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9 Diffusion of Helium in SiC and Implications for Retention of Cosmogenic He

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Abstract

Diffusion of helium has been characterized in silicon carbide of cubic and hexagonal (4H and 6H) forms. Polished sections of SiC were implanted with ^3He at 100 keV at a dose of $1 \times 10^{15}/\text{cm}^2$. The implanted SiC samples were sealed under vacuum in silica glass ampoules, and annealed in 1-atm furnaces. ^3He distributions following all experiments were measured with Nuclear Reaction Analysis using the reaction $^3\text{He}(d,p)^4\text{He}$. For He diffusion in cubic SiC and 4H hexagonal SiC we obtain the following Arrhenius relations:

$$D_{\text{cubic}} = 1.83 \times 10^{-6} \exp(-254 \pm 10 \text{ kJ mol}^{-1}/RT) \text{ m}^2\text{sec}^{-1}.$$

$$D_{4\text{H}} = 4.78 \times 10^{-7} \exp(-255 \pm 29 \text{ kJ mol}^{-1}/RT) \text{ m}^2\text{sec}^{-1}.$$

While He diffusion is considerably slower in SiC than in many silicate phases, He retentivity may be limited under some conditions. For example, helium will be lost from SiC grains over much shorter timescales than potential survival times of SiC presolar grains in the solar nebula. When exposed to impact heating followed by slow cooling, nearly complete loss of He from SiC grains near the site of impact will occur within several hours to a few days. For SiC grains at greater distance from impact sites, He would be better retained, depending on the rapidity of cooling. At tens of km away from a large impactor, where peak T would be $\sim 800\text{K}$, SiC grains would lose about 50% of their He if the grains cooled within a few thousand years, and 5% if they cooled within a few tens of years. At greater distances where heating is more modest (500K and lower), SiC grains would be quite retentive of He even for cases of very slow cooling. Helium would also be retained in cases of impact heating followed by very rapid cooling. For these short heating pulses, $10 \mu\text{m}$ diameter SiC grains would retain more than 50% of their He for peak heating temperatures of 2173, 1973 and 1773K for durations of 3, 10 and 60 seconds, respectively.

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71 Keywords: SiC, helium, diffusion, nuclear reaction analysis, presolar grains

1. Introduction

Silicon carbide is a major constituent of interstellar dust grains (e.g., Bernatowicz et al., 1987; Zinner et al., 1987; Zinner, 2013; Amari et al., 1994). In addition, it has important technological applications in nuclear reactors as cladding or containment materials (e.g., Nozawa et al., 2009; Riccardi et al., 2004; Yvon and Carre, 2009; Snead et al., 2007; Katoh et al., 2012), as well in electronic devices for high temperature, high frequency and high power applications (e.g., Raynaud, 2001).

Because of its importance as a material in nuclear reactor and nuclear waste applications and for electronic devices, the effects of He implantation and subsequent annealing on SiC have been studied extensively (e.g., Chen et al., 2000; Oliviero et al., 2002; 2003; Jiang et al., 2002; Zhang et al., 2003; Vincent et al., 2009; Miro et al., 2011; Barbot et al., 2011; Linez et al., 2013). He migration and defects in SiC structures have also been explored theoretically with density functional theory calculations (e.g., Van Ginhoven et al., 2006; Cheng et al., 2011). Direct profiling to characterize diffusion of implanted ^3He and ^4He in SiC has been undertaken using the techniques of nuclear reaction analysis (NRA) and Elastic Recoil Detection (ERD) (e.g., Miro et al., 2011; Jiang et al., 2002; Smith et al., 2004; Sauvage et al., 2007). He diffusion in SiC has also been characterized through bulk degassing of He-implanted materials (Jung, 1992). However, there are wide variations in He diffusivities determined in the existing experimental studies, and observations have been made of complex behaviors of He in SiC, which have been attributed to trapping-detrapping phenomena and may depend on He implant dose and energy as well as annealing conditions.

In this work, we attempt to further quantify helium diffusion in SiC by examining different SiC structural forms, both cubic and hexagonal (4H and 6H). We conduct experiments over a range of time-temperature conditions to evaluate temperature dependence of He transport, and assess whether measured diffusivities exhibit time invariance at constant T, which could be an indicator of the presence or absence of trapping effects. A similar approach to that used in our earlier investigations (Cherniak et al., 2009; Cherniak and Watson, 2011; 2012; 2013) of He diffusion is taken here, with ion implantation used to introduce ^3He , and ^3He concentrations measured by nuclear reaction analysis (NRA) using the reaction $^3\text{He(d,p)}^4\text{He}$. Relatively low doses of implanted He are used to minimize effects of implantation-induced defects, and to avoid the possibility of He aggregation, which has been associated with high He implant doses. Materials were also characterized with IR reflectance spectroscopy prior to and following ion implantation to assess the effects of He implantation on crystal integrity.

