

# A multi-method, multi-scale theoretical study of He and Ne diffusion in zircon

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Cécile Gautheron, Duval Mbongo Djimbi, Jérôme Roques, Hilal Balout, Richard Ketcham, et al.. A multi-method, multi-scale theoretical study of He and Ne diffusion in zircon. Geochimica et Cosmochimica Acta, 2020, 268, pp.348-367. 10.1016/j.gca.2019.10.007 . hal-02996430

## HAL Id: hal-02996430 https://hal.science/hal-02996430

Submitted on 13 Nov 2020

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1	A multi-method, multi-scale theoretical study of He and Ne
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21	10 figures; 4 Tables
22	2 appendices
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#### 24 Abstract

25 The quantification of He and Ne diffusion behavior in crystals rich in U and Th such as zircon is key for the interpretation of  $(U-Th)/{}^{4}$ He and  $(U-Th)/{}^{21}$ Ne thermochronometric ages. 26 Multiple parameters such as chemical substitution, channel obstruction and damage can modify 27 28 the diffusivity compared to a pristine structure. To investigate the impact of these parameters, 29 we have conducted a theoretical diffusion study combining a series of methods and approaches 30 to address the problem across the necessary range of scales (atomic to crystal size). First, using 31 quantum calculation, we determine the different He and Ne insertion sites, insertion energies 32 and diffusion pathways at the atomic scale for an ideal pristine zircon structure (i.e. damage 33 free). These results serve as input for a 3D random walk simulation of atomic trajectories that 34 provides diffusion coefficients for damage-free zircon crystals. Second, as natural zircon 35 crystals are not perfect, we model the impact of different types of damage and diffusion 36 pathway obstruction at the atomic level on He and Ne diffusion in 3D. The calculated He and 37 Ne diffusion coefficients for pure ZrSiO<sub>4</sub> exhibit strongly anisotropic behavior and very high 38 diffusivity along the c-axis, and with 3D, closure temperatures of -197°C and -202 °C 39 respectively. The results for He are comparable to previous DFT studies but strongly different 40 from experimental diffusion results; results for Ne are similar in this respect. Modelling the 41 impact of different types of damage (vacancies, recoil, fission, voids or fluid inclusions) and 42 obstruction on He and Ne diffusion reveals important implications for the (U-Th)/He and (U-43 Th)/Ne thermochronometers. First, obstruction alone does not significantly modify He and Ne 44 diffusion except to reduce anisotropy. Second, trapping is the primary mechanism altering He 45 and Ne diffusion even at low dose, and we predict the maximal trapping energies for He and Ne to be 164 and 320 kJ/mol, similar to values inferred from experimental data. We also 46 47 propose that the closure temperature increases non-linearly with damage, with effective 48 trapping energy increasing with dose until a threshold, possibly corresponding to a percolation transition, after which retentivity decreases. Based on field data sets we also anticipate a value for this threshold of around  $\sim 2-5 \times 10^{17} \alpha/g$ , lower than previously proposed. We show Ne to be highly blocked by damage and predict similar diffusion behavior to He, but with higher retentivity. We demonstrate the importance of investigating rare gas diffusion at the atomic level for comparison with experimental data, in order to build a predictive diffusion law at different scales.

## 55 1. Introduction

In the last two decades, radiogenic <sup>4</sup>He and nucleogenic <sup>21</sup>Ne have been used for (U-56 57 Th)/<sup>4</sup>He and (U-Th)/<sup>21</sup>Ne thermochronology in different minerals such as apatite, zircon and 58 iron oxides for a broad range of geological applications (e.g. Farley and Flowers, 2012; Farley 59 and Stockli, 2002; Gautheron et al., 2006; Reiners et al., 2002; Shuster et al., 2005; Zeitler et 60 al., 1987). Robust He and Ne age interpretation strongly depends on quantitative knowledge of 61 diffusion behavior in crystals, which is linked to the closure temperature Tc (Dodson, 1973), 62 representing to first order the temperature below which He and Ne are significantly retained 63 during cooling. He and Ne diffusion in crystals theoretically follows a simple Arrhenius law with isotropic or anisotropic diffusion. However, it has been shown that, for apatite and zircon, 64 65 diffusion behavior is highly variable. Experimental data sets have Tc values ranging from 40 to 120°C for He in apatite (Shuster et al., 2006) and from -60 to 190°C for zircon (Guenthner 66 et al., 2013, and references therein). For Ne diffusion in zircon, data are sparse due to analytical 67 68 difficulties, and Tc estimates come only from indirect assessment and one published abstract 69 (Gautheron et al., 2006; van Soest et al., 2013).

Radiation damage is considered to be a primary contributor to this variability, although
the impacts of damage type (alpha, recoil and fission damage) and topology (Frenkel-pair, large
damage and amorphous zone) on He diffusion in zircon are not well defined. In addition to
forming traps for diffusing elements (Farley, 2000), damage can also change diffusive behavior

for even low-damage zircon by reducing the strong anisotropy along the *c*-axis (Bengtson et
al., 2012; Farley, 2007). Similar complications may arise from other imperfections such as
inclusions, voids, and defects (Zeitler et al., 2017; Danišík et al., 2017).

77 The relationship between He diffusivity and dose in zircon suggests another topological effect. Diffusivity has been shown to decrease with increasing dose until a threshold is reached, 78 79 after which it strongly increases with further damage (Guenthner et al., 2013), although recent 80 work suggests that this threshold dose may vary (Anderson et al., 2017). This flip in behavior 81 may be linked to the onset of percolation, in which overlapping damage zones start to form an 82 interconnected network (Salje et al., 1999), essentially dividing the crystal into two transport 83 regimes, one through normal crystal (albeit with imperfections) and one through the damage 84 network (Ketcham et al., 2013). Superimposed on the complexity of diffusion is the process of 85 annealing, which changes the landscape in which diffusion occurs, as it is happening. Recent 86 work suggests that damage annealing in zircon also may depend on dose (Ginster et al., 2019), 87 further highlighting the challenges to understanding the regime in which diffusion operates.

88 As a result of this complexity, there are limits to how much progress can be made using 89 exclusively empirical observations and experiments on incompletely-understood natural 90 materials (e.g., Reiners et al., 2004; Reiners, 2005; Cherniak et al., 2009; Guenthner et al., 2013; 91 Anderson et al., 2017; Ginster et al., 2019; Zeitler et al., 2017; Danišík et al., 2017). A rigorous 92 physical understanding of the diffusion process and how it is affected by imperfections is an 93 indispensible complement for the varied and extensive data gathering currently underway. 94 Although the inevitably chaotic and variable nature of damage zones makes them hard to 95 characterize, transport of He and Ne in the areas between damage zones, and between damaged 96 and undamaged crystal, is accessible through theoretical and computational approaches.

