CONTROLS OF HELIUM DIFFUSION IN CALCITE, ARAGONITE, AND DOLOMITE

by

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3He diffusion rates have been measured and interionic aperture sizes have been estimated for three gem carbonates: calcite, aragonite, and dolomite. Small wafers of calcite, aragonite, and dolomite were implanted with 3MeV of 3He at a dose of $5 \times 10^{15}$ 3He/cm$^2$ and annealed in 1-atm furnaces between 78-400°C. 3He distributions after annealing were measured with nuclear reaction analysis using the reaction $^3$He(d,p)$^4$He. 3He diffusion in calcite has produced the following Arrhenius relationships:

$$D_{\parallel c} = 2.82 \times 10^{-11} \exp(-46.42 \text{ kJ mol}^{-1}/RT) \text{ m}^2\text{sec}^{-1} \quad (146-400°C)$$

$$D_{\perp \text{cleavage}} = 8.14 \times 10^{-9} \exp(-54.53 \text{ kJ mol}^{-1}/RT) \text{ m}^2\text{sec}^{-1} \quad (78-300°C)$$

In calcite, distinct diffusional anisotropy is observed with 3He diffusion normal to cleavage occurring roughly two orders of magnitude faster than diffusion along the c-axis. However, the estimated activation energy of the c-axis (46 kJ/mol) remains comparable to the activation energy calculated normal to cleavage (55 kJ/mol). One 3He diffusion rate of $7 \times 10^{-18}$ m$^2$sec$^{-1}$ at 201°C was collected for dolomite perpendicular to cleavage. This rate is ~2-3 orders of magnitude slower than diffusion in calcite in the same direction. Implanted aragonite samples were annealed at temperatures similar to that of calcite and dolomite samples but for longer periods of time. However, no movement of 3He was observed in aragonite and thus no diffusion rates were able to be collected. Comparing aragonite's heating schedules to that of calcite and dolomite suggests that the upper bound of helium diffusion in aragonite is approximately three orders of magnitude slower than that of calcite; however, distinct structural differences between the lattice structures of calcite and aragonite make such comparisons difficult.

Lattice models of calcite, aragonite, and dolomite were created using CrystalMaker© and MATLAB® in order to estimate the size and distribution of interionic apertures along major crystallographic axes. Of particular interest is the maximum aperture size, i.e. the largest aperture found in each cross-section along the axis of study. Aperture statistics were compared to diffusion rates and axes with relatively slow diffusion rates were found to contain smaller maximum apertures. An aperture-controlled diffusion model is therefore proposed in which diffusion rate along each major crystallographic lattice axis is primarily controlled by the size of the smallest maximum apertures.

Diffusion data and aperture sizes of calcite and dolomite compared to other geochronometers additionally agree well with the aperture controlled diffusion model and may explain the low helium retention rates observed in many natural carbonates. Relatively high rates of diffusion, low activation energy, and low closure temperatures calculated for calcite suggest the mineral may be an excellent low temperature geochronometer for both thermochronology and cosmogenic dating. However, calcite’s highly variable helium retention rates and potentially complicated diffusion dynamics preclude its use until a solid understanding of the helium-calcite system is gained.
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1. INTRODUCTION

Thermochronometry and cosmogenic dating techniques have been used for decades to study tectonics, geomorphology, resource maturation, and many other processes which involve the understanding of absolute cooling histories and exposure ages of specific rocks. For such techniques, either $^4\text{He}$ or $^3\text{He}$ is often measured in minerals, such as apatite (Wolf et al., 1996), titanite (Farley et al., 1999), and zircon (Reiners et al., 2002; Reiners et al., 2004), all of which do not readily lose helium at surface temperatures (i.e. below ~50° C) (Dodson, 1973). Cooling histories and exposures ages can only be found by first knowing the past rate of helium production in a sample, how helium diffuses within that sample, at what temperature significant helium is lost from the minerals in the sample (the closure temperature), the rate of helium loss at a given temperature, and the current amount of helium in the mineral (Ehlers & Farley, 2003).

Since the conceptualization of radiometric dating of calcite (Rutherford, 1905), significant research has focused on experimentally measuring the He retention of natural carbonates to determine their applicability for radiometric dating. These studies have produced a very limited understanding of the extent to which helium remains in carbonates of varying origins and at different temperatures. Results from Amidon et al. (2008) and Copeland et al. (2007) suggest at least some carbonates can adequately retain helium for the purposes of thermochnology and cosmogenic dating. However, it would seem from the conclusions of Fanale & Kulp (1961), Fanale & Schaeffer (1965), Bender et al. (1973), Keevil (1950), and Hobbs and Amidon (unpublished data) that not all calcite and certainly not all carbonates have predictable helium concentrations due to
insufficient He retention, common helium, inherited helium, or complicated microstructures. It is still unclear as to what characteristics separate retentive carbonates from those that are unretentive. Only recently has there been an effort to specifically characterize the diffusive behavior of helium within carbonates and relate that understanding to retention. In particular, results from step heating experiments by Copeland et al. (2007) suggest many carbonates of different origins display similar diffusivities and closure temperatures.

This research therefore aims to determine what factors control He diffusion and retention in calcite, aragonite, and dolomite in order to facilitate the development of straightforward, repeatable thermochronometry and cosmogenic dating methodologies. Specifically, $^3$He implantation, diffusion, and profiling experiments were conducted according to Cherniak et al. (2009) along major crystallographic axes to characterize diffusion. Diffusion data were compared to interionic aperture (i.e. spacing) size and frequency, the hypothesized primary control on diffusion behavior, along the same axes. Diffusional anisotropy, observed from two directions of diffusion in calcite, and the relative diffusion rates of carbonate minerals were found to correlate well with aperture estimates derived from mineral lattice models created in CrystalMaker© and MATLAB®. Activation energies and closure temperatures were calculated from Arrhenius relationships for calcite samples in this study and were found to be much lower than those collected from near-congruous samples by bulk diffusion.
2. THEORY OF HELIUM DIFFUSION

2.1 Sources of Helium

Helium isotope production can be attributed to two main processes. Radioactive series decay of primarily $^{238}\text{U}$, $^{235}\text{U}$, $^{232}\text{Th}$, and $^{147}\text{Sm}$ produce stable $^4\text{He}$ atoms, called alpha particles, at rates unique to the decaying isotope (Figure 1). These most prevalent radioactive isotopes are naturally concentrated in trace amounts in certain accessory minerals that are found in a great variety of rocks, including carbonates, and are thus the primary source of in-situ $^4\text{He}$ (Rutherford, 1905). He derived from the mantle, crust, or metamorphic fluid is often trapped in fluid and gas inclusions of calcite and other minerals but is of varying importance depending on the relative abundance of in-situ $^4\text{He}$ (Farley & Neroda, 1998).

![Simplified model of radioactive alpha decay](image)

**FIGURE 1** Simplified model of radioactive alpha decay. The radioactive and, therefore, unstable $^{235}\text{U}$ nucleus will eventually split spontaneously into two daughter products: $^{231}\text{Th}$ and an alpha particle ($^4\text{He}$). $^{231}\text{Th}$, itself unstable, will eventually radioactively decay as well, producing two new daughter nuclides. This process will continue through the U-series decay chain, producing alpha particles at many decay points, until the relatively large but stable $^{207}\text{Pb}$ nuclide is reached. The average rate at which each radioactive isotope decays is specific to the isotope and is based on its stability. Knowledge of decay rates and the number of parent and daughter products within a sample are central to the application of radiometric dating.
The other stable helium isotope, $^3$He, is much less abundant and typically produced in rocks and soil located less than ~3m below the surface by cosmic-ray spallation reactions. These reactions occur when high-energy neutrons bombard and split the atoms of surface rocks into $^3$He and other nuclides (Figure 2). The rate of cosmogenic $^3$He production at a given point is largely dependent on the cosmic-ray flux which, in turn, is a factor of elevation, burial depth, and latitude (Gosse & Phillips, 2001).

![Spallation in minerals](image)

FIGURE 2 Cartoon of in-situ cosmogenic $^3$He production by spallation reactions. High-energy cosmic rays, particularly high mass, high velocity neutrons that are relatively unhindered by the atmosphere, bombard atoms of surface rock and soil. This impact can split atoms, producing a variety of nuclides including $^3$He.

### 2.2 Basics of Temperature-Driven Noble Gas Diffusion

Noble gas diffusion has been studied in great detail for a number of minerals (see Baxter, 2010). Helium, like other noble gases, is unpolarized and does not typically interact chemically with minerals such as calcite, aragonite, and dolomite. He is also relatively small with an ionic radius of 0.90 Å and 1.08 Å in 4- and 6-fold coordination, respectively (Zhang & Xu, 1995). Despite relatively large disparities in mass (3 Da vs 4
Da), $^3$He and $^4$He have similar diffusion rates, at least in apatite, olivine, and titanite (Shuster et al., 2003).

The behavior of noble gases in minerals has been observed to be highly temperature dependent such that, at low temperatures, noble gases remain essentially trapped within the lattice of minerals; however, with enough energy at higher temperatures, the lattice will distort randomly allowing for the gas to make a diffusion jump within and potentially out of minerals (Harrison & Zeitler, 2005). Diffusion of noble gasses follows Fick’s first law which describes the preferential flux of diffusants from areas of high concentration to those of low concentration proportional to the concentration gradient (Fick, 1855). The rate of noble gas diffusion in minerals continues to increase with temperature as gases become more energetic. Such temperature-dependent diffusion can be modeled using an Arrhenius equation (Equation 1) in which $D$ is the diffusion coefficient, $D_0$ is the frequency factor, $E$ is the activation energy, $R$ is the gas constant, and $T$ is absolute temperature.

$$D = D_0 \exp\left(-\frac{E}{RT}\right)$$

(1)

This relationship can be represented graphically using an Arrhenius diagram (Figure 3) in which log $D_0$ is the x-intercept and the slope of the line is equal to $E/2.303R$ (Harrison & Zeitler, 2005).
Central to isotope geochronology is an understanding of a system’s closure temperature. Simplistically speaking, the closure temperature is the absolute temperature below which the isotope, in this case He, is inactive enough to not diffuse out of the mineral containing it at a significant rate (Dodson, 1973). Ideally, the ages produced by thermochronology represent the time since the sample cooled below the closure temperature. Prolonged heating of a mineral above its closure temperature will result in diffusion of all helium out of the mineral essentially restarting the thermochronological clock. However, if the mineral experiences temperatures near the closure temperature, then only some of the isotopes may be released. In nature, this occurs in a “partial
retention zone” which is defined by a temperature range in which diffusion systems transition to and from an open state to a closed state (Wolf et al., 1998). Without significant corrections for partial retention, isotope geochronology analysis of the rock produces an erroneous age. Relatedly, the cosmogenic $^3$He content of a rock may occasionally be the product of multiple exhumation cycles. It is not unusual for rocks that are brought at or near the surface to be re-buried and eventually exhumed once more. If the rock does not exceed its He closure temperature for very long during burial, then some $^3$He will be inherited from previous exposure to cosmic rays.