2. Experimental Procedure

2.1 Sample Preparation

The silicon carbide samples were single-crystal gem moissanite purchased from a commercial jewelry supplier, SiC in cubic form, grown by the continuous feed physical vapor transport (CF-PVT) method (Chaussende et al., 2005; 2009), and commercially-produced polished slabs of single-crystal hexagonal SiC (both 6H and 4H forms) obtained from the MTI Corporation. The hexagonal and cubic structure SiC samples were cut into pieces 3-4mm on a side using a low-speed saw with a diamond blade. The gem moissanite was polished to 0.3 μm alumina, followed by a chemical polish with colloidal silica to create a flat surface about 3mm

on a side. After polishing and cutting, samples were cleaned ultrasonically in distilled water and ethanol.

2.2 Ion implantation and diffusion experiments

The prepared SiC samples were mounted for ion implantation on an aluminum plate using carbon paint. The samples were implanted at room temperature with 100 keV ^3He ions produced in the Extrion ion implanter at the Ion Beam Laboratory at the University at Albany, with a dose of $1 \times 10^{15} \text{ } ^3\text{He}/\text{cm}^2$. All of the samples were implanted simultaneously, so they received the same implant dose.

Experimental assemblies for diffusion experiments were prepared by sealing the implanted SiC samples in silica glass ampoules under vacuum, along with some Si powder to act as a scavenger for residual oxygen and nitrogen. Experiments were run in 1-atm furnaces at temperatures from 749-1150°C, for times from 30 minutes to 9 days (Table 1). Experiments at temperatures under 1100°C were run in Kanthal-wire wound vertical tube furnaces, monitored with chromel-alumel (type K) thermocouples; those at higher temperatures were run in horizontal tube furnaces with MoSi₂ heating elements, monitored with Pt-Pt10%Rh (type S) thermocouples. In all cases, temperature uncertainties were $\sim \pm 2^\circ\text{C}$. Following diffusion anneals, samples were removed from the furnaces and allowed to cool in air. They were then removed from capsules and cleaned in baths of ethanol.

2.3 NRA analysis

³He distributions in the samples were measured with nuclear reaction analysis using the ³He(d,p)⁴He reaction (e.g., Pronko and Pronko, 1974; Dieumegard et al., 1979; Payne et al., 1989; Paszti, 1992). Analyses were performed at the 4 MeV Dynamitron accelerator at the University at Albany. This nuclear reaction has been used to measure ³He in a variety of minerals and ceramic materials, including apatite (e.g., Miro et al., 2006; Cherniak et al., 2009), zircon (Cherniak et al., 2009), zirconia (Gosset et al., 2002, Costantini et al., 2003; Trocellier et al., 2003a,b), titanite (Cherniak and Watson, 2011), rutile (Cherniak and Watson, 2011), olivine (Cherniak and Watson, 2012) and REE phosphates (Cherniak and Watson, 2013). The protons produced in the reaction, along with backscattered deuterons and products of various (d,p) and (d,α) reactions induced with major elements constituting in the sample, were detected with a solid state surface barrier detector with 1500 μm depletion depth and 100 mm² area positioned at 167.5° with respect to the incident beam. The beamspot incident on sample surfaces was ~1 to 1.5mm on a side. A 7.5 μm thick Kapton foil was placed in front of the detector to stop some of the backscattered deuterons.

For these analyses, we take the approach used in Cherniak et al. (2009), performing analyses over a range of energies to better define the profile. Analyses at 4 or 5 different incident deuteron energies were performed, using energies ranging from 0.5 to 0.9 MeV, with energy steps of 0.1 to 0.2 MeV. Typical beam currents, using a D₂⁺ beam with beamspot ~1.5mm on a side, were 40-60 nA, with 50-100 μC charge collected per energy step. Repeat analyses of the same samples in successive analytical sessions yielded results in good agreement, suggesting little effect on He diffusion profiles from the deuterium used in NRA measurements. The reference sample was implanted at the same time, and with the same implant dose and energy, as the samples used in diffusion anneals. For each energy step, proton yields from the ³He(d,p)⁴He

reaction were measured for both annealed samples and an implanted unannealed reference sample of SiC. From these measurements, ratios of proton yields from the annealed samples and the implanted reference sample were calculated for each energy step.

