had the microprobe calibrated and ready to run whenever I arrived in the morning, and you were very patient with my learning curve. Bob Downs and Chen Li, I never knew Raman spectroscopy could make mineral identification so fast and easy. Without all of you, this dissertation would not have been possible.

Laura, thank you for all of your support, and for tolerating all of the nights and weekends I spent working, especially in the last few months. Without you, all of this would have been much harder. Mom and Dad, without the values and drive you gave me, I would not have been able to get as far as I have. Even though I’ve worked hard on this dissertation, you worked harder and longer to make me who I am now. I would also like to thank all of the friends and family who have helped me throughout the years, but who are too numerous to mention here.
DEDICATION

for Hugh Bernard Weirich
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ABSTRACT

The source of potassium and argon in ordinary chondrites is determined by comparing the argon activation energies of feldspar, pyroxene, and olivine with that of the L chondrites Chico and North West Africa (NWA) 091. In addition, shock pressures of 29 to 55.8 GPa are shown to lower the activation energy of feldspar. Comparable shock pressures lowers the activation energy of pyroxene outside of error, but the variability of this value, even among unshocked samples, makes a clear distinction difficult. The effect of shock on olivine has not been investigated, by myself or others.

Like many ordinary chondrites, Chico and NWA 091 have two major releases of argon, one at low temperature, and the other at high temperature. The low temperature release of Chico contains two releases, which match the activation energies of shocked and unshocked feldspar. The low temperature release of NWA 091 only contains a single release, which matches shocked feldspar. The high temperature release of both Chico and NWA 091 has an activation energy that is similar to pyroxene, but not olivine.

A potassium mass balance of Chico shows that all the potassium in the meteorite is contained in feldspar, and Raman spectroscopy shows this feldspar has not been converted into a high pressure phase, indicating the high temperature release is inclusions in a high temperature mineral. This mineral is probably pyroxene based upon the activation energy, though thin sections provide evidence that feldspar is more closely associated with olivine.
NWA 091 exhibits multiple isochrons, showing the presence of two non-primordial and (probably) non-terrestrial trapped components of argon. The removal of these trapped components reveals a thermal event produced by a collisional impact on the L chondrite parent body at 475 ± 6 Ma (which supports a link between L chondrites and Ordovician fossil meteorites), as well as a similar event at ~800 Ma (which, combined with similar ages on other Solar System objects, suggests an increased impact flux at that time). Chico did not exhibit an isochron, and the age data for Chico is not reported.
The $^{40}\text{Ar}^{39}\text{Ar}$ (hereafter referred to as Ar-Ar) radioactive dating technique (a variation of K-Ar dating) has been applied to meteorites since the 1960’s (Merrihue and Turner, 1966). It is especially useful since the half-life of $^{40}\text{K}$ is 1.25 Ga, meaning it can be applied to K-bearing rocks from about <1 Ma to 4.56 Ga (McDougall and Harrison, 1999). Terrestrial geologists soon realized the usefulness of this technique, and extensive investigation was undertaken to fully understand the Ar-Ar system of terrestrial rocks. However, due to the limited availability and the fine-grained nature of meteorites (thus making mineral separates difficult), the meteoritical community has not performed as many investigations of the details of the technique (such as Ar diffusion rate), and has instead focused on acquiring age data. We have been able to create a rough timeline of the history of the Solar System for a few meteorite types, but only because of the large number of dated meteorites (Bogard, 1995). It is desirable to be able to obtain a more accurate representation of this timeline, as well as develop timelines for rare meteorite types using a smaller set of samples. This requires a more detailed understanding of the basic system. Luckily, some of the techniques developed by the terrestrial community can be applied to meteorites.

The Ar-Ar age can represent the formation age of meteorites, but because meteorites have often experienced past heating, which resets the isotopic system via
diffusional loss of Ar, an age younger than the formation age is often measured. This heating can be caused by the same mechanism that caused thermal metamorphism (probably radioactive decay of short-lived isotopes) (Trieloff et al., 2003), and/or by collisional impacts with other asteroids. Note that some believe collisional impacts caused thermal metamorphism (Rubin, 2004). By investigating heavily shocked meteorites (meteorites which obviously experienced a collisional impact), we have been able to observe trends in the impact history. In addition to identifying individual impacts on various meteorite parent bodies, we have also found an increase in the impact frequency between about 3.5 and 4.0 Ga in H chondrites (Swindle et al., 2009). These H chondrite ages may be related to the hypothesized Lunar Heavy Bombardment that occurred between 3.9 and 4.1 Ga (Bogard and Garrison, 2003). However, the reason for the extended duration in the asteroid belt remains unclear. So the Ar-Ar technique can be used for more than just a reconstruction of the impact history of the asteroid belt throughout Solar System history, because this history has implications for our understanding of the rest of the Solar System.

Because of dozens of analyses of the most common kinds of meteorites (H and L ordinary chondrites), we have been able to broadly identify the age of some impacts. The most striking example is the heavily shocked L chondrites, for which most Ar-Ar ages are between 400 and 600 Ma, with a peak around 500 Ma. With fewer analyses, this peak around 500 Ma would not have been discovered since the error of individual age measurements is typically ≤30 Ma (i.e. less than the 400-600 Ma spread in ages). With just the Ar data alone, it is not possible to determine if the spread in ages is due to
multiple large impacts (large impacts are infrequent, so this is unlikely but possible), or if there is a single impact that is being masked by incomplete resetting, trapped Ar (i.e. Ar that didn’t arise from in situ decay), or some other effect.

Recently, independent confirmation of this impact has been found in fossil meteorites in a quarry in Sweden. Most of the minerals have been replaced and cannot be used for classification. However, the chromite grains survived, and these grains can be used for classification. The oxygen isotopes, chemical composition, and chondrule size are all consistent with L chondrites (Heck et al., 2009). These meteorites have cosmic ray exposure (CRE) ages (i.e. the time it took the meteoroid to travel from the parent body to Earth) of 0.1-1 Ma (errors are ~10~20% depending upon the isotope used), and are found in a rock layer that has an age of 467.3 ± 1.6 Ma. Additionally, the fossil meteorites that are found higher in the stratigraphic column have an older CRE age, definitively showing the fossil L chondrites were all ejected from their parent body at ~470 Ma (Heck et al., 2004; Heck et al., 2008). As a working hypothesis, I will take the fossil meteorites as indication that a large impact occurred at ~470 Ma.

If we assume all L chondrites that have an Ar-Ar age between 400 and 600 Ma were reset by an impact at ~470 Ma, what is the cause for the spread in ages? If the cause can be identified and removed, we can then apply the Ar-Ar technique to a smaller subset of meteorites and still correctly, and confidently, identify a true impact age. This is especially desirable for meteorite types that are rare, and thus for which measuring many meteorites is difficult or impossible. Because most Ar-Ar studies of chondrites have focused on easily acquirable age data, a lot of the more difficult to obtain information has
been given secondary importance, even though this information gives clues that can help interpret (or improve) the age data. Information typically lacking in our knowledge of an Ar-Ar system is

1) the source(s) of K,
2) well-defined diffusion properties of those sources when both shocked and unshocked, and
3) the presence of any trapped (i.e. non-radiogenic) Ar component.

Because chondrites are made of fine-grained material, mineral separation is not usually performed, and instead whole rock samples are used. This feature makes identification of the source(s) of K difficult, even though the K/Ca ratio of an individual release can be determined from the Ar-Ar data. Additionally, there appear to be two domains that contain K with different diffusion parameters and hence different release temperatures (see Chapter 4). The low temperature release has a K/Ca ratio of about 0.1-1, while the high temperature release has a K/Ca ratio of about 0.01-0.1 (Bogard and Hirsch, 1980). The low temperature release is almost certainly the mineral oligoclase feldspar (An$_{10-30}$Or$_{0-15}$) (Deer et al., 1962), but identification of the high temperature release has proven elusive. Possible explanations are a chemical difference, an effect of shock, a change of the diffusion distance from grains to melt veins, and enclosure in a higher temperature mineral (Bogard et al., 1995; Bogard and Hirsch, 1980; Kunz et al., 1997; McCoy et al., 1995). Pyroxene and olivine, the most abundant minerals in L chondrites, are likely candidates for enclosing feldspar or containing trace amounts of K.
To determine which of the above possibilities are important, Chapter 3 details the measurement of the Ar diffusion parameters of feldspar, pyroxene, and olivine as a function of shock pressure. Previous authors have studied the effect of shock on feldspar (Section 3.1), but my measurements have a higher temperature resolution, employ a technique that provides more accurate data, and are performed on a different feldspar composition from that of previous authors. Having determined the Ar diffusion parameters of the major minerals in L chondrites, in Chapter 4 I compare these results with the Ar diffusion parameters of the L chondrites Chico and North West Africa (NWA) 091. Chapter 4 also includes Raman spectroscopy of feldspar, as well as a K mass balance of Chico, to compare what is seen in the Ar data with what is seen in a thin section.

Having addressed 1) and 2) within Chapter 3 and 4, in Chapter 5 I discuss 3) the trapped component of Ar in NWA 091. Normally a trapped component in meteorites cannot be identified because of chlorine activation during irradiation (see Section 2.4.1). However, chlorine activation can be reduced or eliminated by proper shielding, allowing identification of the trapped component, as shown by Korochantseva et al. (2007). They found a non-terrestrial, as well as non-primordial, trapped Ar component in three L chondrites. I irradiated NWA 091 with more appropriate shielding, confirmed the lack of chlorine activation, then performed my own investigation of the trapped component. Like Korochantseva et al. (2007), accounting for a trapped Ar component gives an age identical to 470 Ma, showing the need for a trapped correction in chondrites.
CHAPTER 2

FUNDAMENTALS OF ARGON-ARGON DATING

2.1 Introduction

This chapter is an introduction to the Ar-Ar dating technique, and is heavily based on McDougall and Harrison (1999).

2.2 Basics

The Ar-Ar system is a variation of the K-Ar system. $^{40}$K constitutes about 0.01% of all K and decays to $^{40}$Ar with a half-life of 1.25 Ga. This means the K-Ar system can be used to easily date material between ~1 Ma (limited by the amount of radiogenic Ar) and the beginning of the Solar System (when solids first start appearing). In other words, the K-Ar system can be used to date events over virtually all of Solar System history.

The K-Ar system originally involved a two-part extraction system. The first was complete extraction of Ar by heating, and the second was chemical dissolution and analysis of K. This leads to two complications. The first is that the sensitivity of the instruments used to measure Ar and K are crucial, and the second is that partially reset minerals, or samples with multiple K bearing minerals, can lead to meaningless ages. The Ar-Ar system was discovered in the 1960’s as a side effect of neutron irradiation of meteorites in a nuclear reactor for I-Xe dating (Merrihue and Turner, 1966). The relevant
reaction for Ar-Ar dating is $^{39}\text{K}(n,p)^{39}\text{Ar}$, meaning a $^{39}\text{K}$ atom absorbs a neutron while emitting a proton.

The result is an $^{39}\text{Ar}$ atom that can be extracted and measured simultaneously with the radiogenic $^{40}\text{Ar}$, which solves both of the problems with the K-Ar system. First, the sensitivity of the instrument is not as critical to the age determination, because I no longer need to know the absolute amounts of $^{40}\text{Ar}$ or $^{39}\text{Ar}$. All that matters for the age is the $^{40}\text{Ar}/^{39}\text{Ar}$ ratio, which is independent of the sensitivity. The second problem, partial resetting and multiple K-bearing minerals, is lessened because many heating steps can be performed on a single sample. Because partial resetting often occurs via diffusion, the edges of the partially reset mineral grains will have a lower concentration of $^{40}\text{Ar}$ compared to the interior. The $^{39}\text{Ar}$ will have the same concentration gradient as the K, usually a uniform distribution. Hence, when gas is then later extracted in the laboratory, the $^{40}\text{Ar}/^{39}\text{Ar}$ ratio will increase as Ar is progressively lost from the grains, reflecting the fact that the interiors of the grains are more retentive. For rocks that have multiple K-bearing species, each species will release most of its Ar at a different temperature. By performing multiple extractions, usually each one a higher temperature than the last, I can separate out the gas released from different minerals and grains, as well as identify partial resetting. However, to fully understand the system, the identities and diffusion properties of the grains containing K must be known.
2.3 Collecting Raw Data

The extraction system and data collection are all automated by a software package written by Alan Deino at the Berkeley Geochronology Center. His software is specifically designed for use with Ar-Ar systems. A schematic of the extraction system is shown in Figure 2.1. Inside the component labeled “Furnace” is a tantalum crucible that is surrounded by a tungsten furnace, which is in turn surrounded by coils that have chilled water running through them. The space from the exterior of the crucible to the chilled water coils is kept under a rough vacuum ($10^{-3}$ to $10^{-2}$ torr) to limit oxidation of
the crucible. A type C thermocouple is fed through a hole in the furnace and makes contact with the bottom of the crucible and records the temperature, which is read by a Eurotherm model 2404 temperature controller. The Eurotherm also controls an Electronic Instruments power supply (model TCR 10T500-1-D), and maintains the target temperature using a Proportional-Integral-Derivative (PID) controller. The interior of the crucible and the remaining extraction system is kept at high vacuum ($2\times10^{-8}$ torr).

Directly above the crucible is the sample holder (not shown in Figure 2.1). Pressure valves #1 through #7 allow sample gas to be trapped in various stages of the extraction system for cleanup or analysis. Manual valves (small ovals) are only used during sample exchange to isolate the extraction system from atmospheric gas. Air pipettes are labeled PA, PB, and PC, and pressure valves associated with the air pipettes begin with a “P”. SAES charcoal getters are used to clean the gas prior to analysis in the mass spectrometer. Two stages of gettering are performed, one “cold” (room temperature) the other “hot” (~400°C). The laser extraction portion of the system was not used for any sample extraction in this dissertation.

Gas extraction uses the following procedure. Valve 2 (V2) remains closed all throughout gas extraction. Valve 4 (V4) is closed to isolate the furnace volume from the extraction line. The target temperature is approached linearly in time over ~200 seconds (this helps to preserve the furnace). After attaining the target temperature, that temperature is maintained for ~720 seconds. After power has been cut to the furnace, I allow the crucible to cool to about 500 °C (no wait time for target temperatures ≤500 °C), and then V1, V3, and V5 are closed and V4 and V6 are opened. Cold gettering occurs
for 180 seconds, then V6 is closed, the ion gauge is turned off, and V5 is opened allowing hot gettering to occur for another 180 seconds. Finally, V7 is closed, V6 is opened, and after the gas is allowed to expand for 30 seconds, V6 is closed, and V1 through V5 (minus V2) are opened, and the ion gauge is turned back on. After 300 seconds (while the gas is being analyzed in the mass spectrometer), the process starts over again with a new target temperature. The overlap of runs is such that the mass spectrometer is pumped down for >300 seconds before being used again.

For convenience, I will refer to “mass per charge”, as just “mass” since the isotopes of argon I am interested in measuring are singly charged. Masses measured are 36-40, the baseline (a constant electronic background signal that is measured halfway between mass 39 and 40), and other masses that indicate potential interferences (no interferences were detected). For each mass, a series of “counts” (the amount of charges per second) are recorded, along with the clock time of each count, starting with mass 40 and proceeding to lower masses. The magnet then sweeps back to mass 40, and another cycle begins. Using all the recorded cycles, the trend for each mass is fit with either a linear or parabolic trend (whichever is more appropriate), and then extrapolated back to time zero (i.e. when the gas was originally released into the mass spectrometer).

Mass 37 is limited to fewer counts and cycles than the other masses because each decay of an $^{37}$Ar atom that has been implanted into the detector leads to an energy cascade that contributes to the electronic background signal. With a half-life of 35 days, the $^{37}$Ar can become a significant contribution to the baseline, which increases the error of all masses.
2.4 Converting Raw Data to Useful Data

2.4.1 Ar Sources

Because there are many contributions to the various Ar isotopes, I here list those sources relevant to this dissertation.

*Atmospheric argon:* This is the Ar that is found in the atmosphere. It can be adsorbed onto grain surfaces, or can be incorporated into the entire grain if formed on Earth. The $^{40}\text{Ar}/^{36}\text{Ar}$ is very well determined to be $295.5 \pm 0.5$, while $^{38}\text{Ar}/^{36}\text{Ar}$ is $0.1869 \pm 0.0004$ (Nier, 1950; Steiger and Jager, 1977).

*Radiogenic argon ($^{40}\text{Ar}^*$):* This is the argon produced by decay of $^{40}\text{K}$, and is used to determine the age of the rock.

*Trapped argon:* This term is somewhat nebulous in its use. McDougall and Harrison (1999) use it to mean the component that is incorporated into the rock during formation. For terrestrial materials, that is often atmospheric argon, but it can have other sources (mantle argon for instance). Meteorites typically have a primordial component called Q, which has $^{40}\text{Ar}/^{36}\text{Ar} < 1$, and $^{38}\text{Ar}/^{36}\text{Ar} = 0.1873 \pm 0.0007$ (Busemann et al., 2000). However, some authors use the term to mean any $^{40}\text{Ar}$ that is not radiogenic or atmospheric, so caution is needed. For this dissertation I will use the term “trapped argon” to be any component that has an identifiable $^{40}\text{Ar}/^{36}\text{Ar}$ and/or $^{38}\text{Ar}/^{36}\text{Ar}$ ratio that
isn’t cosmogenic. Hence my usage of the term will not indicate how or when the source was incorporated into the rock.

_Cosmogenic argon:_ This is $^{38}\text{Ar}$ and $^{36}\text{Ar}$ that is produced by cosmic ray spallation off K, Ca, and Fe. The ratio depends on the relative concentration of K, Ca, and Fe, and burial depth, but a typical meteoritic value is $^{38}\text{Ar}/^{36}\text{Ar} = 1.54$ (in calculations I assume an uncertainty of 0.02) (Wieler, 2002). Terrestrial rocks, even surface rocks, typically don’t contain much cosmogenic argon due to atmospheric shielding.

_Neutron-induced (Reactor-produced) argon:_ This is argon produced during neutron bombardment in a nuclear reactor from K, Ca, and Cl. Sample monitors are included during irradiation to identify many of these sources. Monitors used are identified in the relevant chapter. Removing the unwanted neutron-induced argon

<table>
<thead>
<tr>
<th>Table 2.1. Argon sources</th>
<th>Isotope</th>
<th>Atmo.</th>
<th>Radiogenic</th>
<th>Trapped</th>
<th>Cosmogenic</th>
<th>Reactor-produced$^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{40}\text{Ar}$</td>
<td>#</td>
<td>#</td>
<td># (sometimes)</td>
<td>#</td>
<td>$^{40}\text{K}(n,p)^{40}\text{Ar}$</td>
<td></td>
</tr>
<tr>
<td>$^{39}\text{Ar}$</td>
<td>#</td>
<td>#</td>
<td>#</td>
<td>#</td>
<td>$^{39}\text{K}(n,p)^{39}\text{Ar}$, $^{42}\text{Ca}(n,\alpha)^{39}\text{Ar}$</td>
<td></td>
</tr>
<tr>
<td>$^{38}\text{Ar}$</td>
<td>#</td>
<td>#</td>
<td>#</td>
<td>#</td>
<td>$^{39}\text{K}(n,nd)^{38}\text{Ar}$, $^{42}\text{Ca}(n,\alpha)^{38}\text{Ar}$, $^{37}\text{Cl}(n,\gamma)^{38}\text{Cl} \rightarrow ^{38}\text{Ar}$</td>
<td></td>
</tr>
<tr>
<td>$^{37}\text{Ar}$</td>
<td>#</td>
<td>#</td>
<td>#</td>
<td>#</td>
<td>$^{40}\text{Ca}(n,\alpha)^{37}\text{Ar}$</td>
<td></td>
</tr>
<tr>
<td>$^{36}\text{Ar}$</td>
<td>#</td>
<td>#</td>
<td>#</td>
<td>#</td>
<td>$^{40}\text{Ca}(n,\alpha)^{36}\text{Ar}$, $^{35}\text{Cl}(n,\gamma)^{36}\text{Cl} \rightarrow ^{36}\text{Ar}$</td>
<td></td>
</tr>
</tbody>
</table>

# Indicates presence of isotope. $^1^{36}\text{Cl}$ decays to $^{36}\text{Ar}$ with a half-life of 0.3 Ma, $^{36}\text{Cl}$ contribution to Ar is usually negligible. $^{38}\text{Cl}$ decays to $^{38}\text{Ar}$ with a half-life of 37.3 min, $^{38}\text{Cl}$ decay is complete by the time samples are analyzed.
sources (anything other than $^{39}$K-induced $^{39}$Ar and $^{40}$Ca-induced $^{37}$Ar) is one of the first steps in data reduction.