### 2.3 Mineral Structures of Calcite, Aragonite, and Dolomite

Calcite (CaCO$_3$) (Figure 4a) is a widely abundant mineral found in sedimentary, metamorphic, and igneous rocks and has highly variable crystallographic- and micro-structure. Most commonly, calcite is trigonal with prominent, perfect cleavage along [10$ar{1}$1] faces and strong twinning often along [01$ar{1}$2] and [0001]. Optically continuous, gem quality samples used in this study are assumed to have this “ideal” structure with relatively few imperfections or inclusions. Calcite additionally has over 800 different morphologies including many that are crystalline, granular, stalactitic, concretionary, massive, and rhombohedral. Similarly, calcite twinning ranges from fibrous, to granular, lamellar, or compact (Nesse, 2000).

Dolomite, CaMg(CO$_3$)$_2$ (Figure 4c), is the principle mineral of dolostone and metadolostone and is often a secondary component of calcite-dominated limestone and marble. Dolomite has the same trigonal lattice structure as calcite but replaces every other sheet of Ca with Mg, resulting in slightly different atomic and ionic radii as well as unit cell dimensions. Cleavages, however, remain perfect along the same three faces, [10$ar{1}$1].
Twinning behavior is similar to calcite as well, with twins common on [0001], [1010], and [11\(\overline{2}0\)]. Lamellar twins are notably found on [02\(\overline{2}1\)]. Dolomite morphology is frequently rhombohedral, prismatic, granular, or massive (Nesse, 2000).

Aragonite (Figure 4b) is the second most common polymorph of CaCO\(_3\), second only to calcite, and is formed in a much more specific range of low-temperature, near surface environments. Aragonite is typical of speleothems, geyser deposits, marine oolites, and as a replacement mineral in a variety of rocks. The orthorhombic mineral lattice structure differs from calcite and dolomite, as are aragonite’s most defined [010] cleavage and [110] cyclical twinning. Crystals are often prismatic, stalactic, or tabular (Nesse, 2000).

![Figure 4](image_url)  
**FIGURE 4** Idealized ball and stick models of (a) calcite, (b) aragonite, and (c) dolomite lattices. Carbon atoms are represented as black spheres, oxygen is red, calcium is green, and magnesium is blue. Atom spheres are not representative of ionic radii size.

### 2.4 Anisotropic Diffusion

One essential aspect to understanding helium diffusion in calcite, aragonite, and dolomite is determining if helium preferentially moves through their lattices in specific directions. Such directed movement of diffusants is commonly referred to as anisotropic diffusion. \(^3\)He diffusion has been characterized for minerals such as olivine (Cherniak &
Watson, 2012), rutile, titanite (Cherniak & Watson, 2011), zircon, and apatite (Cherniak et al., 2009) according to step-heating and direct helium distribution profiling experiments conducted along major crystallographic axes of gem-quality samples. From these experiments, diffusion of $^3$He was found to be significantly anisotropic in olivine, rutile, and zircon but relatively isotropic for the axes measured in apatite and titanite. For anisotropic minerals, anisotropy was linked to regularly oriented, relatively large interatomic openings (apertures) in the mineral structure which are thought to facilitate diffusion. This relation suggests anisotropy is primarily a factor of atomic aperture and that interconnected, large aperture spaces within minerals define “fast paths” for $^3$He to move along – all of which has a large impact on the bulk He diffusion dynamics of these minerals. The ideal calcite, aragonite, and dolomite lattices contain similar, large-aperture openings oriented along cleavages. Strong anisotropy in apatite, zircon, and olivine associated with “fast paths” suggests calcite, aragonite, and dolomite may exhibit analogous anisotropic diffusion along cleavages.

2.5 Multiple Diffusion Domains

Previous research suggests calcite, aragonite, and dolomite commonly contain multiple diffusion domains (MDD) which may supersede, define, or complicate the potential controls on and effects of anisotropy. The MDD theory states that the retentive properties of a mineral are attributed to multiple diffusion domains within which He and other diffusants are trapped at low energies. It is theorized that larger domains typically require more energy than smaller domains to release helium. The effects of multiple diffusion domains, namely inconsistent jumps in the rate of gas release with increasing temperature, are thought to have been observed in sporadic release of argon from
potassium feldspars (Lovera & Richter, 1989) and alkali feldspars (Parsons et al., 1999); however, relatively little is known about what defines the size, shape, or retention of domains in these minerals.

In one study by Copeland et al. (2007), step-heating experiments were conducted on 23 natural and synthetic calcite and dolomite samples of sedimentary, metamorphic, and igneous origin. Step-heating and subsequent outgassing of each sample was conducted to produce Arrhenius diagrams from which bulk diffusion rates and closure temperatures were determined. Two key observations were made of the diffusion data: (1) Diffusion rates, activation energies, and closure temperatures were highly similar across sample types, suggesting He diffusivity in carbonates is independent of sample genesis and He source. (2) Several samples displayed anomalously non-linear Arrhenius curves, particularly in retrograde heat steps. Copeland et al. (2007) interpret the Arrhenius behavior as indicative of MDD behavior as it mimics the shape of Arrhenius plots for argon behavior in feldspars. Importantly, the observation of probable MDD behavior in single crystal samples implies that effective domain sizes are at least sometimes less than or equal to that of crystals; however, little else about the size, shape, or retention of domains in carbonates or feldspars from these data. Further investigation is needed to better define diffusion domains in these minerals.
3. PREVIOUS RETENTION EXPERIMENTS

3.1 Early Work

The study of helium diffusion in carbonates has historically focused on how well measured He/U ratios in natural samples match expected He/U ratios based on other age controls and a known rate of radioactive decay. The goal of these experiments has been to determine if these samples retain helium consistently enough to be used as a reliable geochronometer. However, such experimentation has produced inconsistent and conflicting data, reflecting the theoretical complexity of diffusion dynamics in carbonates (Bender et al., 1973; Bender, 1973; Copeland et al., 2007; Fanale & Kulp, 1961; Fanale & Schaeffer, 1965; Keevil, 1950).

Keevil (1940) presented theoretical evidence for calcite’s ability to retain He alpha particles produced by radioactive decay of uranium at low temperatures. However, when natural carbonate samples were first studied, measured He concentrations were often greater than expected according to U/Th ratios and other age controls (Keevil, 1950). It is likely that these experiments introduced significant error by inaccurate and/or imprecise methods used to measure the small volume of He released. Interestingly, carbonates were one of the only minerals in the study which produced excess He. It is probable that no attempt was made to remove He-bearing gas inclusions, commonly found in calcite, or to somehow account for their presence when calculating He content.

Later experiments by Fanale & Kulp (1961) incorporated new and supposedly more accurate techniques to measure He in marble, Iceland spar, and fossilized shells; yet, He concentrations were similarly inconsistent with predictions based on U/Th ratios. Calcite from samples formed at low temperatures (shells and spar) released less than a
quarter of the He expected while calcite from marbles produced ~6-12 times more He than predicted. As of yet, there has been no well-evidenced explanation for this drastic discrepancy in He content. It is unclear if fundamental differences in the structure, composition, formational environment, or post-formational environment of samples can sufficiently control $^3$He production, capture, or retention so as to explain this study’s results. A better understanding of helium diffusion dynamics in calcite and other carbonates is therefore needed to limit the number of possible influences on He content.

3.2 Aragonite Corals

Attempts to determine the age of aragonite corals from He/U concentrations were promising – with He/U measurements consistent with U/Th ratios and stratigraphy in most cases (Fanale and Schaeffer, 1965; Bender, 1973; Bender et al, 1973). However, a limited understanding of the spatial distribution of alpha producers in the microstructure of these corals meant potentially significant uncertainties in the accuracy of ages derived from any alphachronology technique (Fanale & Schaeffer, 1965).

3.3 Carbonate Bulk Diffusion Experiments

In recent years, the question of He retention has been revisited by Copeland et al. (2007) with new bulk-degassing experiments on a range of natural carbonates. For these experiments, untreated natural samples were measured for their $^4$He, U, Th, and Sm content as $^4$He in samples is assumed to have derived primarily from in-situ U, Th, and Sm series decay. (U-Th-Sm)/He ages were calculated for each sample and compared to apatite fission-track ages or stratigraphic relationships. Ages determined by Copeland et al.’s analysis varied considerably (e.g. 126.7 ± 7.5 Ma to 1525 ± 93 Ma for the same unit) and most were not consistent with apatite fission-track data; however, samples with more
alpha producers (>0.3 ppm U) generally produced more reasonable ages. The many inconsistencies found in this study between (U-Th-Sm)/He ages and other age controls remain unresolved by Copeland et al. (2007) but are speculated to be a product of either lost He during burial-induced heating or common He being incorporated into the samples via inclusions. Putting such uncertainties aside, the interpretation presented by Copeland et al. is that calcites of all origins retain He well and yield reasonable (U-Th-Sm)/He ages if kept below the average closure temperature of ~70° C and given sufficient alpha producers. These conclusions contrast sharply with the observation of Fanale & Kulp (1961) that large and regular disparities in He retention exist between metamorphic and low-temperature calcite.

3.4 Pamir and Sierra Nevadan Calcite

The potential seen by Copeland et al. for calcite to retain helium is consistent with recent field-based experiments measuring cosmogenic $^3$He in natural samples from Pamir but is further complicated by similar cosmogenic studies of Sierra Nevadan samples. These data also appear to show inconsistent retention of $^3$He by calcite that is independent of major and trace element compositions, suggesting the importance of one or more non-compositional factors in determining He retention and diffusion rates.

For example, a set of optically opaque, microcrystalline calcite samples from river terraces in the Pamir produced reasonable $^3$He ages when compared to U-series disequilibria ages of carbonate (Amidon et al., 2008). In contrast, ~20 samples of coarse-grained, optically clear calcite from a pair of marble-rich moraines in Laurel Canyon of the Sierra Nevada (Figure 5) displayed highly variable $^3$He concentrations (Table 1) (Hobbs and Amidon unpublished data). The two moraines are thought to be of Tahoe
(145ka) and Tioga (18ka) age and to have experienced the same $^3$He production rate of 984±84 atoms/yr (Rood et al., 2011; Vermeesch, 2007). Given perfect $^3$He retention, such an age difference would suggest that Tahoe-aged samples should have $^3$He concentrations almost eight times that of Tioga-aged samples; however, the Sierra Nevadan samples as a whole displayed roughly the same range of $^3$He concentrations regardless of origin.

Assuming a reasonable theoretical $^3$He production rate, each Tahoe-aged sample contained at least seven times less $^3$He than expected. It is interpreted that low $^3$He in Tahoe samples indicates significant $^3$He loss prior to bulk degassing experiments and therefore poor $^3$He retention by these samples. This apparent large variation in helium retention of Sierra Nevadan samples is also consistent with the mixed results of past He/U experiments on corals (Fanale & Kulp, 1961). Furthermore, ICAP-AES analysis of Sierra Nevadan marbles and Pamir samples revealed no obvious link between $^3$He retention and the abundance of impurities (Appendix A).