The measured ratios were converted into diffusivities by first evaluating the loss of diffusant from an implanted profile as a function of Dt . For a semi-infinite medium with the concentration of diffusant equal to zero at $x = 0$, the distribution of the implanted species can be described as a function of depth x and time t as (Ryssel and Ruge, 1986):

$$N(x,t) = \frac{N_m/2}{\sqrt{\left(1 + \frac{2Dt}{\Delta R^2}\right)}} \left(\exp\left[-\frac{(x-R)^2}{2\Delta R^2 + 4Dt}\right] \times \left[1 + \operatorname{erf}\left(\frac{\frac{R\sqrt{4Dt}}{\sqrt{2}\Delta R} + \frac{x\sqrt{2}\Delta R}{\sqrt{4Dt}}}{\sqrt{2\Delta R^2 + 4Dt}}\right)\right] - \exp\left[-\frac{(x+R)^2}{2\Delta R^2 + 4Dt}\right] \times \left[1 + \operatorname{erf}\left(\frac{\frac{R\sqrt{4Dt}}{\sqrt{2}\Delta R} - \frac{x\sqrt{2}\Delta R}{\sqrt{4Dt}}}{\sqrt{2\Delta R^2 + 4Dt}}\right)\right] \right) \quad (1)$$

where D is the diffusion coefficient, N_m is the maximum concentration of the implanted species (in an unannealed sample), R is the range (depth in the material) of implanted species, and ΔR is the range straggle (full width at half-maximum width of the initial implanted distribution).

Values of R and ΔR for ^3He from the Monte-Carlo simulation program SRIM 2006 (Ziegler, 2006) are 3830 and 600 Å for SiC; the value for N_m is ~ 0.09 at% for the implanted dose of $1 \times 10^{15}/\text{cm}^2$.

Proton yields from the nuclear reaction at each beam energy are related to the ^3He distribution by taking into consideration the cross-section of the reaction as a function of energy (and depth in the material) over the depth sampled by the beam, the number of deuterons impinging on the target, the energy loss with depth of the deuterons as they traverse the SiC samples, and the solid angle subtended by the detector, as outlined in Cherniak et al. (2009). The proton yields for the ^3He distribution in the unannealed implanted reference sample are also evaluated in this manner, and compared with those for annealed implanted samples. Using the

equations above, a relationship can be calculated for each incident beam energy which directly relates the ratio of proton yields for an implanted untreated sample and an annealed sample to a specific value of Dt . Since the duration of the experiment for the annealed sample is known, a value of D can then be determined. Uncertainties in diffusivities are determined from counting statistics from the detected proton signals and the variance of calculated diffusivities among incident beam energies used for each sample, which also take into consideration the uncertainties associated with stopping powers in the materials for the incident deuterons and the implanted helium.

2. 4. Fourier Transform Infrared Spectroscopy

Reflectance Fourier transform infrared (FTIR) spectroscopy was used to probe changes to the SiC crystal lattices caused by ion implantation and subsequent diffusion annealing. The incident infrared beam was not polarized. Reflectance FTIR spectra were measured using a Bruker Hyperion infrared microscope with KBR beamsplitters and an MCT detector, attached to a Bruker Vertex 70 spectrometer. The spectrometer compartment was purged with 'dried' air. Backgrounds were collected on a gold-coated mirror. The incident IR beam was apertured to obtain sample intensities of ~ 1 . Knife-edge apertures were adjusted to focus a $\sim 200 \times 200 \mu\text{m}$ IR beam with near-normal incidence on the prepared crystal surfaces.

3. Results

³He diffusion coefficients for silicon carbide are presented in Table 1 and plotted in [figure 1](#). A fit to the data for the cubic SiC over the temperature range 749-1150°C yields an activation energy of 254 ± 10 kJ/mol and pre-exponential factor of 1.83×10^{-6} m²/sec ($\log D_0 = -5.738 \pm 0.426$). Diffusion parameters for the hexagonal structures agree within uncertainties with those for the cubic structure; a fit to the 4H SiC data yields a pre-exponential factor of 4.78×10^{-7} m²/sec ($\log D_0 = -6.320 \pm 1.299$) and an activation energy of 255 ± 29 kJ/mol, while a fit to both the 6H and 4H forms results in a pre-exponential factor of 1.39×10^{-7} m²/sec ($\log D_0 = -6.856 \pm 0.869$) and an activation energy of 244 ± 19 kJ/mol). The activation energy for He diffusion in SiC is much higher, and diffusivities much lower, than for most silicate minerals. For example, the activation energy for He diffusion in olivine (for diffusion parallel to c) is 159 kJ/mol (Cherniak and Watson, 2012), and He diffusivities are ~5 orders of magnitude greater than that for SiC at 800°C.