97 Several studies have been conducted using Density Functional Theory (DFT)
98 calculations to quantify the He diffusion coefficient in damage-free zircon (Reich et al., 2007;

Saadoune and De Leeuw, 2009; Saadoune et al., 2009). Independent studies consistently find that He is not expected to be retained in the zircon structure at Earth-surface temperatures; for example, Bengtson et al. (2012) calculate  $T_c \sim -150^{\circ}C$  along the crystallographic *c*-axis. However, recent DFT studies on He and Ne diffusion in apatite and hematite give results more similar to experimental data on real specimens, supporting the veracity and applicability of this theoretical approach (Balout et al., 2017a; Djimbi et al., 2015; Gerin et al., 2017).

105 In this contribution, we investigate He and Ne diffusion in zircon from atomic to grain 106 scales using a coordinated series of methodologies developed in recent studies (Djimbi et al., 107 2015, Balout et al., 2017a, b; Gerin et al., 2017) to examine important factors that can modify 108 diffusion rates, including trapping, anisotropy, and path obstruction. As no published Ne 109 diffusion data exist, we use DFT at the atomic scale to build and optimize the ideal zircon unit 110 cell accounting for quantum features, and we inventory the insertion and interstitial sites. Once 111 these sites are identified, we combine the DFT approach with the Nudged Elastic Band (NEB) 112 method to determine the migration energies between them. We complete our atomic-scale characterization using Transition State Theory (TST) to compute jump rates between sites. To 113 114 extend to a larger scale spanning defects, DFT and TST outputs are used in a Kinetic Monte 115 Carlo (KMC) simulation to determine the diffusion trajectories and the effective diffusion 116 coefficients in 3D. We then compare our results with published experimental data and 117 investigate the processes that can modify He and Ne diffusion in zircon. We simulate and 118 evaluate different hypotheses, such as trapping of He and Ne in damage, and diffusion pathway 119 obstruction, in 3D, and their impact on closure temperature. Finally, we discuss the model 120 implications for the (U-Th)/He and (U-Th)/Ne thermochronometers.

121

## 2. Methods, the multi-scale approach

We first provide a general summary of our methods and how they interact with each other, as illustrated in Figure 1. Density Functional Theory (DFT) is a computational modeling

124 method to calculate the energy of interacting atoms by calculating their external electronic 125 configuration. This is done by solving the Schrödinger equation for the electrons using 126 functionals of the electron density. The DFT just solves static problems, atoms at given 127 positions, and does not include dynamics, contrary to molecular dynamics. However, in contrast 128 to molecular dynamics it includes the quantum effects for the electrons, thereby providing the 129 most accurate energy estimation of an ensemble of interacting atoms. Due to the high 130 calculation time, requiring cluster computing, the number of considered atoms remains small 131 (<150 atoms) compared to a real crystal, and therefore a super-cell containing a small number 132 of motionless atoms is used and an infinite repetition of this super-cell is assumed to represent 133 an infinite lattice. The stable position of the atoms for a crystal lattice is found by nudging atom 134 positions until the total energy is minimized. In the same way, an insertion site for He or Ne is 135 found by inserting it into a pre-computed lattice and finding the positions with the minimum 136 energy with respect to displacement after relaxation of the neighboring atoms.

137 He and Ne atoms can statistically jump between insertion sites when they vibrate as a 138 consequence of the finite temperature. This is a dynamical process, beyond the scope of DFT, 139 which addresses static configurations only. Therefore, another approach has to be followed, 140 namely the Transition State Theory (TST), which computes the jumps statistically. It is based 141 on a full mapping of the energy field encountered when the inserted atom moves along its path 142 to its neighboring site, as delivered by the DFT analysis. This approach is valid because the 143 Born-Oppenheimer approximation allows consideration of the motion of atoms as quasi-144 stationary from the electron viewpoint.

The ideal pristine crystal represented by DFT and TST does not capture all the properties of a natural one, which will always contain defects, distortions, dislocations and substitutions, and typically mineral and/or fluid inclusions. However, even in a highly degraded crystal, diffusion occurs in pristine lattice for at least some length scale. The approach we

149 develop here is to consider the ideal case and see how it should be amended when alterations 150 of the pristine lattice are added. Only when significant amorphisation takes place does this 151 approach become invalid. The alteration of the ideal lattice by vacancies, interstitial atoms, and 152 substitutions breaks the periodicity of the lattice and introduces heterogeneity over length scales 153 much larger than the lattice cell dimension. Their effects on diffusion depend on their energy 154 and their topology. Therefore, the easiest way to study them is the simulation of diffusion by 155 random walk over many lattice cells spanning many defects. For this we use the Kinetic Monte 156 Carlo method (KMC), which operates at the mesoscopic level and delivers diffusion 157 coefficients for a heterogeneous medium, based on the energetics of the DFT and the transition 158 rates of the TST (Figure 1). Finally, to compute He and Ne ages in crystals the diffusion 159 equation has to be solved at the macroscopic level using the diffusivities delivered by KMC, or 160 directly by DFT and TST in case of an ideal crystal.

In summary, DFT calculates the mapping of energy as a function of atom location. TST then computes the transition rates by using this mapping and by making use of thermodynamic equilibrium in phase space. KMC then quantifies the effect of randomly distributed alterations of the crystal-like traps or obstructions, independently of the mechanism producing them (interstitial atoms, substitutions, etc.). This pipeline delivers bulk diffusion coefficients for solving the 3D diffusion equation for a finite grain, as illustrated in Figure 1.

167

## 2.1 Density Functional Theory

Following the approach described in detail by Djimbi et al. (2015), we use the Periodic Density Functional Theory (DFT; Hohenberg and Kohn, 1964; Kohn and Sham, 1965), as implemented in the Vienna Ab-initio Simulation Package (VASP) (Kresse and Furthmüller, 1996; Kresse and Hafner, 1993), for all structural optimization and insertion site investigations of both He- and Ne-doped zircon lattices. All parameters were optimized on the zircon unit cell, and the relaxed unit cell geometrical parameters are in good agreement with experimental values. To minimize the volume relaxation effect due to the incorporation of Ne and He atoms, and to avoid interactions between He or Ne with neighboring cells, the zircon unit cell was duplicated along each spatial direction, resulting in a  $2\times2\times2$  super cell consisting of 192 atoms (Figure 2A and 2B). We determine the insertion energy of He and Ne in each interstitial site by relaxing the structure with the help of the gradient technique at constant volume. The insertion energy is defined as the energy needed to bring the He or Ne from outside the crystal into the interstitial site. It is calculated as:

$$E_{ins} = E_{He+zircon} - (E_{zircon} + E_{He})$$
(Eq. 1)

182 where  $E_{He+zircon}$ ,  $E_{zircon}$  and  $E_{He}$  are respectively the absolute energy of the system with He 183 or Ne in the zircon host lattice, the absolute energy of the host lattice, and the energy of the 184 isolated He or Ne atom.