<table>
<thead>
<tr>
<th>Tioga</th>
<th>$^3$He Mat/g</th>
<th>Tahoe</th>
<th>$^3$He Mat/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCI1</td>
<td>4.0</td>
<td>LCT1</td>
<td>5.0</td>
</tr>
<tr>
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<tr>
<td>Expected</td>
<td>17.7±1.5</td>
<td>Expected</td>
<td>142.7±12.1</td>
</tr>
</tbody>
</table>

TABLE 1 $^3$He concentrations of Sierra Nevadan calcites and wollastonite (LCT4W). Average $^3$He concentrations of Tahoe samples are calculate with LCT4W excluded. Expected concentrations are based on 100% retention rate, a 18ka Tioga moraine age, 145ka Tahoe moraine age, and a production rate of 984±84 atoms/yr for all samples. From Hobbs and Amidon (unpublished data).
One marble taken from the older Tahoe moraine was found to be particularly rich in wollastonite, a calcium inosilicate (CaSiO$_3$). Wollastonite grains were isolated with HCL and measured for $^3$He separately. $^3$He concentration in wollastonite grains were more than double that of the most concentrated calcite sample but still between expected concentrations for the Tahoe and Tioga moraines. These findings largely preclude the possibility that improper age assignments to moraines resulted in an inaccurately high expected $^3$He concentration. Also, since the wollastonite-rich sample was collected along with the rest of the marble samples, it is unlikely that environmental factors, such as prolonged burial of most samples, can fully account for low $^3$He concentrations in the Sierra Nevadan calcite. Instead, the lack of helium appears to be caused by diffusive loss at surface temperatures.
FIGURE 5 Sampling locations of marbles from the Sierra Nevada Mountains, California. Marbles labeled LCI and LCT were collected from two north-west-trending moraines thought to be of Tioga (18Ka) And Tahoe (145Ka) age, respectively.
4. GOALS AND OBJECTIVES

4.1 Summary of Questions

The purpose of this research is to understand the primary controls of helium retention and diffusion in calcite, aragonite, and dolomite – a critical hurdle in developing new cosmogenic dating and thermochronometry techniques which use helium in carbonates as a geochronometer. One of the most fundamental aspects of diffusion dynamics is the relative diffusivities along different mineralogical axes. Determining to what extent diffusion is isotropic or anisotropic should provide great insight into what controls bulk diffusion rates, retention, or even diffusion domains. Anisotropy has been identified in a number of minerals with large aperture openings in their mineral structure. The a- and b-axes of calcite and dolomite as well as the c-axis of aragonite are fairly “open” and appear to have more large, interconnected apertures than other directions. Gem-quality samples, assumed to have nearly perfect structures, are therefore hypothesized to contain many interconnected fast paths along these axes and thus display significantly anisotropic He diffusion.

In addition to anisotropy, diffusion domains are another key area of study which need further clarification. Comparing Amidon et al. (2008) with Hobbs and Amidon (unpublished data) may shed some light on what defines diffusion domains and also the question of anisotropic diffusion in carbonates. Optically continuous, gem-like calcite from marbles in the Sierra Nevada appears to display low He-retentivity while opaque, microcrystalline calcite from Pamir limestones seems to retain helium relatively well. Based on the contrasting structures and retention of these calcites, it is hypothesized that randomly oriented microcrystalline structures promote the retention of $^3$He possibly by
(1) creating diffusion domains defined by relatively short intergranular boundaries and/or
(2) inhibiting anisotropic diffusion along fast paths in the mineral lattice. While these hypotheses will not be tested directly or fully in this study, characterization of diffusion behavior in terms of anisotropy is the first step toward understanding diffusion domains.

4.2 Experimental Summary

To test if helium diffuses more readily along specific axes in calcite, aragonite, and dolomite, the rate of diffusion along multiple unique crystal axes must be isolated and measured. Ion implantation and profiling experiments, used by Cherniak and Watson (2005), allow for such controlled measurements to be taken. A set of similar experiments were therefore conducted parallel to the a-axis, b-axis, c-axis, and perpendicular to cleavage of gem calcite, aragonite, and dolomite. The diffusivities observed from each axis were then compared to assess anisotropy. Interionic aperture size and frequency estimates collected from calcite, aragonite, and dolomite mineral lattice models were finally compared to diffusion data in order to test the influence of aperture characteristics on diffusion behavior.
5. METHODOLOGIES

The characterization of helium diffusion in calcite, aragonite, and dolomite was approached in two main steps. (1) To detect anisotropic diffusion, profiling experiments were run in which diffusion rates were measured separately along the three cleavages and the c-axis of gem-quality samples. (2) Mineral lattice models were made to estimate the size and distribution of interionic apertures and to assess their relation to experimentally derived diffusion data.

5.1 Profiling Experiments

To test if helium diffuses more quickly along certain axes in calcite, aragonite, and dolomite, the rate of diffusion along specific crystal axes must be isolated and measured. Ion implantation, used by Cherniak and Watson, allows for a narrow plane of $^3$He to be implanted into a gem-quality crystal at a specific orientation. If that sample is heated, the narrow band of helium will become wider as helium diffuses. Nuclear reaction analysis (NRA) enables the study of the implanted helium plane shape before and after diffusion is induced by heating. Anisotropy along a specific axis should manifest in a wider distribution of implanted He along that axis and a narrower distribution of helium along all other axes. For this study, 18 samples, heated at 14 different schedules, were analyzed by NRA (Cherniak et al., 2009).

Sample Preparation

Wafers (~2x2x3mm) of gem-quality calcite, aragonite, and dolomite, assumed to be compositionally pure and possess a consistent atomic structure, were selected and prepared for $^3$He profiling experiments. Gem-calcite, purchased from Commercial Crystal Labs, was cut along either the c-axis [001] or cleaved along one of three cleavage...
faces [1011]. Unpolished dolomite samples from Oberdorf, Styria, Austria via the Smithsonian (USNM R12596) were cleaved along the same cleavage faces. Aragonite (Morocco) samples from the RPI collection were either cleaved along cleavage (b-axis) [010] or cut along the c-axis [001] and then polished with 1 µm alumina and further polished manually with colloidal silica. After polishing, samples were washed for approximately five minutes in an ultrasonic bath of distilled water and ethanol before being implanted with $^3$He.

**Implantation and Step-heating**

Ion implantation was conducted using the Extrion ion implanter at Ion Beam Laboratory at the University of Albany. Polished samples were mounted to an aluminum plate with carbon paint, placed in the implanter, and implanted with 3 MeV $^3$He at doses of $5 \times 10^{15}$ $^3$He/cm$^2$. Implantation effectively emplaced a thin plane of $^3$He atoms oriented perpendicular to the implantation direction and slightly beyond the surface of implantation (Figure 6). Implanted samples were placed individually into platinum capsules in preparation for step-heating. Samples were annealed at constant temperatures ($\pm 2 ^\circ$C) from 78 to 400°C in 1-atm, Kanthal-wound furnaces for 15 minutes to ~4 days and monitored using chromel–alumel (type K) thermocouples (Table 2).
FIGURE 6 Simplified cartoon depicting direct profiling procedure. Cut samples, potentially containing natural helium, are first heated (fully annealed) until all helium in the lattice is thought to be released. A narrow surface of $^3$He is then implanted into the sample which, if “profiled” along the length of the crystal, would appear as a sharp peak in He concentration that is surrounded by background levels of He. Heating this sample according to a specific time and temperature schedule results in helium diffusion perpendicular to the narrow surface. The outcome of diffusion is a dispersed and broad He profile. The relative change in the He profile as a result of heating is thereby a measure a mineral’s diffusivity in the direction perpendicular to the implantation surface.

**Nuclear Reaction Analysis**

Following step-heating, the $^3$He distributions of annealed and unannealed samples were compared by nuclear reaction analysis using the 4 MeV Dynamitron accelerator at the University at Albany. $^3$He is indirectly measured by detecting highly energetic protons produced by the $^3$He(d,p)$^4$He reaction induced by the accelerator beam (Figure 7). This analysis can only produce a short, high-resolution profile of $^3$He and, therefore, must be repeated over a range of depths to measure, at high-resolution, the entire peak of $^3$He in a sample. Each sample was thus analyzed at four or five regularly spaced energies between 0.5 to 1.0 MeV. For each profile taken, the ratio of total protons detected in annealed samples to detected protons in unannealed samples was calculated and converted to diffusivities following Cherniak et al., (2009). Arrhenius plots of diffusion data were made for each sample and used to determine their respective activation energies. Counting statistics of protons produced by the $^3$He(d,p)$^4$He reaction and the
variation between diffusivities derived from different incident beam energies are used to calculate diffusional uncertainty.

5.2 Aperture Modeling

To better quantify the size, frequency, and distribution of inter-ionic apertures in calcite, aragonite, and dolomite and assess their relation to diffusion rates, the ionic structures of these carbonates were modeled in CrystalMaker© and analyzed by a pair of specialized MATLAB® programs (Appendix B-C). Atomic spacing determined by high temperature X-ray diffraction (Antao & Hassan, 2010; Markgraf & Reeder, 1985; Reeder & Markgraf, 1986) and commonly used ionic radii (Shannon & Prewitt, 1969; Shannon, 1976) were loaded into the CrystalMaker© modeling program and used to project a 2x2x2 “supercell” of each mineral with dimensions double that of a unit cell (Figure 8). The

![FIGURE 7 Example spectrum of detections made by nuclear reaction analysis at one energy. The isolated peak near channel 1600 represent protons produced by ³He(d,p)⁴He reaction while the low-energy counts are backscatter deuterium and other products of (d,p) and (d,α) reactions. Multiple spectra such as this must be made for a single sample, one for each incident energy (depth). From Cherniak 2009.](image-url)
coordinates of each atom center in these supercells were imported into the ‘xtal_section’ MATLAB® program. This program projected spherical atoms in a three-dimensional lattice using the same coordinates and radii. To visualize the inter-ionic apertures along the principal axes of each mineral, perpendicular cross-sections spaced 0.025Å apart were taken of the three dimensional model (Figure 9). The output of these cross-sections, one or more circles representing slices of atom spheres, were subsequently assessed for interionic apertures by the second program, ‘mat_stat’, which measured and collected statistics on aperture sizing of each slice (Figure 10).

FIGURE 8 Aragonite 2x2x2 supercell as displayed in crystalmaker. The lattice is oriented such that the [001] face is facing out, the origin is in the top left, the b-axis is vertical, and the a-axis is horizontal.
The ‘mat_stat’ program begins by taking the convex hull of the atom sections captured in the cross-section to effectively delineate the “outline” of the lattice slice and consider only the space inside the lattice. To measure apertures within the cross-section, the largest possible circle is fit between the atom slices displayed and is tested to ensure that it does not overlap with any pre-existing atoms (Figure 10). The first circle fit is considered the maximum aperture for this particular cross-section. The cross-section is then evaluated to determine if any more circles of the same size can fit in the image without overlapping any existing atom circles or aperture circles. Once it is known that no more circles of this size can fit within the image, circles with radii 0.01Å smaller are tested to see if they can fit between the atom circles and the larger aperture circles. Smaller apertures continue to be tested and saved for the next round of aperture size test until, at last, apertures of 0.1Å radii are evaluated and analysis of the cross-section is complete. The position and radius size of each aperture circle in the cross-section is recorded and used to assess and compare aperture distributions with other the cross-sections throughout the entire lattice.
FIGURE 9 Diagram of the aperture modeling procedure. Here, cross-sections are taken perpendicular to the c-axis of calcite in order to find apertures along the c-axis. Red rectangles within the calcite lattice indicate where a small subset of the slices (numbered boxes) are taken. Numbered boxes show, in cross-section, the extent of ionic radii of atoms which make up the calcite lattice at these slices.