2.4.2 Reactor and Decay Corrections

Contributions from K and Ca are easily removed by including samples of K$_2$SO$_4$ and CaF$_2$ in the irradiation package. These samples will only have atmospheric and reactor-produced Ar (the K$_2$SO$_4$ was previously melted to remove $^{40}$Ar$^*$. Atmospheric Ar can be removed by assuming all $^{40}$Ar is atmospheric in the CaF$_2$, and all $^{36}$Ar is atmospheric in the K$_2$SO$_4$. Removing Cl-derived Ar is unfortunately difficult. This is because the fast decay rate of $^{38}$Cl (half-life of 37.3 min) ensures complete decay to $^{38}$Ar, while the slow decay rate of $^{36}$Cl (half-life of 0.3 Ma) ensures almost no decay. However, I can limit Cl-derived Ar by using cadmium shielding, which blocks thermal neutrons. Because reactions on K and Ca require high energy neutrons, Ar production from these elements is largely unaffected by cadmium shielding.

The reactor-induced Ar I am interested in keeping is K-derived $^{39}$Ar and Ca-derived $^{37}$Ar. However, both of these isotopes of Ar are radioactive. $^{39}$Ar has a half-life of 269 years, while that of $^{37}$Ar is 35.1 days (Stoenner et al., 1965). After measurement, these isotopes are corrected for decay to the time immediately after irradiation.

2.4.3 Separating Cosmogenic Ar

Assuming there is no Cl-produced Ar in an irradiated sample, the cosmogenic spallation contribution to $^{38}$Ar and $^{36}$Ar can be identified. The presence of Cl-produced Ar is identifiable if the measured $^{38}$Ar/$^{36}$Ar ratio is $>$1.5. Although a ratio lower than 1.5
does not guarantee the absence of Cl-produced Ar, one can assume that is the case, since that will maximize the ultimate correction for trapped Ar. Atmospheric and trapped Ar have nearly the same $^{38}\text{Ar}/^{36}\text{Ar}$ ratio, hence I can treat them as equal. I can then perform a simple component balance between a cosmogenic $^{38}\text{Ar}/^{36}\text{Ar}$ ratio of 1.54, and an atmospheric/trapped ratio of 0.19.

If Cl-produced Ar is present, I can still identify spallation assuming there are a few temperature steps that contain only the spallation signature in $^{36}\text{Ar}$. Ar spallation is produced from K, Ca, and to a lesser extent Fe ($^{36}\text{Ar}$ production from Fe is 1-3% that of K and Ca, depending upon burial depth (Hohenberg et al., 1978)). Because most atmospheric gas is released at low temperature, while most of the Ca-derived $^{37}\text{Ar}$ is released at high temperature (>1000 °C), the high temperature steps are the most promising. The high temperature steps also have the added benefit of a K/Ca ratio that is <<1, resulting in a negligible contribution of K-derived spallation. The only remaining contribution, then, is Fe-derived spallation. For H or L ordinary chondrites, the relative abundance of Fe and Ca, along with the spallation production rates for those elements, indicate that at >1000 °C the Ca contribution is >70% of the total Ar spallation (Hohenberg et al., 1978; Mason, 1965). Therefore, I look for the minimum $^{36}\text{Ar}/^{37}\text{Ar}$ ratio. If I see multiple temperature steps that have the same ratio, then presumably I am seeing Ca-spallation dominated $^{36}\text{Ar}$. Based on the amount of $^{37}\text{Ar}$, I can then remove an appropriate amount of $^{36}\text{Ar}$ from the remaining extractions. Removing Ca spallation does, however, leave the spallation contribution from K and Fe (especially important at low T, where the K/Ca ratio is ~0.5). At the very least, I have removed the largest
spallation contribution to $^{36}$Ar, and now have enough information to determine the cosmic ray exposure age.

2.4.4 J Factor

Whether or not I can identify and remove the spallogenic Ar, I can still convert the measured $^{40}$Ar/$^{39}$Ar ratio into an apparent age. However, I need to be cautious when interpreting the apparent age if I have not removed the trapped component (more on that topic in Section 2.5.2). Whatever components contribute to the $^{40}$Ar/$^{39}$Ar ratio, that ratio can be converted into an apparent age by what is called the J factor, a term that describes the efficiency of conversion of $^{39}$K to $^{39}$Ar during neutron irradiation. The J factor is determined by including a monitor mineral of a well-known fully-reset age in the irradiation package. I use the biotite GA1550 (98.79 ± 0.96 Ma), the hornblende Mmhb-1 (519.4 ± 2.5 Ma) and the hornblende PP-20, a recollection of HB3gr (1072 ± 11 Ma) (McDougall and Harrison, 1999). The J factor is determined by the following equation:

$$J = \frac{e^{\lambda t_{mm}} - 1}{(^{40}Ar* / ^{39}Ar)_{mm}}$$ (2.1)

where $\lambda$ is the decay constant for $^{40}$K, $t_{mm}$ is the age of the monitor mineral, and $(^{40}Ar* / ^{39}Ar)_{mm}$ is the measured $^{40}$Ar*/$^{39}$Ar value of the monitor mineral. To convert the $^{40}$Ar/$^{39}$Ar value of the sample into an apparent age, I use the following equation:

$$t_a = \frac{1}{\lambda} \times \ln \left(1 + J \times (^{40}Ar / ^{39}Ar)\right)$$ (2.2)

where $t_a$ is the apparent age and $(^{40}Ar / ^{39}Ar)_a$ is the $^{40}$Ar/$^{39}$Ar of the sample.
2.5 Interpreting the Ar Data

2.5.1 Reverse Isochron Plot

Once I have reduced the $^{40}\text{Ar}$ and $^{36}\text{Ar}$ down to only the trapped and radiogenic sources, I can then plot each extraction on an isochron plot ($^{40}\text{Ar}/^{36}\text{Ar}$ vs. $^{39}\text{Ar}/^{36}\text{Ar}$). However, because $^{36}\text{Ar}$ is usually the least well-determined isotope (and usually has the largest error due to multiple corrections), I instead use a reverse isochron plot ($^{36}\text{Ar}/^{40}\text{Ar}$ vs. $^{39}\text{Ar}/^{40}\text{Ar}$). An example is shown in Figure 2.2. The resulting line will have a y-intercept equal to the trapped Ar, while the x-intercept can be used to determine the age of the rock. If there are multiple trapped sources that are separated by temperature, then more than one line may be seen in the data (Korochantseva et al., 2007). However, this technique only works for samples that are not partially reset, and have no cosmogenic component (or have one that can be identified and removed). Hence, the reverse isochron plot is usually only used to determine the trapped component of $^{40}\text{Ar}$ (if one can be identified). For an age spectrum, I use a plateau plot, as seen in the next section.

2.5.2 Plateau Plot

Because of issues mentioned in Section 2.5.1, the age is usually determined from a plateau plot, which plots apparent age vs. the percentage of $^{39}\text{Ar}$ released (Figure 2.3). If the trapped component has been removed and the sample is completely reset, the individual steps will all have the same apparent age, forming a plateau. If a plateau is formed, then that is likely to be the age of the resetting event, or the formation age, depending on the history of the sample. If the sample is partially reset, then the gas
released first will have a lower apparent age than the gas released later. If a trapped component is present throughout the entire release, then the ages will scatter and be meaningless. Even if there is no trapped component, atmospheric gas is usually adsorbed on grain surfaces, and is released during the first few extractions. If no atmospheric correction has been applied, the first few extractions typically have ages much older than the remaining extractions.

2.5.3 Release Plot

The reverse isochron and plateau plots do not contain any temperature information. One way to display this information is to plot the Ar released as a function of temperature. However, this will make it difficult to compare a sample to samples that were extracted with a different heating schedule. To normalize the data, I divide the Ar
released by the difference in temperature between the previous extraction (0 °C if this is the first extraction) and the duration of the laboratory heating pulse. The result is similar to Figure 2.4. This plot can also give a crude interpretation of how many Ar domains are present in the sample, though it is difficult to impossible to determine if there are domains overlapping in temperature. Still, it is useful when used in tandem with the Arrhenius plot (Section 2.5.4).

2.5.4 Arrhenius Plot

The major portion of this dissertation is concerned with measuring the diffusion rate of Ar bearing minerals. At first glance, it may seem strange to determine the

![Plateau Plot for NWA 091](image)
diffusion rate using a technique that never measures distance. Therefore, a basic description of this process is given below.

The Arrhenius equation (equation 2.3), along with a shape model for the mineral grains, provides us with a way to determine the diffusion coefficient (D) for each temperature extraction. Spherical grains are often a good assumption for irregularly shaped grains. In order for another shape model to be a better approximation, such as plane sheet or cylindrical, the mineral must prefer a particularly non-spherical shape (such as phyllosilicates). The Arrhenius equation describes how D varies as a function of temperature. There are two unknown variables, the activation energy (E) and the frequency factor (D₀). These values are often collectively referred to as the diffusion parameters. The Arrhenius equation is:

\[ D = D_0 \times e^{\frac{-E}{RT}} \]  

\[(2.3)\]
where R is the gas constant and T is temperature. Because I must assume a shape model, I can only measure D/a², where “a” is the diffusion distance (usually the radius of the grain). However this is easily fixed by just dividing both sides of (2.3) by a². To turn the raw data (amount of gas released by each extraction) into something usable, I normalize the data by dividing each extraction by the total amount of gas released by the sample, and then convert the raw data into log D/a² at each temperature by assuming spherical grains and a behavior that follows (2.3), the details of which can be found in McDougall and Harrison (1999), pages 145-146. By plotting the data as log D/a² vs. 1/T (called an Arrhenius Plot), the result will be a straight line with a slope proportional to E and the intercept equal to log D₀/a², if the proper conditions have been meet (Figure 2.5). The most important of these conditions, at least as far as the samples in this dissertation are concerned, are A) a single chemical phase with B) a constant grain size that C) remains stable during heating, and D) has a uniform distribution of Ar inside in the grain.

The third condition (stability during heating) is only a concern when dealing with hydrated minerals. In this dissertation I will only be measuring feldspar, pyroxene, olivine, and chondrites, none of which involve hydrated minerals. Therefore, this will not be discussed further, though one should remember that linear behavior will break down above the melting temperature. Samples that violate condition B) (constant grain size) will, assuming discrete grain sizes, result in portions of the Arrhenius plot having linear behavior when a single domain is outgassing. If the smallest grain size can outgas without too much contribution from larger grains, the diffusion parameters can still be extracted. Samples that have a more continuous distribution of grain sizes will result in a
semi-linear behavior, but the measured $E$ would be lower than the real value. This is because each subsequent extraction contains gas from a larger grain size, which then gives a smaller $\log D/a^2$. D) (uniform distribution of Ar) is not an issue because I used reactor-produced isotopes from samples that do not have chemically zoned grains. However, most of my samples violate A) (single chemical phase) and B) (constant grain size), and require domain separation. The technique for domain separation is discussed in Chapter 3.

Figure 2.5. An example of an Arrhenius plot. Determined using phase separation on the low temperature release of $^{39}$Ar (see Chapter 4). Error bars are typically smaller than the symbols. The deviation from linearity at higher temperatures is due to a contribution from the higher temperature release.
CHAPTER 3

DIFFUSION OF ARGON IN ALBITE, PYROXENE, AND OLIVINE: SHOCKED AND UNSHOCKED

3.1 Introduction

To identify the K domains of L chondrites, I must know the diffusion parameters of any potential K-bearing minerals, or any mineral that may be enclosing a K-bearing mineral. Feldspar is an obvious choice for a K-bearing mineral in L chondrites. The two most abundant silicates in L chondrites, olivine and pyroxene, are the best candidates for enclosing feldspar, or for containing a trace amount of K that can still account for a large percentage of the K budget.

Another complicating factor in identification of K-bearing domains in L chondrites is the effect of shock, which could disrupt the mineral structure. To provide a basis for comparison of the diffusion rate of Ar in L chondrites, I used step-heating to measure the diffusion parameters of albite, pyroxene, and olivine as a function of shock. Because I actually measure the frequency factor ($D_0$) divided by the square of the diffusion distance (the latter of which can vary between samples), it is more straightforward to compare the activation energy ($E$) of the various chemistries and shock pressures (see 2.5.4). Previous work on each mineral is discussed below.
Feldspar:

Feldspar is a major mineral used for Ar-Ar dating and has been investigated more than other minerals. There are three “states” of feldspathic material relevant to this study, structural feldspar, diapeletic glass (maskelynite), and normal glass. Diapeletic glass is formed by a shock event above ~30 GPa converting the structure to a disordered state without causing melting, while higher shock pressures (~45 GPa) will cause melting that produces normal glass (Stöffler et al., 1991). Ar diffusion in structural feldspar has been well studied, especially orthoclase (the K endmember of feldspar), which has an E of about 45 kcal/mol (Lovera et al., 1997; McDougall and Harrison, 1999; Wartho et al., 1999). Plagioclase has been less well studied, but recent work on an unshocked sample has shown the E of individual grains have a real composition-independent variation of ~37 to ~43 kcal/mol, in both An$_{40}$ and An$_{70}$ (Cassata et al., 2009). Ar diffusion in normal glass formed from feldspar has been found to have an E of 29-35 kcal/mol, depending upon the composition (Carroll, 1991).

Jessberger and Ostertag (1982) investigated the effect of shock pressures between 30 and 45 GPa on irradiated samples of Ca-rich plagioclase (An$_{67}$). Despite complete transformation to diapeletic glass of all shocked samples, they found no obvious change in the Ar release plot (E was not reported). Stephan and Jessberger (1992) found a continual decrease of E as shock pressure increases in both experimentally shocked oligoclase (An$_{10-30}$Or$_{0-10}$) from northwest Argentina and naturally-shocked K-rich feldspar from the Haughton impact structure in Canada. However, they were using radiogenic $^{40}$Ar to determine E, and $^{40}$Ar may not be homogeneously distributed (Section
2.5.4) if the samples are partially reset. Indeed, some of their samples do appear to exhibit partial resetting. Hence, I redid their calculations using $^{37}$Ar from the oligoclase, and $^{39}$Ar from the K-rich feldspar, though there are many potential problems (low statistical significance, possibility of continuous grain size distribution, possible contamination in the oligoclase separate, no unshocked analog for the K-rich feldspar, etc.). The result for the oligoclase is that generally there seems to be no effect of shock up to 60GPa, though the second highest shock pressure did give an $E$ as low as 36 kcal/mol. The remaining samples all clustered around 45 kcal/mol. For the K-rich feldspar, all three samples (shock pressures between ~28 and 45-50 GPa) gave an $E$ between 23 and 35 kcal/mol. However, because I cannot compare these samples to an unshocked sample, I cannot rule out a grain size effect. The lack of a shock effect in the oligoclase is surprising considering Weiss et al. (2002) found the $E$ of $^{39}$Ar (presumably from maskelynite) in ALH 84001 to be ~18 kcal/mol. Cassata et al. (2010) found a value of 30-33 kcal/mol in ALH 84001, which is higher than that found by Weiss et al. (2002), but still indicates a lowering of the $E$. Most of the feldspathic material in ALH 84001 is An$_{30-40}$ though some is also Ab$_{46}$An$_3$ (Greenwood and McSween, 2001).

In summary, previous studies indicate that the $E$ of Ca-rich feldspar (An$_{>70}$) is not affected by shock, the $E$ in K-rich feldspar is affected by shock, and the $E$ of Na-rich feldspar (An$_{<40}$) may be affected.
Pyroxene:

Pyroxene, not having as much importance in the K-Ar system, has not been as thoroughly investigated. Thomas et al. (2008) found single crystal enstatite pyroxene to have a very low Ar E (7.6 kcal/mol). However, Thomas et al. (2008) acknowledge they get unexpected results given what we know about diffusion of other gases in other minerals. Additionally, they did not measure Ar via diffusional release. Instead, they diffused Ar into pyroxene in a pressurized vessel, and measured the Ar concentration via Rutherford backscattering spectrometry, which only profiles the first few tens of nm from the surface. Thus, their results may not be directly comparable since in-situ Ar may have a different siting, and hence a different diffusion pathway. Therefore, I will not discuss the Thomas et al. (2008) results further.

Bogard (2009) used step-heating on Martian meteorites and determined the Ar E of three Shergottite pyroxene separates to be ~65 kcal/mol, and that of two Nakhlite pyroxene separates to be ~160 kcal/mol. Cassata et al. (2010) found the pyroxene in ALH 84001 to have an Ar E of ~100 kcal/mol. Shock pressures of the Shergottites are ~29.5 to ~45 GPa, one of the Nakhlites is 5-14 GPa and the other is of unknown shock pressure, and ALH 84001 is 32 GPa (Fritz et al., 2005). It is not known whether the large difference in E between these meteorites is due to shock pressure, or some other difference (such as composition).

Because of the limited data on Ar diffusion, He diffusion may be a useful comparison. Trull and Kurz (1993) used isothermal heating to find the He E of unshocked clinopyroxene to be 69.3 ± 9.6 kcal/mol. This value is indistinguishable from
the Ar E in the Shergottite samples, though given the difference in mass and radius between Ar and He, a similarity may be a cause for caution.

Olivine:

Thomas et al. (2008) also investigated the Ar E of unshocked single crystal forsterite olivine, and also found a very low E (10 kcal/mol), though for the same reason stated above I will not discuss their work further. The only other measurement of Ar diffusion in olivine gave an E of 32 kcal/mol for ion implanted Ar (Futagami et al., 1993). Experiments performed by Trull and Kurz (1993) (isothermal heating) and Shuster et al. (2004) (step-heating), found the He E of unshocked olivine to be 100.3 ± 4.8 kcal/mol (Fo89) and ~35–~45 kcal/mol (Fo75–Fo80), respectively. The reason for such a large discrepancy is under debate (Baxter, 2010). Shocked samples of olivine have not been analyzed.

There are two main reasons for making my own measurements of these minerals. First, my analyses have a much higher temperature resolution, and second, Bogard (2009), Jessberger and Ostertag (1982), Stephan and Jessberger (1992), and Futagami et al., (1993) did not control for the effect of a continuous grain size distribution, which can result in an erroneously low E (See 2.5.4). Cassata et al. (2010) did use duplicate temperature steps, but did not investigate the effect of shock pressure on any of the silicates. Most of my experiments are conducted with re-ex extractions at each temperature
step to confirm that a single domain or grain size is outgassing. This technique is
described by Lovera et al. (1997) and allows me to detect if I am measuring an
erroneously low E. For this study, I used terrestrial samples of an albite (a rock almost
wholly albite) and pyroxenite (a rock almost wholly pyroxene) that had been
experimentally shocked up to ~60 GPa, and analyzed spectroscopically (Johnson et al.,
2002). For olivine, I used a separate of the Springwater pallasite, although this meteorite
has an unknown shock pressure.

3.2 Methods

3.2.1 Microprobe Data

I used a Cameca SX-50 with 4 wavelength dispersive spectrometers at the
University of Arizona to determine the elemental composition of major minerals in thin
sections of unshocked albite and pyroxenite. X-ray dot maps of the thin sections were
also generated using the same instrument. Thin sections of shocked material were
unfortunately not available for analysis. Feldspar in the albite rock was measured with
two different conditions to prevent volatilization of Na and K. The first condition was an
accelerating voltage of 15 kV, a beam current of 6 nA, a spot size of 2 µm, and a 10 s
counting time for Na and K. The second condition was an accelerating voltage of 15 kV,
a beam current of 20 nA, a spot size of 2 µm, and a 20 s counting time for Si, Mg, Al, Ca,
Mn, Fe, Cr, and Ti (with P added to the list for K-rich feldspar). The remaining silicates
in the albite rock were measured with a single condition of 15 kV, 20 nA, 1 µm, and 20
s for Na, Si, Mg, Al, K, Ca, Mn, P, Fe, Cr, and Ti. Silicates in the pyroxenite were
measured using the same conditions as silicates in the albitite, though P was not measured. Outliers that had totals more than three $\sigma$ away from the average were not included in any statistical analysis.

3.2.2 Determination of Modal Abundances Using X-ray Dot Maps

X-ray dot maps of Na, Mg, Al, Si, K, Ca, and Fe were made for the albitite and pyroxenite. Additionally, X-ray dot maps of Ba and Mn were made for the albitite and pyroxene, respectively, but provided no useful information for my purposes. The variability of minerals in both rocks can be captured by judicious choice of three elements. Each element map was then imported into a single RGB channel of Photoshop, giving a three-color map of each rock. This map was then smoothed using the “Median” filter to eliminate noise, and the number of pixels belonging to each mineral was counted. The total number of pixels in each rock was determined by a backscattered electron (BSE) image of the same resolution. The modal abundance of each mineral was then determined by dividing the number of pixels of each mineral by the total number of pixels in the rock.

3.2.3 Ar Sample Preparation

The feldspar and pyroxene samples received from J. R. Johnson had previously been crushed to a fine powder; mostly $\sim 20$ µm in diameter, though with some grains up to 250 µm in diameter. To limit the variability of grain sizes, and because dealing with radioactive powder can be dangerous, the samples were sieved. To eliminate the fine powder, samples were swirled around in a 50 mL beaker of methanol, allowed to sit for a
few seconds, and then the liquid plus suspended grains were decanted into another container. This was done until the decanted liquid was clear. The remaining grains were then washed multiple times in acetone and allowed to dry. Mesh sieves were used to separate the grains into size fractions of 150-250 µm, 75-150 µm, and 38-75 µm. Each time a new chemistry or shock stage was handled all surfaces and equipment were cleaned to prevent cross-contamination. I was only able to find enough shocked material for analysis in the 38-75 and 75-150 µm size fractions. The Springwater olivine samples had already been separated previously. All samples were wrapped in Al foil prior to irradiation. A second preparation of unshocked pyroxenite was performed, and from this preparation high-Ca pyroxene was picked from the 150-250 µm size fraction, and also wrapped in Al foil. The remaining high-Ca depleted material was set aside and not used.