Time series (i.e., experiments run at a constant temperature but for different amounts of time) are a standard means to evaluate whether there are any contributions from non-diffusive transport processes that could result in a variation with annealing time of values determined for D. The time series ([figure 2](#)) for SiC at 850°C shows similar values for diffusivities in the 6H SiC for times differing by nearly an order of magnitude. These data suggest that the dominant process being measured is volume diffusion, and that diffusion behavior is consistent with the assumptions made in the diffusion model. The figure also illustrates the similarity of He diffusivities for different forms of SiC, as diffusivities for 6H, 4H and gem moissanite samples are the same within experimental uncertainty.

4. Discussion

4.1 Comparison with previous He diffusion studies and consideration of the effects of ion implantation

Several studies have investigated He diffusion in both single-crystal and polycrystalline SiC. These data are summarized, along with results from the present work, in [figure 3](#). In addition, there has been exploration of the effects of He ion implantation on SiC, with investigations of the creation of defects and the aggregation and transport of the implanted helium; studies of these phenomena are also discussed below.

Jung (1992) investigated the bulk release of He from high energy (5-28 MeV) implants in polycrystalline SiC. The material was predominately the 6H form of SiC, with ~10% free Si. From the degassing spectra, Jung (1992) obtained an Arrhenius relation of $D = 1.1 \times 10^{-6} \exp(-136 \text{ kJ mol}^{-1}/RT)$. It was noted that complete outgassing did not occur and some helium was retained in the samples, likely at grain boundaries.

Sauvage et al. (2007) also investigated He diffusion in polycrystalline SiC (primarily in the 6H form). They implanted ^3He at energies of 500 keV and doses of $5 \times 10^{15}/\text{cm}^2$ and $1 \times 10^{15}/\text{cm}^2$, which results in a maximum He concentration of ~ 0.35 at% for the former dose. Changes in ^3He in the samples with heating were measured with nuclear reaction analysis using the $^3\text{He}(d,\alpha)^1\text{H}$ and $^3\text{He}(d,p)^4\text{He}$ reactions. A diffusivity of $8 \pm 1 \times 10^{-17} \text{ m}^2/\text{sec}$ was determined at 1300°C, with similar values found for both implant doses.

Miro et al. (2011) studied diffusion of He in single-crystal SiC of 4H and 6H forms, implanting SiC with 3 MeV ^3He at a dose of $1 \times 10^{16}/\text{cm}^2$, which yields a peak He concentration of ~ 0.33 at%. The changes in distributions of implanted ^3He were measured with NRA, using the $^3\text{He}(d,p)^4\text{He}$ reaction. They observed complex behavior, which they attributed to trapping

and detrapping of He. They fit the He concentration distributions determined from the NRA spectra with a model incorporating two diffusivities, D_1 , a low apparent diffusivity with little temperature dependence, which they ascribed to a trapping/detrapping mechanism, and D_2 , a faster diffusivity with a significant temperature dependence. They observed little evidence of He migration at temperatures less than 1100°C. For the D_2 component, they determined activation energies ranging from 318 ± 39 to 396 ± 39 kJ/mol. Miro et al. (2011) argued that He diffusion occurs in the ion-implanted SiC either through a substitutional mechanism involving vacancy-assisted migration, or a dissociative mechanism involving helium-vacancy ($\text{He}_n\text{-V}_m$) clusters in which He atoms are trapped at defects, with interstitial migration only occurring at low temperatures, and for samples with low amounts of implantation-induced damage.

In addition to these experimental studies, helium migration in SiC has also been investigated with models using density functional theory. Van Ginhoven et al. (2006) performed density functional theory calculations of He migration in 3C-SiC, which yielded an activation energy of 2.5 eV (241 kJ/mol) for interstitial migration; these authors note that movement on interstitial sites is thought to be the dominant long-range migration pathway within single crystal SiC. Our activation energies for He diffusion are similar to those determined in this work.