Following the measurement of apertures, statistics were collected for each axis along which apertures were measured. The maximum aperture size within each cross-section along an axis was collected, displayed as normalized probability plots (Figure 10), and used to calculate several important statistics. For each axis, the very smallest and largest of the maximum apertures along an axis was recorded. Likewise, the median size of the maximum apertures from each cross-section was determined. Additionally, the percentage of maximum apertures larger than an interstitial $^3$He atom (0.9Å) was collected.

For each axis, average ionic porosity is calculated by taking the amount of interionic void space in a given cross-section, dividing it by the area within that cross-
section’s convex hull, and averaging over all cross-sections of a given mineral axis. The average aperture fill along an axis is a similar metric that uses the total area of all apertures in a given cross-section instead of void space. In this way, the effectiveness of the aperture filling can be assessed.

FIGURE 10 Once the position and extent of atoms making up the mineral lattice are determined for a given slice (top left), the largest non-overlapping circle is fit between the lattice to approximate the maximum aperture (top right). This process is duplicated for each slice along the axis in consideration in order to make aperture frequency diagrams (bottom right) and normalized probability plots of maximum aperture (bottom left).

This sequence was run for calcite, aragonite, and dolomite along their respective a-, b-, and c-axes, and additionally perpendicular to each mineral’s cleavage. It is important to note that the b-axis of aragonite is perpendicular to its cleavage plane and thus the two orientations are referred to interchangeably.
6. RESULTS

6.1 Profiling Experiments

Diffusion coefficients of $^3$He for calcite and dolomite are presented in Table 2 and plotted as a function of temperature in Figure 11. Diffusion was detected in all 15 calcite samples, one dolomite sample, but neither of the two aragonite samples. For the samples which did not display significant movement of $^3$He as a result of heating, no diffusion rates were calculated.

<table>
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<th>D (m²s⁻¹)</th>
<th>log D</th>
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<td>250</td>
<td>48.50</td>
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TABLE 2 Heating schedules and respective diffusion rates of carbonate samples. No diffusion rates were able to be calculated for aragonite due to inadequate $^3$He movement. Uncertainties of 0.3 logD are typically associated with diffusion rates collected by NRA analysis at the implant dosage and incident energies used.
Arrhenius behavior is suggested by the gem calcite data for both diffusion along the c-axis and diffusion normal to cleavage. By applying a least squares fit to the data sets, an activation energy of 46 kJ/mol and pre-exponential factor (D₀) of 2.82×10⁻¹¹ m²/s (Log D₀ = -9.846) is estimated for diffusion parallel to the c axis from 146-400 °C. For diffusion normal to cleavage between 78-300 °C., the activation energy is comparable at 55 kJ/mol with a pre-exponential factor of 8.15×10⁻⁹ m²/s (Log D₀ = -8.089). Due to the fact that only one diffusion rate was calculated for dolomite and no diffusion was measured for aragonite, no activation energy was able to be calculated for these minerals. However, the comparable heating schedules for dolomite and calcite suggest that diffusion perpendicular to cleavage in dolomite is several orders of magnitude slower than that of calcite in the same direction. Insignificant ³He diffusion in aragonite at comparable heating schedules is indicative of substantially slower diffusion rates in the directions tested.

Aragonite was annealed at 200°C and 250°C for substantially longer than calcite and dolomite samples at the comparable temperatures. Total diffusion is a product of both diffusion rate and time, with diffusion increasing linearly with time. Because aragonite was annealed 100 times longer than calcite at 250°C with no detection, it is reasonable to assume aragonite diffusion is, at the very least, 2 orders of magnitude slower. However, considering aragonite’s 250°C anneal was approximately as long as the 200°C dolomite anneal, it seems likely that aragonite diffusion is significantly slower than diffusion in dolomite. Assuming, for a moment, that ³He diffusion in both aragonite and dolomite have similar temperature sensitivities as diffusion in calcite, diffusion in aragonite is estimated to be around an order of magnitude or more slower than that of dolomite. As
dolomite is already nearly two orders of magnitude slower than calcite, aragonite, by extension, is therefore estimated to be at least three orders of magnitude slower than calcite.

FIGURE 11 Arrhenius plot of $^3$He diffusion in calcite with relation to that of dolomite. A least squares line of fit is applied to each the two calcite dataset and used to calculate activation energy and $D_0$. Error bars represent estimated uncertainties of 0.3LogD.

$^3$He diffusion normal to cleavage in calcite that was annealed at 201°C for 50 minutes was measured a total of three times in three separate samples. Diffusion rates for
these samples range by almost an order of magnitude and provide a sense of the diffusional variability between samples. Uncertainties, though not calculated for these specific samples, are typically on the order of ±0.3 log D based on uncertainties from similar methods (Cherniak et al., 2009).

6.2 Aperture Modeling

Analysis of calcite, aragonite, and dolomite lattice models has produced interionic aperture measurements along a, b, c, and perpendicular to cleavage for the minerals. Summary statistics of aperture data from each modeled mineral axis are presented in (Table 3), aperture frequency diagrams of each mineral axis are displayed in Figure 12, and normalized probability plots of the maximum aperture sizes of each cross-section for each mineral axis are found in Figure 13.

<table>
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<th><strong>Calcite</strong></th>
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<th><strong>Dolomite</strong></th>
<th></th>
<th><strong>Aragonite</strong></th>
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<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
<td>Cleaved</td>
<td>A</td>
</tr>
<tr>
<td><strong>General</strong></td>
<td></td>
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<tr>
<td>Minimum (Å)</td>
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<td><strong>0.92</strong></td>
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<td>90%</td>
<td><strong>61%</strong></td>
<td><strong>100%</strong></td>
<td>92%</td>
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**TABLE 3** Summary of statistics collected from the MATLAB aperture modeling program. **Boldface** indicates mineral axes that were experimentally tested, the maximum values for each mineral are highlighted in green, and the minimum values are highlighted in orange.

Aperture trends for calcite and dolomite are largely similar as expected for similar lattice structures. Aragonite aperture sizes are comparable but follow different trends due
to significant lattice dissimilarities. The apertures normal to cleavage and along the a-axis of calcite and dolomite and along the c-axis of aragonite are generally the largest out of the axes modeled. For each axis, at least 61% of maximum apertures were found to be larger than a $^{3}$He atom (0.9 Å), and in several cases 100% of maximum apertures were larger than 0.9 Å.

Smallest maximum aperture size, the statistic most strongly correlated by Cherniak and Watson with differences in diffusion rates between minerals, appears to vary significantly between the major axes of calcite, aragonite, and dolomite. The smallest maximum apertures sizes of calcite normal to cleavage and along the a-axis exceeded the size of interstitial $^{3}$He atoms as does the smallest maximum aperture size of aragonite’s c-axis. Calcite’s absolute smallest maximum aperture radius, 0.56 Å, is found along the b-axis. 0.50 Å is the smallest maximum aperture radius of dolomite and occurs along the c-axis. Aragonite has a smallest maximum aperture radius of 0.76 Å along the a-axis.

Comparing the median size of the maximum aperture radii associated with each mineral axis, there is significant variation between the axes of individual minerals and also often between the equivalent axes of each mineral. The median maximum aperture radii in dolomite ranges from 1.19 Å along the b-axis to 1.37 Å along the a-axis. Similarly, the median maximum apertures for calcite fall between1.17 Å along the b-axis to 0.71 Å along the a-axis. Interestingly, aragonite has both the smallest median maximum aperture of all three minerals (0.96 Å along the a-axis) and the largest median maximum aperture (1.67 Å along its c-axis).
Aperture frequency diagrams (Figure 12) display the frequency of apertures along an axis with brighter areas representing a higher frequency of apertures or a larger number of slices with an aperture there. Diagrams from each mineral axis show very similar aperture frequency patterns for calcite and dolomite, as expected. Along the a-axis, calcite has slightly better aligned apertures than dolomite as evidenced by the greater brightness and larger size of the regular aperture triplets seen lined up along the a-axis. Along the c-axis, the frequent apertures in calcite appear to be noticeably larger and more regularly positioned than those in dolomite. The same is true for apertures found perpendicular to calcite and dolomite cleavage. It is difficult to assess which of the calcite and dolomite axes have the biggest and brightest areas, indicative of many large apertures in a row. The c-axis hosts some of the most regularly positioned large apertures; however the brightest of these areas is somewhat low compared to other axes, suggesting these apertures are less common despite their regular alignment. For calcite and dolomite the a- and b-axes have the brightest areas. The bright rectangular areas are small, regularly spaced, and oriented parallel to the a- and b-axes.

Aragonite’s aperture frequencies are understandably quite different due to the large structural dissimilarities of its lattice. The a-axis hosts the largest, most aligned, interconnected, and therefore brightest aperture regions. The c-axis has relatively small but somewhat bright regions that are laterally connected to one another by slightly less bright lines which, together, form a hexagonal pattern. The b-axis (normal to cleavage) has many large, well defined, but somewhat infrequent apertures.
FIGURE 12 Aperture frequency diagrams of each modeled mineral-axis combination. The brightness of each pixel is a measure of the percentage of cross-sections in which the pixel was part of an aperture circle. Lighter areas represent lines through the lattice which were frequently unoccupied by atoms with white being paths that were entirely unobstructed through the axes modeled. Plot axes labels denote pixel distances in units of Åx50. Note that the plots for aragonite along b and perpendicular to c are identical as these are the same crystallographic directions.
Normalized probability plots of maximum aperture radii from each slice along mineral axes (Figure 13) allow for easy comparison of the size and frequency of the maximum apertures of each mineral axis. In each plot, the apertures to the farthest left are the smallest of the maximum apertures collected for a specific mineral axis. Conceptually, these are thought to be the smallest apertures that a particle would have to pass through while traveling along the axis specified. Information about the largest maximum apertures may be artificially inflated by artifacts of the modeling procedure. The largest radius, low frequency outliers in the plots are therefore ignored in this study.

As with aperture frequency diagrams, the normalized probability plots of maximum aperture radii for calcite and dolomite are largely similar. For calcite and dolomite, the greatest proportion of large maximum apertures are found along the a-axis while the most small maximum apertures are along the c-axis. Along the a-axis, the sizes of maximum apertures are more broadly distributed across a wider range of sizes for dolomite than calcite. Maximum aperture distributions for the b-axis of calcite and dolomite are nearly identical. Despite having the smallest maximum apertures, the majority of maximum apertures along the b-axis of calcite and dolomite are noticeably larger than that lower bound. The c-axis of calcite and dolomite have significantly more small (0.5-75 Å) maximum apertures than the b-axis. Along the c-axis, the smallest few maximum apertures of calcite are slightly larger (by ~0.1 Å) than the smallest maximum apertures of dolomite. Normal to cleavage, calcite and dolomite maximum apertures have a similar range of sizes; however, dolomites apertures are distributed noticeably more towards the small end.
Aragonite maximum aperture probability plots are unlike those of calcite and dolomite. The c-axis of aragonite definitively contains the largest maximum apertures as they are all larger than the vast majority of maximum apertures found in other directions of aragonite. The c-axis, as well, has the largest maximum apertures of all minerals by a considerable margin. The a-axis of aragonite has slightly smaller maximum apertures than the b-axis.