3.2.4 Ar Data Collection

Ar data collection followed the procedure in Chapter 2.3, though for these samples the $^{37}\text{Ar}$ was not limited. This was done because of the low amount of Ca in these samples, and because I wanted to ensure accurate counting statistics on $^{37}\text{Ar}$. Samples were dispersed throughout three tubes. Tube 1: samples A1 to B9; Tube 2: samples B10, B11, J1-J3, and T1; and Tube 3: T2 to T11. All three tubes were irradiated at the U.S. Geological Survey Training Research and Isotope Production, General Atomics (USGS TRIGA) in Denver, CO. A J factor of $6.81 \times 10^{-3} \pm 2.8 \times 10^{-4}$ for Tube 1 was determined by averaging three samples of the Ar-Ar geochronology standard PP-20 [hornblende, 1074 Ma], while a J factor of $6.88 \times 10^{-3} \pm 2.9 \times 10^{-4}$ for Tube 2 was determined by averaging three samples of PP-20 and one sample of GA1550 [biotite,
98.79 Ma]. For Tube 3, I chose a J factor that varied linearly from the top to the bottom of the tube. This gave a J value between $7.097 \times 10^{-3}$ and $7.174 \times 10^{-3}$, each with an error of $2.0 \times 10^{-5}$, which was determined by three samples of PP-20 and one sample of Mmhb-1 [hornblende, 523.1 Ma]. Reactor correction values were: $(^{39}\text{Ar}/^{37}\text{Ar})_{\text{Ca}}$ of $7.61 \times 10^{-4} \pm 2.5 \times 10^{-5}$; $(^{36}\text{Ar}/^{37}\text{Ar})_{\text{Ca}}$ of $2.73 \times 10^{-4} \pm 1.6 \times 10^{-5}$; $(^{40}\text{Ar}/^{39}\text{Ar})_{K}$ of $6.9 \times 10^{-3} \pm 2.5 \times 10^{-3}$. All listed errors are 1σ. While $^{40}\text{Ar}$ was measured for the albitite and pyroxenite, high blanks and low $^{40}\text{Ar}$ abundance lead to large errors. Hence, we focus our attention on the radioactive isotopes $^{39}\text{Ar}$ and $^{37}\text{Ar}$.

To ensure accurate temperature (T) measurements, pure metals with various melting temperatures were melted in the crucible to calibrate T. Metals used, along with their melting temperatures, were; tin (231.91 °C), lead (327.5 °C), aluminum (660.37 °C), gold (1064.43 °C), copper (1083.4 °C), and nickel (1453 °C). Via visual examination, two pieces of each metal were used to confirm the melting temperature. Results are shown below in Figure 3.1. A linear fit of the data was used, giving a conversion equation of,

$$T_{\text{real}} = 1.15 \times T_{\text{measured}} - 72.5$$

where $T_{\text{real}}$ and $T_{\text{measured}}$ are both in °C. The error of $T_{\text{real}}$ was assumed to be the same as the error in $T_{\text{measured}}$ (usually ~5 °C). This temperature correction is needed because, during the time period when these samples were analyzed, there was only a small gap between the bottom of the crucible and the bottom of the furnace. This creates a sharp temperature gradient along the length of the thermocouple, which then acts as a heat sink, and results in a temperature reading lower than that at the tip of the thermocouple. For
samples analyzed in Chapters 4 and 5, the gap between the furnace and crucible was widened, and calibration with melting metals showed that no correction was needed.

In the albite, applying the temperature correction lowers $E$ and $\log D_0/a^2$ by about 4σ, or ~8%--30%. The correction is much less important in the pyroxenite samples, where the correction is <1σ.

3.2.5 Measurement of Diffusion Parameters

The basics of diffusion were described in Section 2.5.4. Here, the technique of domain separation and the conversion of raw data into diffusion data is described in more detail. Domain separation usually just involves phase separation. This is because the initial gas released from each phase only comes from the smallest grains (the larger grains have not yet begun to substantially outgas), often making the need for size separation unnecessary. To help aid in identification of a change in domain (either size

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**Figure 3.1. Temperature calibration of the extraction system.**
or chemical), re-extractions were performed at each temperature (Lovera et al., 1997). If the re-extract did not agree with the first extraction, I then knew I was seeing an influence from a second domain as the first domain was becoming exhausted.

There are three conditions that can aid in phase separation, assuming multiple chemical phases are present in the sample. The first is gas releases that are separated by temperature. In this case some extractions will have little or no gas, while the preceding extractions (lower temperature) and later extractions (higher temperature) have more gas. This is illustrated in Figure 2.4, which shows one release <1000 °C and another release >1000 °C, with a local minimum of gas released at ~1000 °C. If the mineral phases are not separated by temperature, then extracting meaningful data is very difficult, and phase separation is typically not performed. Secondly, if the minerals contain both K and Ca, the different releases can be identified by a change in the K/Ca ratio. Thirdly, if a mass balance has been performed on either K or Ca, then I can check the amount of gas released by each phase, and compare it to the amount of K or Ca in the rock that is from that mineral. Multiple grain sizes are not a major issue, as discussed on the previous page, but as I get to higher temperatures the slope will drop off as gas from the larger grains lowers the measured log D/a². As long as I exclude the extractions with multiple grain sizes from the line fit, accurate diffusion parameters can still be determined by measuring the slope and intercept of the resulting line. Finally, if the mineral does not remain stable during heating, for example due to melting or dehydration, reliable diffusion parameters cannot be obtained. Fortunately, multiple extractions below the
melting or desiccation temperature can easily be performed, and the minerals I am interested in measuring all remain stable below their melting temperatures.

After I have identified the general temperature range over which each domain outgases, I remove extractions that are at or below the blank level within error, usually at the very beginning (rarely) or end (very common) of each heating schedule. While these points will not affect the overall data, they result in cluttered graphs. Rather than arbitrarily choosing which of the remaining extractions form a straight line, a more quantitative approach is used, and to do that I need error bars on each measurement. I have propagated errors throughout the entire set of extractions from a given sample using the method of Lovera et al. (1997). In addition to the error associated with measuring the gas, I also need errors in the temperature and the heating duration. First, I look at the error in the heating duration. The sample outgases while heating up to the target temperature, as well as when cooling back down to room temperature. The amount of gas lost obviously depends upon the diffusion parameters, but reasonable estimates indicate that the amount lost during ramp up and cool down can be comparable to a maximum of an additional 30 s of heating. Hence I used a heating duration error of 30 s. For the temperature error, I measured the variability of the target temperature during each extraction, and combined this value via the square root of the sum of the squares with the error of $T_{\text{real}}$ (see Equation 3.1 and its description). The error in $T_{\text{real}}$ has been assumed to be 5 °C. The error cannot be much larger than this value, because otherwise the $q$ values (see below) are too close to 1, indicating an overestimation of the error. While this is not
a rigorous determination, a 5 °C temperature error is commonly assumed (Cassata et al., 2009; Lovera et al., 1997). Thus I have errors in both y (log D/a^2) and x (1/T).

With errors assigned to each data point on the Arrhenius plot, I can determine how good a fit the points are to a straight line, via the goodness-of-fit parameter (q) defined by Press et al. (1992). This parameter uses the incomplete gamma function and gives the probability that the calculated chi-squared value would be that poor by chance (higher q means higher probability of linear behavior, q value is between 0 and 1).

Rather than choosing data points that give the highest q (which is sometimes only 3 or 4 points), I instead choose data points that give the highest q*N, where N is the number of data points included in the fit. Usually the difference in E between highest q and highest q*N is within error, though in a few cases E differs by ~30% (this doesn’t explain outliers in Tables 3.3 and 3.6-8). Using the maximum q*N allows me to maximize both the number of points in the fit and the linear behavior, without including points that contain gas from another domain. Although three unique temperatures provide enough information to form a line with one degree of freedom, I require at least four unique temperatures to ensure the line has statistical significance, which is defined as having a q >0.001.

To be sure I have excluded all points that have a contribution from another phase, I chose many different cutoff temperatures between the two phases, each time excluding gas below any particular cutoff temperature from my diffusion calculations. Excluding gas requires the recalculation of the log D/a^2. Each recalculation then requires its own Arrhenius plot. Within each Arrhenius plot, I can determine which set of points give the
largest q*N. Further procedural information for determining which points to include in the domain separation is given in the Section for each sample. Whichever Arrhenius plot gave the maximum q*N was chosen to represent the temperature range over which the mineral of interest was outgassing, and this subset of the data points was chosen to represent the most accurate measurement of the diffusion parameters.

In a few cases, the above procedure will remove too much gas. This has the effect of lowering the log D/\(a^2\) of the first few points of the remaining steps, creating an artificial curvature to the Arrhenius plot (Figure 3.2). Additionally, the re-extracts no longer give the same value within 1\(\sigma\) error. The errors on each measurement are large enough that these first few points will often be considered to be part of a line (sometimes even the largest q*N), though including them in the fit will produce an erroneous slope and intercept that are both too high. I note the cases for which this occurs, and chose a lower cutoff temperature that still has a large q*N.

3.3. Results

3.3.1 Albitite

Samples of albitite were collected near Szklary, Poland, in Lower Silesia (Muszynski and Natkaniec-Nowak, 1992). Shocked and unshocked samples were prepared for Ar analysis as noted in Section 3.2.3.
3.3.1.1 K and Ca Domains in the Unshocked Albitite

Microprobe measurements of the chemical composition of major minerals, as well as their modal abundances, are given in Table 3.1. An elemental map of the albitite is given in Figure 3.3. By multiplying the K and Ca wt% in each mineral by the mineral’s abundance in the rock, I can determine the contribution of each mineral to the whole rock K and Ca ppm (Table 3.2). The low abundance of K and Ca in the albite means I have to be careful about measuring the diffusion parameters, because small amounts of K- or Ca-rich minerals can contain a significant percentage of the total amount of the element. In order for the Arrhenius plot to provide accurate results, Ar from other minerals must be mathematically “removed”. To help identify the gas that belongs to each mineral, I compare the quantity of K and Ca as measured by the microprobe and mineral abundance
with the quantity of K and Ca in each temperature release from the unshocked samples (Table 3.2).

Ca-derived $^{37}$Ar is more easily interpretable than K-derived $^{39}$Ar because the domains are more separated by temperature (Figure 3.4). A description of how the phase separation is performed is given in Section 3.3.1.2. Examination of Table 3.2 shows that the first release and the hydrated Mg- and Al-rich silicate have total Ca abundances that overlap at 2σ. The second release and the albite also have the same amount of Ca, to within 20%. However, there is a third release of $^{37}$Ar that cannot be accounted for in the thin section. This cannot be contamination because all the crushed material (shocked and unshocked), as well as the unshocked whole rock, have the same amount of Ca. Even if all the crushed material was contaminated to exactly the same degree (which would be

<table>
<thead>
<tr>
<th>Table 3.1. Albitite Composition and Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element (wt%)/Mineral</td>
</tr>
<tr>
<td>-----------------------</td>
</tr>
<tr>
<td>Na</td>
</tr>
<tr>
<td>K</td>
</tr>
<tr>
<td>Si</td>
</tr>
<tr>
<td>Mg</td>
</tr>
<tr>
<td>Al</td>
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<tr>
<td>Ca</td>
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<tr>
<td>Fe</td>
</tr>
<tr>
<td>Cr</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>Total</td>
</tr>
<tr>
<td>Modal Abundance (%)</td>
</tr>
</tbody>
</table>

* Four of the measurements didn’t include P.
very unlikely), the whole rock samples should only have contamination on the surface. Surface contamination would make up a much smaller portion of the overall Ca and result in the whole rock samples having lower total Ca, which is not seen. A possible explanation is a high-Ca mineral with low modal abundance that was much more abundant in the samples used for Ar analysis that in the thin section. While there was a

Figure 3.3. Three-element map of the albitite. Mg is mapped to red, K to green, and Na to blue. The color scheme can also be used as a mineral map, blue is Na-feldspar, green is K-feldspar, and red is the hydrated Mg- and Al- rich silicate. Left and right portions are two different slices.
single grain of plagioclase found in the thin section, it was nowhere near the ~2% modal abundance needed to account for the third release. Muszynski and Natkaniec-Nowak (1992) list amphibole (which can have as much as 8-9 wt% Ca) as a trace mineral in the rock (<0.1 vol%), though again it would need to be much more abundant in our samples to account for the third release. While identification of all three releases would be preferable, the temperature separation means the third release does not affect the phase separation of the second release. The second release is certainly from the albite because the total amount of Ca matches between the Ar and microprobe data, and because the K/Ca ratio as measured by the microprobe also matches the K/Ca ratio of the second release. While this cannot be seen in Table 3.2 due to difficulty in separating $^{39}$Ar into a 1st and 2nd release, it can be seen by plotting the K/Ca ratio for each step as a function of $^{37}$Ar released (Figure 3.5).

| Table 3.2. K and Ca Mass Balance of the Albite |
|---|---|---|---|---|
| **Ar Data from Unshocked Albite** | **Microprobe Data from Albite** |
| Release | K ppm$^a$ | Ca ppm$^a$ | Mineral | K ppm$^a$ | Ca ppm$^a$ |
| *1$^{st}$ | 1554 ± 332$^b$ | 64 ± 18 | Mg-rich | 4 ± 1 | 32 ± 11 |
| *2$^{nd}$ | 2547 ± 328 | | Ab | 1262 ± 388 | 3010 ± 486 |
| *3$^{rd}$ | 718 ± 290 | 1247 ± 254 | Or | 1824 ± 300 | 2 ± 6 |
| Total$^c$ | 2294 ± 616 | 3866 ± 305 | Total | 3090 ± 490 | 3044 ± 486 |

$^a$ The ppm values are relative to the mass of total rock, not the individual mineral or release. $^b$ Gas from the 1st and 2nd release cannot be effectively separated, and is all included in the 1st release. $^c$ Totals are calculated by average and standard deviation of all samples, not by summing the above columns together. * For the Ca ppm, the temperature range for the 2nd release is given in Table 3.3, while the temperature range for the 1st and 3rd releases are below and above the range of the second release, respectively. For the K ppm, the 1st release is < ~1020 °C, while the 3rd release is >~1020 °C.
As we will see, getting accurate diffusion parameters from the K-derived $^{39}\text{Ar}$ is not really feasible. While there appears to only be two releases of $^{39}\text{Ar}$ in Figure 3.4, plotting the K/Ca ratio as a function of $^\%$ $^{37}\text{Ar}$ (Figure 3.5) shows there are in fact three releases of $^{39}\text{Ar}$. The first release is exhausted quickly, and has a very high K/Ca ratio. The second release, as in the case of $^{37}\text{Ar}$, has a K/Ca ratio that matches the albite (for most of the points), while the third release has a K/Ca ratio that is between the first and second release. All three releases have non-negligible overlap, so proper phase separation cannot be performed. The distinction between the first and second release in

Figure 3.4. Release plot for sample B11, showing multiple releases. Open symbols are $^{39}\text{Ar}$, closed symbols are $^{37}\text{Ar}$. The first release is shown as blue diamonds, the second release by red squares ($^{37}\text{Ar}$ only), and the third release by green triangles. Due to overlap of the first and second release in $^{39}\text{Ar}$, a distinction is not made between the releases.
Figure 3.5. Ar data of the K/Ca ratio vs. %$^{37}$Ar released. Three releases are present, but all three exhibit temperature overlap preventing rigorous separation. The transition from “Ar 1” to “Ar 2” is arbitrarily chosen for visual effect. “Ar 3” is the third release from Figure 3.4. The microprobe data for the albite (red line, with standard error of the mean for errors) is included for reference. K/Ca is a ratio of wt%.

Figure 3.5 has been arbitrarily chosen for visual representation, and the points in the third release are identical with those for the third release in Figure 3.4.

I cannot compare the amount of $^{39}$Ar in each release with the K concentration of each mineral because I cannot perform proper phase separation. I can, however, put limits on the amount of $^{39}$Ar in the second release. The maximum amount of $^{39}$Ar in the second release will be all the gas released below 1000 °C. This is the gas indicated in the first release in Figure 3.4. The minimum amount of $^{39}$Ar in the second release will be the gas that has a K/Ca ratio within 2$\sigma$ of the value measured by the microprobe. For sample B11, the second release of $^{39}$Ar then has a concentration of 770-1710 K ppm. These limits are within 2$\sigma$ of the K concentration measured by the albite in the microprobe,
further proof showing the second release is from the albite. The $^{39}$Ar in the third release is a little less than half the K attributable to Or in the microprobe data, but because the error bars overlap at 2σ they are probably the same.

The source of the first release of $^{39}$Ar is difficult to determine with the limited data. One possibility is that the first and third release are both due to Or, and I am just seeing a grain size effect. Small grains would outgas at low temperature, while the large grains would outgas at high temperature. Another possibility is mica, which Muszynski and Natkaniec-Nowak (1992) found in abundances up to 0.3 vol% in the albitite. Mica can have up to ~9 wt% K, which means ~0.5 vol% would be needed to account for the first portion. Again, I was not able to identify all sources of $^{39}$Ar. However, I do have positive identification of the major source as albite, since the K/Ca ratio and amount of K of the second grouping matches that of the albite. Unfortunately, because of the overlap of the first and second release in $^{39}$Ar, separating the $^{39}$Ar into domains and measuring the diffusion parameters will not give accurate results.

In summary, I could not positively identify all major carriers of K and Ca, though possibilities for the unidentified domains were provided. The shocked albite Ar release (Sect. 3.3.1.3) may provide some confirmation that the high T releases of $^{39}$Ar and $^{37}$Ar are K-feldspar and plagioclase, respectively, but it is by no means certain. Regardless, lack of positive identification of all Ar releases will not affect the results for albite because I have identified the gas release that belongs to albite. This allows me to separate the second release from the first and third releases, but only for $^{37}$Ar. In the case of $^{37}$Ar, it is very straightforward and accurate because all three releases are well
separated by temperature. In the case of $^{39}\text{Ar}$, I could only identify rough portions of the three releases. After phase separation of $^{37}\text{Ar}$, the resulting gas has the same amount of Ca as found in the albite with the microprobe. In the case of $^{39}\text{Ar}$, the resulting gas has limits that are within $2\sigma$ of the K in the albite as measured by the microprobe. Additionally, many of the steps give the same K/Ca ratio, which also match the albite microprobe data. Because separating the $^{37}\text{Ar}$ from the albite into its own domain was the most straightforward, it will also provide the most accurate measurement for the diffusion parameters of albite.

3.3.1.2 Criteria for Phase Separation in Albite

Before fitting a straight line to the Ar data, the gas from each mineral phase must be separated into its own domain. This phase separation was briefly described above. Even though the three phases have mostly been separated by temperature, there is still some question about exactly what temperature constitutes the cutoff between two domains. In reality, there probably is no exact temperature cutoff, and instead at least a few steps contain gas from both domains. However, partitioning the gas from a single step into multiple domains would only be accurate if I already knew the diffusion parameters for each phase. I could guess at the percentage of gas that belonged to each domain, but that’s still a guess and could artificially impact our result. Having a set of criteria choose a particular cutoff, while not perfect, at least does not introduce human error.

As an example, I will describe the phase separation for $^{37}\text{Ar}$ from B11. The cutoff between the 1st and 2nd release, which I will call the low T cutoff, is determined in the
following way. I first examine the release plot (Figure 3.4) and see that the low T cutoff should be about 500 °C. I create an Arrhenius plot for multiple low T cutoffs around 500 °C. Figure 3.6 shows the two most promising low T cutoffs.

For each Arrhenius plot, I then consider the linear portion that includes the first point in the plot, and then select the one that gives the maximum q*N (Section 3.2.5). This is to ensure I include as much of the low T data as possible, since it will be less influenced by any grain size effect. In the case of sample B11, using 502 °C as a cutoff leads to a higher q*N than using a 530 °C cutoff. A good way to confirm if I have properly removed gas from a different domain is if pairs of extractions become more similar. Indeed, the pairs of extractions at an x-axis value of 13 are more similar in the “502 °C Cutoff” as compared to “Original”. The next step is to find the high T cutoff, which separates the 2\textsuperscript{nd} release from the 3\textsuperscript{rd} release.

Figure 3.6. Various low-temperature cutoffs showing the effect on the log \( D/a^2 \) of individual measurements.
Again, I examine the release plot (Figure 3.4) and see that the high T cutoff should be about 1000 °C. I create an Arrhenius Plot for multiple high T cutoffs around 1000 °C, which also excludes points below the low T cutoff. Figure 3.7 shows the two most promising high T cutoffs. In the case of B11, the highest q*N occurs for a high T cutoff of 960 °C. The linear portion determined by the highest q*N extends from 502° to 874° (i.e. not all the way up to the high T cutoff) and gives an E of 46.36 ± 0.60 kcal/mol.