Our diffusivities differ significantly from those determined for He diffusion in polycrystalline SiC. They are about 2 orders of magnitude faster than the findings of Sauvage et al. (2007), and more than 6 orders of magnitude slower than those from the measurements of Jung (1992). This discrepancy is not surprising, given typical differences between grain-boundary and lattice diffusion rates, and the possibility of contributions from multiple fast transport paths that may exist and enhance He loss rates and diffusivities derived from bulk degassing measurements like those of Jung (1992). In the case of Sauvage et al. (2007), grain

boundaries may act as traps for He (e.g., Vincent et al., 2009) in the polycrystalline SiC and inhibit He loss from samples, thus lowering apparent diffusivities.

In comparing our findings to the results of Miro et al. (2011) for single crystal SiC, we measure diffusivities about 3 orders of magnitude faster than their D_1 diffusivities estimated for the trapping/detrapping mechanism, but the values of D_2 they determine are similar in magnitude to our diffusivities, but with larger activation energies for diffusion, although it must be noted that the activation energies determined by Miro et al. (2011) are not very well-constrained because of the limited range of temperatures investigated in their study. There are some important differences between our experiments and those of Miro et al. (2011), which may affect the degree of damage and relative significance of different He transport processes. The implant doses of Miro et al. (2011) are an order of magnitude greater than those used in our work, and maximum He concentrations are about a factor of 4 smaller in our samples than in those of Miro et al. (2011); the greater damage induced by the higher implant dose, as well as the higher concentration of He, may increase the likelihood of trapping. In contrast to the observations of Miro et al. (2011) we see movement of He following anneals at temperatures below 1100°C, and measure consistent diffusivities for a time series of anneals at constant temperature, again in contrast to observations of Miro et al. (2011) who observe scatter among their diffusion data at constant temperature but differing annealing times.

While SiC exhibits high-temperature stability and generally good resistance against irradiation (e.g., Giancarli et al., 1998; Bockstedte et al., 2010), helium implantation, especially at high doses, can affect these materials. In an examination of He implanted 6H SiC (50 keV energy, doses of 2×10^{14} and $1 \times 10^{15}/\text{cm}^2$), Linez et al. (2013) probed defect distributions with positron annihilation spectroscopy, finding that the main defects produced are $V_{\text{Si}}V_{\text{C}}$

divacancies. They also noted trapping in divacancies during low-temperature annealing, with detrapping occurring at ~850 and 950°C, respectively, for the two doses, as well as growth of larger defects (e.g., $V_{Si}V_CV_{Si}$) in the samples exposed to the higher He fluence. Given the differences in energy between our implants and those of Linez et al. (2013), maximum values for He concentration and defects produced will be ~20% lower for our samples with an equivalent implant dose given the differences in He distribution. Although low-dose He implantation can produce some defects, Linez et al. (2015) reported little lattice damage in 6H-SiC, as evaluated by channeling measurements, for implantation of 50 keV ^3He at a dose of $1 \times 10^{15}/\text{cm}^2$. In another study investigating radiation damage effects on He-implanted SiC, Jiang et al. (2002) conducted RBS/channeling studies of 6H-SiC implanted with 50 keV He at 300K at various doses ranging from 7.4×10^{14} to $2.5 \times 10^{16}/\text{cm}^2$. For the low end of these doses, in the range similar to those used in our work, Jiang et al. (2002) observed only a small relative degree of disorder of the of Si sublattice (about 0.05 relative Si sublattice disorder, with 1.0 corresponding to full amorphization), consistent with the observations of Linez et al. (2015). They also found no evidence of He bubbles in these single-crystal materials over the range of He implantation doses investigated.

At high He implant doses, however, there can be aggregations of He and bubble formation in SiC. For example, Beaufort et al. (2002; 2003) and Oliviero et al. (2003) observed bubble formation following high-fluence implantation of He (doses ranging from 5×10^{16} - $1 \times 10^{17}/\text{cm}^2$) into 4H-SiC. Helium-vacancy complexes formed as a result of room-temperature implantation may lead to lattice expansion in cases of high implant doses (Oliviero et al, 2003) where He concentrations exceed 0.5% (Leclerc et al., 2008), but such doses are more than five times the implant dose used in the present work. Zhang et al. (2003) observed bubble formation after

implantation of 30 keV He, finding that there is a critical fluence at a dose of $\sim 5 \times 10^{15} \text{ cm}^{-2}$, with He bubble formation likely above this implant dose. Vincent et al. (2009) also observed bubble formation at a dose of $5 \times 10^{15} \text{ cm}^{-2}$ for 500 keV implants, but bubble formation was only seen in polycrystalline α -SiC (mostly of the 6H structure) but not in single-crystal 6H SiC. Helium was totally released from single crystals during a 30 minute anneal of their samples at 1300°C (loss consistent with our diffusion data), but in the polycrystalline samples some He remained trapped at grain boundaries.