Comparing maximum apertures normal to cleavage from all three minerals, aragonite easily has the smallest maximum apertures. As mentioned earlier, dolomite has a smaller absolute smallest maximum aperture than calcite as well as smaller maximum apertures, in general.
FIGURE 13 Normalized probability plots depicting maximum aperture radii (Å) for all cross-sections of each of the 11 principle axis-mineral combinations as determined by MATLAB® program. Y-axis of each plot represents the fraction of maximum apertures within the size bins defined on X-axis. All axes are of the same scale. Note that the plots for aragonite along b and perpendicular to c are identical as these are the same crystallographic directions.
7. DISCUSSION

7.1 Interpretation of Diffusion Data

It is clear that gem calcite samples display significant diffusional anisotropy as rates of $^3$He diffusion are consistently two orders of magnitude lower along the c-axis as compared to perpendicular to cleavage. This finding is solid evidence that a structurally and compositionally perfect calcite crystal should always display such anisotropy. Furthermore, imperfect, natural grains of calcite likely exhibit similar anisotropic diffusion behavior, modified by imperfections. Assuming a constant 10°C/Ma cooling rate and a spherical diffusion radius of 75 µm, typical of apatite, calcite closure temperatures of -32°C and -44°C were calculated from diffusion trends along the c-axis and perpendicular to cleavage, respectively.

Dolomite, which possesses a similar lattice structure to that of calcite, is predicted to express similar diffusional patterns. Assuming dolomite follows these same anisotropic trends and that the one collected data point is an accurate representation of $^3$He diffusion rates perpendicular to cleavage at 200°C, it would follow that diffusion in the dolomite sample is 2 to 3 orders of magnitude slower in all directions than the calcite sample. This prediction is, of course, ignorant of the slight structural differences between samples and implies the physical properties of the lattice structure are the only important control on diffusion rates.

As previously suggested, diffusion of aragonite is likely too slow to have been measured at the heating schedules evaluated. The large structural differences compared to calcite and dolomite makes predicting diffusional patterns of aragonite difficult; however,
we can glean some understanding from the aragonite heating schedules which did not exhibit discernible $^3$He movement.

### 7.2 Aperture Size and Diffusion Rate

The most exciting outcome of this research is an opportunity to assess the control of ionic aperture size on diffusion rates in carbonates. Noble gas diffusion through solids has traditionally been conceptualized with a direct interstitial diffusion mechanism in mind (F. Fanale & Kulp, 1961; Keevil, 1940). Cherniak and Watson (2011), for instance, describe crystal lattices as a “molecular sieve” in which the rate of helium diffusion is directly controlled by the metaphorical sieve size or the lattice aperture size. In this way, the size and frequency of the smallest maximum apertures, ideally the smallest gates through which He atoms must pass through, should be the most important factor in qualitatively predicting the relative diffusion rates of different minerals along different axes.

The diffusion and aperture size data for calcite, aragonite, and dolomite, albeit limited, seems to suggest an aperture-dependent diffusion model as predicted. Comparing the smallest and median maximum aperture sizes, the axes with smaller sizes generally exhibited slower diffusion rates. Normalized probability plots of maximum aperture radii also demonstrate a correlation between more small apertures and slower diffusion rates. Aperture frequency diagrams, however, do not clearly show a relationship between many large, well-aligned apertures and faster diffusion rates.

It is important to focus first on the carbonate mineral axes for which we ran profiling experiments. Looking first at calcite, we see a marked difference between the c-axis and normal to cleavage directions in the size distribution of maximum apertures.
Maximum aperture probability plots indicate the c-axis direction exhibits a vastly higher frequency of small (0.5-1 Å) maximum apertures. Dissimilar maximum aperture size distributions fit very well with the marked diffusional anisotropy observed from the same directions. Differences in maximum aperture sizes between these two directions are not obvious, however, in aperture frequency diagrams which show much better alignment and frequency of apertures along the c-axis.

Having addressed the intra-mineral comparisons, it follows that there be an inter-mineral investigation of the aperture-diffusion relationship. Starting with the normal to cleavage direction for calcite, aragonite, and dolomite, we can again see large distinctions in the size distributions of maximum apertures between the minerals which follow the hierarchy relative diffusion rate trends. Aragonite, which demonstrated the slowest diffusion, has only 80% of its maximum apertures normal to cleavage exceeding typical interstitial helium sizes while 100% of calcite and 99% of dolomite maximum apertures in this direction are larger than helium. $^3$He diffusion perpendicular to cleavage in dolomite was 2-3 orders of magnitude slower than calcite and, as expected, the dolomite lattice has relatively smaller maximum apertures compared to calcite in this direction. This observation is yet more strong evidence supporting a molecular sieve diffusion model. Relatively slower diffusion in one mineral appears to be the product of smaller maximum aperture sizes and frequency, at least in this specific case. Again, the size and brightness of aperture frequency diagrams are not accurate predictors of relative diffusion rates as the aragonite diagram is generally brighter with better defined aperture shapes despite demonstrating slower diffusion.
Focusing on the c-axis direction, we see similar, though more subtle, trends. The smallest maximum apertures of dolomite are slightly (0.1 Å) smaller than those of calcite and only account for ~7.5% of the maximum apertures recorded for dolomite. Aperture frequency diagrams also seem to predict faster diffusion rates as calcite demonstrates larger frequently aligned apertures along the c-axis than dolomite. The differences in maximum aperture size, frequency, and distribution suggest slightly slower $^3$He diffusion along the c-axis of dolomite than the c-axis of calcite. Interestingly, in this direction, aragonite has vastly larger maximum apertures than calcite and dolomite such that roughly half of the maximum apertures of calcite are smaller than the smallest maximum aperture of aragonite (1.31Å). This significant difference in aperture size does not seem to affect the relative diffusion rates perpendicular to cleavage.

Looking now at mineral axes for which no $^3$He diffusion rates were collected, we see a wide range of maximum aperture trends as well as well-aligned but isolated high frequency apertures. The b-axis of both calcite and dolomite demonstrate the smallest maximum apertures of all directions considered but the low frequency of those apertures suggests slightly larger apertures may be more important and that diffusion should be faster than the c-axis. Assuming that diffusion follows smallest maximum aperture trends, the a-axis of calcite is predicted to facilitate faster diffusion rates compared to calcite’s other directions. Dolomite, however, may not demonstrate this same trend due to the higher frequency of apertures smaller than 1.0 Å along the a-axis compared to normal to cleavage. Aragonite again is predicted to have slower diffusion along the a-axis than its two counterparts due to smaller maximum apertures.
7.3 Comparison to Other Studies

Profiling Results for Other Geochronometers

At the temperatures measured (78-400°C), our calcite and dolomite samples demonstrated higher diffusion rates than several other geochronometers (apatite, zircon, titanite, monazite, and rutile) measured by similar methods (Figure 14). As well, activation energies determined for $^3$He diffusion along the two calcite axes measured, 46-55 kJ/mol, are significantly lower than activations energies of the other geochronometers (117-148 kJ/mol) (Cherniak et al., 2009; Cherniak & Watson, 2011). A combination of relatively low activation energy and high diffusion rates of carbonates is unsurprising and may explain their generally low $^3$He retentively. If $^3$He requires less energy to begin diffusing and diffusion occurs at relatively fast rate, then it is expected that much of the $^3$He produced in a mineral will easily leave the sample at low temperatures. Calcite’s low Arrhenius slope also means that diffusion rate does not scale much with increasing temperature and is almost always high relative to other geochronometers.

Diffusional anisotropy observed in rutile of roughly the same magnitude as calcite is matched by smallest maximum aperture sizes that are highly dissimilar (0.61Å and 0.31Å). The scale of smallest maximum aperture differences in calcite (0.92Å vs 0.66Å) is on par with that observed in rutile and suggests aperture size has a similar amount of influence on diffusion rate for these two minerals. Likewise, the size of the smallest maximum apertures in carbonates is comparable to other geochronometers. Although diffusion rates in carbonates are generally faster than in these other minerals, their smallest maximum apertures are not always larger. This suggests aperture size has a similar effect on diffusion rate for all these minerals; however, the effect is not fully
described by only minimum aperture size and frequency along major axes. It would seem there are other secondary statistics and factors influencing the relative diffusion rates in these geochronometers.

**FIGURE 14** Comparison of He diffusion in calcite, dolomite, apatite, zircon (Cherniak et al., 2009), titanite, rutile (Cherniak & Watson, 2011), and monatize (Cherniak & Watson, 2010). Listed adjacent to mineral axis labels are the associated minimum aperture sizes reported by Cherniak & Watson (2011). Modified from Cherniak & Watson (2011).

*Bulk Diffusion of Calcite*

Activation energies calculated from gem calcites in this study are \( \sim \frac{1}{3} \) to \( \frac{1}{4} \) that of activation energies derived from bulk diffusion measurement of natural and synthetic
carbonates reported by Copeland et al. 2007. Relatedly, closure temperatures estimated for gem calcite in this study are significantly lower (by ~100°C) than those calculated for carbonates studied by Copeland et al.

Specific comparisons can be drawn from the two samples of CCL gem calcite, the same calcite used in this study, for which Copeland et al. also reported diffusion data (Figure 15). Activation energies were calculated for all but one of the 23 samples studied by Copeland et al. The sample in question, one of the CCL calcites (CCL-H6), was excluded on the basis that the data formed an anomalously low slope when plotted on an Arrhenius diagram. This slope, though not quantified, is much closer to the slopes for our CCL samples than to slopes for other samples studied by Copeland et al. Copeland et al. suggests the Arrhenius trends observed at the lower temperatures for each sample relate only to smaller diffusion domains. The authors therefore interpret the low slope of CCL-H6 to be a product of minimal output of He from small domains compared to other samples. Little further interpretation is provided about CCL-H6 other than a statement that, within a single hand sample, there may be significant variation in the distribution of helium between different sized diffusion domains.
It remains unclear why CCL samples would exhibit such markedly different diffusive behaviors when subjected to the same conditions and measured using the same procedures. CCL samples used by Copeland et al. came from the same 6cm hand sample and were relatively large (0.55-1.21mm) compared to hypothesized diffusion domains sizes. It is possible that significant deformation was incurred in one sample during sample preparation which altered the morphology of diffusion domains. Alternatively, as Copeland et al. suggests, the distribution of helium may be highly variable for some reason. Perhaps large diffusion domains serve as a helium “sink” in which a disproportionately large proportion of helium atoms are trapped at low temperatures. If the distribution of large diffusion domains is highly variable within a hand sample, then the distribution of helium may therefore be variable as well.