3.3.1.3 K and Ca Domains in Shocked Albite

The shocked albite is easier to reduce, because there are only two releases of K and Ca. Evidently the shock caused the albite and the unidentified third release to release their Ar in tandem, because the shocked samples have the same amount of Ca and K as the unshocked samples. At this time I cannot determine if the shock caused the albite to absorb the third release, or if the two domains remained physically separated but with the
same diffusion parameters. All unshocked samples were reduced in a similar manner to the shocked.

3.3.1.4 $^{37}$Ar Diffusion in Albite

The $^{39}$Ar and $^{37}$Ar data should give the same results for the Na-rich feldspar. Because most of the $^{37}$Ar is from the albite, it is more robust and reliable and will be examined first. The $^{39}$Ar data has a large contribution from K-feldspar and is harder to interpret. Thus, $^{39}$Ar will be discussed further in its own section. The samples that deviated from the conditions mentioned in Section 3.3.1.2 are listed in Appendix A.

Unshocked samples all give about the same $E$ (Table 3.3), and an unweighted average gives $49 \pm 7$ kcal/mol, or $46.0 \pm 2.8$ kcal/mol, if the most extreme outlier is
removed (both errors are 1σ standard deviations). An unweighted average for \( \log D_0/a^2 \) gives 4.9 ± 1.4 s\(^{-1}\), or 4.3 ± 0.6 s\(^{-1}\) if the largest outlier is removed. While the intercepts for the unshocked samples have about a factor of two spread, there is no correlation with sieve size. Instead, high intercept values correlate with high E values, while low intercept values correlate with low E values. The diameters of the albite grains are 60-160 µm, which spans the range of both sieve sizes. This range of grain sizes would create a range of \( \log D_0/a^2 \) values that differ by about 0.9, which is comparable to the error seen in \( \log D_0/a^2 \). Still, because the \( \log D_0/a^2 \) values do not correlate with sieve size, I prefer to average all the values together. The E for the unshocked samples is over the same range as what has been seen by previous authors (See Section 3.1). If grain size is
the diffusion distance, then the $D_0$ values for these samples is about that seen in plagioclase (Cassata et al., 2009), but significantly larger than that seen in K-feldspar (McDougall and Harrison, 1999).

The shocked samples show an obvious change in the diffusion parameters. Because they do not change between 29 and 55.8 GPa, the transformation must have been complete by 29 GPa, unlike the results observed by other authors (Velde et al., 1989). Unweighted averages give $24.5 \pm 2.4$ kcal/mol for $E$ and $1.1 \pm 0.7$ s$^{-1}$ for $\log D_0/a^2$.

3.3.1.5 $^{39}$Ar diffusion in Albite

Because the diffusion parameters of albite as measured by $^{37}$Ar are so very close to the accepted diffusion parameters of K-feldspar, one would expect the $^{39}$Ar data, being composed of K-feldspar and albite, to be identical to the $^{37}$Ar data. However, as noted above, there are problems with overlapping releases that I cannot remove. A crude attempt to delineate the releases of the unshocked samples does give $E$ values of 30 to 50 kcal/mole for the Ab release, but I will not discuss $^{39}$Ar further since $^{37}$Ar is a much better measurement.

3.3.2 Pyroxenite

Samples of pyroxenite were collected from the Stillwater Complex in Montana (Raedeke and McCallum, 1984). Three types of samples from this rock were run for Ar analysis. The first two are shocked and unshocked whole rock samples. The third type of sample was high-Ca Pyx picked from the unshocked pyroxenite.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Shock (GPa)</th>
<th>Sieve size (µm)</th>
<th>Low T Cutoff (°C)</th>
<th>High T Cutoff (°C)</th>
<th>T range (°C)</th>
<th>E (kcal/mol)</th>
<th>log D₀/a² (1/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1 and A4</td>
<td>0</td>
<td>38-75</td>
<td>559</td>
<td>960</td>
<td>559-731</td>
<td>49.20±2.02</td>
<td>5.16±0.49</td>
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<tr>
<td>A3</td>
<td>0</td>
<td>38-75</td>
<td>502</td>
<td>960</td>
<td>502-931</td>
<td>43.57±0.63</td>
<td>3.81±0.14</td>
</tr>
<tr>
<td>B10*</td>
<td>0</td>
<td>75-150</td>
<td>502</td>
<td>1019</td>
<td>502-961</td>
<td>42.61±0.77</td>
<td>3.60±0.18</td>
</tr>
<tr>
<td>B11</td>
<td>0</td>
<td>75-150</td>
<td>502</td>
<td>960</td>
<td>502-874</td>
<td>46.36±0.60</td>
<td>4.29±0.14</td>
</tr>
<tr>
<td>B6</td>
<td>0</td>
<td>Whole rock</td>
<td>588</td>
<td>960</td>
<td>588-874</td>
<td>62.51±1.06</td>
<td>7.45±0.23</td>
</tr>
<tr>
<td>B7</td>
<td>0</td>
<td>Whole rock</td>
<td>502</td>
<td>1019</td>
<td>502-846</td>
<td>48.16±0.86</td>
<td>4.64±0.20</td>
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<tr>
<td>A6</td>
<td>29</td>
<td>38-75</td>
<td>330</td>
<td>-</td>
<td>330-674</td>
<td>22.17±0.46</td>
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<tr>
<td>A7</td>
<td>29</td>
<td>38-75</td>
<td>330</td>
<td>-</td>
<td>330-617</td>
<td>25.81±0.73</td>
<td>1.46±0.22</td>
</tr>
<tr>
<td>B1</td>
<td>44.6</td>
<td>38-75</td>
<td>388</td>
<td>-</td>
<td>388-617</td>
<td>28.99±0.67</td>
<td>2.27±0.19</td>
</tr>
<tr>
<td>B2</td>
<td>44.6</td>
<td>38-75</td>
<td>330</td>
<td>-</td>
<td>330-473</td>
<td>22.62±1.22</td>
<td>0.41±0.39</td>
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<tr>
<td>B3</td>
<td>55.8</td>
<td>38-75</td>
<td>330</td>
<td>-</td>
<td>330-674</td>
<td>25.01±0.37</td>
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<tr>
<td>B4*</td>
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<tr>
<td>B5</td>
<td>55.8</td>
<td>38-75</td>
<td>330</td>
<td>-</td>
<td>330-617</td>
<td>24.19±0.59</td>
<td>0.92±0.17</td>
</tr>
</tbody>
</table>

* Sample B4 and B10 did not have re-extractions performed, so are considered less reliable.
3.3.2.1 Ca Domains in Pyroxenite

Microprobe analysis has shown there are three types of pyroxenes (Pyx) in the pyroxenite; high-Ca Pyx, low-Ca Pyx, and pigeonite (although I do not have structural information, the composition is consistent with this). None of the three types of pyroxene had any K above the detection limit using the microprobe, so for both the microprobe measurements and the Ar analysis, I will mostly ignore K (i.e. $^{39}$Ar). A Ca mass balance
on the thin section gives ~50% more Ca than is seen in the average whole rock Ar analysis, probably indicating the thin section was not large enough to be representative. I was only able to make a thin section from a small piece of whole rock (~2.7 mm in size), and the high-Ca Pyx grain size was ~500 μm, while the other two pyroxenes were even larger. Nonetheless, the thin section indicates ~80% of the $^{37}$Ar is in high-Ca Pyx, with the remaining $^{37}$Ar coming from pigeonite (the Ca content of the low-Ca Pyx is too low to contribute).

Since the whole rock samples used in Ar analysis give a lower Ca wt% than indicated by the thin section, but about twice that found in the pigeonite (Table 3.4), I know that high-Ca Pyx was present, but with an abundance lower than that in the thin section. The extremes will come when I assume no low-Ca Pyx on the one hand, and no pigeonite on the other. If I use the Ar data, a sample with no pigeonite gives a high-Ca

<table>
<thead>
<tr>
<th>Table 3.4 Pyroxene mineral composition and abundance</th>
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<tbody>
<tr>
<td>Element (wt%)/ Mineral</td>
</tr>
<tr>
<td>------------------------</td>
</tr>
<tr>
<td>Na</td>
</tr>
<tr>
<td>K</td>
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<td>Si</td>
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<td>Cr</td>
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<td>Ti</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>Total</td>
</tr>
<tr>
<td>Abundance (%)</td>
</tr>
</tbody>
</table>
Pyx modal abundance of ~10% (which would amount to 100% of the $^{37}$Ar coming from high-Ca Pyx), while no low-Ca Pyx in the samples gives a high-Ca Pyx modal abundance of ~5% (which would amount to ~50% of the $^{37}$Ar coming from high-Ca Pyx). So to summarize, 50-100% of the $^{37}$Ar comes from high-Ca Pyx, with the remaining from pigeonite. The modal abundance of the thin section indicates 80% of the $^{37}$Ar is from high-Ca Pyx, but is not necessarily representative of the whole rock.

For the picked high-Ca Pyx samples, I have much better agreement with the values measured in the microprobe. Microprobe measurements on the high-Ca Pyx give 16.05 wt% Ca, well within error of the samples used for Ar analysis.

3.3.2.2 Criteria for Phase Separation in Pyroxene

For the pyroxene samples, I only have two releases, so I only require a low T cutoff. The first release contains only 1-5% of the total $^{37}$Ar, and based upon the
$^{39}$Ar/$^{37}$Ar ratio it is probably interstitial feldspar, though a thorough investigation of the interstitial feldspar was not undertaken. In the albite samples I choose the largest $q*N$ that included the first point. This was done to avoid any grain size effect. The pyroxene samples, on the other hand, do not appear to have a significant grain size effect. More importantly, the high E means that the low temperature steps have very little gas in them, causing a two-fold effect. First it makes the contribution from feldspar harder to identify. Second, if I erroneously choose a low T cutoff that is too high, I remove a large portion of the gas from the pyroxene, artificially increasing the E.

In an attempt to only extract Ar from pyroxene at low temperature, for some splits I chose an irregular heating schedule that rises to about 1100 °C (the melting temperature of alkali-rich feldspar) and then drops back to about 1000 °C before rising again. The idea is to exhaust gas from the feldspar, then drop back down in temperature and get a reading from the pyroxene without a contribution from feldspar. Because of this, samples with an irregular heating schedule have some temperatures with four (or more) extractions. To avoid confusion, I refer to the first two extractions of a temperature as the “1st pair”, and the second two extractions (which were performed after extractions at higher temperatures) as the “2nd pair”, etc.

If I choose a low T cutoff using the conditions from the albite (i.e. the largest $q*N$ that also includes the first point), the result usually yields a cutoff that excludes the 1st pair of extractions, but includes the 2nd pair of extractions. On the surface this would seem to confirm that the 1st pair of extractions had contamination from another domain, and that temperature cycling exhausted the feldspar leaving pyroxene as the only
contributor to the 2\textsuperscript{nd} pair of extractions. However, upon closer inspection one finds that at temperatures above those used for temperature cycling, the log $D/a^2$ of the re-extractions are no longer the same as those of the original extraction to within error. This indicates that I have removed gas that actually belongs to the pyroxene. For the pyroxene samples, then, I use conditions similar to the albite for the low T cutoff, but only require the highest $q*N$, without regard for whether or not it includes the first point. This has the effect of giving more weight to the high temperature steps, whose log $D/a^2$ is less affected by which low T cutoff is selected.

3.3.2.3 $^{37}$Ar Diffusion in High-Ca Pyroxene

Two of the high-Ca Pyx samples were well behaved, and a straight application of the procedures in Section 3.3.2.2 was followed. The third is described in Appendix A.

Table 3.6 gives the diffusion parameters for high-Ca pyroxene samples.

Combining the albite samples was simple because all had the same behavior. In the case of high-Ca Pyx, this doesn’t capture the true variation of the samples, because J3 seems to have a different behavior from J1 and J2. Nonetheless, $E$ and log $D_o/a^2$ have overlapping 1σ error bars for all three samples, so I average the slopes and intercepts of all three samples, giving an $E$ of 102.0 ± 1.8 kcal/mol and a log $D_o/a^2$ of 9.9 ± 0.6 s\textsuperscript{-1}.

3.3.2.4 $^{37}$Ar Diffusion in Whole Rock Pyroxene

A summary of the diffusion parameters for whole rock Pyx is listed in Table 3.7. Most samples followed the procedure of Section 3.3.2.2, those that deviated from the standard procedure are listed in Appendix A.
The unshocked pyroxene, like the unshocked high-Ca pyroxene, has a few outliers, though the majority of the samples are closely grouped. Because the pyroxene samples do not all cluster together, combining the diffusion parameters into a single set depends on the method chosen. I performed four different combinations, which gave an E range of 124.6-134.1 kcal/mol and a log $D_0/a^2$ range of 13.39-14.55 s$^{-1}$. These numbers were determined by the following methods; averaging all the slopes and intercepts

![Unshocked high-Ca Pyroxene](image)

Figure 3.11. Phase separated unshocked high-Ca pyroxene. Labels correspond to the internal identifier (see Table 3.6).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shock (GPa)</th>
<th>Sieve size (µm)</th>
<th>Low T Cutoff (°C)</th>
<th>T range (°C)</th>
<th>E (kcal/mol)</th>
<th>log $D_0/a^2$ (1/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>J1</td>
<td>0</td>
<td>150-250</td>
<td>846</td>
<td>903-1133</td>
<td>100.8±4.3</td>
<td>9.48±0.73</td>
</tr>
<tr>
<td>J2</td>
<td>0</td>
<td>150-250</td>
<td>731</td>
<td>903-1105</td>
<td>101.3±4.1</td>
<td>9.63±0.71</td>
</tr>
<tr>
<td>J3*</td>
<td>0</td>
<td>150-250</td>
<td>1017</td>
<td>1017-1133</td>
<td>104.0±5.6</td>
<td>10.54±0.91</td>
</tr>
</tbody>
</table>

*Irregular behavior outside this temperature range

Table 3.6 High-Ca Pyroxene Diffusion
Figure 3.12. Phase separated unshocked pyroxene. Most samples cluster together, though there are two outliers. Labels correspond to the internal identifier (see Table 3.7).

Figure 3.13. Phase separated shocked pyroxene. Clustering is less obvious, outliers are still present. Labels correspond to the internal identifier (see Table 3.7).
together, taking all the x-y points from the linear portions of each sample (or in the case of samples T8 and T9, points from the low T cutoff to the extractions with the most gas) and fitting a line to all samples, and doing the previous two methods without samples T8 and T9 (i.e. the outliers). The preferred method is averaging all the slopes and intercepts together, but leaving out T8 and T9. This ensures all samples are weighted equally (instead of by the number of extractions in each sample), but does not give any weight to the outliers. This gives an E of $131 \pm 10$ kcal/mol and a log $D_0/\sigma^2$ of $13.7 \pm 1.3$ s$^{-1}$.

The shocked pyroxene has a clustering as well, and the diffusion parameters are determined using methods similar to that of the unshocked pyroxene. Here, the linear combinations are performed both with and without T1 and T4 (using a 903 °C cutoff with
a T range of 903-1191 °C), and I also average the slopes and intercepts of T2, T3, and T5. The E range is then 82.1-103.6 kcal/mol and the log $D_0/a^2$ range is 6.9-10.5 s$^{-1}$. For the same reasons as the unshocked pyroxene, the preferred method is to average the slopes and intercepts of the samples that have a linear portion. This gives an E of 82 ± 8 kcal/mol and a log $D_0/a^2$ of 6.9 ± 1.4 s$^{-1}$.

3.3.3 Olivine

For the olivine samples, I did not use reactor-produced Ar because very little Ca or K can be incorporated into the structure. Instead I used cosmogenically produced Ar from Fe-produced spallation (See 2.4.3) in the Springwater pallasite. Because these samples did not need to be irradiated prior to analysis, Cl-derived Ar cannot interfere with separating cosmogenic Ar from terrestrial Ar. The $^{38}$Ar and $^{36}$Ar was separated into air and spallation by assuming values slightly different from that in Chapter 2. Here I used a $^{38}$Ar/$^{36}$Ar of 0.1879 ± 0.0004 for air, and 1.50 ± 0.05 for spallation, which are the same as Chapter 2 to within 2σ. For diffusion analysis, $^{38}$Ar was used, though $^{36}$Ar would have given identical results due to the separation procedure forcing the $^{38}$Ar/$^{36}$Ar ratio to become ~1.5.

3.3.3.1 Criteria for Phase Separation in Olivine

Unfortunately these samples were analyzed before I started using the double extraction technique. This means there is the potential for a grain size effect. The grains used for analysis were 1-2 mm in diameter, and up to ~10 grains were used for each aliquot. This size is smaller than the average diameter of 3.6 mm (Nininger, 1932), so
Table 3.7. Pyroxene Diffusion

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shock (GPa)</th>
<th>Sieve size (µm)</th>
<th>Low T Cutoff (°C)</th>
<th>T range (°C)</th>
<th>E (kcal/mol)</th>
<th>log D_0/a² (1/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T6</td>
<td>0</td>
<td>75-150</td>
<td>960</td>
<td>960-1133</td>
<td>146.7±7.9</td>
<td>15.99±1.30</td>
</tr>
<tr>
<td>T6B</td>
<td>0</td>
<td>75-150</td>
<td>960</td>
<td>1017 (2nd pair)-1162</td>
<td>122.2±7.1</td>
<td>12.82±1.13</td>
</tr>
<tr>
<td>T7</td>
<td>0</td>
<td>75-150</td>
<td>903</td>
<td>1105-1248</td>
<td>129.3±5.1</td>
<td>13.55±0.78</td>
</tr>
<tr>
<td>T8</td>
<td>0</td>
<td>75-150</td>
<td>1018</td>
<td>1076-1249</td>
<td>48.8±1.9</td>
<td>2.11±0.29</td>
</tr>
<tr>
<td>T9*</td>
<td>0</td>
<td>38-75</td>
<td>846</td>
<td>846-1018</td>
<td>169.0±6.0</td>
<td>22.92±1.09</td>
</tr>
<tr>
<td>T10</td>
<td>0</td>
<td>38-75</td>
<td>1076 (1st pair)</td>
<td>1076 (2nd pair)-1277</td>
<td>125.1±3.0</td>
<td>12.65±0.45</td>
</tr>
<tr>
<td>T11</td>
<td>0</td>
<td>38-75</td>
<td>846</td>
<td>960 (3rd pair)-1219</td>
<td>131.0±4.2</td>
<td>13.69±0.67</td>
</tr>
<tr>
<td>T4</td>
<td>30</td>
<td>75-150</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T5</td>
<td>30</td>
<td>38-75</td>
<td>960</td>
<td>1018-1191</td>
<td>83.9±3.0</td>
<td>7.30±0.47</td>
</tr>
<tr>
<td>T1</td>
<td>60</td>
<td>75-150</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T2</td>
<td>60</td>
<td>75-150</td>
<td>1076 (1st pair)</td>
<td>1076 (2nd pair)-1162</td>
<td>73.6±5.5</td>
<td>5.34±0.86</td>
</tr>
<tr>
<td>T3</td>
<td>60</td>
<td>75-150</td>
<td>960 (1st pair)</td>
<td>1018 (1st pair)-1191</td>
<td>88.93±2.88</td>
<td>8.08±0.47</td>
</tr>
</tbody>
</table>

* Very small q, so while not statistically significant given the errors, T9 does follow a general linear trend.
aggregate grains should not occur. This does mean there could be up to a factor of two spread in the domain size, but that should result in minimal deviation from the true value. In addition to single extractions, the olivine samples also have a lower temperature resolution. This results in the largest q*N never selecting more than four unique temperatures. To reduce the chance of random alignment, I instead choose the cutoff and linear portion based upon the largest N that also gave a q value above 0.001. If the largest N occurred in two different fits, I choose the fit with the larger q because it forms the straightest line. These criteria have the effect of selecting the largest temperature range that also had the most linear behavior. In all cases the diffusion parameters acquired using these conditions were the same as the largest q*N to within 2σ, except for one E which was the same to within 3σ.

3.3.3.2 $^{38}$Ar Diffusion in Olivine

A summary of the diffusion parameters for olivine are listed in Table 3.8. All samples followed the procedure of Section 3.3.3.1.