The above studies suggest that the SiC samples in our experiments experienced little damage from He implantation at the energy and dose used in this work, which is also supported by measurements made with reflectance Fourier transform infrared spectroscopy. Spectra of implanted and unimplanted 6H SiC have virtually identical spectra, indicating little effect on Si-C bonding environments. While reflectance Fourier transform infrared spectroscopy does have limitations in its sensitivity, these findings are consistent with the relatively high resistance of SiC to irradiation effects (e.g., Giancarli et al., 1998; Bockstedte et al., 2010) and observations from other studies cited above.

5. Cosmochemical implications

The He content of presolar SiC grains is used to determine the cosmic ray exposure age, i.e., the travel time of a grain from its parent star to the early Solar System. Helium is produced in a presolar grain due to induced spallation reactions from the irradiation with galactic cosmic rays. Cosmic ray exposure ages have been determined by Heck et al. (2009; 2015). To better understand how SiC grains retain their cosmogenic He, we apply our measurements and discuss potential diffusional losses of He during the early Solar System.

5.1 Timescales for He loss and survival times of presolar SiC grains

Mendybaev et al. (2002) have explored the volatilization of SiC grains exposed to gas mixtures under reducing conditions to evaluate the survivability of presolar grains in the solar nebula. They conclude that under an oxygen fugacity at six log units below the IW buffer, a 10 μ m diameter SiC grain would survive several thousand years at 900°C, ~10yr at 1100°C, ~10d at 1300°C, and ~10h at 1400°C. In [figure 4](#) we plot the fraction of He retained as a function of time for 10 μ m diameter SiC grains experiencing the temperatures above. For these calculations, we assume spherical geometry for the grains, and use the Arrhenius relations for He diffusion in both cubic (Figure 4a) and hexagonal (Figure 4b) forms of SiC. The fraction of total He diffusing from a sphere of radius a for isothermal heating at a given time and temperature can be determined from eq. 6.20 in Crank (1975) in terms of the dimensionless parameter Dt/a^2 , where D is the diffusion coefficient and t is the time. In all cases, helium will be lost from SiC grains over much shorter timescales than potential survival times of SiC presolar grains: virtually all He (99%) will be lost from 10 μ m grains in ~14d at 900°C, ~7h at 1100°C, ~30 min at 1300°C and ~10min at 1400°C. For hexagonal SiC, the times for essentially complete loss of He would be ~50d, ~30h, ~2h, and ~40min at 900, 1100, 1300, and 1400°C, respectively.

5.2 Impact Heating

Davison et al. (2012) have modeled impacts between planetesimals to investigate post-impact thermal histories of parent bodies and evaluate the importance of impact heating on their

thermal evolution. We can use the findings from these simulations to approximate reasonable scenarios for heating of SiC grains following impact events and assess the likelihood of these grains retaining helium. We use a simple model in which we consider the thermal histories to approximate skewed parabolas with specific values of peak temperature and thermal event duration, and use the expressions of Watson and Cherniak (2013) to determine the extent of diffusive exchange for grains of different sizes exposed to different thermal histories, which will depend on the relative sizes of the impactor and parent body, the velocity of the impactor, the porosity of the parent body, as well as the distance of the grains from the impact site and how quickly they will cool.

The expression from Watson and Cherniak (2013) for heating and cooling along a parabolic trajectory can be applied for both symmetric and "skewed" parabolic trajectories, as long as the total duration of the heating event (τ) and maximum temperature of heating (T_{pk}) are the same. In this case, with a rapid rise to peak temperature due to the impact, the duration of the heating event (τ) is predominately in the cooling portion of the trajectory. This simplified model assumes no production of the diffusing species during the thermal event, and an initially uniform distribution of the diffusant. The expression determines the value ζ , which is directly related to the fractional loss of diffusant from a spherical grain, as a function of τ , T_{pk} , the grain radius (a) and the diffusion parameters E_a and D_0 :

$$\log \zeta = \log \left[\frac{D_0 \tau}{a^2} \right] + \frac{140}{T_{pk}} - \frac{0.437 E_a}{RT_{pk}} - 0.8 \quad (2)$$