185 We use the Nudged Elastic Band (NEB) (Jónsson et al., 1998; Mills et al., 1995) method 186 to determine the migration energy between insertion sites. NEB is an efficient approach to 187 estimating the minimum energy path (MEP) and the migration energy between two interstitial sites  $(E_{mia}^{ij})$ , which is defined as the difference in energy from when the atom is at the saddle 188 189 point to when it is in the insertion site. It is also called the barrier energy. The NEB is a chain-190 of-states method (Elber and Karplus, 1987; Pratt, 1986) found by constructing a series of system 191 images between states. Adjacent images are linked by a spring force to ensure the continuity of 192 the path, thus mimicking an elastic band. In this study, all NEB calculations are performed with a spring constant of -5  $eV/Å^2$ . 193

194

## 2.2. Transition State Theory

195 Interstitial diffusion occurs through a random walk of an atom from one site in the 196 crystal lattice to another neighboring free one. The atom needs enough energy to accomplish 197 this motion; as there is an energy barrier to overcome, diffusion is a thermally activated process. As already mentioned, this dynamical process cannot be directly calculated by DFT, which addresses static configurations. However, as the motion occurs in thermodynamic equilibrium the canonical ensemble is assumed in phase space. This leads to the transition state theory (Vineyard, 1957; Voter, 1986; Wert and Zener, 1949), in which the atomic motion is controlled by the jump probabilities,  $\Gamma$ , which depend exponentially on temperature.

203 
$$\Gamma^{ij} = \nu_0 e^{-\frac{E_{mig}'}{k_B T}}$$
 (Eq. 2)

204 With 
$$\nu_0 = \frac{\prod_{i=1}^{3N} \nu_i^{init}}{\prod_{i=1}^{3N-1} \nu_i^*} \xrightarrow{\text{Vineyard approx.}} \approx \frac{\prod_{i=1}^{3} \nu_i^{init}}{\prod_{i=1}^{2} \nu_i^*}$$
 (Eq. 3)

205 And 
$$E_{mig}^{ij} = E^* - E^{init}$$
 (Eq. 4)

Where  $v_0$  is the attempt frequency;  $v_i^{init}$  and  $v_i^*$  are the normal mode frequencies at, 206 respectively, the initial and transition states;  $E_{mig}^{ij}$  represents the migration energies; and N is 207 208 the number of atoms in the system. For a molecule with N atoms there are 3N degrees of 209 freedom. For a non-linear molecule three degrees of freedom can be assigned to translation of 210 a body as a whole  $(T_x, T_y, T_z)$  and three to rotations  $(R_x, R_y, R_z)$ . The remaining motions of the 211 atoms are displacements of the atoms from their mean positions. These fundamental vibrations 212 are referred to as "normal modes". Thus, a non-linear molecule has 3N-6 normal modes. In the 213 insertion location, the energy is minimum, and therefore the energy has an upward curvature 214 for any displacement of the inserted atom. This 3D-curvature can be expressed with three 215 eigenvalues, which translate directly to the three normal frequencies. This translation is exactly 216 the same as for any harmonic oscillator like a pendulum. At the saddle point, the same features 217 apply, but only transverse motion relative to the transition path is involved, and therefore there 218 are two frequencies. According to the Vineyard (1957) approximation, for one atom (He or Ne), 219 the energetics of other atoms are not affected by the position of the migrating atom being 220 considered. The TST allows thus provides a well-understood theoretical approach for 221 calculating the frequency factor (Figure 1).

#### 222 2.3. Kinetic Monte Carlo Method

223 In a pristine lattice, the activation energy  $(E_a)$  corresponds to the migration energy 224 obtained from DFT, and the frequency factor  $(D_0)$  can be extracted directly from the TST 225 formulas (Fig. 1). However, when obstructions occur the diffusivity depends on their topology, 226 and a simulation over macroscopic crystals has to be run to determine the modified diffusion 227 coefficients. The Kinetic Monte Carlo (KMC) method (Bortz et al., 1975; Gillespie, 1976) is 228 particularly apt for our purposes because it can be used to extend simulation to time scales far beyond the vibrational period and lengths much larger than the cell size. The KMC simulates, 229 230 at a given temperature, a random walk over the interstitial sites based on the microscopic jump 231 probabilities ( $\Gamma$ ), which have been calculated from TST using the DFT results (Fig. 1). In 232 addition, it takes into account potential obstructions and traps, as well as anisotropy.

233 For a selected temperature, one He (or Ne) atom is placed randomly in one available insertion site. For the possible diffusion directions, with the calculated jumping frequencies 234 235 given by the TST, we randomly choose a number to simulate the jumping time for each 236 direction. The distribution of jumping times follows an exponential decay. The jump direction 237 with the lowest time is chosen, the time and coordinate are updated, and the time is added to 238 the total travel time. This is repeated m times for each atom, and n trajectories (atoms) are 239 simulated, using the method of Djimbi et al. (2015). For each trajectory, the total time is 240 computed as the sum of the residence times in each site between jumps. The diffusion coefficient is obtained by averaging over the ensemble of *n* trajectories. If  $\langle x^2 \rangle$ ,  $\langle y^2 \rangle$ ,  $\langle z^2 \rangle$  are 241 242 the averages over the trajectories of the squares of distances between initial and final points in 243 x, y and z, <t> is the average time of the trajectories, and if we denote as  $D_x$ ,  $D_y$ ,  $D_z$  the diffusion 244 coefficient along the axes, then according to the Einstein relation.

$$245 D_x = \frac{\langle x^2 \rangle}{2\langle t \rangle}$$

246 
$$D_y = \frac{\langle y^2 \rangle}{2\langle t \rangle}$$
 (Eq. 5)

$$D_z = \frac{\langle z^2 \rangle}{2\langle t \rangle}$$

From the above relations the diffusion coefficients can be assessed even in the case of anisotropic diffusion, as is necessary for zircon. The temperature dependence is obtained by running the random walk at different temperatures.

To account for highly anisotropic behavior along the *c* axis and its possible obstruction, the random walk operates on a sub-lattice of  $128 \times 128 \times 4096$  interstitial sites. When an atom jumps against an edge of the sub-lattice it is automatically re-inserted into the opposite side, so that the geometry can be considered as infinite with a periodicity given by the size of the sublattice. Obstructions are simulated by inhibiting some fraction of sites randomly distributed over the sub-lattice.

#### 257 2.4 3D diffusion modeling

Finally, these two descriptions provide a bulk diffusion coefficient, which is used to calculate the diffusion over a finite grain where the surface is taken into account by solving in 3D the diffusion equation appropriate to surface boundary conditions. A modified version of the rare gas 3D diffusion code published in Gautheron and Tassan-Got (2010) and used in subsequent studies (Djimbi et al., 2015; Gautheron et al., 2009; 2012) has been implemented to simulate He and Ne diffusion in zircon. This code solves the diffusion equation by a Monte Carlo method at the macroscopic level, using the diffusivity extracted from the KMC simulation. This approach accounts for crystal surface boundaries, which is not possible in theKMC code.