Sample S1 has a higher D/a² at low temperature compared to the other two samples. However, the amounts of $^{38}$Ar are very similar, indicating I do not have contamination. Phase separation leads to diffusion parameters that are close to, but smaller than, the other two splits. Without any justification for exclusion, I accept S1 as a valid measurement. Averaging all three samples together gives an E of 44 ± 7 kcal/mol and a log D₀/a² of 0.8 ± 0.9 s⁻¹. Even though olivine is a high-temperature mineral, an E for Ar in olivine lower than in pyroxene is not surprising, since Mg and Fe equilibrate
Table 3.8. Olivine Diffusion

<table>
<thead>
<tr>
<th>Sample</th>
<th>Low T Cutoff (°C)</th>
<th>T range (°C)</th>
<th>E (kcal/mol)</th>
<th>log D₀/a² (1/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1*</td>
<td>900</td>
<td>1000-1400</td>
<td>36.46 ± 0.98</td>
<td>-0.14 ± 0.15</td>
</tr>
<tr>
<td>S2</td>
<td>600</td>
<td>600-1200</td>
<td>51.06 ± 0.76</td>
<td>1.63 ± 0.15</td>
</tr>
<tr>
<td>S3</td>
<td>700</td>
<td>900-1200</td>
<td>44.71 ± 1.37</td>
<td>1.02 ± 0.22</td>
</tr>
</tbody>
</table>

*Low temperature behavior is different from the other two samples, the high temperature behavior is still similar.

faster in olivine than pyroxene (Huss et al., 2006). What is a little surprising is if the characteristic diffusion distance is the grain size for both the unshocked albite and the olivine, the diffusion rate of the olivine would only be an order of magnitude slower than that of the feldspar. However, it is unknown what role the grain size actually plays in these samples.
3.4 Conclusions

I found experimental shock to have an obvious and reproducible effect on the Ar diffusion of albite, lowering E from ~45 to ~25 kcal/mol. The unshocked albite has an E the same as unshocked orthoclase. Shocked albite has an E lower than that found in normal glass (Carroll, 1991), and intermediate to previous measurements of maskelynite in ALH 84001 (Cassata et al., 2010; Weiss et al., 2002). It is unclear why the oligoclase samples of (Stephan and Jessberger, 1992) do not seem to be affected by shock, or if Ca-rich feldspar truly is shock resistant (Jessberger and Ostertag, 1982).
I found Ar diffusion in a mixture of low-Ca and high-Ca pyroxene to be affected by shock, lowering E from ~130 to ~80 kcal/mol. This difference is probably real. However, samples of both shocked and unshocked pyroxenite have outliers that look similar to each other, making a clear distinction difficult. Surprisingly, unshocked high-Ca pyroxene has an intermediate E of ~100 kcal/mol, nearly the same as the pyroxene in ALH 84001 (Cassata et al., 2010). All of the pyroxene Ar E values are intermediate to those of pyroxene separates in Shergottites and Nakhlites (Bogard, 2009). I found Ar diffusion in olivine to have an E of ~45 kcal/mol, higher than that measured via Ar ion implantation (Futagami et al., 1993), and intermediate to those of previous determinations of the He E (Shuster et al., 2004; Trull and Kurz, 1993). A summary of the E values for all shocked and unshocked compositions is given in Figure 3.16.
4.1 Introduction

For some time now it has been known that step-heating experiments on ordinary chondrites produce two releases of Ar. This is graphically demonstrated in Figure 4.1. The K/Ca ratio of the lower temperature release (<~1000 °C) is always very similar to that of microprobe measurements of the feldspar. However, the higher temperature release (>~1000 °C) has never been identified, though there are many suggestions. Possible explanations are a chemical difference, an effect of shock, a change of the diffusion distance from grains to melt veins, and enclosure in a higher temperature mineral (Bogard et al., 1995; Bogard and Hirsch, 1980; Kunz et al., 1997; McCoy et al., 1995). Pyroxene and/or olivine, being the most abundant minerals in L chondrites, are the most likely high temperature candidates for enclosing feldspar or containing trace amounts of K.

Given what we have learned so far, I can say a few things about the above suggestions. Shock is known to convert feldspar to maskelynite, and in the last chapter I showed that maskelynite has a higher diffusion rate than structural feldspar, and thus cannot be the high temperature release. However, there are other high-pressure phases of feldspar, such as feldspar that has been converted to a hollandite structure (Liu, 1978;
While feldspar with a hollandite structure has been seen in L chondrites (Gillet et al., 2000), this mineral is rare in natural samples. Thus, shock is still a potential, though unlikely, candidate for the high temperature release. Previous work on the diffusion parameters of the ordinary chondrite releases has shown the low temperature release has an Ar activation energy (E) between 20 and 50 kcal/mol, while the high temperature release is >70 kcal/mole (Bogard et al., 1995; Bogard and Hirsch, 1995).
1980; Kunz et al., 1997; Turner et al., 1978). Because the E for the high T release is higher than that of feldspar, and because feldspathic glass has a lower E than that of crystalline feldspar (Chapter 3), a change of diffusion distance is not a valid explanation for the high temperature release, and will not be considered further. Exploring the other possibilities will be the goal of this chapter.

Chapter 3 established the groundwork that is needed to understand the Ar releases of ordinary chondrites. I do not compare the findings from Chapter 3 to previous Ar diffusion work on ordinary chondrites because those studies did not have a second extraction at each temperature. As shown in Chapter 2, this means a grain size effect could compromise the measured diffusion parameters. Therefore, I have performed step-heating experiments on NWA 091 and Chico using two (or more) extractions at each temperature, and I have acquired a much higher temperature resolution than previous authors, both of which give me a more detailed picture of the meteorites’ diffusion properties. Additionally, because I will be analyzing the meteorites with the same setup that I used in Chapter 3, we will not need to worry about inter-laboratory differences.

A straight comparison of the Ar diffusion parameters of meteorites with diffusion parameters of known chemistry and shock pressure will not definitively determine the source of K. One reason is the diffusion parameters of K in a high temperature mineral will be very similar to that of feldspar enclosed in a high temperature mineral, because either way the Ar must diffuse through the high temperature mineral. Another reason is the Ar diffusion parameters of NaAlSi$_3$O$_8$-hollandite could be very similar to pyroxene or olivine. Synthetic NaAlSi$_3$O$_8$-hollandite forms at $\sim$1025 °C and 12-24 GPa (depending
upon chemistry), though it is only rarely found in natural samples and hence has not been well studied for Ar-Ar chronology (Gillet et al., 2000; Tomioka et al., 2000). To distinguish between these two scenarios, I will perform a K mass balance on host material from the Chico meteorite, and also perform Raman spectroscopy on the feldspar of Chico. This will provide enough information to discriminate between the various possible K sources of the high temperature release.

4.2 Methods

4.2.1 Sample Description

The petrology and Ar-Ar age of the Chico meteorite have been well studied (Bogard et al., 1995), and I selected it precisely for this reason. While much of this meteorite is impact melt, I chose to analyze the host material because it has a larger grain size, making microprobe and Raman data easier to acquire. Additionally, I knew the host contained two releases of Ar (Bogard et al., 1995), making it a good candidate to study the source of the high temperature release. The host is classed as an L6 S6, the latter of which translates to a shock pressure of 45-75 GPa (Stöffler et al., 1991). This is at the higher end of the pressures investigated in Chapter 3. I also analyzed Northwest Africa (NWA) 091, an L6 S4 (Grossman and Zipfel, 2001), which translates into 15-35 GPa. While not much is known about this meteorite, it does provide a shock pressure at the lower end of the pressures investigated in Chapter 3.
4.2.2 Microprobe Data

Like the samples in the previous chapter, a thin section of Chico was scanned with an X-ray dot map, and major minerals were analyzed with point analyses using the Cameca SX-50 with 4 wavelength dispersive spectrometers at the University of Arizona. Na-rich feldspar was measured with the same conditions as the feldspar in Chapter 3, but instead of using a 2 µm spot size, I used a 5 µm spot size, and no measurements analyzed P. A few Na-rich feldspar measurements used a 20 µm spot size, 4 nA beam current, and 8 s counting time for the Na and K, but the remaining conditions were the same as the other feldspar measurements in this meteorite. Both sets of Na-rich feldspar measurements give values that are the same to within 1σ, and will not be differentiated in the text. A small feldspathic phase was measured with the same conditions, though with a spot size of 2 µm instead of 20 µm. Mafics were measured with the same conditions as the mafics in Chapter 3. Melt veins were measured with the same conditions as the mafics, but with a spot size of 20 µm, and without measuring P.

4.2.3 Determination of Modal Abundances Using X-ray Dot Maps

X-ray dot maps of Na, Al, Si, Mg, Fe, P, Cr, and Ca were made of an entire thin section of the Chico meteorite. Adobe Photoshop was used to determine the mineral abundance (vol%) of feldspar, low-Ca pyroxene, high-Ca pyroxene, olivine, chromite, Ca phosphates, kamacite, troilite + taenite (lack of a S map prevented distinction), and a mixture of feldspar + other silicates from the elemental maps. The technique used to assign a category to each pixel was taken from Knight et al. (2002), a brief description of
which follows. For elements that did not have a very large signal (e.g. Na and Al in pyroxene), the noise was often enough to drown out the signal in some of the pixels. The “Median” noise reduction filter was used to remove this effect by averaging the pixel brightness with all adjacent pixels. For each elemental map, a threshold brightness was then chosen to convert the map into a binary file. All pixels brighter than this value were set to maximum brightness, while all pixels dimmer than this value were set to zero brightness.

Mineral maps were constructed by “multiplying” pixels of elements that are expected in the mineral and then “subtracting” those of elements that should not be present. For example, a feldspar map was created by multiplying Na, Al, and Si, and then subtracting Mg. Olivine was distinguished from pyroxene by creating two Si maps with different threshold settings, and troilite + taenite was distinguished from kamacite using the same technique with Fe. A “mixed phase” map was created for pixels that contained a mixture of feldspar and other silicate minerals by multiplying maps of Si, Mg, Ca, and Al. The “mixed phase” map probably indicates feldspar grains that are smaller than the pixel footprint. Melt veins did not end up in the “mixed phase” map, but were instead identified as one of the other minerals. Fortunately, the low melt vein abundance means the melt vein contribution will be small.

Assigning an error to each measurement is difficult. Some pixels did not end up in any of the assigned mineral bins (including the mixed phase bin). When calculating a vol%, I did not include these pixels in the total. The mixed phase bin contains 3% of total pixels, hence the listed vol% for most minerals is slightly underestimated. The
largest error from the mixed phase bin for all of the minerals is ~1.5 wt%, which occurs when the bin contains equal amounts of two different minerals (a large contribution from a single mineral would place it in the appropriate bin). Another source of error is the threshold levels for each element. Choosing extreme, but reasonable, threshold levels for the various elements only produces minor differences in the calculated vol%. For feldspar, the difference is ~0.2 vol%. Finally, because S and Ni were not measured, distinguishing between troilite and taenite was not possible, and some kamacite was probably put in the troilite + taenite bin. While this does not affect the measured vol% of other minerals, it will affect the calculated wt%. However, the effect on the feldspar abundance is <1wt% (see Section 4.3.1), less than the error introduced by the mixed phase bin. Altogether, I estimate the error is not better than the error in XRD measurements, which is typically ±2 wt% with well-matched standards (Dunn et al., 2010). Assigning a robust number to any of the abundances is difficult, but a conservative estimate is ±2% (absolute) for abundances >4 wt%, and ±50% (relative) for abundances <4 wt%.

High resolution X-ray dot maps of Na, Al, K, and Fe were taken in about ten different locations of the Chico thin section, each about 1 mm$^2$ in area. In these maps, very small grains with a high K abundance can be seen. The modal abundance of the grains is very small, and does not affect the K budget significantly. To show this minor effect, I wish to determine an upper limit to the modal abundance of these grains, and used a process similar to that used in the large maps described above. However, here I only used the K maps, and instead of the “Median” noise reduction filter, I instead used
the “Despeckle” noise reduction filter to preserve as much detail as possible. I adjusted the threshold brightness to the lowest reasonable value, which produces an upper limit to the modal abundance of the K-rich grains.

4.2.4 Raman Spectroscopy

Raman spectroscopy uses a laser to excite the vibrational, rotational, and other low frequency modes (such as libration) of a mineral. A fraction of the incident light will inelastically scatter off a molecule, and either impart or remove energy from the molecule. The former is known as Stokes scattering, while the latter is known as anti-Stokes scattering. This change in energy also changes the energy of the scattering photon. The change in photon wavelength is represented by the Raman shift (in cm\(^{-1}\)), which is determined by

\[
\Delta \lambda = \left( \frac{1}{\lambda_0} - \frac{1}{\lambda_1} \right)
\]  

(4.1)

where \(\lambda_0\) is the laser wavelength and \(\lambda_1\) is the Raman spectrum wavelength. To get the Raman spectrum, intensity is plotted versus Raman shift. The Raman spectrum is unique for each mineral, and is used to determine structural state. I performed Raman spectroscopy using Stokes scattering on Chico feldspar/glass with Prof. R. Downs at the University of Arizona using a Thermo Nicolet Almega microRaman system with an excitation wavelength of 532 nm and partial polarization. Using a different laser frequency will produce different peak intensities, but will not change the location of the peaks. Therefore, a spectrum collected with any laser frequency can be used for mineral identification. Feldspar grain locations are determined with Figure 4.3, and I found that
the feldspar grains are visible with reflected light. The feldspar grains appear darker than
the surrounding grains, which makes aiming with the Olympus microscope easy. The
optics of this microscope are also used to focus the laser. Although the spot size of the
beam is only a few microns, the pointing of the microscope is uncertain. Hence the
spectrum sometimes exhibited peaks from adjacent pyroxene and olivine. The major
peaks of pyroxene and olivine are easily distinguishable from feldspar, and do not affect
the interpretation.

4.2.5 Ar-Ar Data Collection

Ar data collection followed the procedure in Section 2.3. As in Chapter 3, I used
two extractions at each temperature for all samples. In addition, for some samples I also
used temperature cycling. Because I used temperature cycling along with two extractions
per temperature, some temperatures ended up with four extractions.

In Chapter 3 a temperature calibration was performed, and a large temperature
mismatch between the measured and true value was found. After completing all analysis
for Chapter 3, we investigated the cause of this mismatch, which turned out to be an issue
with the positioning of the thermocouple. As described in Section 2.3, a tungsten furnace
surrounds the tantalum crucible, and the thermocouple is fed in through the bottom of the
furnace and makes contact with the bottom of the crucible. The problem was that our
thermocouple tips were too close to the bottom of the furnace, resulting in a temperature
gradient. The higher the furnace temperature, the larger the gradient, and the lower the
resulting measured temperature. We raised the bottom of the crucible to allow the
thermocouple tips to be positioned deeper into the furnace, which eliminated the effect of
the temperature gradient. This was confirmed by melting a second set of metals. Hence, the temperatures in this chapter do not need to be corrected.

Whole rock chips of NWA 091 and Chico, and splits of the standards CaF$_2$, K$_2$SO$_4$, and PP-20 (hornblende, 1074 ± 4 Ma) were wrapped in Al foil and sealed in a quartz tube. Samples were irradiated at the Cadmium-Line, In-Core Irradiation Tube (CLICIT) reactor at Oregon State University. Measured reactor correction values were:

- $(^{39}\text{Ar}/^{37}\text{Ar})_{\text{Ca}}$ of $6.75 \times 10^{-4} \pm 6 \times 10^{-6}$;
- $(^{38}\text{Ar}/^{37}\text{Ar})_{\text{Ca}}$ of $2.05 \times 10^{-5} \pm 1.1 \times 10^{-6}$;
- $(^{36}\text{Ar}/^{37}\text{Ar})_{\text{Ca}}$ of $2.77 \times 10^{-4} \pm 2 \times 10^{-6}$;
- $(^{38}\text{Ar}/^{39}\text{Ar})_{\text{K}}$ of $1.225 \times 10^{-2} \pm 4 \times 10^{-5}$.

The measured value for $(^{40}\text{Ar}/^{39}\text{Ar})_{\text{K}}$ is negative and zero to within error, which means atmospheric argon is dominating the release. I instead use $1.1 \times 10^{-3} \pm 1.2 \times 10^{-3}$, the value for the CLICIT reactor as measured by Renne et al. (1998). While this value is still zero to within error, it is positive and thus more reliable. The other reactor correction values were the same as Renne et al. (1998) to within error.

Unfortunately, the mass discrimination value of 0.997 ± 0.006 per AMU was only reliably determined for the time period over which a little less than half of the samples were analyzed. However, because mass discrimination does not change rapidly with time, I have assumed the same mass discrimination value for all samples. Two samples of the Ar-Ar geochronology standard PP-20 were placed at each end of the quartz tube. To determine the J factor for each meteorite split, I first averaged the samples of PP-20 at each end together to get a value of $8.81 \times 10^{-3} \pm 1.3 \times 10^{-4}$ at one end, and $9.25 \times 10^{-3} \pm 6 \times 10^{-5}$ at the other. The J factor for each meteorite split is then determined from a linear interpolation between these two values. Measuring the K/Ca production ratio is
uncertain. One K salt (K$_2$SO$_4$) gives a $^{39}$Ar production rate ~3 times that of the other two K salts. Averaging all three salts together gives a K/Ca ratio of ~5, excluding the outlier gives a ratio of ~2.88. However, most reactors give a K/Ca ratio of ~1.8. If, instead of using the K salts to get the $^{39}$Ar production rate, I use the PP-20, I get a K/Ca production ratio of 1.9 ± 0.4. This value is much more reasonable, and is the value I use for this irradiation package.

4.3 Results

4.3.1 K Mass Balance

A K mass balance was performed on host material from the Chico L6 impact melt breccia. This involved determining the abundance and K concentration of all K-bearing minerals. A mineral map (description of creation in Section 4.2.3) is shown in Figure 4.2, and mineral abundances of those minerals are found in Table 4.1. To convert mineral vol% to wt%, I used the following densities (in g/cm$^3$): feldspar, 2.7; troilite, 4.6; chromite, 4.8; Fe-Ni metal, 7.95; other minerals (including mixed phases), 3.3. Because a distinction between taenite and troilite could not be made, I performed two different conversions from vol% to wt%, one with no troilite, and the other with no taenite (Table 4.1). Comparison with Mason (1965) shows that this meteorite has typical mineral abundances for an L chondrite. Because the melt vein abundance was not captured in Figure 4.2, the melt veins have been indicated in Figure 4.3. The melt vein abundance is small enough that any misidentification as another mineral (Section 4.2.3) will be within error.
I performed microprobe measurements of the major silicates, which are found in Table 4.2. I was only able to find a K signal in the melt veins and two feldspathic phases (one is chemically oligoclase and the other is undetermined, but enriched in K). If a feldspathic phase is structurally feldspar, it will have five cations for every eight oxygen...
The feldspathic phases do not seem to be structural feldspar, due to a cation number that is typically less than 5. The K-enriched phase has an average cation number of 4.77, with the highest being 4.9, though this could just be due to missing an important cation during analysis, as evidenced by the low element totals (Table 4.2). The oligoclase-like phase is much closer, but still has an average cation number of 4.94, with only four of 27 measurements equal to 5.0. Since the element totals of the oligoclase-like phase are ~100, this would suggest the meteorite does not have structural feldspar (but see Section 4.3.2). To determine the nature of the K-enriched phase, a more thorough investigation would be needed. However, this phase is not necessary to perform a K mass balance. Table 4.3 combines the microprobe data with the mineral abundance to get

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chico vol%</th>
<th>Chico wt% (no troilite)</th>
<th>Chico wt% (no taenite)</th>
<th>Average L chondrite wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olivine</td>
<td>47.7</td>
<td>43.7</td>
<td>46.5</td>
<td>47.0</td>
</tr>
<tr>
<td>Low-Ca Pyroxene</td>
<td>24.8</td>
<td>22.7</td>
<td>24.2</td>
<td>22.7</td>
</tr>
<tr>
<td>High-Ca Pyroxene</td>
<td>3.6</td>
<td>3.3</td>
<td>3.5</td>
<td>4.6</td>
</tr>
<tr>
<td>Feldspar</td>
<td>12.5</td>
<td>9.4</td>
<td>10.0</td>
<td>10.7</td>
</tr>
<tr>
<td>Kamacite</td>
<td>1.5</td>
<td>3.2</td>
<td>3.4</td>
<td>7.5^b</td>
</tr>
<tr>
<td>Taenite</td>
<td>6.5^c</td>
<td>14.4</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>Troilite</td>
<td>n.a.</td>
<td>8.9</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>Chromite</td>
<td>0.4</td>
<td>0.5</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Apatite</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.6</td>
</tr>
<tr>
<td>Mixed Phases</td>
<td>3.1</td>
<td>2.8</td>
<td>3.0</td>
<td>n.a.</td>
</tr>
<tr>
<td><strong>Totals</strong></td>
<td><strong>100.1</strong></td>
<td><strong>100.0</strong></td>
<td><strong>100.1</strong></td>
<td><strong>99.8</strong></td>
</tr>
<tr>
<td>Melt Veins^d</td>
<td>1.5</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>K-enriched Phase</td>
<td>&lt;0.02</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

^a From (Mason, 1965), contains 0.2 wt% ilmenite  
^b No distinction is made between kamacite and taenite  
^c The distinction between taenite and troilite could not be made due to lack of a S map  
^d Melt veins registered as one of the other minerals, not as a mixed phase  
^e Vol% is converted to wt% using the specific gravities mentioned in the text
the total K concentration of Chico. The oligoclase-like phase dominates the K budget of the meteorite. The K-enriched phase has a negligible contribution to the overall K budget, and the melt vein contribution (while not fully accounted for) would be a second order effect. The maximum K contribution from olivine, low-Ca pyroxene, and high-Ca
Table 4.2. Chico Major Silicate Mineral Composition