In [figure 5](#), results of calculations using this equation are shown for 10 μm diameter grains of cubic SiC. For the calculations, we use values from the impact heating models of Davison et al. (2012) for a planetesimal with a 250km radius and 50% porosity, with large (10% of the

radius of the planetesimal) or small (1% of the radius of the planetesimal) impactors with impact velocities of 4 km/s. For the case of the large impactor, we use a value of 1400K for peak temperature, and 1300K for the small impactor for regions on the planetesimal close to the impact site. Nearly complete loss of He from SiC grains near the site of impact will occur within one to several days, respectively, for the large and small impactors. It should be emphasized, however, that only a small fraction of the impacted planetesimal experiences these extreme conditions, and that most of the body undergoing impact heating would be heated to much more modest temperatures. For SiC grains at distance from the impact site, helium would be better retained, depending on the rapidity of cooling. For example, at 30km away from a large impactor (or 3.5km from a small impactor), where peak T would be $\sim 800\text{K}$, SiC grains would lose about 5% of their He if the grains cooled within a few tens of years, 50% in a few thousand years, and nearly all within a few tens of thousands of years. For grains 40km from a large impactor, with a peak T of 700K, SiC grains would lose about 5% of their He if they cooled within a few thousand years, 50% in several hundred thousand years, and nearly all within ~ 10 Ma. Calculations of post-impact thermal histories by Davison et al. (2012) yield median cooling rates of 1 K/Ma and 128.8 K/Ma for large and small impactors, respectively, suggesting that SiC grains on planetisimals within the distances from an impactor noted above will retain little helium. However, grains at greater distance from the impact site (e.g., 65km and 7.0km for large and small impactors, respectively, heated to $\sim 400\text{K}$), would experience little He loss even with very slow cooling.

We can also consider the case where SiC grains cool very rapidly after impact heating, for example when they are not on or within a larger body where they would experience slow cooling. Equation 2 can still be used for such scenarios, as it has been demonstrated (Young et

al., 2013) that this expression is valid for heating event durations as short as a few seconds. In figure 6, we plot curves showing the fraction of He lost as a function of peak temperature for heating events from 3-60 seconds, with curves calculated using eq. 2 and Arrhenius parameters for cubic SiC. For these short heating pulses, SiC grains will be relatively retentive of He; for example, 10 μm diameter SiC grains will retain more than 50% of their He for peak heating temperatures of 2173, 1973 and 1773K for durations of 3, 10 and 60 seconds, respectively.

Conclusion

In this study, we have characterized helium diffusion in silicon carbide of cubic and hexagonal (4H and 6H) forms, using ion implantation to introduce ^3He and Nuclear Reaction Analysis to measure distributions of ^3He following diffusion anneals. Our findings indicate that retentivity of cosmogenic helium may be limited under some conditions relevant to presolar grains. For example, helium would be lost from SiC grains over much shorter timescales than potential survival times of SiC presolar grains in the solar nebula. When exposed to impact heating followed by slow cooling, nearly complete loss of He from SiC grains near the site of impact would occur within several hours to a few days. For SiC grains at greater distance from impact sites, He would be better retained, depending on the rapidity of cooling. Grains experiencing only modest heating ($\sim 500\text{K}$ or lower) would retain nearly all of their He even when undergoing very slow cooling. For impact heating followed by very rapid cooling, He retention would be significant even for high-temperature short heating pulses.

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582 Table 1. ^3He Diffusion in SiC