267 **3.** Results

#### 268 3.1. Investigation of He and Ne interstitial sites

269 Zircon crystallizes as a body-centered tetragonal unit cell, with a structure consisting of 270 a chain of alternating edge-sharing (SiO<sub>4</sub>) tetrahedral and (ZrO<sub>8</sub>) triangular dodecahedra 271 parallel to c-axis (Figure 2A and 2B). The lateral connection of these chains provides two types 272 of possible sites  $(S_1 \text{ and } S_1)$  into which He or Ne atoms can be inserted; these insertion site 273 positions, and the diffusion pathways between them, are identical He and Ne. The connection 274 of these interstitial sites provides open channels along each direction in which He or Ne could 275 diffuse (Figure 2A' and 2B'). In this part of our analysis, a periodic–DFT is run first to build 276 an optimized model of zircon. Next, the model is used to identify diffusion channels and all 277 possible interstitial insertion sites for both He and Ne atoms. As mentioned above, a  $2 \times 2 \times 2$ 278 supercell was optimized as the host lattice (Figure 2), which was large enough to simulate and 279 study the He and Ne insertion in the zircon crystal lattice free of boundary effects.

280 The *c*-axis channel is formed by alternating edge-sharing  $SiO_4$  tetrahedron and  $ZrO_8$ 281 dodecahedron units (Figure 2A), and Figure 2A' illustrates the different He (or Ne) insertion 282 sites along this pathway. In each *c*-channel four sites are inventoried for each lattice cell and 283 they are energetically identical due to the symmetries of the crystal. They are spaced by 1.5 Å. 284 Two types of sites are recognized:  $S_1$ , which allows a jump to an adjacent c channel along a 285 (jump along b forbidden), and  $S_1$ , which allows a jump along b to an adjacent c channel. Along c, the sites form a sequence  $S_1$ - $S_1$ '- $S_1$ - $S_1$ ' ... (Figure 2A'). Therefore, along a, diffusion 286 287 pathways connect  $S_1$  sites. The same applies along b with the  $S_1$ ' sites. The channels along the 288 a- and b-axis are energetically identical and they will be noted a/b-(axis or channel) for 289 simplicity. To move along the a/b-axis, He (or Ne) atoms have to pass through a rhombic

290 (Rhom.) or rectangular (Rect.) gap as shown on Figure 2B'. The former is formed by the 291 intersection of Zr - Zr and O - O diagonals. The latter is formed by the intersection of Si - Siand O – O diagonals, and its area is much larger than the rhombic gap. Each channel consists 292 293 of an alternating series of the two gap types (Figure 2B'); for example, along a the sequence is 294 S1-Rhom.-S1-Rect.-S1-Rhom.-S1-Rect. configuration This makes the *a*/*b*-channels 295 considerably less diffusive than the *c*-axis due to the narrow rhombic gaps.

After channel determination, the two possible interstitial sites, called  $S_1$  and  $S_1$ ', were optimized. They are structurally symmetrical and energetically equivalent. Only one interstitial site environment exists for He and Ne, an octahedral-like site formed by the six oxygen atoms. The interatomic He – O distances have three different values of 2.02, 2.22 and 2.36 Å. For the Ne insertion case, the Ne atom is located 2.16, 2.30 and 2.42 Å from neighboring oxygen atoms. These larger distances are due to the larger size of the Ne atom, making the relaxation effect important for Ne.

The insertion energies calculated based on equation 1 for He and Ne in the different insertion sites are listed in Table 1. The derived helium insertion energy is 1.46 eV, which is in good agreement with other DFT calculations performed by Saadoune et al. (2009) and for comparison obtained insertion value in hematite is given (Balout et al., 2017a, b). In the case of Ne, the insertion energy of 3.10 eV is almost twice that calculated for He. This is related to the larger atomic radius of Ne, which must repel the neighboring atoms more to enter the interstitial site.

310 3.2. Migra

## Migration Energies (E<sub>mig</sub>)

In the *c*-channel, since the inter-site distance  $S_1 - S_1$ ' is about 1.5 Å, only one image is taken between the two sites for the NEB calculation. Figure 3A and 3A' present the migration energies path results along the *c*-channel for He and Ne migration, respectively. The migration energies, reported in Table 2, are 0.24 eV for He (Figure 3A) and 0.22 eV (Figure 3A') for the 315 Ne atom. According to a (b)-channel structures, the  $S_1(S_1)$  sites are separated on one side by 316 a rhombic gap and on the other by a rectangular one. Hence, two NEB calculations were performed for He and Ne migration, corresponding to the energy necessary to pass through 317 318 each gap. For NEB calculation in this channel we start with a linear path composed of a series 319 of 4 images connecting the two  $S_1(S_1)$  sites. After the relaxation process we found that the 320 migration energy between the sites separated by the rectangular gap is equal to 0.66 and 1.53 321 eV for He and Ne atoms, respectively (Table 2; Figure 3B). For the rhombic gap, we find a 322 migration energy of 2.60 eV for He, but for Ne the NEB calculation indicated that no migration 323 is possible (Figure 3B'). Figure 4 illustrates the sequence of the interstitial sites along c and 324 how they are connected to the pathways along *a* and *b*.

The paradoxical result is that along c the energy barrier for Ne is lower than for He, even though its radius is larger as already recognized in the insertion energy calculation. This can be understood by noting that the height of the barrier is a difference in energy. For Ne both the energy in the interstitial site and at the top of the barrier are higher in comparison to He, reflecting the atom radius effect, but this does not say anything about the difference. As a conclusion, contrary to the insertion energy, the activation energy is not well controlled by the ionic or atomic radius. This outcome was already evident in Farley (2007).

According to our results, one can say that, at low temperature, in an ideal crystal He and Ne will diffuse mainly along the *c*-channel. However, as temperature increases, there will be competition between the probability of jumping the 0.24 eV barrier and the 0.66 eV barrier in the case of He diffusion. For Ne-diffusion, however, even at high temperature diffusion along the *c*-axis remains strongly favored.

#### 337 3.3. Ideal lattice results

Using Transition State Theory as presented in section 2, the attempt frequencies v,
which allow determination of relative jump probabilities, were calculated for each jump case.

All calculated jump probabilities are provided in Table 3. From the parameters listed in this
table, the diffusion coefficient along the *c*-axis can be derived analytically for a pristine crystal:

342 
$$D_z = \nu. a^2. \exp\left(-\frac{E_{mig}}{k_B T}\right)$$
(Eq. 6)

343 with a=1.5 Å. In the same way the diffusivity along *a* and *b* for an undamaged crystal and for 344 practical temperatures (T<10<sup>4</sup> K) is obtained as:

345 
$$D_{xy} = \frac{v.a^2}{4} \cdot \exp\left(-\frac{E_{rect}}{k_B T}\right)$$
(Eq. 7)

with *a*=3.35 Å. The factor 4 accounts for the fact that only one site over four allows a jump in
a given direction (Fig. 4), as crossing the rhombic diamond is quasi-forbidden.