Also perplexing is why diffusion data for CCL samples collected by profiling experiments is so dissimilar to data collected by bulk diffusion. These procedures are
obviously quite different in the parameters that are directly evaluated and also the scale at which measurements are taken (Figure 16). While bulk diffusion measures all helium which escapes from an entire sample, helium profiling evaluates the movement of helium within a sample along a single direction. Bulk diffusion is arguably the more comprehensive of the two techniques as the entire range of diffusion factors (aperture size, fast paths, MDD, along grain diffusion, etc.) fully affect the measurement taken. Likewise, bulk diffusion is almost certainly more analogous to helium loss and retention as these phenomena occur at a whole-rock scale. It is quite possible that the limited scale of profiling, on the order of micrometers, does not accurately capture the range of diffusional phenomena which naturally occur within a hand sample. If the measurement scale of profile experiments is smaller than that of important diffusion domains or fast paths, then diffusion data collected by profiling may not be applicable for whole-rock processes such as helium retention.
FIGURE 16 Cartoon illustrating several proposed noble gas diffusion concepts as well as key conceptual differences thought to be associated with A) profiling experiments and B) bulk diffusion experiments. Helium is shown to move differently depending on the microstructural features that they encounter. The general trend is for gasses to move preferentially out of the main body of the regular mineral lattice and into pores and “fast paths” such as fractures, cleavages, and other relatively wide, open surfaces. Diffusion rates out of the crystal are uniform for the basic lattice but greater where fast paths reach the surface. A) The outcome of profiling experiments is a measure of diffusion in a single direction. B) Bulk diffusion experiments measure the total helium released from the sample, regardless of the diffusion path. Modified from Cheriak and Watson, 2012.

7.4 Mechanisms of Diffusion

As with rutile and zircon, activation energies of calcite do not differ much with direction despite significant diffusional anisotropy. This suggests He atoms experience similar energetic hurdles with net movement in any direction, perhaps because movement in one direction necessitates intermediate jumps in other directions or because single jumps occur in non-orthogonal directions.

Given the many possible paths through a mineral lattice and considering how varied adjacent interstitial zones can be, it seems highly likely that many different
winding paths are taken by $^3$He atoms moving from point a to point b. These paths would logically involve helium jumping in directions that are not parallel to the net movement direction. If diffusion rate is anisotropic, then it is reasonable to assume helium tends to jump in one direction more than others (Figure 17). If this is the case, then the net diffusion rate in one direction is likely helped or inhibited by jumps in other directions.

FIGURE 17 A hypothetical path taken by a “wandering” helium atom. Although the path from start to end is not direct, the helium atom tends to move preferentially downward. This behavior, if accurate of natural phenomena, would result in observed anisotropy.

Suppose, for a moment, that helium can only move along the a- and c-axes and that diffusion is fastest along the a-axis of a calcite and slowest along the c. The net diffusion rate perpendicular to cleavage would therefore be a product of jumps in both the a and c directions. This rate would be more influenced by the ease or rate of diffusion in the a direction because the net diffusion vector (normal to cleavage) is closer aligned with
the a-axis than with the c-axis. With this hypothetical scenario in mind, it follows that the net diffusion rate in any direction is a product of the ease or likelihood of diffusion in all directions.

Another, non-exclusive possibility is that the jumps made by $^3$He through apertures are not perfectly aligned with a major crystallographic axis but are instead oblique or entirely random, containing several directional components (Cherniak & Watson, 2011). Such non-orthogonal movement brings to question the mechanisms by which He atoms diffuse within minerals. Most noble gas diffusion models describe diffusion as occurring by primarily direct interstitial movement that is strongly limited by the position and extent of the atomic components of the mineral (Fanale & Kulp, 1961). These models allow for slightly oblique jumps by noble gases from one interstitial domain, through a restricting aperture, and into another interstitial region of the lattice. These jumps are thought to be made possible by a momentary increase in the energy budget of the diffusion atom and by the atoms defining the target aperture moving aside slightly for an equally brief period so that the diffusing particle may be allowed through (Keevil, 1940).

Perhaps we should assess the ability for the restricting lattice to temporarily accommodate the passage of diffusing particles in addition to the typical size of apertures when diffusion is not even occurring. In most cases, it is probable that larger apertures allow for more accommodation and at a lower energy cost. Alternatively, the movement of helium from one interstitial area to another is less mechanical in nature and, instead, $^3$He often jumps “through” atoms regardless of where the relevant aperture are. The ease at which jumps in certain direction are made could still be dictated by the positions of
atoms in the lattice; however, the range of possible jump vectors may be greater than is typically thought.

If any of these conceptual models are accurate, we must consider the ease of diffusion in all directions to understand the overall rate of diffusion of many He atoms in one direction. For calcite, it may be that the a- and c-axes are the most important axes in terms of aperture size and diffusion rate. These directions have, after all, the largest and smallest maximum apertures of the four principle axes of calcite. The a- and c-axes might exhibit the most anisotropic diffusion trends while simultaneously interfering with the diffusion behavior observed along b-axis and normal to cleavage. Diffusional normal to cleavage, for instance, may be faster than diffusion along the c-axis simply because the diffusion vector is closer to the hypothetically more diffusive a-axis than the potentially slowest c-axis.

7.5 Potential for Calcite as Geochronometers

Low activation energies, low Arrhenius slopes, and high diffusivities have significant implications for the usefulness of calcite as a geochronometer. First, a low closure temperature means the information gathered from helium concentrations in calcite is only applicable to relatively low temperatures such as those experienced at the surface or at shallow depth. A low temperature calcite geochronometer could prove invaluable as there currently exist few low-temperature thermochronometers and very few with closure temperatures below 100°C. When doing thermochronometry, having an additional geochronometer with a unique and well-understood temperature sensitivity range would allow for far better constrained time-temperature paths to be created as the effective “window” of observation is broadened to include that of calcite.
Second, individual calcite samples may have a smaller partial retention zone (PRZ) than other geochronometers due to the high diffusion rates and low activation energies; however, small variations in structure between natural calcites may result in a relatively wide range of PRZ’s. Variation in macro-scale mineral structure may therefore be just as, if not more, important than micron-scale diffusion characteristics for determining the effective PRZ for large calcite crystals. Slight differences in the maximum temperature experienced by natural samples (on the order of a few degrees Celsius), compounded by grain- or subgrain-scale structure differences may therefore explain the large variability in retention between natural carbonate samples with similar helium production rates. The complexity of such a system, although difficult to initially understand, may prove to be a powerful tool which provides increased range and precision of thermal history estimates. It is therefore important to reiterate the need for a well-defined model of helium diffusion in calcite.

A narrow PRZ also means that He-retention in calcite should be more sensitive to minor changes in temperature than other minerals. For example, equilibrium age is the apparent age of a sample when the sample’s helium concentration reaches equilibrium between production and diffusive loss at a constant temperature. If temperature changes in a sample, due to a change in environment (e.g. burial or exhumation), calcite should reach its equilibrium age more quickly than other geochronometers because activation energy is lower and diffusion occurs more quickly. This may mean that even small changes in temperature or burial depth have a strong effect on the helium concentration of calcite, potentially making calcite sensitive to minor cooling events triggered by a
short-lived pulse of exhumation or other regional thermal disturbances (Copeland et al., 2007).

7.6 Uncertainty in Diffusion Data

A few important characteristics of the diffusion data collected severely limit the extent to which broad-scale interpretations can be made. This study provides multiple diffusion rates for just one mineral, calcite, and only in two directions of a particular sample. We cannot assume all calcites behave equivalently to our gem calcite though it is likely most exhibit similar anisotropy trends and have diffusivities within a few orders of magnitude. The dolomite data presented has these same problems and the additional uncertainties associated with having only a single data point. Notably, it is uncertain what the reproducibility of the one point is or what diffusional trends exist with increasing temperature or with changing diffusion direction. Uncertainties for these experiments are typically within the range of ±0.3 log D and are a combination of instrument uncertainty and variability in the multiple diffusivities calculated for a given sample. However, diffusion rate along a given direction can vary beyond the range of uncertainty as demonstrated by diffusion rates calculated for calcite perpendicular to cleavage at 200°C. Similarly, we can only speculate qualitatively on the relative diffusion rates for aragonite as no significant He movement has been observed at the heating schedules evaluated.

There are additionally uncertainties when comparing our carbonate diffusion data to that of other minerals. The range in temperatures for which diffusion rates of our samples were measured only overlaps slightly with many of these other minerals. The exception to this trend is apatite diffusion, which was measured directly between ~150-450°C (Cherniak et al., 2009; Cherniak & Watson, 2011).
8. NEXT STEPS

8.1 Complete Diffusion Dataset

Although this research has provided invaluable first order information on the rates and controls on diffusion in carbonates, there remain a number of crucially important tasks to be completed. First and foremost, a more complete description of the directional $^3$He diffusion rates for calcite, aragonite, and dolomite must be made. Diffusion rates along the a- and b-axes of calcite should be collected to assess the importance of each mineral axis on diffusion in other directions, to understand the defining component of bulk diffusion, and to better interpret trends in activation energy. With data for only two directions of diffusion in calcite, we cannot confidently determine if the diffusion rates in these unique crystallographic directions are entirely independent of one another or if profile experiments along one direction are significantly influenced by diffusion rates in other directions. Similarly, the impact of one direction’s diffusion rate on the bulk diffusion rate of the mineral cannot, at the moment, be determined. Currently, activation energy has been estimated for two directions of diffusion in calcite. Having estimations for three or four directions should more definitively determine if activation energies are relatively consistent between calcite axes despite diffusion anisotropy and could potentially allow for a more conclusive interpretation of such trends.

Diffusion along the a-, b-, and c-axis, and perpendicular to cleavage has also yet to be finalized for aragonite and dolomite. This data will allow us to know if dolomite follows the same diffusional trends as calcite, particularly in reference to diffusional anisotropy. Similar trends would provide more evidence for a structure-controlled diffusion model and further support the need to assess aperture size and related
parameters in order to understand $^3$He diffusion dynamics. Diffusion data for aragonite will, of course, tell us just how much slower $^3$He diffusion is for the calcite polymorph as well as test how consistent activation energy is over several directions of another carbonate with a different lattice structure. With diffusion trends for three or more unique directions in all three carbonates, the influence of lattice structure, composition, and other more specific mineral characteristics on directional and bulk diffusion can be more thoroughly assessed.

**Bulk Diffusion and Cylinder Models**

As previously implied, it would be useful to collect bulk diffusion data on these same carbonate samples and compare it to three or more directional diffusion rates. This could provide insight on the contributions of each direction’s diffusion rate on bulk diffusion as well as help build or assess the accuracy of diffusion models which estimate bulk diffusion or the diffusion rate in directions not directly measured. Such models have been created for anisotropic argon diffusion in mica and halogen-hydroxyl exchange in apatite (Watson et al., 2010), as well as $^3$He diffusion in rutile, titanite, zircon, and apatite (Cherniak et al., 2009; Cherniak & Watson, 2011). These models, which consider anisotropic diffusion within a cylinder, benefit from experimentally derived bulk diffusion data and also diffusion data for multiple unique directions. Developing a well parameterized diffusion model is useful for applying knowledge of diffusion trends from our carbonate samples to other, less studied, samples.