<table>
<thead>
<tr>
<th>Element (wt%)</th>
<th>Oligoclase-like (n=27)</th>
<th>K-enriched (n=4)</th>
<th>Olivine (n=10)</th>
<th>Low-Ca Pyx (n=10)</th>
<th>High-Ca Pyx (n=10)</th>
<th>Melt vein (n=15)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>6.64 ± 0.51</td>
<td>1.79 ± 1.79</td>
<td>&lt;0.01</td>
<td>0.04 ± 0.02</td>
<td>0.35 ± 0.08</td>
<td>1.31 ± 0.58</td>
</tr>
<tr>
<td>K</td>
<td>0.51 ± 0.12</td>
<td>2.17 ± 0.82</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.10 ± 0.05</td>
</tr>
<tr>
<td>Si</td>
<td>31.44 ± 1.25</td>
<td>30.91 ± 2.11</td>
<td>17.74 ± 0.13</td>
<td>25.76 ± 0.23</td>
<td>24.89 ± 0.44</td>
<td>21.49 ± 2.06</td>
</tr>
<tr>
<td>Mg</td>
<td>0.08 ± 0.08</td>
<td>3.71 ± 2.25</td>
<td>23.28 ± 0.24</td>
<td>17.12 ± 0.30</td>
<td>10.22 ± 0.57</td>
<td>14.88 ± 1.11</td>
</tr>
<tr>
<td>Al</td>
<td>10.65 ± 0.76</td>
<td>6.70 ± 0.44</td>
<td>&lt;0.01</td>
<td>0.13 ± 0.04</td>
<td>0.40 ± 0.15</td>
<td>2.15 ± 0.84</td>
</tr>
<tr>
<td>Ca</td>
<td>1.84 ± 0.71</td>
<td>0.66 ± 0.81</td>
<td>0.07 ± 0.02</td>
<td>0.96 ± 0.40</td>
<td>14.46 ± 1.87</td>
<td>1.92 ± 1.52</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt;0.01</td>
<td>0.08 ± 0.02</td>
<td>0.37 ± 0.03</td>
<td>0.38 ± 0.02</td>
<td>0.20 ± 0.05</td>
<td>0.31 ± 0.05</td>
</tr>
<tr>
<td>P</td>
<td>n.a.</td>
<td>n.a.</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.02</td>
<td>n.a.</td>
</tr>
<tr>
<td>Fe</td>
<td>0.74 ± 0.43</td>
<td>3.38 ± 1.55</td>
<td>17.70 ± 0.26</td>
<td>10.50 ± 0.34</td>
<td>4.91 ± 1.54</td>
<td>14.79 ± 2.84</td>
</tr>
<tr>
<td>Cr</td>
<td>&lt;0.02</td>
<td>0.06 ± 0.07</td>
<td>0.05 ± 0.02</td>
<td>0.17 ± 0.07</td>
<td>0.61 ± 0.08</td>
<td>0.17 ± 0.13</td>
</tr>
<tr>
<td>Ti</td>
<td>0.10 ± 0.06</td>
<td>0.11 ± 0.03</td>
<td>&lt;0.03</td>
<td>0.12 ± 0.04</td>
<td>0.23 ± 0.09</td>
<td>0.07 ± 0.04</td>
</tr>
<tr>
<td>O</td>
<td>48.79 ± 0.80</td>
<td>46.04 ± 1.55</td>
<td>40.80 ± 0.23</td>
<td>44.42 ± 0.40</td>
<td>43.26 ± 0.52</td>
<td>41.88 ± 1.38</td>
</tr>
<tr>
<td>Total</td>
<td>100.81 ± 1.16</td>
<td>95.60 ± 2.01</td>
<td>100.06 ± 0.49</td>
<td>99.60 ± 0.82</td>
<td>99.53 ± 0.82</td>
<td>99.06 ± 1.25</td>
</tr>
</tbody>
</table>

n.a.=not available
For entries listed as <0.0X, all measurements are zero or below detection, strongly indicating 0 wt%.

a Detection limit is 0.02, all measurements are at least twice detection, large variability is due to a few large values
b Detection limit is 0.07, some measurements are above detection, some below
c Detection limit is ~0.58, one measurement is below detection
d Detection limit is 0.05, some measurements are above detection, some below
e Detection limit is 0.03, some measurements are above detection, some below
f Detection limit is 0.06, some measurements are above detection, some below
pyroxene is listed in Table 4.3. Realistically though, these three minerals probably have virtually no K at all, since they had no measurement above the detection limit of ~0.007 wt% K.

### 4.3.2 Raman Spectroscopy of Chico

The transformation of feldspar (ordered) to diaplectic glass (disordered) has a distinct effect on vibrational modes. Velde et al. (1989) and Heymann and Hörz (1990) studied the effect of this transformation on the Raman spectra and found it to cause progressive line broadening, decrease in line intensity, and the loss of low signal lines. Additionally, Velde et al. (1989) found heavily shocked albite to have three types of spectra; normal feldspar, disturbed feldspar, and glass. These three types are shown in Figure 4.4. The disturbed feldspar spectra are accompanied by spectra of glass, which they attribute to inter-layering of crystalline and glassy zones. Another possible shock
Figure 4.4. Different types of spectra found in the 50 GPa post shock sample of albite. The lower spectrum shows crystalline zones that change to a glassy state in the uppermost spectrum. (With kind permission from Springer Science+Business Media: Velde et al. (1989), Figure 2.)

The effect could be the transformation to structural hollandite, as is seen Figure 4.5 (Gillet et al., 2000).
I collected Raman spectra of the feldspathic phase in Chico, the results of which are shown in Figure 4.6 and Figure 4.7. Eighteen of the twenty spectra collected from
Chico are of nearly pure feldspar like spectrum C) (Figure 4.6) or a mixture of feldspar and pyroxene/olivine like spectrum D) (Figure 4.7), the remaining two are shown as spectra A) and B) (Figure 4.6). Spectra A) and B) have broad, shallow lines similar to feldspar, but lack the broad lines at ~580, ~780, and ~1090 cm$^{-1}$ that are seen in Figure 4.4. This could be evidence of near complete conversion to glass, but the curved baseline indicates I have background luminescence, which could be masking the lines. Ultimately, spectra A) and B) do not tell me much, but they are included for completeness.

Figure 4.6. Three Raman spectra of Chico feldspathic phases, along with an oligoclase standard. The other 17 spectra were all very similar to C), though many exhibited obvious peaks from pyroxene or olivine (Figure 4.7). Note the peak at ~570 cm$^{-1}$, which is present in nearly all of the spectra.
Spectrum C), and the others like it, appear to be mostly crystalline. Spectrum C) has peaks at 281, 477, 509, 572, 793, and 1102 cm\(^{-1}\) that are nearly identical with those found in the middle spectra of Figure 4.4. There is another peak at 408 cm\(^{-1}\), which coincides with feldspar, and is also present in most of the other spectra. However, many spectra have peaks from pyroxene, one of which is at 401 cm\(^{-1}\) (Figure 4.7). While there are no other pyroxene lines present in spectrum C), different orientations of grains can cause some lines to disappear (i.e. that mode is not excited), so I will be cautious and disregard the line at 408 cm\(^{-1}\). Finally, spectrum C) has a peak at 962 cm\(^{-1}\), which is probably due to an olivine peak at 965 cm\(^{-1}\), and should also be disregarded. All spectra
contain a very broad peak at ~280 cm\(^{-1}\), and sharper peaks at ~480 and ~510 cm\(^{-1}\). Most spectra contain a peak at ~580 cm\(^{-1}\), while some contain a peak at ~790 and/or ~1100 cm\(^{-1}\). In the region from 200 to 400 cm\(^{-1}\), none of the spectra contain lines that can be definitively interpreted as coming from feldspar, except for the line at ~280 cm\(^{-1}\).

Given the lack of all but one line between 200 and 400 cm\(^{-1}\), a very broad line at 280 cm\(^{-1}\), and the presence of broad lines at ~580, ~790, and ~1100 cm\(^{-1}\), there is the possibility of a small amount of glass in all the spectra. All spectra have a very strong signal from crystalline feldspar, and no evidence of hollandite is seen. The line broadening that is seen in the major lines indicates the crystalline feldspar has Si/Al and K/Na disordering (Bendel and Schmidt, 2008).

4.3.3 Diffusion Parameters of Shocked Meteorites

4.3.3.1 Criteria for Phase Separation

The criteria I follow are essentially the same as those found in Chapter 3. For the low temperature (T) release I use the same criteria as Section 3.3.1.2, and for the high T release I use the same criteria as in Section 3.3.2.2. The procedure is briefly repeated here.

I perform phase separation on the low temperature (T) release first. First, I examine the release plot of a sample to determine the range of reasonable low T cutoffs. I then create an Arrhenius plot for each low T cutoff, and choose the value that gives the largest q*\(N\) (Section 3.2.5) that also includes at least four different temperatures and the first point in the plot. I then examine the release plot again to determine reasonable high
T cutoffs, usually the temperatures where the $^{39}$Ar released stops decreasing and begins increasing. I then create an Arrhenius plot for each high T cutoff, incorporating the previously determined low T cutoff. Again I choose the largest q*N that includes at least four different temperatures and the first point.

Next I perform phase separation on the high T release. The high T release will have its own low T cutoff, which will be of a higher temperature than that of any extractions in the low T release. I again choose the low T cutoff that gives the largest q*N, but here I relax the requirement of including the first point in the release. This loosened requirement gives more weight to the high temperature extractions that are less affected by the particular cutoff chosen.

4.3.3.2 Diffusion Parameters of Chico

I am interested in both the K-derived $^{39}$Ar and the Ca-derived $^{37}$Ar. The release plot for sample A4 is shown in Figure 4.8. Both isotopes show an obvious change of domain around 900 to 950 °C. A potential change of domain can be spotted around 575 °C, where the slope of both isotopes changes sharply. The isotopes mirror one another fairly well until about 1100 °C, where $^{39}$Ar drops much more rapidly than $^{37}$Ar. An Arrhenius plot of Chico sample A4 is shown in Figure 4.9. Notice that at 575 °C (11.8 K$^{-1}$ in Figure 4.9) the slope increases here as well. This is a good indication that there are two releases below 1000°C in the Chico meteorite, though because they overlap so much, phase separation is impossible. In the other sample of Chico (A2), this second low T release is seen in $^{39}$Ar, but does not appear to be present in $^{37}$Ar, though it could just be a problem of lower temperature resolution. Because phase separation is
Figure 4.8. Plot of $^{39}$Ar (or $^{37}$Ar) released, normalized by the heating duration and difference in temperature.

Figure 4.9. Arrhenius plot for $^{39}$Ar and $^{37}$Ar. Note that, in this plot, $^{39}$Ar and $^{37}$Ar are different at low temperature.
impossible, I will continue to refer to the gas below 1000 °C as the low T release, even though it technically contains two overlapping releases.

The criteria of Section 4.3.3.1 were followed as closely as possible, but given the overlapping releases, modifications are required. Rather than trying to separate the gas below 1000 °C into two releases, I instead left it as a single release, but fitted a line to both linear portions. While a lack of phase separation will often lead to erroneous values for $\log D_0/a^2$, the shape and slope of the linear portions are only mildly affected (see the difference between $^{39}$Ar and $^{37}$Ar in Figure 4.9, and the similarity of $^{39}$Ar and $^{37}$Ar in Figure 4.10). Deviations from the criteria in Section 4.3.3.1 are listed in Appendix A. Results are shown in Figure 4.10 and Table 4.4. Note that sample A4 used temperature cycling, while sample A2 did not. As mentioned in Section 4.2.5, I used two extractions at each temperature, which means temperature cycling produces four extractions for some temperatures. To avoid confusion I refer to the first two extractions as the “1st pair” and the second two as the “2nd pair”.

4.3.3.3 Diffusion Parameters of NWA 091

As in the case of Chico, I am interested in both $^{39}$Ar and $^{37}$Ar for NWA 091. The release plot for NWA 091 is shown in Figure 4.11. Like Chico, there is an obvious change of domain around 850-950 °C in $^{39}$Ar and $^{37}$Ar. Also like Chico, at high temperature $^{39}$Ar drops more rapidly than $^{37}$Ar, though in this case the $^{39}$Ar begins dropping at a lower temperature (~1025 °C instead of ~1100 °C). Unlike Chico, the low temperature (T) domain of $^{39}$Ar appears to only have a single release. $^{37}$Ar at low T in Figure 4.11 is a bit more complicated. There is a sharp rise in $^{37}$Ar from ~475 °C to 525
°C, and then a rapid drop back down to a mostly flat profile. Evidently a Ca-bearing/K-free domain began outgassing and was quickly exhausted. The other split of NWA 091 did not have a Ca-bearing/K-free domain at low temperature; instead $^{39}$Ar and $^{37}$Ar mirror each other quite nicely. Presumably this domain is a fluke, perhaps a single grain of anorthite.

An Arrhenius plot of NWA 091 is shown in Figure 4.12. The Arrhenius plot confirms that the low temperature release of $^{39}$Ar is indeed only a single release; there is no change of slope. The presence of another release in $^{37}$Ar is also confirmed in the low temperature regime, and we can now see that the E (slope) for the intervening release is
<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Low T Cutoff (°C)</th>
<th>High T Cutoff (°C)</th>
<th>T range (°C)</th>
<th>E (kcal/mol)</th>
<th>log $D_0/a^2$ (1/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A4-$^{39}$Ar</td>
<td>1st low T line</td>
<td>400</td>
<td>900 (1st pair)</td>
<td>400-525</td>
<td>28.42±1.27</td>
<td>0.97±0.38 $^a$</td>
</tr>
<tr>
<td>A4-$^{37}$Ar</td>
<td>1st low T line</td>
<td>400</td>
<td>900 (1st pair)</td>
<td>400-575</td>
<td>27.05±0.99</td>
<td>0.18±0.29 $^a$</td>
</tr>
<tr>
<td>A4-$^{39}$Ar</td>
<td>2nd low T line</td>
<td>400</td>
<td>900 (1st pair)</td>
<td>575-700</td>
<td>53.83±2.10</td>
<td>7.40±0.51 $^a$</td>
</tr>
<tr>
<td>A4-$^{37}$Ar</td>
<td>2nd low T line</td>
<td>400</td>
<td>900 (1st pair)</td>
<td>575-700</td>
<td>56.56±2.29</td>
<td>7.77±0.55 $^a$</td>
</tr>
<tr>
<td>A4-$^{39}$Ar</td>
<td>High T line</td>
<td>900 (2nd pair)</td>
<td>-</td>
<td>925-1085</td>
<td>140.1±4.1</td>
<td>17.6±0.7</td>
</tr>
<tr>
<td>A4-$^{37}$Ar</td>
<td>High T line</td>
<td>950 (1st pair)</td>
<td>-</td>
<td>950 (2nd pair) -1125</td>
<td>130.9±3.5</td>
<td>15.4±0.6</td>
</tr>
<tr>
<td>A2-$^{39}$Ar</td>
<td>1st low T line</td>
<td>350</td>
<td>900</td>
<td>350-500</td>
<td>19.96±0.99</td>
<td>-1.19±0.31 $^a$</td>
</tr>
<tr>
<td>A2-$^{37}$Ar</td>
<td>2nd low T line</td>
<td>350</td>
<td>900</td>
<td>600-750</td>
<td>47.06±1.75</td>
<td>5.72±0.40 $^a$</td>
</tr>
<tr>
<td>A2-$^{39}$Ar</td>
<td>Low T line</td>
<td>500</td>
<td>900</td>
<td>500-750</td>
<td>47.52±0.93</td>
<td>5.27±0.23 $^a$</td>
</tr>
<tr>
<td>A2-$^{37}$Ar</td>
<td>High T line</td>
<td>950</td>
<td>-</td>
<td>950-1100</td>
<td>75.07±3.27</td>
<td>6.25±0.56</td>
</tr>
<tr>
<td>A2-$^{37}$Ar</td>
<td>High T line</td>
<td>1000</td>
<td>-</td>
<td>1000-1350</td>
<td>90.90 $^b$</td>
<td>8.34 $^b$</td>
</tr>
</tbody>
</table>

$^a$Because proper phase separation was not possible, these values may be inaccurate.  
$^b$A statistically significant line could not be determined for the high T release of A2, values are only provided as a rough comparison.
Figure 4.11. Normalized $^{39}$Ar (or $^{37}$Ar) released divided by the heating duration and difference in temperature.

Figure 4.12. Arrhenius plot for $^{39}$Ar and $^{37}$Ar.
larger than the main low temperature $^{37}$Ar release. The small number of points prevents a rigorous determination of the slope for the intervening release, but it is in the range of 40-60 kcal/mole, probably indicating unshocked anorthite due to the Ca-rich but K-free nature of the source. Because this release is quickly exhausted, it must be from a single grain size. Multiple grain sizes would extend the release over a larger temperature range.

Because the source is a single grain size that is not present in the other sample, I propose the release is due to a single grain of anorthite that just happened to be in the split I analyzed, and is not representative of the entire meteorite.

The criteria for phase separation in Section 4.3.3.1 were followed as closely as possible, deviations are listed in Appendix A. The results are shown in Figure 4.13, and Table 4.5. Note that sample B5 used temperature cycling, while sample B1 did not.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Low T Cutoff (°C)</th>
<th>High T Cutoff (°C)</th>
<th>T range (°C)</th>
<th>E (kcal/mol)</th>
<th>log D_0/a^2 (1/s)</th>
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<tr>
<td>B5-^{39}Ar</td>
<td>Low T line</td>
<td>400</td>
<td>850</td>
<td>400-675</td>
<td>27.33±0.46</td>
<td>1.43±0.13</td>
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<tr>
<td>B5-^{37}Ar</td>
<td>1st low T line</td>
<td>400</td>
<td>800</td>
<td>400-475</td>
<td>19.21±2.05</td>
<td>-0.98±0.63^a</td>
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<td>2nd low T line</td>
<td>400</td>
<td>800</td>
<td>625-750</td>
<td>24.02±1.29</td>
<td>0.65±0.29^a</td>
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<tr>
<td>B5-^{39}Ar</td>
<td>High T line</td>
<td>900 (1st pair)</td>
<td>-</td>
<td>925-1050</td>
<td>112.4±5.1</td>
<td>13.6±0.9</td>
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<tr>
<td>B5-^{39}Ar</td>
<td>High T line</td>
<td>950 (1st pair)</td>
<td>-</td>
<td>925-1060</td>
<td>111.8±3.8</td>
<td>12.6±0.66</td>
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<tr>
<td>B1-^{39}Ar</td>
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<td>850</td>
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<td>30.69±0.39</td>
<td>2.24±0.10</td>
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<tr>
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<td>450-600</td>
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<td>3.23±0.36^b</td>
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<td>16.4±0.9</td>
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<td>-</td>
<td>950-1100</td>
<td>110.9±4.4</td>
<td>12.3±0.7</td>
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</tbody>
</table>

^a Because proper phase separation was not possible, these values may be inaccurate. ^b Only one statistically significant choice, but this choice is probably removing too much of the gas, artificially increasing these values.
4.4 Discussion

A combination of the results of Table 4.4 and Table 4.5 are shown in Table 4.6. The similarity of the Ar activation energies of NWA 091, the 1st low temperature release of Chico, and shocked feldspar (Chapter 3), show that both meteorites have feldspar that has been converted to maskelynite by shock. The maskelynite contains 35-40% of the $^{39}$Ar in NWA 091, and 3-5% of the $^{39}$Ar in Chico, depending upon the split. The 2nd low temperature release of Chico has an Ar E that matches unshocked feldspar, to within 1σ. The unshocked feldspar in Chico contains 55-60% of the $^{39}$Ar. The low temperature Ar measurements of Chico are completely consistent with the Raman spectra (Section 4.3.2), which indicate the feldspathic material is indeed dominated by structural (though disordered) feldspar, and may also exhibit a signature from glass. The lack of an obvious Raman signal from glass (Figure 4.4) is somewhat troubling, but given the low abundance of glass in Chico (~5% of the $^{39}$Ar), and the fact that glass and crystal are intimately mixed, it is not clear that an obvious signal should be present. If small amounts of glass are indeed mixed with the feldspar, it may explain the mildly low cation numbers found via the microprobe (Section 4.3.1). Without further investigation, the issue cannot be resolved.

The structural state indicated by Ar diffusion and Raman spectroscopy is at odds with the classification scheme for these meteorites (Section 4.2.1). NWA 091, classed as an S4, should not have maskelynite. However, the shock could be heterogeneous, which would indicate a higher shock stage for this meteorite. Chico, classed as an S6, should
have normal glass, when in fact it has structural feldspar. In this case the shock classification is not wrong, ~60% of the meteorite is impact melt indicating a very high shock pressure. More likely, post-impact cooling allowed re-crystallization of most of the feldspar.

Both Chico and NWA 091 show that the high temperature release has an E that is much too high for feldspar, and is similar to that of unshocked pyroxene (Chapter 3). However, as shown in Section 4.3.1, the pyroxene does not contain measurable K. Rather, the K in the feldspar can account for all the K in the meteorite. Because the Raman spectra have no indication of a high-pressure phase of feldspar, pyroxene with feldspar inclusions is the best explanation of the Ar data.