348 We get respectively for He and Ne:

349 
$$D_{z,He} = 1.6 \times 10^{-7} exp\left(-\frac{0.24}{k_BT}\right) m^2/s$$
 (Eq. 8)

350 
$$D_{xy,He} = 1.5 \times 10^{-7} exp\left(-\frac{0.66}{k_BT}\right) m^2/s$$
 (Eq. 9)

351

352 
$$D_{z,Ne} = 1.2 \times 10^{-8} exp\left(-\frac{0.22}{k_BT}\right) m^2/s$$
 (Eq. 10)

353 
$$D_{xy,Ne} = 1.1 \times 10^{-7} exp\left(-\frac{1.53}{k_BT}\right) m^2/s$$
 (Eq. 11)

From these results one can conclude that Ne diffusivity is slightly higher at low temperature than He diffusivity in a perfect zircon host lattice. In addition, the diffusivity is highly anisotropic and diffusion occurs essentially along the *c*-axis. The anisotropy is even stronger in the Ne case due to the high energy barrier when crossing the rectangular gap.

358 **4. Discussion** 

## 359 4.1. He and Ne diffusion in non-damaged zircon structure

#### 360 **4.1.1. Comparison to previous calculations**

Helium diffusivity in zircon, calculated by DFT and molecular dynamics, has already
been reported (Bengtson et al., 2012; Reich et al., 2007; Saadoune et al., 2009), and for

363 comparison the insertion energy and barriers are listed respectively in Tables 1 and 2. It is interesting to point out that only Bengtson et al. (2012) recognizes the 1.5 Å inter-site distance 364 along the c-axis, which results from the crystal symmetries. Reich et al. (2007) and Saadoune 365 366 et al. (2009) missed this feature although a dip is visible in the energy landscape for the former, 367 indicating that the minimal energy path was not found along the *c*-axis. Concerning the 368 migration energies, which have the strongest impact on the diffusivity, we are in good 369 agreement with Saadoune et al. (2009) along the c-axis, and at variance with the other 370 calculations. Although we found the same energy pattern along this channel as Bengtson et al. 371 (2012), our migration energy is lower. As the variations of the energy along this channel are 372 small the computations of the barrier are very sensitive to the finding of the minimum energy 373 path. When comparing to the previous calculations along the a/b directions we find the same 374 barrier across the rhombic gaps, but a higher one through the rectangular gap (0.66 instead of 375 ~0.45 eV, Figure 4, Table 2), for a reason which is not elucidated. We will see later that this is 376 barrier is the one that mainly controls the diffusivity in zircon in practical situations.

377 Concerning He diffusivity, differences exist with respect to the other calculations 378 beyond the migration energy. Reich et al. (2007) and Saadoune et al. (2009) used a 1D formula 379 which is known to be inadequate because it assumes that the energetic shape around the 380 interstitial site and the saddle-point is the same. However, this assumption only acts on the pre-381 exponential factor and its impact is limited. Bengtson et al. (2012) did not use this assumption 382 but assumed that along a/b the higher barrier (~2.6 eV) dominates, disregarding the relatively 383 easy intermediate jump along c that can bypass this barrier. This explains why they obtained a 384 very low diffusivity along a/b.

385

#### 4.1.2. Comparison to experimental data

For Ne only one abstract reports diffusion data, with an  $E_a$  value of ~339 kJ/mol and closure temperature of 396-410°C for a 10°C/Ma cooling rate (van Soest et al., 2013). This 388 value is much higher than that computed in this work. Similarly, He diffusion data obtained on 389 natural zircon crystals present significantly higher apparent activation energies than obtained 390 by theoretical studies. In addition, measured (U-Th)/He and (U-Th)/Ne zircon ages confirm that 391 He and Ne are strongly retained in this mineral. For illustration, Figure 5 presents some He 392 diffusion data obtained on natural zircon crystals (e.g., Reiners et al., 2004; Cherniak et al., 393 2009; Guenthner et al., 2013) compared to our data for a pristine zircon. In detail, Figure 5 394 shows the distribution of activation energy, frequency factor and closure temperature for He 395 obtained for natural zircon, and the deduced activation energy for Ne needed to explain a (U-396 Th)/Ne age (Gautheron et al., 2006). The authors based their estimate on the known thermal 397 history of the Gold Butte, Nevada area (Reiners et al., 2000) and measured ZNe ages (777±122 398 and 963±164 Ma) that are much older than the ZHe age (19.1±1.5 and 16.7±1.3 Ma 399 respectively). From this, they deduced a closure temperature for Ne in zircon of  $\sim 400 \pm 50^{\circ}$ C, 400 similar to the diffusion data from Van Soest et al. (2013). The activation energy for Ne in zircon 401 should thus be greater than the one for He (i.e., >170 kJ/mol), as Ne appears much more strongly 402 retained than He (Figure 5), in contradiction with the result of our calculation in which a larger diffusivity is found along c. Based on the linear relationship between  $E_a$  and closure 403 404 temperature, for Ne we can anticipate an activation energy value above ~170 kJ/mol, but we 405 cannot clearly define the upper limit, and the lower limit is below the value determined by van 406 Soest et al. (2013).

407 **4.2.** 

## Processes modifying He and Ne diffusion

A strong discrepancy exists between results obtained using theoretical and experimental approaches, leading to a misinterpretation of the validity of the theoretical method. However, recent DFT studies on He and Ne diffusion in apatite (Djimbi et al., 2015) and hematite (Balout et al., 2017a; b), which produce expectations consistent with experiments, bring a strong credit to this theoretical approach. If the discrepancy is not due to a methodological issue, additional features and processes are likely to be modifying He and Ne diffusion in zircon, as already
discussed by Reich et al. (2007), Saadoune et al. (2009) and Bengtson et al. (2012).

415 Until now, our calculation has only considered an ideal pristine crystal, but in real 416 crystals defects are present and change local diffusion properties. The defects can be 417 substitutions in which an atom of the ideal lattice (Zr usually) is exchanged for another, such 418 as a rare earth element. Another type is Frenkel pairs, consisting of an atom knocked out from 419 its original lattice site, leaving a vacancy, and inserted somewhere else. Frenkel pairs are 420 thermally activated and exist at any temperature, meaning that they can be created and 421 recombined by thermal motion. They are highly enhanced by irradiation due to the decay of U 422 and Th. The first effect of the alpha particle, and more strongly, the recoiling daughter is to 423 create Frenkel pairs by knocking atoms out of the lattice. For high radiation doses the density 424 of vacancies and interstitial atoms becomes high enough to make the lattice unstable, collapsing 425 it into amorphized zones. The diffusivity in such zones is not known and only hypotheses can 426 be proposed. Dislocations are yet another likely pervasive defect type that can alter diffusional 427 pathways. The detailed description of these defects is far beyond the scope of this work. 428 Similarly, meso-scale features that may alter diffusivity and retention, such as mineral and fluid 429 inclusions, are also beyond our scope. Our methodology is based on a simple modeling of their 430 effect on the diffusion of inserted He and Ne atoms, by considering that they diffuse in an ideal 431 crystal (Figure 6A) until they find some defect altering the diffusion (Figure 6B and 6C). We 432 address only two phenomena, obstruction and trapping.