### 8.2 Additional Modeling Applications

In addition to a more complete understanding of carbonate diffusion rates, this research highlights the possibility for more advanced means of evaluating diffusional
controls. For instance, the aperture modeling used to assess aperture size is almost certainly an overly-simplified representation of lattice natural systems and may not capture all the most important factors effecting $^3$He diffusion rate.

*Electron Density Clouds*

One major assumption of our and similar aperture models is that ions in a crystal lattice have consistent physical dimensions that influence noble gas diffusion. In our model, oxygen atoms, regardless of their immediate neighbors, are thereby assumed to have an ionic radius of 1.21Å. This assumption ignores, for example, the expected change in radius size for dolomite which has oxygens neighbored by a plane of Mg on one side and a plane of much larger Ca on the other. Additionally, more complex electron cloud geometries, consisting of several differently shaped suborbital probability clouds, are not included in our simplified model. Of course, our model also does not account for changes in electron cloud shape due to varying external forcing of surrounding that are dependent on position within the crystal lattice.

Skinner et al. (1994) presents evidence for non-spherical electron density clouds in calcite (Figure 18) whose shapes vary significantly for those used in our lattice model. If these more complex shapes were incorporated into the calcite model and lattices for other minerals, then the maximum aperture statistics for these axes could be drastically different. It is also possible that the effects of cloud densities are significant and that a less binary diffusion model should be considered. If the lowest density regions of certain atoms are relatively large but were still included in the ionic radius we used, then the significance of that low density region would be overstated by our binary model.
A density dependent model could account for non-spherical electron shapes and inconsistent distance-electron probability relationships. Unfortunately, it does not appear that reliable and consistently presented data exists at the moment for most of the minerals for which profiling experiments have been conducted. Until such information is available, we must find other means of estimating or compensating for the complex characteristics of electron clouds or choose to ignore these potentially important factors when modeling.

![Diagram of Charge Density](image)

**FIGURE 18** Charge density for calcite within the (10\(\overline{1}4\)) cleavage plane. Contours are spaced at 0.05 Bohr\(^{-3}\) and are in the range 0.05-0.5 Bohr\(^{-3}\). From Skinner et al. (1994).

*Least Cost Path Modeling/Modeling 3D Diffusion Paths*

One aspect that is not fully considered in our assessment of aperture size-dependent diffusion is the continuity of the three-dimensional paths along which that
helium travels in a mineral. While size and frequency of apertures was quantified for calcite, aragonite, and dolomite, the interconnectedness of such apertures was only visualized with aperture frequency diagrams and not quantitatively evaluated. It follows that although a hypothetical mineral lattice may have regular large apertures, if large apertures are spatially isolated from one another with relatively small apertures in between, the overall helium diffusion rate may not be greater than that of a mineral with many interconnected, moderately sized apertures.

A potential solution to simultaneously consider aperture size, frequency, and interconnectedness is to implement a type of three-dimensional least cost path modeling in the least restrictive path through a mineral lattice is evaluated (Figure 19). Costs associated with movement would be based on hypothesized controls on diffusion rate, such as aperture size. The model which produces paths whose relative costs and directions best mimic experimental diffusion rate data should logically incorporate mineral characteristics that most control diffusion rate. For example, a least cost path model could be built in which $^3$He atoms are partially restricted by aperture size such that smaller apertures cost more “points” to move through. By comparing all the potential paths a $^3$He atom could take through a three-dimensional lattice to get from one side to the other, the relatively likelihood that a $^3$He atom, given the parameters of the model, will take any one path can be estimated. Hopefully, after running the models for a number of unique starting and ending points, the relative costs of $^3$He movement along different mineral axes in the model are found to be highly similar to the relative diffusion rates of actual $^3$He along the same axes of real samples. If such similarities are found,
then the sources of the modeled costs in the least cost path model are likely to be representative of the true controls on $^3$He diffusion rates in real life.

![Figure 19: Cartoon illustrating the basic concept of a least path. Here, the main cost in this model is distance traveled and the objective is to move through the lattice from one side to the other. The helium atom is therefore shown to be taking the shortest path.](image)

A great advantage of a least cost path model is that numerous controls on diffusion rate can be incorporated into the model at the same time. For instance, costs can be added based on the probabilistic electron cloud densities that have both a spatial (aperture) component and a gradational density component. This allows for more flexibility in the number of model-able scenarios that a helium atom could potentially encounter while diffusing through a mineral lattice.
9. CONCLUSIONS

$^3$He diffusion rates have been measured by implantation and NRA analysis for diffusion along the c-axis of calcite, perpendicular to calcite cleavage, and perpendicular to dolomite cleavage. Profiling experiments conducted on aragonite did not produce diffusion rates but did help to estimate a maximum diffusion rate of 3-4 orders of magnitude slower than calcite. Importantly, diffusional anisotropy has been observed in calcite and, in general, carbonates demonstrate higher diffusion rates and lower activation energies compared to several other common geochronometers. These comparisons help to understand that the relatively low helium retention of natural carbonates is likely due to high rates of helium diffusion at low temperatures.

This study also investigates the major controls on diffusion rates and anisotropic behavior in carbonates by comparing diffusion data to interionic apertures within these minerals. Aperture size and distribution along several major crystallographic axes were assessed using 3-D and 2-D mineral lattice models created in CrystalMaker® and MATLAB®. The size frequency of maximum apertures, i.e. the largest apertures encountered by helium atoms moving along an axis, appears to be related to the relative intra- and inter-mineral diffusion rates along major axes. As indicated by other mineral systems and predicted for carbonates, the size and frequency of the smallest maximum apertures exhibit the closest correlation with diffusion rates.

At the moment, continued study of helium diffusion dynamics in carbonates appears to be a worth-while investigation considering the potential for a new low-temperature geochronometer with a unique and versatile effective temperature range. The greatest challenges in reaching this goal are the incredible structural variability between
natural samples at a micro- and macro-scale and the subsequent likelihood of intricate scale-dependent diffusion controls. This study provides crucial first order descriptions of direction-specific helium diffusion in carbonates and a framework for continued research on the topic. Significant work has yet to be done to complete the dataset of diffusion rates along major axes of calcite, aragonite, and dolomite, which are essential to making strong conclusions on the diffusive trends in these minerals. Likewise, simplistic mineral lattice models used to estimate aperture size appear to be predictive of the basic hierarchy of relative diffusion rates; however, the predictive accuracy and precision of these models could certainly benefit from the integration of more complex concepts such as electron density clouds and least cost path modeling.
Works Cited


## APPENDIX

### Appendix A:

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**Major elements compositions of Sierra Nevada marbles and Pamir limestones as collected by ICAP-AES (left) alongside their respective $^4$He and $^3$He concentrations from bulk degassing measurement collected at the Farley lab at CalTech (Hobbs and Amidon, unpublished data).**

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Appendix B:

Crystal sectioning program modified from Will Amidon’s ‘xtal_section’ (2013)

%%% Daniel Hobbs (March 2013)
%%% Modified from Will Amidon's 'xtal_section' code (January 2013)

%%This code mimics Bruce Watson's code for sectioning crystals
%%%***this code only works for minerals where C is orthogonal to A and B**
clear all

%%%CHANGE THESE INPUTS BEFORE STARTING%%%%%%%%%%%%%%%%%%%%
cfile=dlmread('aragonite2.0.txt');  %coordinate input file
%radii=[0.066 0.197 0.077];      %radii of Ox, Ca, Cb (Ang)
radii=[1.21 1.14 0.29];         %radii of Ox, Ca, Cb (Ang)
nclr_list=[1 1 0;1 0 1;0 1 1];    %create a 3x3 array where each row is RGB
color vector (ox, ca, cb)
axlength=2*[4.9635 8.0024 5.7760]; % list of a b and c axial lengths (ang)
ab_ang=90;  %angle between A and B axes (deg). Both must be orthogonal to C!!
slice_interval=0.025; %interval of slices (Ang)
n_vect=[1 0 0];   %vector defining the plane to be sliced in orthogonal coords
%this loop converts coordinates and extracts radii
for j=1:length(cfile)
   xyz(j,1:3)=cfile(j,1:3).*axlength;  %convert from fract. coords to crystal
   coordinates in angstroms
   xyz_orj(j,1:3)=[xyz(j,1)+xyz(j,2)*cosd(ab_ang)  xyz(j,2)*sind(ab_ang)
  .xyz(j,3)];    %convert from crystal coordinates to orthogonal coordinates
   dist(j)=sqrt(xyz_orj(j,:)*xyz_orj(j,:)');  %compute distance of each point
from origin
end

%%determine how far the slicing needs to go by projecting each point
%onto the normal vector
t_vect=n_vect*100;  % this is just to make the slicing vector long enough
start=min(dist)-max(radii);  %define the distance from origin to start slicing
pd_max=0;  %set up a minimum max distance
for i=1:length(dist)
   pdv=((t_vect'*xyz_orj(i,:)'/(t_vect'*t_vect')).*t_vect;  %project each point
onto the slicing vector
   pd=sqrt(pdv*pdv');  %determine the distance of projected point from origin
   if pd>pd_max
      %determine if the point exceeds the existing max
      distance
datax_max=0-start+max(radii);  % if yes, assign this point as the new
max and adjust for start
%This loop begins slicing
numsllices=ceil(pd_max/slice_interval);  %determine number of slices

for i=1:numsllices
    %establish equation of each slicing plane
    scalar(i)=start+(i*slice_interval);  %distance from origin in A
    xyz0(i,:)=n_vect.*scalar(i);  %point in plane where origin vector intersects
    d(i)=-n_vect*xyz0(i,:)';  %negative d assumes ax+by+cz-d=0
    %equation of plane ax+by+cz-ax0-by0-cz0=0  ax+by+cz-d=0  where
d=ax0+by0+cz0  n_vect*[x,y,z]-n_vect*xyz0
    %points in plane satisfy ax+y+z=d

    cnt=0;  %set up a counter
    %start looping over all points
    for j=1:length(xyz_ort)  %loop over all j points
        %establish distance from each point to the plane
        D=|a*xp+b*yp+c*zp+d|/sqrt(a^2+b^2+c^2)
        %http://mathworld.wolfram.com/Point-PlaneDistance.html
        D(j,i)=abs(n_vect*xyz_ort(j,1:3)'+d(i))/sqrt(n_vect*n_vect');

        if D(j,i)<cfile(j,4)  %determine if point j intersects plane
            cnt=cnt+1;
            %extract coordinates of projected point
            %following: http://www.9math.com/book/projection-point-plane
            t0(j,i)=-(n_vect*xyz_ort(j,:)'+d(i))/(n_vect*n_vect');  %distance of projected point
            xyzr_prj(i).xyz(j,1:3)=xyz_ort(j,1:3)+n_vect.*t0(j,i);
            %coordinates of projected point
            xyzr_prj(i).r(j)=sqrt(cfile(j,4)^2-D(j,i)^2);  %create array with radii of atoms as projected on plane
            xyzr_prj(i).clr(j,1:3)=nclr_list(find(radii==cfile(j,4)),1:3);  %Identify points by radii then create array of RGB color vectors.
            else     %if point does not intersect, write placeholder "no data" values
                xyzr_prj(i).xyz(j,1:3)=[-99 -99 -99];
                xyzr_prj(i).r(j)=-99;
                xyzr_prj(i).clr(j,1:3)=-999;
            end
        end
    end
end