To demonstrate how well the measured diffusion parameters capture the actual release pattern, Figure 4.14 shows a model as well as actual $^{39}$Ar data from NWA 091 split B5. The model was built using the heating schedule for split B5, the measured diffusion parameters from Table 4.5 for split B5, and by partitioning the gas <850 °C into

<table>
<thead>
<tr>
<th>Table 4.6 Diffusion Summary</th>
<th>Chico</th>
<th>NWA 091</th>
</tr>
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<tr>
<td></td>
<td>E (kcal/mol)</td>
<td>log D₀/a²</td>
</tr>
<tr>
<td>1st Low T Release</td>
<td>25.13±4.54</td>
<td>-0.01±1.10 a</td>
</tr>
<tr>
<td>2nd Low T Release</td>
<td>51.24±4.70</td>
<td>6.54±1.23 a</td>
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<tr>
<td>High T Release</td>
<td>135.5±6.5 b</td>
<td>16.5±1.5 b</td>
</tr>
</tbody>
</table>

a Probably not accurate due to lack of proper phase separation. b Excludes results from A2. $^{37}$Ar lacks statistical significance, and $^{39}$Ar appears to be an outlier. Including $^{39}$Ar from A2 gives an E of ~115±35 kcal/mol and log D₀/a² of ~13±6 1/s. c Includes all results (even the questionable ones), a more careful picking would only produce changes within error.
the low temperature domain, and the gas >850 °C into the high temperature domain. If I were to instead use the E values for shocked feldspar and unshocked pyroxene (Chapter 3), and treat $\log D_0/a^2$ as a free parameter, an equally good fit can be obtained using values that are within 1σ of the measured $\log D_0/a^2$ for the low T release, and within 2σ for the high T release.

The low T release is a very good fit; only the first few points are different. This difference is probably due to smaller grains that are quickly exhausted, or due to alteration phases. The high T release is a good fit until ~1025 °C, where the measured Ar drops off rapidly but the model rolls over before dropping. A mismatch at high T is not unexpected, since feldspar grains enclosed by pyroxene violates condition D) from
Chapter 2, which requires the $^{39}\text{Ar}$ to be evenly distributed in the diffusing medium. The release plot for Ca-derived $^{37}\text{Ar}$, however, does indeed roll over just as the model, showing that we have properly described the Ar release from pyroxene. Evidently this simple model does not capture the true behavior of feldspar enclosed in pyroxene. Another feature that the model does not capture is the increase of $^{39}\text{Ar}$ at 1150 °C. Presumably there is another domain at high T, though due to the low temperature resolution it cannot be identified via the Arrhenius plot. It could be due to either a larger grain size of pyroxene, or to another chemical domain such as olivine. A precise fit cannot be obtained with either scenario, but larger pyroxene grains seem to work better than olivine.

While the data indicate that the high T release is from feldspar grains enclosed in pyroxene, is this actually seen in the thin section? A three-element map of Chico is shown in Figure 4.15. Although the map is limited to two dimensions, some generalizations can be made. While I do see some feldspar that could be enclosed by pyroxene, more seems to be enclosed by or associated with olivine. Other maps of Chico show the same story. While there are problems with the idea of feldspar enclosed in pyroxene, enclosure of feldspar in a higher temperature mineral is still a valid conclusion.

To resolve this issue, further work would be needed. Examining thin sections can give a rough estimate of the percentage of feldspar grains enclosed in a higher temperature mineral. However, enclosure in two-dimensions does not guarantee enclosure in three-dimensions, so this value would only give an upper limit. To get an accurate answer, a three–dimensional view is needed, and synchrotron X-ray computed
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Microtomography can provide this view. Resolutions of one to tens of µm per voxel can be attained, and the lower end is enough to resolve individual grains of feldspar (Ebel and Rivers, 2007). If it is shown that a large percentage of the feldspar grains are not

Figure 4.15. Combined three-element map of Chico. Fe is mapped to red, Al to green, and Na to blue. Feldspar is blue/green, Fe-Ni metal is bright red, olivine is intermediate red, and low-Ca pyroxene is dim red. White circles indicate examples of potential inclusions. A melt vein is visible in the upper right corner.
enclosed in pyroxene or olivine, then all current suggestions will have been eliminated. However, my work would still show that the only source of radiogenic $^{40}\text{Ar}$ is the feldspar, and because interstitial feldspar by itself cannot explain the release $>1000 \degree \text{C}$, it would require something external to the feldspar to change the diffusion rate, though at this time how that could occur is a mystery.
CHAPTER 5

ARGON-ARGON AGE OF NWA 091

5.1 Introduction

Most unshocked ordinary chondritic (OC) meteorites give Ar-Ar ages of 4.4-4.5 Ga, attesting to cooling within the first ~100 Ma after formation (Trieloff et al., 2003; Turner et al., 1978). Heavily shocked OCs, on the other hand, often have ages much younger, usually <1.3 Ga (Bogard, 1995). The lack of young unshocked chondrites indicates the only thermal events on these parent bodies after ~4.4 Ga are due to collisional impacts. In addition to the timing of the collision on the parent body, we would like to know about the trip from the asteroid to Earth. After a collision ejects a meteorite from its parent body, cosmic rays bombard the meteorite at depths up to ~1 m. These cosmic rays break apart atomic nuclei, producing a host of cosmogenic isotopes. Since we know the production rate of these isotopes, we can measure them and determine the duration of the transit from the parent body to Earth, the cosmic ray exposure (CRE) age. An important point to remember is the impact that resets the Ar-Ar chronometer is typically not the impact that sends the meteorite to Earth, since the CRE ages for OCs are typically <50 Ma, while Ar-Ar ages are much older (Bogard, 1995).

For the shocked L chondrites, about half the Ar-Ar ages are at ~500 Ma, indicating a large collision at that time, possibly large enough to cause break up of the
parent body (Bogard, 1995; Bogard and Hirsch, 1980; Bogard et al., 1976; Heymann, 1967; Kunz et al., 1997; McConville et al., 1988). However, rather than a tight clustering of ages, there is a spread from about 400 Ma to 600 Ma, which is larger than the uncertainty for individual meteorites. While trapped argon is always a concern, and is a likely source of the older ages, identification of trapped Ar is often hampered by Cl activation during neutron bombardment (see 2.4.3). What was needed was a new discovery to shed light on the spread in apparent ages.

That discovery came in the form of fossil meteorites found in a Swedish quarry (Schmitz et al., 2001). Fossil meteorites are meteorites that fell to Earth and were then buried before deteriorating on the surface. In this case, meteorites fell to the ocean floor and were then buried under sediment. Most of the minerals have been replaced, though relict chromite grains exist and the oxygen isotopes, chemical composition, and chondrule size are all consistent with L chondrites (Heck et al., 2009). These fossil meteorites have very short CRE ages of 0.1-1 Ma (errors are ~10--20% depending upon the isotope used), and are found in a limestone layer that is 467.3 ± 1.6 Ma (Heck et al., 2004; Heck et al., 2008). Additionally, these CRE ages increase with higher stratigraphy. These results show that at ~470 Ma, meteorites were ejected from their host body, and meteorites that were in space longer did indeed fall to Earth at a later time. As a working hypothesis, I will assume the fossil meteorites were ejected from the L chondrite parent body during a large impact. Because the Ar-Ar age of many L chondrites are ~500 Ma, it was suspected these meteorites were also involved in the impact that ejected the fossil meteorites at ~470 Ma. Korochantseva et al (2007) was able to identify a trapped
component in a set of L chondrites, and the removal this component gave a weighted average of $470 \pm 6$ Ma, the same as the age of the limestone. The identification of the trapped component was only possible because of Cd-shielding during neutron irradiation, which blocked thermal neutrons, neutrons with the energy range that interacts with Cl (see 2.4.2).

While not nearly as dramatic as the ~500 Ma event on the L chondrite parent body, there is also evidence for an ~800 Ma impact event on the Moon. Impact glasses from different Apollo landing sites, with different chemistries (and hence different source regions), give a tight cluster of ages near 800 Ma (Zellner et al., 2009). This is also the accepted age of the Copernicus event (Bogard et al., 1994). In addition, Cat Mountain (L chondrite) and LAP 031308 (H chondrite), both have Ar-Ar ages close to 800 Ma (Kring et al., 1996; Swindle et al., 2009). The lunar impact glasses combined with the chondrites suggests the possibility of an increase in the impact flux at this time (Zellner et al., 2009).

NWA 091 and Chico, both L chondrites, were irradiated with Cd shielding to provide an opportunity to search for multiple trapped Ar components. Chico, however, was large enough that some of the spallation products were thermalized neutrons capable of interacting with Cl, and this interaction produced $^{38}$Ar during the transit to Earth (Garrison et al., 1992). Because Chico is not a good candidate to search for trapped Ar, I limited my search to NWA 091.
5.2 Ar-Ar Data Collection

All details related to the samples of NWA 091 discussed in this chapter can be found in Section 4.2.5. While I used different splits for diffusion and age analyses, all samples were irradiated in the same quartz tube, so the same reactor parameters (including corrections and method of calculating J values) were used. Errors include uncertainty in J, but not in the decay constant.

5.3 Results

5.3.1 Data Reduction without Using $^{38}$Ar

In this section I reduce the Ar-Ar data using various suggestions that have been used in the past. All of these techniques warrant caution, but are included here to show the techniques most frequently used on meteorites. Here I show the plateau plot without a trapped correction, a reverse isochron without spallation correction, an attempt to remove spallation using the minimum $^{36}$Ar/$^{37}$Ar ratio, and a three-isotope plot normalized to $^{37}$Ar.

Even without a spallation correction, authors often try to glean as much information as possible from a sample by creating a plateau plot and isochron (Bogard et al., 2010). If a trapped component is present, but not removed, the apparent age of each extraction will be artificially old. A reverse isochron can identify this trapped component, but if one does not first remove spallation the resulting $^{36}$Ar/$^{40}$Ar ratio for each extraction will be raised. However, the x-intercept can be pushed one way or another depending upon whether spallation comes out in extractions that have a high or
low $^{39}$Ar/$^{40}$Ar ratio. Figure 5.1 shows the plateau plot with no trapped correction. I can see the effect of trapped gas below $\sim$40% $^{39}$Ar released in all three splits, manifested as decreasing ages with each successive extraction. The gas above $\sim$40% $^{39}$Ar released appears to be partially reset, though the whole spectrum could also be interpreted as a saddle shaped plateau, which would indicate trapped gas at both low and high temperatures.

Figure 5.2 shows the reverse isochron with no spallation correction for split B4, which has the highest temperature resolution of the three splits. As with Section 5.3.2, I will only give a detailed description of split B4, though the story is very similar for the other two splits. Figure 5.2 shows that we do indeed have two trapped components, indicated by the two linear portions with different y-intercepts. The blue filled diamonds form a linear pattern, but the green triangles seem as though they could be part of this line.
as well. All of these points correspond to extractions less than \(\sim 1200 \, ^\circ C\), or \(\sim 90\%\) $^{39}$Ar released. A weighted fit to the blue filled diamonds gives an isochron age of \(\sim 500 \pm 30\) Ma, and the q value (i.e. the goodness of fit, Section 3.2.5) gives a nearly perfect line within error. Fitting the blue filled diamonds along with the green triangles gives an isochron age of \(\sim 420 \pm 10\) Ma, and a q value that indicates it is certainly not a statistically reasonable linear fit. As a side note, the age error is based solely upon the number and error of individual points, hence we need a q value to indicate if the result means anything.

Figure 5.2. Reverse isochron without a spallation correction for NWA 091 split B4. Blue filled diamonds and red squares form linear patterns. Green triangles and blue filled diamonds do not form a statistically rigorous line, but are still similar. With the exception of two green triangles, all filled points with the same color and shape are consecutive extractions. Blue open diamonds are not included in any of the fits. Even without a spallation correction two trapped components are visible, but aren’t as linear as after spallation correction.
These two isochrons nearly span the range of reported ages for most shocked L chondrites, though the best fit gives an age of ~500 Ma, the same (but now known to be slightly old, see Section 5.3.2.3) age that was previously thought to be the catastrophic impact age. The other, steeper, linear portion (red squares) gives an age of ~800 ± ~60 Ma. The other two splits show a similar story, and the best-fit ages are ~470 ± 30 Ma for split B2 and ~550 ± 35 Ma for split B3, though no steeper linear portion is found in these splits. An unweighted average of all three splits, with standard deviation for errors, gives ~505 ± 40 Ma.

One technique to remove the contribution to $^{36}$Ar from spallation is to assume that the spallation is all due to Ca and that the $^{36}$Ar in the extraction with the minimum $^{36}$Ar/$^{37}$Ar ratio is all due to spallation (see Section 2.4.3), and remove that fraction of gas from all extractions (Benedix et al., 2008; Garrison et al., 2000; Swindle et al., 2009). There are two potential problems with this technique. The first is that there is no independent check to see if in fact the minimum $^{36}$Ar/$^{37}$Ar ratio has no trapped gas. If this assumption is wrong, too much $^{36}$Ar will be removed. Even if that assumption is correct, it will not fully correct extractions that have a large spallation contribution from K and/or Fe. As with no removal of spallation, the resulting age can be pushed either direction depending upon the specifics of the sample.

For split B4, the minimum $^{36}$Ar/$^{37}$Ar occurs for two extractions, both well within 1σ of each other, at ~0.01. After applying this correction, many of the points that were close to the shallow linear portion in Figure 5.2 are now well below the resulting line, a strong indication I have removed too much $^{36}$Ar. For the points that remain, I get an
isochron age of $\sim 535 \pm 15$ Ma, again older than the fossil meteorites and about what is seen for many shocked L chondrites. The steeper portion now gives an isochron age of $\sim 900 \pm 65$ Ma. The other two splits give $\sim 520 \pm 30$ Ma for split B2 and $\sim 510 \pm 30$ Ma for split B3, again with no steeper linear portion. An unweighted average of the three splits together, with standard deviation for errors, gives $\sim 520 \pm 10$ Ma. Again, I get an age very close to 500 Ma.

One final technique has been used on a few meteorites (Bogard et al., 2010), though it is unclear why it gives any meaningful age at all. This technique is to make an isochron plot of $^{40}$Ar/$^{37}$Ar vs. $^{39}$Ar/$^{37}$Ar, with the slope of any linear portion giving the age. In order for this technique to work, it requires the trapped Ar to be correlated with Ca for at least a portion of the release, which would be surprising.

As is seen in Figure 5.3, there is indeed an obvious linear portion in split B4 (indicated by closed symbols), and the isochron age is $476 \pm 28$ Ma. The linear portion of the gas is released between $\sim 900$ and 1200 °C, and corresponds to the temperature range over which pyroxene releases its gas (Chapter 4). Evidently the trapped Ar is contained in the pyroxene, and is correlated with Ca. Reasonable fits for split B2 give ages from $\sim 400$ to $\sim 475$ Ma with individual errors of $\sim 20$ to $\sim 35$ Ma. While that does seem promising, the more reasonable fits for B2 are at the lower end of the isochron ages, and split B3 has no linear portion at all. Without good criteria for which isochron of B2 to pick, I pick an age in the middle, and make sure the error bars are large enough to encompass both extremes. This gives an age of $\sim 440 \pm 40$ Ma for B2. An unweighted average of B2 and B4, with standard deviation for errors, is then $\sim 455 \pm 25$ Ma.
Though this result is reasonable (though with fairly large errors), there remains the question of why trapped Ar would be correlated with Ca.

All of the above techniques leave something to be desired. After averaging all the splits together, the different techniques give a range of 455-520 Ma. For an individual technique on an individual split, I can often get a similar range of ages, depending upon which points I include in the linear fit. Previous authors have often only run a single split of a meteorite, which makes deciding on an age even more subjective. In order to give an accurate and precise age for a meteorite, a better technique is needed.
5.3.2 Data Reduction with Spallation Correction

All three splits of NWA 091 have very similar release patterns for all isotopes of Ar. For this reason, I will only give a detailed description of split B4, which had more extractions than the other two splits. Where relevant, differences between splits are discussed. A summary of all three splits is given in Section 5.3.2.3.

5.3.2.1 Identification and Removal of Spallation

In order to properly distinguish trapped $^{36}$Ar from spallation-produced $^{36}$Ar, we must use $^{38}$Ar (see 2.4.3). In order to receive useful information from $^{38}$Ar, I must make sure $^{38}$Ar does not contain Cl-activated argon. Hence, I utilize Figure 5.4. In a plot of $^{37}$Ar/$^{36}$Ar vs. $^{38}$Ar/$^{36}$Ar, a two-component mixture will form a straight line. In this case, the first component is trapped gas ($^{37}$Ar/$^{36}$Ar=0 and $^{38}$Ar/$^{36}$Ar=0.187) and the second is Ca-spallation ($^{37}$Ar/$^{36}$Ar is inversely proportional to the CRE age and $^{38}$Ar/$^{36}$Ar=1.54). Any deviation from a straight line is due either to large contributions from K and/or Fe spallation, or Cl activation.

First, I note that no extraction has a $^{38}$Ar/$^{36}$Ar ratio above the spallation value of 1.54. If there were extractions with such a high $^{38}$Ar/$^{36}$Ar ratio, it would be an obvious sign of Cl activation, because that reaction would produce only $^{38}$Ar (again, see 2.4.3). In fact, none have a $^{38}$Ar/$^{36}$Ar above 0.7, indicating that all extractions have a significant amount of trapped gas, further confirmation that using the method of the maximum measured $^{37}$Ar/$^{36}$Ar ratio to remove spallation would lead to erroneous values.

The linearity of most of the extractions in Figure 5.4 suggests that any deviation from a $^{38}$Ar/$^{36}$Ar of 0.187 for those extractions is indeed due to Ca spallation. For the six
extractions that do not fall on the line, obvious culprits are spallation from K and/or Fe, and Cl activation. The $^{39}\text{Ar}/^{37}\text{Ar}$ ratio of these six extractions is lower than previous extractions, which would seem to rule out K spallation. These six extractions were all consecutively released between 850-1050 °C, around the eutectic temperature of the troilite/Fe-Ni metal system, hinting at Fe spallation. Cl activation is still a possibility, though below I show this is not the case.

I have two choices to remove the $^{36}\text{Ar}$ due to spallation. The first is to extrapolate the linear portion of Figure 5.4 to a $^{38}\text{Ar}/^{36}\text{Ar}$ of 1.54, and use that value of $^{37}\text{Ar}/^{36}\text{Ar}$ to subtract out the Ca-spallation. The other method is to use only $^{38}\text{Ar}$ and $^{36}\text{Ar}$, and assume the measured $^{38}\text{Ar}/^{36}\text{Ar}$ ratio for each extraction is due to mixing various amounts of trapped gas ($^{38}\text{Ar}/^{36}\text{Ar}$ of 0.187) and K/Ca/Fe spallation ($^{38}\text{Ar}/^{36}\text{Ar}$ of 1.54). I use the

Figure 5.4. Plot showing the relationship between $^{38}\text{Ar}$, $^{37}\text{Ar}$, and $^{36}\text{Ar}$. Diamonds (closed) indicate extractions that form a straight line, while squares (open) indicate extractions that deviate from a straight line. An unweighted fit to the closed diamonds is also shown.
latter method because it incorporates spallation from all three elements instead of just Ca, though the former method gives very similar results. The spallation-corrected reverse isochron is shown in Figure 5.5. The biggest difference between the two methods of spallation reduction occurs, unsurprisingly, for the six extractions that fell off the line in Figure 5.4. Three of the six extractions are the rightmost closed blue diamonds of Figure 5.5, which are now colinear with the rest of the points, which suggests that Fe spallation was indeed the culprit. The other three extractions are the open blue diamonds between a $^{39}\text{Ar}/^{40}\text{Ar}$ ratio of 0.015 and 0.02, which are now close to, but still slightly above, the line. Cl contamination does not explain these extractions, because that would have the effect of removing too much $^{36}\text{Ar}$, causing them to fall below the line. These extractions remain a mystery, though they are now at least within 2σ of the line.

5.3.2.2 Identification and Removal of Trapped Gas

Having removed the contribution from spallation, I can now determine the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of the trapped component, and thus determine the plateau age of NWA 091 split B4. To do this, I actually reduce the data twice. I first include all the gas that reasonably forms a line in the reverse isochron plot, excluding the problematic extractions discussed in the above paragraph, and perform the full reduction with that data (i.e. trapped component and plateau age). I then determine which extractions have an age that is zero to within 2σ, and perform the entire reduction again without these extractions. The reason for excluding the extractions that have an age of zero to within 2σ is because I do not wish to include gas that has been partially reset. Additionally, these extractions have large errors, and will only inflate the final error without providing
For each split, the first and second reductions give plateau ages that are the same to within 1σ.

For each instance of line fitting on the reverse isochron plot, I perform a weighted fit of the previously selected values. In both cases the q (i.e. the goodness of fit, Section 3.2.5) does indeed indicate a statistically significant line. The intercept of this line then gives the $^{36}\text{Ar}^{40}\text{Ar}$ ratio for the trapped component. I then use this trapped $^{36}\text{Ar}^{40}\text{Ar}$ ratio and the measured amounts of $^{36}\text{Ar}$ to calculate the amount of trapped $^{40}\text{Ar}$ in each step, which I then subtract from the total amount of $^{40}\text{Ar}$, leaving only radiogenic $^{40}\text{Ar}$.