Obstruction may occur when an interstitial atom, knocked out due to irradiation for example, is already in an interstitial site, preventing He or Ne from entering the site. This mechanism is efficient for slowing down diffusion along fast pathways along the *c*-axis in zircon, because it requires the atom to jump over higher barriers to span long distances. The motion is illustrated in Figure 6B, whereas Figure 6A shows the ideal case where the jumps 438 occur primarily along the *c*-axis due to the low barrier. Obstruction can also result from 439 chemical substitutions that alter the energetics along the diffusion pathway. This has been 440 shown to occur for Cl-rich apatite compared to F-apatite (Djimbi et al., 2015), although the 441 authors demonstrate that a significant effect on diffusion only occurs at a relatively high 442 substitution level (some dozens of percent of the halogen sites) in that mineral. For zircon, Hf 443 substitution can be quite important (some wt% percent, e.g., Hanchar and van Westrenen, 2007) 444 and will modify He diffusivity. Dislocations could also lead to obstruction by a local shrinking 445 of the original cell. In Figure 6B for example, the He atom first diffuses along the c-axis and 446 crosses the rhombic gap but is then blocked due to the obstruction. Finally, the He atom will go 447 back as it will demand too much energy to cross the rectangular gap, where the migration energy 448 is 2.6 eV (251 kJ/mol). As already emphasized in Djimbi et al. (2015), obstruction is very 449 efficient in reducing diffusion anisotropy, which is an important feature in the case of zircon.

450 The other effect we consider is trapping. This phenomenon has been already considered 451 in several works (Farley, 2000; Shuster et al., 2006; Gautheron et al., 2009; Flowers et al., 2009; 452 Shuster and Farley, 2009; Gerin et al., 2017) and can result from different kinds of defects. 453 When vacancies are created, in particular under irradiation, they offer more space to the 454 diffusing atom at lower energy. Therefore additional energy, noted ( $\Delta Ea_T$ ), is necessary to 455 extract it from its location and bring it to a normal interstitial site. In general, trapping may 456 occur in any situation where the interstitial atom has more space to be accommodated. The 457 amorphized zones could offer this more open space and serve as He and Ne storage. If the zones 458 are not interconnected, diffusion still occurs through an ideal lattice endowed with trapping 459 volumes. Even substitutions in some cases can act as traps. Saadoune and de Leeuw (2009) demonstrate that when U<sup>4+</sup> and Pu<sup>4+</sup> are present at the percent level in the zircon lattice in the 460 461 vicinity of an He insertion site, U and Pu increase He solubility by decreasing He insertion 462 energy, leading to a trapping effect.

Radiation damage is the favored mechanism producing trapping because it creates 463 464 vacancies, and in the case of zircon amorphized zones (Figure 6C). This mechanism was 465 initially proposed for apatite, where radiation damage strongly influences He diffusion by 466 trapping He inside damage (Farley, 2000; Shuster et al., 2006). As a guideline, the maximum available trapping energy corresponds to a case where the diffusing atom is far from its 467 468 neighbors, such as in a cavity (large damage, voids, fluid inclusions). Any short distance to its 469 neighbors will repel it and increase its energy, thereby reducing ( $\Delta Ea_T$ ). The extreme case where 470 the atom is far from any other atom is equivalent to an atom outside of the crystal, and in this 471 case the trapping energy is merely the insertion energy. Therefore, the maximal trapping energy 472 is the insertion energy. The only exception to this rule would occur if atoms in the crystal would 473 interact with the He or Ne by attracting it. Gerin et al. (2017) described the energetics of this 474 process for apatite but similar conclusions can be drawn for zircon. As the insertion energy is 475 1.46 and 3.1 eV for He and Ne respectively, one can infer that the maximal trapping energy for 476 large damage such as recoil damage ( $\Delta Ea_T$ ) will be respectively 1.46 eV (with global Ea 1.7 477 eV = 1.46+0.24 eV; 164 kJ/mol) and 3.31 eV (with global *Ea* 3.32 eV = 3.10+0.22 eV; 320) 478 kJ/mol). In crystals with real damage, different geometries of defects are present, entailing a 479 distribution of  $\Delta Ea_T$ . In addition, when radiation damage accumulates vacancies can connect 480 creating larger spaces, increasing the trapping energy. Figure 6C illustrates a diffusion 481 trajectory with different topologies of damage, with small damage (such as point defects), single 482 recoil damage or recoil damage clusters. The  $\Delta Ea_T$  will be different for each case according to 483 the available free space. An important feature of trapping is that, unlike obstruction, it has no 484 effect on the anisotropy of diffusion, so that it cannot be responsible for the reduction of the 485 anisotropy in case of zircon, although it has the capability to reduce diffusivity strongly, and 486 may be spatially associated with other defects.

487

## 4.3. Impact of blocking pathways, i.e. obstruction, on He and Ne diffusion in zircon

It is expected that atoms displaced into the *c*-axis channel as a result of radiation damage strongly affects diffusion along *c*, which is quasi-free at normal temperature in an ideal lattice. In this section, we test the obstruction model using the KMC method and discuss the impact of obstructed pathways on He and Ne diffusion coefficients, by using the model described in section 2.3; additional details are given in Appendix A.

493 Figure 7 presents the dependence of the diffusion coefficient  $D_{a,b}$  and  $D_c$  (respectively 494 along a, b and c-axis) as a function of inverse temperature for a set of fractions of obstructed 495 sites (1, 5, 10, 20%). We define the obstruction level as the fraction of sites occupied. In the 496 hypothesis of obstructions produced by displaced atoms, the obstruction level is the fraction of 497 displaced atoms multiplied by 1.5, because there are 1.5 more atoms than interstitial sites S1 498 and S1'. Therefore, the considered set of obstruction levels corresponds respectively to 0.7, 3.3, 499 7, 13% of displaced atoms. Table 4 provides all obtained diffusion coefficients (*Ea* and  $D_0$ ) 500 along the *a/b*-axis and *c*-axis and associated closure temperatures

501 Along *a*- and *b*-channels the diffusion coefficient  $(D_{a,b} \text{ or } D_{x,y})$  is only slightly affected 502 by the amount of obstruction (Figure 7A). The curves do not diverge significantly from each 503 other; at most the 20% case reduces the diffusivity slightly, keeping the same slope defined by 504 the barrier of 0.66 eV. Along the *c*-channel, obstruction strongly affects diffusivity ( $D_c$  or  $D_z$ ), 505 especially at low temperature where the slope of the diffusion behavior changes significantly 506 (Figure 7B). An important result is that, surprisingly, the impact of obstruction on 3D diffusion 507 is higher at low temperature with an important deviation from the ideal lattice. As the fraction 508 of obstruction increases the dependence moves closer to the a/b diffusivity. For T<300°C all 509 the curves are almost straight lines parallel to the a/b Arrhenius law, implying similar activation 510 energy, but with  $D_0$  scaling down as the level of obstruction increases.