		$T(^{\circ}\text{C})$	$time(sec)$	$D(m^2sec^{-1})$	$\log D$	+/-
583	<i>Gem Moissanite:</i>					
	SiC-BW-2	850	9.36×10^4	4.19×10^{-19}	-18.31	0.22
584	<i>Cubic:</i>					
	SiC-BW-3a	749	5.18×10^5	2.05×10^{-19}	-18.69	0.18
	SiC-BW-4	951	1.44×10^4	1.99×10^{-17}	-16.70	0.25
	SiC-BW-5	650	1.93×10^6	8.24×10^{-21}	-20.08	0.22
	SiC-BW-6	1050	3.90×10^3	2.08×10^{-16}	-15.68	0.18
	SiC-BW-7	1150	1.80×10^3	8.89×10^{-16}	-15.05	0.10
585	<i>4H:</i>					
	SiC-BW-3c	749	5.18×10^5	1.01×10^{-19}	-18.96	0.28
	SiC-BW-8	850	9.18×10^4	5.17×10^{-19}	-18.29	0.23
	SiC-BW-15	850	3.53×10^5	2.22×10^{-19}	-18.65	0.29
	SiC-BW-9	950	9.00×10^3	4.73×10^{-18}	-17.32	0.18
	SiC-BW-10	1051	2.10×10^3	8.26×10^{-17}	-16.08	0.25
586	<i>6H:</i>					
	SiC-BW-3b	749	5.18×10^5	7.48×10^{-20}	-19.13	0.18
	SiC-BW-11	850	8.64×10^4	6.23×10^{-19}	-18.21	0.25
	SiC-BW-16	850	2.59×10^5	4.34×10^{-19}	-18.36	0.21
	SiC-BW-12	850	4.21×10^5	4.29×10^{-19}	-18.37	0.30
	SiC-BW-17	850	8.24×10^5	2.89×10^{-19}	-18.54	0.29
	SiC-BW-13	950	9.00×10^3	1.19×10^{-17}	-16.92	0.23
	SiC-BW-14	1050	2.10×10^3	1.99×10^{-17}	-16.70	0.32

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Captions for Figures

Figure 1. Arrhenius plot for helium diffusion in SiC. A fit to the data for the cubic SiC over the temperature range 749-1150°C results in an activation energy of 254 ± 10 kJ/mol and pre-exponential factor of 1.83×10^{-6} m²/sec. Diffusion rates in the hexagonal structures do not differ greatly, with diffusion parameters in agreement within uncertainties with those for the cubic structure; a fit to the 4H SiC data yields a pre-exponential factor of 4.78×10^{-7} m²/sec and an activation energy of 255 ± 29 kJ/mol.

Figure 2. Time series for He diffusion in SiC at 850°C. He diffusion coefficients in the 6H form of SiC have consistent values for annealing times differing by nearly an order of magnitude, suggesting that volume diffusion of He is the dominant process being measured. Note also the similarities of diffusivities for the 6H, 4H and gem moissanite samples, indicating little effect of differences in SiC structure on He diffusivities.

Figure 3. Summary of measurements of diffusion of He in SiC, comparing the findings from the present study with reported helium diffusivities from experiments on polycrystalline SiC by Jung(1992) and Sauvage et al. (2007), and single-crystal SiC by Miro et al. (2011). See text for discussion.

Figure 4. Time-temperature conditions for He loss from 10µm diameter grains of cubic (Figure 4a) and hexagonal (Figure 4b) forms of SiC. Virtually all He will be lost from 10µm grains of cubic SiC in ~20 d at 900°C, 10h at 1100°C, ~40 min at 1300°C and ~10min at 1400°C; for

hexagonal SiC, the times would be ~ 60d, ~2d, ~3h, and ~50min at 900, 1100, 1300, and 1400°C, respectively. In all cases, helium would be lost from SiC grains over much shorter timescales than potential survival times of SiC presolar grains in the solar nebula.

Figure 5. Calculations evaluating helium retention in 10 μm diameter SiC grains following heating from an impactor and slow cooling. The calculations, using the modeling results of Davison et al. (2012), consider a 250km radius planetesimal with 50% porosity, with large (10% of the radius of the planetesimal) or small (1% of the radius of the planetesimal) impactors with an impact velocity of 4 km/s. For the case of the large impactor, we use a value of 1400K for peak temperature near the impact site, and 1300K for the case of the small impactor. Nearly complete loss of He from SiC grains near the site of impact will occur within several hours and a few days, respectively, for the large and small impactors. For SiC grains at distance from the impact site, He would be better retained, depending on the rapidity of cooling. For example, at 30km away from a large impactor, where peak T would be ~800K, SiC grains would lose about 50% of their He if the grains cooled within a few thousand years, and 5% if they cooled within a few tens of years. Grains a greater distance from the impact site that experience only modest heating (~500K or lower) would retain nearly all of their He even when undergoing very slow cooling.

Figure 6. Calculations evaluating helium retention in 10 μm diameter SiC grains following rapid heating events due to impact. The calculations use equation 2 with diffusion parameters for cubic SiC, and consider He retention as a function of peak temperature of heating. For these short heating pulses, SiC grains will be relatively retentive of He; for example 10 μm diameter

639 SiC grains will retain more than 50% of their He for peak heating temperatures of 2173, 1973
640 and 1773K for durations of 3, 10 and 60 seconds, respectively.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6