For the plateau plot, the plateau age is calculated by summing together gas from all the

Figure 5.5. Reverse isochron after $^{36}\text{Ar}$ spallation removal. One trapped component is represented by blue diamonds (open or closed), the other by red squares. A green line shows the weighted fit of the closed blue diamonds, while a purple line shows the weighted fit of the red squares.
extractions that were included in the linear fit. Various alternative methods of calculating a plateau age (weighting by errors of individual extractions, weighting by number of extractions, etc.) all give plateaus ages that are within the stated errors. For split B4, the final selection of points is indicated by closed symbols in Figure 5.5, and the final plateau plot is shown in Figure 5.6. Also shown in Figure 5.5 are the two linear fits showing the two trapped components.

The above scenario works very well for splits B2 and B4. Split B3 requires special treatment. After the first round of data reduction, one of the extractions on the plateau plot falls below the plateau and has fairly large errors, but not so large that they overlap zero at 2\(\sigma\). I do not wish to include extractions with partial resetting, yet at the same time this extraction has a very small amount of \(^{39}\)Ar and thus provides the most accurate measurement of the trapped component. Ultimately I have decided to reduce the data both with and without this extraction, and refer to these two reductions as “reduction 1” and “reduction 2”, respectively. Note that neither of these reductions include the points whose apparent age is within 2\(\sigma\) of zero.

5.3.2.3 Comparison of Splits

The trapped component and plateau ages for all splits are listed in Table 5.1, and all plateau plots are shown in Figure 5.7. B3 in Figure 5.7 shows the plateau plot for “reduction 2”. Isochron ages are not reported here, but are the same as the plateau ages within error, as they should be, given the mathematical relationship between the two presentations. The first 3% of the gas of B2 and B4, and the first 5-7% of gas in B3, had a very large trapped contribution to the total \(^{40}\)Ar, and hence after the removal of trapped
gas those steps have very large errors on the plateau plot. Some of this gas also probably contained adsorbed terrestrial air. Hence, it is not used to calculate the plateau ages, though in split B3 we did include a small amount of it for one of the reductions. The gas that is released between ~32 and ~42 %$^{39}$Ar released (depending on the split) gives an apparent age less than the plateau. On the reverse isochron plots, these extractions correspond to values that are slightly above the linear fit, and on the release plots they correspond to a transition from the low temperature to high temperature release (see Figure 4.11 for the same effect in a different split). These extractions probably indicate weathering or partial resetting, and are also not included in either the plateau age or the linear fit on the reverse isochron. Including the first few extractions of each split and the
gas between the high and low temperature release produces a ~3–12 Ma change in the plateau age, but increases the error bars from ~10 Ma to ~20–27 Ma.

The plateau plots of the three splits are all very consistent, though split B4 deviates from the other two splits above ~90% $^{39}$Ar released. This is because low resolution prevented me from identifying a second trapped component in the other two splits. Hence, I used a single trapped component for the entire release, when I most
likely have two components for all three splits. Because I “removed” a trapped component that had an inappropriately high $^{40}$Ar/$^{36}$Ar, these splits have an apparent age $\leq 500$ Ma above $90\%$ $^{39}$Ar released. If I were to use the second trapped component identified in split B4, and apply it to the last 10% of gas released in the other two splits, three of the four large extractions in split B2 are 800 Ma to within 2σ, and the large extraction in split B3 is ~1100 Ma. While B3 gives a high temperature age that is not consistent with an 800 Ma event, B2 does hint at an event at 800 Ma, indicating this event is probably real.

The gas below ~90% $^{39}$Ar released forms an unquestionable plateau, and all three splits agree on the age to within 1σ. To combine both reductions for B3, I average the plateau ages together, and use the largest error of the two samples. This gives 476.0 ± 14.5 Ma. Now, I can combine the three splits together to form a mean age weighted by the inverse of the errors, with a final error equal to the inverse sum of the squared errors. This gives an event at 475.4 ± 5.9 Ma. Interestingly, the gas from ~5-30% $^{39}$Ar was identified in Chapter 4 as corresponding to shocked feldspar, while that of the gas from ~40-90% $^{39}$Ar released was identified as corresponding to feldspar enclosed in pyroxene. Both of these Ar domains contribute to the ~470 Ma plateau age above. The gas above ~90% $^{39}$Ar released corresponds to the second high temperature release mentioned in Chapter 4, whose release pattern could not be easily modeled, and gives a plateau age of ~800 Ma.
5.4 Discussion

5.4.1 Trapped Ar

All three splits have a trapped Ar component that has a $^{40}\text{Ar} / ^{36}\text{Ar} < 290$, confirming the need to remove a trapped component to obtain an accurate plateau age. Split B3 “reduction 2” has a trapped $^{40}\text{Ar} / ^{36}\text{Ar}$ ratio that has overlapping 1σ error bars with terrestrial air, but the other reduction and the other two splits don’t overlap until >2σ. This component appears to be distinct from air, but is close enough to warrant suspicion.

Korochantseva et al. (2007) noted that the low temperature isochron they identified could be due to slightly fractioned terrestrial argon acquired through weathering. In the case of NWA 091, that is more difficult because the gas from ~40-90% $^{39}\text{Ar}$ released is the gas that is identified in Chapter 4 as originating from feldspar enclosed in pyroxene, and is certainly not the low temperature gas. The linearity of the isochron referenced to $^{37}\text{Ar}$ shows that the trapped component is indeed contained in the pyroxene. Pyroxene is resilient to weathering, and furthermore, weathering should cause loss of radiogenic $^{40}\text{Ar}$, something which is not seen. The other explanation by Korochantseva et al. (2007) for the trapped Ar component is an equilibration between primordial argon (Section 2.4.1) and mobilized radiogenic argon. While this does explain my results, it begs another question. In order for a heating event to cause equilibration of argon, instead of simply causing argon to be lost to space, a non-zero argon pressure must be maintained at the grain surface. While this is certainly possible, it is currently unclear how that would occur, and why the $^{40}\text{Ar} / ^{36}\text{Ar}$ ratio would be so close to air.
In addition to a trapped component that appears to be contained in feldspar enclosed in pyroxene, a second trapped component (which is definitely not terrestrial) is found in the gas that corresponds to the second high temperature release identified in Section 4.4. The source of this Ar domain is unknown, but based upon the results in Chapter 4, it appears to be either feldspar enclosed in large pyroxene grains, or feldspar enclosed in olivine. Because it has a trapped component that is different from the first high temperature release, a chemical difference between these two releases is highly suggestive. Figure 4.15 indicated Chico may contain feldspar enclosed in olivine, and this second trapped component may indicate NWA 091 also contains feldspar enclosed in olivine.

5.4.2 Significance of Plateau Ages

Korochantseva et al. (2007) was able to link L chondrites to Ordovician fossil chondrites by identifying and removing a non-terrestrial and non-primordial trapped Ar component from the measured $^{40}$Ar. Here I have presented the first independent confirmation of that link. Although other plausible data reduction techniques give relatively precise ages that scatter around the stratigraphic age of the fossil meteorites, using multiple samples and best-practice data reduction yields an age that agrees with the fossil meteorites, with relatively small uncertainties. Additionally, I have shown that NWA 091 records evidence of an event at 800 Ma, which coincides with a large scale resetting event on the Moon, as well as the age of some H and L chondrites (Zellner et al., 2009).
CHAPTER 6

CONCLUSIONS

The goal of this dissertation was to determine
1) the source(s) of K in L chondrites
2) well-defined diffusion properties of those sources when both shocked and unshocked, and
3) the presence of any trapped (i.e. non-radiogenic) Ar component.

All three of these points have been addressed. The dominant source of K in ordinary chondrites is oligoclase feldspar, which I determined via a K mass balance of the Chico meteorite based on electron microprobe measurements. Neither pyroxene nor olivine have any measurable K, and the amount of K contained in the feldspar matches the amount of K as determined by Ar analysis. Raman spectroscopy of the feldspar in Chico shows that the feldspar is structural feldspar, and not maskelynite or NaAlSi₃O₈-hollandite.

The Ar diffusion experiments I performed on terrestrial albite show that shock has an obvious effect on the activation energy (E). The E for unshocked albite is 46.0 ± 2.8 kcal/mol, while the E for all shock pressures ≥29 GPa and ≤55.8 GPa are 24.5 ± 2.4 kcal/mol. The Ar diffusion experiments on the terrestrial pyroxene show a somewhat similar story. For a rock of three different pyroxene compositions, I get an E of 130.9 ±
9.5 kcal/mol for the unshocked rock, and an E of 82.1 ± 7.8 kcal/mole for the shock pressures of 30 and 60 GPa. However the story is not so simple, because a high-Ca pyroxene mineral separate from the unshocked rock gives an E of 105.0 ± 1.8 kcal/mol. Furthermore, about one of every three pyroxene splits give a diffusion rate that is unusually high, and often does not follow a simple Arrhenius behavior. So while it does appear that shock lowers the E, the variability of the splits cautions against drawing strong conclusions. Naturally shocked pyroxene samples seem to have an even wider range of E than seen here, perhaps suggesting an effect due to composition instead of shock. Further work is needed to accurately determine the E of both shocked and unshocked pyroxene, but with the data in hand I can say that pyroxene has a very large E, typically >80 kcal/mol. The effect of shock on Ar diffusion in olivine was not determined, but the results presented here and from earlier work give an E of 30-45 kcal/mol.

The Ar diffusion parameters of whole rock splits of Chico and NWA 091 confirm that the low temperature release in both samples is due to feldspar. In the case of Chico, most of the gas is from structural feldspar, though a small amount is also from shocked feldspar. NWA 091 has only shocked feldspar at low temperature. In both NWA 091 and Chico, the high temperature release has an E very similar to that of pyroxene. I created a two-domain model using diffusion parameters similar to shocked feldspar and pyroxene, and this model mimics the data for NWA 091 fairly well. Since all of the K in meteorites appears to be in the feldspar, the logical conclusion is that the high temperature release is due to feldspar enclosed in pyroxene, and hence forced to outgas as
pyroxene. At temperatures above ~1200 °C, NWA 091 gives a behavior different from that of the simple model, indicating there is another domain (either size or chemical) at high temperature. I would need higher temperature resolution over this portion of the release to perfect the diffusion model. Looking at the thin section of Chico, I do indeed see feldspar that appears to be enclosed in pyroxene, but I also see feldspar that appears to be enclosed by olivine, and olivine seems to enclose more feldspar than the pyroxene. This is opposite to what the diffusion parameters tell me. To resolve this issue, a more thorough examination of more thin sections from more meteorites is needed, and tomography data would be ideal since it gives a three-dimensional image. Regardless of which mineral, if any, encloses a large fraction of the feldspar, this work shows that the high temperature release is indeed from the feldspar, and something external to the feldspar seems to be required to retain radiogenic $^{40}$Ar at that temperature.

The Ar-Ar plateau age of 475 ± 6 Ma for NWA 091 confirms the link between L chondrites and fossil meteorites from Sweden, indicating a collisional impact on the L chondrite parent body at ~470 Ma. This plateau is only visible after removal of a trapped Ar component that is close in composition to air, but given that this trapped Ar is contained in pyroxene, it is unlikely to be terrestrial contamination. A second trapped Ar component, which is definitely not air, is found in the gas released above ~1200 °C and gives a plateau age at ~800 Ma. This gas corresponds to the portion of the release curve that was not captured by the simple two-domain diffusion model, and since it has a different trapped component, I propose it is due to a different chemical domain, probably olivine. The plateau age of ~800 Ma is not unique in the collisional impact record, but
instead corresponds to ages on the Moon, as well as some H and L chondrites, suggesting an increased impact flux at that time.
APPENDIX A

DEVIATIONS FROM NORMAL PHASE SEPARATION

Albite:

B10: In this sample, the largest q*N occurred at a Low temperature (T) cutoff of 445 °C. However, the 445 °C steps had very large errors. Hence I choose the second highest q*N, which was 502 °C, and gave the same E to within 2σ. I have less data for this sample than for most because only the 502 °C temperature had a re-extract. All other temperatures only had a single extraction. Nonetheless, it is included along with the other unshocked samples.

A6: The highest q*N occurs for a Low T cutoff of 445 °C. However this leads to an obvious curve of the Arrhenius plot (see last paragraph of Section 3.2.5), so I choose a low T cutoff of 330 °C.

A7: The largest q*N occurs for a cutoff of 445 °C and gives an E of 32.1 ± 1.2 kcal/mol, but that corresponds to cutting out 10% of the gas. Additionally, this sample is the same shock pressure and grain size as A6, which showed a curve of the Arrhenius plot at a 445 °C cutoff. Both of the cutoff temperatures below 445 °C also give decent q*N, so I choose the larger of those two, giving a cutoff of 330 °C, while only cutting out 1.58% of the gas.
B2: Another sample for which it is difficult to determine $E$. This sample has the same behavior as A7, and is given the same treatment.

B4: No re-extracts were performed on this sample, so one should be a little cautious. Highest $q^*N$ occurs with no cutoff, and gives an $E$ of $21.8 \pm 0.3$ kcal/mol. However, for consistency with other samples, I choose a low $T$ cutoff of $330 ^\circ C$, which still gives a high $q^*N$ and only raises the $E$ to $22.7 \pm 0.4$ kcal/mol.

B5: Despite being linear on an Arrhenius plot, this sample gives problems with the usual procedure as well. The highest $q^*N$ occurs when no gas is removed. The second highest $q^*N$ occurs at a cutoff of $330 ^\circ C$. The former gives an $E$ of $20.6 \pm 0.7$ kcal/mol, while the latter gives an $E$ of $24.2 \pm 0.6$ kcal/mol, so it makes a difference. Because B3 (which is the same shock pressure) and all of the other shocked samples have a cutoff of at least $330 ^\circ C$, that is the cutoff I choose.

High-Ca Pyroxene:

J3: This sample has about 13% less Ca than the other two samples, so I probably have a different modal abundance from the other samples, though it’s still mostly high-Ca Pyx. This sample also appears to have two releases, the first of which contains ~20% of the total $^{37}$Ar. This is too much to be from a low-Ca phase, because a sample that had 20%
of the Ca in pigeonite and 80% of the Ca from high-Ca Pyx would only have ~3.5 wt% Ca, much lower than the actual 14.82 wt% Ca. Additionally, because the first and second releases do not have the same E, it is not due to a grain size effect.

The best I can do is separate it into two releases and measure values. Based upon the largest q*N, the low T cutoff for the first release should be 903 °C. The high T cutoff within reasonable values has no effect on E to within error. I’m choosing to include 1017 °C in the low T release because without it I would not have four unique temperatures. I then get an E of 207 ± 15 kcal/mol for the first release. For the high T release, I choose a cutoff of 1017 °C because it produces the highest q*N. This does mean the 1017 °C steps are included in both releases, but given the inherent difficulty of this sample it is the best I can do. The highest q*N is over five unique temperatures, and gives an E of 104 ± 6 kcal/mol. Given the odd nature of this sample, the stability of E in the high T release, and similarity of E in the high T release as compared to other samples, I believe I should tentatively ignore the low T release.

Whole Rock Pyroxene:

T1: No linear trend found.

T2: This sample used temperature ramping, and hence had two sets of extractions for some temperatures. The highest q*N occurs for a low T cutoff of 1019 °C (2nd pair), which excludes the 1076 °C (1st pair), cutting out gas from a high temperature. Each
time the low T cutoff is lowered the E also lowers outside of error, probably indicating I’m cutting out gas that belongs in the domain, which artificially increases the E. If the low T cutoff is 1076 °C (1st pair) or lower, the E only changes within error. Hence, I require the low T cutoff to be 1076 °C (1st pair) or lower. With this limit, the highest \( q^*N \) then gives 1076 °C (1st) for the low T cutoff. This results in an E of 73.6 kcal/mol, which is ~50 kcal/mol less than the unlimited highest \( q^*N \).

T4: No linear trend found.

T7: This sample has the same behavior and T2, and is given the same treatment. The highest \( q^*N \) then occurs for a low T cutoff of 903 °C, and gives an E of 129 kcal/mol, which is ~30kcal/mol less than the unlimited highest \( q^*N \).

T8: Most D/a\(^2\) values deviate by about one order of magnitude from the other whole rock Pyx samples (Figure 3.12). It does give a good linear portion that has four unique temperatures, but the resulting E is about a factor of three less than the other samples.

T9: This sample also has D/a\(^2\) values that deviate about one order of magnitude from the other whole rock Pyx samples (Figure 3.12). Additionally, the only points that form a line give a \( q^*N \) that is about an order of magnitude lower than any other pyroxene sample, and the q itself is getting close to a value that would disqualify the points from forming a line. Nonetheless, it does (barely) meet the criteria for a line.
Chico Meteorite:

A4, low T release, $^{37}$Ar: The largest q*N for the first and second linear portions occur at different high T cutoffs. Because all the diffusion parameters are the same to within error, I choose the temperature step that has the least amount of gas prior to the temperature cycle. This is 900 °C (1st pair).

A2, low T release, $^{39}$Ar: The largest q*N occurs for a low T cutoff of 450 °C, however this constitutes nearly all the gas in the first linear portion, and probably artificially increases the E of both portions. Hence, I choose the second largest q*N, which occurs for a low T cutoff of 350 °C. If I were to instead choose the largest q*N, the first and second linear portions then have an E of ~32 and ~51 kcal/mol, respectively. However, this requires the 600 °C steps to be part of both linear portions, and choosing this higher cutoff is probably artificially increasing the E by removing too much gas (see Figure 3.2), so it is not used.

A2, low T release, $^{37}$Ar: The highest q*N occurs for a high T cutoff of 1050 °C, though the resulting line definitely has curvature (see last paragraph of Section 3.2.5). Here I choose a high T cutoff of 900 °C because the largest q*N for that cutoff then constitutes six different temperatures (other high T cutoffs give a largest q*N of only five different temperatures). Choosing a different high T cutoff would only produce changes within error.
A4, high T release, $^{39}$Ar: The highest $q^*N$ occurs for a low T cutoff of $925^\circ$C, though I suspect that cutoff removes too much gas. The second highest $q^*N$ occurs for a low T cutoff of $900^\circ$C (2$^{nd}$ pair) and gives an $E$ of $\sim140$ kcal/mol, which is $\sim20$ kcal/mol less than for the highest $q^*N$. Cutoffs less than $900^\circ$C (2$^{nd}$ pair) give diffusion parameters that are the same to within error, further indication I should not use a cutoff of $925^\circ$C.

A4, high T release, $^{37}$Ar: Same argument as for the $^{39}$Ar from this sample. A low T cutoff of $950^\circ$C (1$^{st}$ pair) gives an $E$ of $\sim130$ kcal/mol, which is $\sim20$ kcal/mol less than the highest $q^*N$.

A2, high T release, $^{37}$Ar: None of the cutoffs give anything that is statistically a line. Here I choose the most points that seemed to visually follow a line, though I caution against drawing any strong conclusions from this result.

NWA 091 Meteorite:

B5, low T release, $^{37}$Ar: As described in Section 4.3.3.3, this release includes gas from another phase, but due to temperature overlap and the small number of points available it cannot be separated out from the main release. Additionally, because this phase begins outgassing at a low temperature, the range for low temperature cutoffs contain a
significant amount of gas from two different releases, and the largest q*N is no longer a valid tool. Rather than using arbitrary criteria, I instead chose the same cutoff that was determined for the low T release of $^{39}$Ar, which is 400 °C. The high T cutoff is determined using the normal criteria.

B1, low T release, $^{37}$Ar: Only the 450 °C cutoff produces a set that is statistically a line. If I were to ignore the statistical analysis and choose a 400 °C cutoff, the E would be ~24 kcal/mol, instead of ~36 kcal/mol. This drastic change in E indicates I’m probably removing too much of the gas (see Figure 3.2). Additionally, the later extractions do not fall reasonably close to the linear extrapolation determined from a 450 °C cutoff, though they do fall right on top of the linear extrapolation created from a 400 °C cutoff. The small q for the 400 °C cutoff stems from the re-extracts only having overlapping errors at the ~3σ level. Neither cutoff is ideal, so I choose the only cutoff that matches the criteria in Section 4.3.3.1.

B5, high T release, $^{39}$Ar: The highest q*N occurs for a low T cutoff of 900 °C (2nd pair), but the E is >2σ away from the E of the next lowest cutoff, probably indicating that cutoff is artificially increasing the E. The second highest q*N occurs for a low T cutoff of 850 °C, but here temperature cycling gives values for log D/a2 that are different by ~3σ. For this release I instead choose the third highest q*N, a low T cutoff of 900 °C (1st pair), because temperature cycling then gives values for log D/a2 that are the same to within 2σ. Compared to a cutoff of 900 °C (1st pair), which gives ~112 kcal/mol, a cutoff
of 850 °C gives an $E \sim 10$ kcal/mol lower, while a cutoff of 900 °C (2\textsuperscript{nd} pair) gives an $E \sim 53$ kcal/mol higher.

B5, high T release, \textsuperscript{37}Ar: Here again, the largest q*N occurs for a low T cutoff of 900 °C (2\textsuperscript{nd} pair), but gives an $E$ that’s probably too high. The second highest q*N is for a low T cutoff of 950 °C (1\textsuperscript{st} pair), and during temperature cycling this cutoff also gives values for log D/a\textsuperscript{2} that are the same to 2σ. The result for 950° (1\textsuperscript{st} pair) is $\sim 32$ kcal/mol less than that of the highest q*N, which gives $\sim 144$ kcal/mol.
REFERENCES