511 As soon as the latter exceeds 1%, He diffusion along the *c*-axis is significantly blocked 512 leading to a change in diffusivity. One particular outcome is that the anisotropy, which was 513 very strong in the ideal lattice, is reduced by a factor depending of the level of obstruction, but 514 almost independent of the temperature. For example, at 10% obstruction the anisotropy drops 515 down to 20. It is worth noting that the above key trends are observed experimentally by 516 Guenthner et al. (2013), who show that He activation energy orthogonal to c is only slightly 517 affected by damage, whereas with increasing damage diffusion along c approaches a constant 518 *Ea* close to that of the transverse direction. This experimental effect is reproduced by our 519 calculation. It reduces the anisotropy, compared to ideal crystal, and cannot be explained by a 520 trapping effect alone. However, our modeled activation energy in any direction remains much 521 smaller (64 kJ/mol) in comparison to those measured in natural zircon (Reiners et al., 2004; 522 Guenthner et al., 2013), which are around 169 kJ/mol.

523 In conclusion, although obstruction strongly slows down He diffusion along c, it is not 524 the primary parameter that drives retentivity of He in natural zircons. However, obstruction is 525 the main parameter acting on the anisotropy of diffusion, reducing it strongly with respect to 526 the ideal lattice case.

527 For Ne the change of diffusivity with obstruction is not progressive but total. At 528 obstruction levels as low as 1%, Ne diffusion is already frozen because the activation energy 529 along the a- and b-axes is so high (147 kJ/mol, Table 3). Nevertheless, as with He, diffusion 530 pathway obstruction alone cannot reproduce the inferred natural Ne diffusion behavior of 531 zircon; as described in section 4.2, an activation energy >180 kJ/mol is necessary to reproduce 532 Ne ages (Gautheron et al., 2006), well above the maximum activation energy of ~147 kJ/mol 533 obtainable from obstruction. Thus, for He and Ne, pathway obstruction mechanisms are not 534 sufficient to block He and Ne diffusion in zircon to the degree observed in natural specimens.

#### 535 4.4. Impact of traps on He and Ne diffusion in zircon

In this section, the trapping model is tested and the amount of trapping energy necessaryto reproduce the inferred natural He and Ne diffusion coefficients is discussed. For this purpose,

the model published in Gerin et al. (2017) is used where the diffusion coefficient modified by damage, denoted  $\tilde{D}$ , follows a formula (eq. 12) that includes a trapping term:

540 
$$\tilde{D}(x,t) = \frac{D(T)}{\left[1 + f \times \exp\left(\frac{\Delta E_{aT}}{RT}\right)\right]}$$
(Eq. 12)

541 Where D(T) is the diffusion coefficient of undamaged zircon (data from this study), f is 542 the damage fraction ranging from 0 to 1, representing the normalized amount of displaced atoms 543 in the structure, and  $\Delta E_{aT}$  is the additional activation energy necessary for an He or Ne atom to 544 jump out of the trap to the next insertion site. Appendix B provides a complete explanation and 545 demonstration of the equation, and the conversion between damage fraction and alpha dose. In 546 this study, the trapping model is correct only if damage stays as an isolated trap and does not 547 form a percolating network connecting to the grain surface, as then it would not be a trap 548 anymore.

549 The evolution of the simulated He closure temperature using Eq. 12 to account for 550 equivalent alpha dose is reported in Figure 8A, for a 60-µm radius spherical grain. The 551 simulation was done for  $\Delta E_a$  values of 40, 80, 120 and 140 kJ/mol, where 140 kJ/mol is the 552 maximum predicted value from the insertion energy ( $\Delta E_{aT}$ ) (see section 4.2). One can observe 553 from Figure 8A that a minimum  $\Delta E_a$  of 120 kJ/mol is necessary to reproduce retentive behavior 554 in low-damage zircon of Guenthner et al. (2013). Interestingly, the activation energies and 555 closure temperatures reported in Figure 8B are similar to those reported for natural samples in 556 Figure 5B, lending support to the idea that our calculations have reproduced the natural range 557 of trap diffusivities quite accurately. For Ne, a similar simulation was done for the same 60-µm 558 radius zircon, and results are reported in Figure 8C and D for  $\Delta E_a$  of 160, 200 and 300 kJ/mol, 559 as these values bracket the needed trapping to reproduce the inferred Ne closure temperature. 560 One can note that a trapping energy of  $\geq 200 \text{ kJ/mol}$  is necessary to reproduce the inferred Ne 561 closure temperature. The data from van Soest et al. (2013) could not be used in this figure as the required information are not given in the conference paper. However, we note that the sum of the insertion and migration energies we calculated for Ne corresponds to 320 kJ/mol, which is comparable with the van Soest et al. (2013) value, and compatible with their Tc range if  $D_0$ is adjusted.

566 For He, closure temperature will increase with the equivalent alpha-dose for relatively 567 low trapping energy  $\Delta Ea$  (<40 kJ/mol). It seems paradoxical that the closure temperature 568 depends only slightly on the damage fraction, as illustrated in Figure 8A, but this is well 569 understood as this fraction shows up in the pre-exponential factor f in Eq. 12, whereas the 570 activation energy is in the exponential, giving rise to a much stronger effect. In other words 571 when the trapping energy is high most of the helium is trapped, whatever the number of traps 572 provided it is higher than the number of helium atoms, and only a high temperature (some 573 hundreds of °C during geological time) can extract them from the traps. This effect has been 574 seen with the DFT calculation in zircon (Saadoune and De Leeuw, 2009) and apatite (Gerin et 575 al., 2017), yet the damage topology between the two minerals is different. However, in the case 576 of zircon a higher trapping energy is needed to reproduce experimental data with respect to 577 expectations and calculations for apatite (~30-40 kJ/mol for apatite (Gerin et al., 2017; Shuster 578 and Farley, 2009) compared to 120-140 kJ/mol for zircon). The difference can be explained by 579 the higher insertion energy for He and even higher for Ne (Table 1) in zircon compared to 580 apatite (~0.6 to 1 eV; Djimbi et al., 2015), as modification of the crystal structure during damage 581 creation will produce a site more energetically favorable compared to the lattice. In this case, 582 the insertion energy strongly drops, leading to an increase of the trapping energy until a 583 threshold  $\Delta E_{aT}$ . The higher necessary trapping energy can be explained by the damage topology 584 in zircon, as the crystal structure behaves quite differently than apatite. It is well known that 585 natural apatites are almost always crystalline in contrast to zircon, which is often reported to be

partially or fully metamict (e.g. Ewing et al., 2003); additional infomation on damage can be 586 587 found in Appendix B.

588 4.5.