%This part does a coordinate transformation to convert the 3-d coordinates where
each point intersects the slicing plane into to 2-d coordinates
%Follows:  http://mathforum.org/library/drcmath/view/51727.html

for i=1:length(xyzr_prj)
p_vect(i,:)=find_perp(xyz0(i,:)); %find a vector within the the plane
cp(i,:)=cross(xyz0(i,1:3),p_vect(i,1:3)); %take a cross product

%find basis vectors for new coordinate system
e1(i,:)= (1/sqrt(p_vect(i,1:3)'*p_vect(i,1:3))).*p_vect(i,1:3);
e2(i,:)= (1/sqrt(cp(i,1:3)'*cp(i,1:3))).*cp(i,1:3);
e12=[e1(i,1:3)' e2(i,1:3)'];
%put new basis vectors into single array
og(i,:)=xyz0(i,1:3); %define origin of new coordinate system

%solve for x and y
for k=1:size(xyzr_prj(i).xyz,1);
    offset(i).offset(k,1:3)=xyzr_prj(i).xyz(k,1:3)-og(i,1:3); % Compute
distance between points and new origin
    xy(i).xy(k,1:2)=e12\offset(i).offset(k,1:3)'; % do an inversion to
solve for new X Y coord
    xy(i).r(k,1)=xyzr_prj(i).r(k); % copy radii into final file
    xy(i).clr(k,1:3)=xyzr_prj(i).clr(k,1:3); % copy color code into final
file
end
if scalar(i)<0
    xy(i).xy(:,2)= xy(i).xy(:,2)*-1;
end
end
xy %this is the structure that holds the data: X,Y,radius, and color code.
%Note that it is a matlab structure and not an array. The syntax is
%different.

Test_name = mfilename;
mat_stat

Appendix C:
Crystal sectioning program ‘mat_stat’

% This program provides aperture statistics for mineral lattices analyzed...
% by Will Amidon's code, xtal_section.m

% Daniel Hobbs
% March 2013

% For model results see stats(2,1)

%%%%%%%%%%%%%%%%%% CHECK THESE INPUTS BEFORE STARTING %%%%%%%%%%%%%%%%%%%%
Mag = 50; % Number of pixels per angstrom
HeMax = 3*Mag; % Max aperture radius to test (angstroms*Mag)
HeInt = 0.01*Mag; % Size interval btxn each test aperture radius (angstroms*Mag)
HeMin = 0.1*Mag;  % Min aperture radius to test (angstroms*Mag)

boundary = [];  
xmax = 0;  
xmin = 1000;  
ymax = 0;  
ymin = 1000;  
clear DistFromEdge stats  
clf  
clc

for vv = 1:numslices
    if isempty(find(xy(1,vv).xy(:,1)>-98))
        continue  
    end
    xxyyarray = xy(1,vv).xy(:,1);  % look at the xy.xy array from xtal_section  
    [xyrows] = find(xxyyarray>-98);  % find rows with real data  
    xyrawcords = Mag.*(xy(1,vv).xy(xyrows,1:2));  % multiply those rows by magnification number

    xmax = max(xmax, max(xyrawcords(:,1)));  
xmin = min(xmin, min(xyrawcords(:,1)));  
ymax = max(ymax, max(xyrawcords(:,2)));  
ymin = min(ymin, min(xyrawcords(:,2)));  
    if ymin < -4000
        'help'
    end
end

rows = ceil(ymax-ymin)+1;  % Define the output matrix size. Must be same as 'distFromCenter'

for v = 1:numslices
    if isempty(find(xy(1,v).xy(:,1)>-98))
        continue  
    end
    slice = v

    xxyyarray = xy(1,v).xy(:,1);  % look at the xy.xy array from xtal_section  
    [xyrows] = find(xxyyarray>-98);  % find rows with real data  
    xyrawcords = Mag.*(xy(1,v).xy(xyrows,1:2));  % multiply those rows by magnification number
% trans xy coords so minimums = 1

xyarray = xy(1,v).r(:,1); % look at the xy.r array from xtal_section

[radrows] = find(xyarray>-98); % find rows with real data

radii = ceil(Mag.*(xy(1,v).r(radrows,1))); % mult. rows by mag # and round up

%%%%%%%%%%%%%%%%%%%%%%  Plot atom slices %%%%%%%%%%%%%%%%%%%%%%%%%%%%%

circlemat = 0; % Clear previous slice

[xMat,yMat] = meshgrid(1:cols,1:rows);

for z = 1:length(radii)
    distFromCenter = sqrt((xMat-xycords(z,1)).^2 + (yMat-xycords(z,2)).^2);
    % For each cell, calculate distance from circle center
    circlemat = distFromCenter<=radii(z,1) | circlemat; % Make logical matrix based on if each cell distance is <= radii
end

%%%%%%%%%%%%%%%%%%%%%%  Make boundary defined by atom centers %%%%%%%%

centers = zeros(rows, cols);

if isempty(boundary) && length(radii) == 1
    continue
elseif isempty(boundary) && length(radii) == 2 %v == 1 || v == 2;
    boundary = ~bwconvhull(circlemat); % make convex hull from the two atoms
    circlemat = logical(circlemat + boundary); % ignore area outside convex hull when testing
else
    centers = zeros(rows,cols);
    for gg = 1:length(xycords)
        centers(ceil(xycords(gg,2)),ceil(xycords(gg,1))) = 1; % ...find center points of all atoms
    end
    boundary = ~bwconvhull(centers); % make convex hull from center points
else
    % use old border b/c you can't make one with just one atom and using two is inaccurate
    elseif ~isequal(xyrawcords, Mag.*(xy(1,(v-1)).xy(xyrows,1:2))) % if new atoms appear...
        centers = zeros(rows,cols);
        for gg = 1:length(xycords)
            centers(ceil(xycords(gg,2)),ceil(xycords(gg,1))) = 1; % ...find center points of all atoms
        end
        boundary = ~bwconvhull(centers); % make convex hull from center points
    else % length(radii) < 3
        % if new atoms appear...
        centers = zeros(rows,cols);
        for gg = 1:length(xycords)
            centers(ceil(xycords(gg,2)),ceil(xycords(gg,1))) = 1; % ...find center points of all atoms
        end
        boundary = ~bwconvhull(centers); % make convex hull from center points
    end
end

circlemat = logical(circlemat + boundary); % ignore area outside convex hull when testing
% save a copy of slice before aperture testing
preapp = single(circlemat);

% For each pixel, find distance from nearest occupied pixel
EdgeDists = bwdist(circlemat);
circlemat = preapp;

%%%%%%%%%%%%%%%%% Find apertures %%%%%%%%%%%%%%%%%
%%% Determine slice porosity (count total black space)...
stats(1,v).porosity = (length(find(circlemat==0)))/(length(find(boundary==0)));
stats(2,1).porosities(1,v) = stats(1,v).porosity;  % add to list of each slice porosity
stat = [0 0 0];

%%% Starting with the largest apertures, fit circles
for q = HeMax:-HeInt:HeMin
    endofline = 0;
    while isempty(find(EdgeDists > q)) == false && endofline == 0  % Check if min DFE is greater than radius of test aperture
        [ro,co]=find(EdgeDists > q);   % Store coords of centers of circles that could fit
        %%% make test circle at each potential circle center
        for aa = 1:length(ro)
            if circlemat(ro(aa),co(aa))==0
                DFC = sqrt((xMat-co(aa)).^2 + (yMat-ro(aa)).^2);
                circle = DFC <= q;
                circle = single(circle);
                circletest = circle + circlemat;

                %%% check for overlap with existing atom slices or approved test circle
                if isempty(find(circletest==2));  % if no overlap
                    circlemat = circletest;  % update circlemat with new circle included
                    EdgeDists = min(EdgeDists,(DFC - q));  % update EdgeDists matrix with new circle included
                    stat = [stat;q/Mag co(aa) ro(aa)];  % save q, t(x), w(y) in temp stats output
                    break;
                end

            if aa == length(ro)  % just in case no circle fits
                endofline = 1
            end
        end
    end
end
if length(stat) > 3
endthing = circlemat - preapp;
histogram = histogram + endthing;
stats(1,v).xy = stat(2:length(stat),2:3); % copy to stats structure array
stats(1,v).r = stat(2:length(stat),1);
stats(1,v).max = stat(2,:);
stats(2,1).maxes(v,:) = stat(2,:);
stats(1,v).ap_porosity = 
(length(find(endthing>0)))/(length(find(boundary==0)))); % what % of available pore space got filled by ap circles?
stats(2,1).ap_porosities(1,v) = stats(1,v).ap_porosity; % add to list of aperture porosities
end
end
% save stats output for entire thing
stats(2,1).histogram = histogram;
stats(2,1).hist_norm = histogram./numslices; % histogram with counts normalized to reflect percentages
stats(2,1).avg_ap_porosity = mean(stats(2,1).ap_porosities(1,:)); % average % of available pore space filled by aperture circles
stats(2,1).minmax = 
stats(2,1).maxes(find(stats(2,1).maxes(:,1)==min(stats(2,1).maxes(find(stats(2,1).maxes(:,1)),1)),1)),:);
stats(2,1).countminmax = length(stats(2,1).minmax(:,1));
stats(2,1).maxmax = 
stats(2,1).maxes(find(stats(2,1).maxes(:,1)==max(stats(2,1).maxes(:,1)),1)),:);
stats(2,1).countmaxmax = length(find(stats(2,1).maxes==max(stats(2,1).maxes(:,1))));
stats(2,1).avg_porosity = mean(stats(2,1).porosities(1,:));
stats(2,1).medmax = median(stats(2,1).maxes(:,1));
stats(2,1).bigger_than_He = length(find(stats(2,1).maxes(:,1) > .9))/length((stats(2,1).maxes(:,1)));
stats(2,1).summary_column = [stats(2,1).avg_ap_porosity(1,1);
stats(2,1).minmax(1,1); stats(2,1).countminmax; stats(2,1).maxmax(1,1); stats(2,1).medmax(1,1);
stats(2,1).bigger_than_He(1,1)];
save(sprintf('%s_stats.mat',Test_name)) %,'stats', 'histogram', 'Test_name', 'numslices', 'HeMax')
iptsetpref('ImshowAxesVisible','on')
imshow(stats(2,1).hist_norm,[0 1])
colorbar
print('-dtiff',sprintf('%s_hist.tif',Test_name))
bar(0:.05:HeMax/Mag,histc(stats(2,1).maxes(find(stats(2,1).maxes(:,1)),1),0:.05 :HeMax/Mag)/numslices)
xlabel('Maximum Aperture Radii of All Slices')
ylabel('Count')% hh = findobj(gca,'Type','patch');
axis([0 1.5 0 0.5])
set(gca,'xtick',[0:.25:1.5],'xminor.tick','on','TickDir','out')
% set(hh,'FaceColor','b','EdgeColor','k')
print('-dtiff',sprintf('%s_maxes.tif',Test_name))