## Damage percolation threshold

589 For zircon, at high dose, several authors have reported that damage overlap or 590 percolation may create amorphous zones (e.g. Ewing et al., 2003; Pidgeon, 2014; Salje et al., 1999). The more recent amorphous-crystal threshold has been estimated to be at ~ $2.2 \times 10^{18} \alpha/g$ 591 592 (Pidgeon, 2014), which has been interepreted as the recoil percolation damage threshold (Trachenko et al., 2003). The transition to rapidly rising diffusivity occurs at  $\sim 2 \times 10^{18}$   $\alpha/g$  in the 593 594 diffusivity data set used by Guenthner et al. (2013), although data by Anderson et al. (2017) suggest a lower value at  $2-5 \times 10^{17}$   $\alpha/g$ . In addition, Ketcham et al. (2013) calculated that alpha 595 recoil and fission damage percolate at different thresholds than previously assumed ( $\sim 2 \times 10^{16}$ 596 and  $\sim 2 \times 10^{17}$   $\alpha/g$  for alpha-recoil damage in 6-8-step decay chains and isolated decays (no-597 chain) respectively, and  $\sim 2 \times 10^{18} \alpha/g$  for fission tracks), due to the elongate nature of recoil and 598 599 fission damage not taken into account by Trachenko et al. (2003).

600 Recent ZHe data measured in Hercynian granites from the Pyrenees (Bosch et al., 2016; 601 Vacherat et al., 2016) exhibit age versus maximum alpha dose correlations that suggest that this retentivity maximum may be reached at ~2-5×10<sup>17</sup>  $\alpha/g$  (Figure 9). It is not straightforward to 602 603 estimate the effective alpha dose needed to explain an age-eU pattern, so we have provided two 604 solutions. First, as an end-member over-estimate, we simply retain all damage for each grain 605 throughout its entire history since crystallization at 305 Ma (U/Pb age); the dose can be no 606 higher than this (Figure 9A). Second, we posit that the divergence of measured ages was due to 607 a reheating and partial resetting event at some time in the past that caused more He loss in the 608 less retentive grains, and so we should consider only the possible damage production prior to 609 that event. A conservative estimate for its timing is the age of the youngest grain, leading to the 610 relationship shown in Figure 9B. Even this dose is likely to be a significant over-estimate of 611 the pertinent dose for explaining the spread in ages, as it presumes that after crystallization 612 damage retention began immediately.

613 The implied transition dose from increasing to decreasing He retentivity is significantly 614 lower than to the one considered in the RDAAM model of Guenthner et al. (2013) and is closer 615 to the no-chain alpha recoil percolation level calculated by Ketcham et al. (2013). The no-chain 616 case is a possibly more appropriate approximation for connectivity that leads to fast pathways, 617 as the connectivity due to U and Th decay chains is "tip to tip", and thus dominated by 618 potentially obstructed regions at the boundaries of tracks. The dose range over which the non-619 chain percolating network expands to encompass the majority of recoil damage roughly 620 coincides with the negative dose-age correlation in the Pyrenean samples, in the range 2 to  $5 \times 10^{17}$   $\alpha/g$ , significantly below the dose range where the Guenthner et al. (2013) model 621 postulates a fall in retentivity (above  $\sim 2 \times 10^{18} \alpha/g$ ). Such a lower alpha dose threshold for 622 623 percolation can also explain why samples in old and stable crustal blocks (Reiners et al., 2005) 624 often displays only negative correlations between ZHe and eU (a proxy used for the alpha dose). 625 In such cases the maximum potential retentivity that connects negative and positive correlations 626 could not be documented because it would correspond to very low and atypical U concentrations for zircon. 627

628 We infer from the Pyrenean samples that the recoil damage threshold will be at a value 629 ranging around  $\sim 2-5 \times 10^{17} \alpha/g$ , as already proposed by Anderson et al. (2017), far below the 630  $\sim 2 \times 10^{18} \alpha/g$  proposed by Guenthner et al. (2013).

#### 631 4.6. Implication for zircon (U-Th)/He and (U-Th)/Ne thermochronometry

He and Ne diffusion coefficients in 3D obtained in this study and the investigation of
mechanisms that can modify He and Ne diffusivity demonstrate that obstruction and trapping
alter diffusivity significantly (Figure 10). Based on atomic investigation of He diffusion

635 energetics, we can predict how He will diffuse in the zircon structure. Figure 10A provides a 636 schematic illustration of a diffusion pathway as postulated by our work. The He atom will 637 diffuse primarily along the *c*-axis following a random diffusion pathway. He diffusion is 638 facilitated along the *c*-axis because of the low migration energy; obstruction could slightly 639 change the trajectory but the He atom can diffuse easily along the *a*-axis to get around any 640 obstructed pathway. Following the example pathway of Figure 10A, the He atom is trapped in 641 a large defect (i.e. recoil damage, voids, fluid inclusion), with a very low insertion energy 642 (potentially approaching 0). The He atom will need a maximum activation energy of 1.7 eV 643 (<164 kJ/mol) to go back to the crystal lattice (Fig. 10A). After that He diffuses again easily in 644 the lattice from site to site along the a-axis and c-axis (passage through the rhombic gap is 645 insignificant due to high migration energy, Fig. 4), until it reaches a second large energy well. 646 In this case the damage is connected to other damage extending to the crystal surface (Fig. 647 10A). In terms of energy, we can infer from our model that in the connected area, because the 648 lattice is distorted, the migration energy may be lowered. He insertion energy is thus very low 649 and the He atom will diffuse in the connected damage zone with lower energy barriers. In Figure 650 10A, we predict that the He migration in the damage ranges from 1.4 to 0.9 eV (135 to 87 651 kJ/mol). Indeed, several geological studies show that for high damage dose, ZHe ages are 652 similar to AFT ages (see Fig. 9 for the Pyrenean case example), and in some cases are even 653 younger or equivalent to AHe ages (Johnson et al., 2017). This implies that at high dose (> $10^{18}$ 654  $\alpha/g$ ), He retentivity is low in damage zone, with Tc of 110 to 50°C and thus Ea of 135 to 90 655 kJ/mol. We thus anticipate that, as opposed to the harmonic averaging model by Guenthner et 656 al. (2013), diffusivity in zircon after the percolation transition may be controlled by the 657 energetics and topology of the damage network.

Figure 10B combines our modeling of trapping and obstruction with natural data interms of the closure temperature evolution as a function of the alpha dose. First, obstruction of

diffusion pathways reduces diffusivity, not as efficiently as trapping but possibly enough to 660 661 play a role in addition to it. Indeed, at sufficient obstruction levels (> 20% for He and 1% for 662 Ne), diffusion for He and Ne will be only possible when it includes a component of motion 663 along the *a*- and *b*-axis (Table 3). The resulting diffusion behavior will still not be retentive enough to reproduce natural data, however. He and Ne global activation energy Ea values are 664 665 respectively 63 kJ/mol and 147 kJ/mol, while values of 120-140 kJ/mol and >180 kJ/mol are 666 needed (Figure 10B for He). The 20% obstruction level corresponds to 13% of atoms displaced (and so to an equivalent dose of  $\sim 10^{18} \alpha/g$ ) as explained in Appendix B, and corresponds to an 667 equivalent closure temperature of approximately -75°C assuming a D<sub>0</sub> of  $1.5 \times 10^{-7}$  m<sup>2</sup>/s. This 668 669 value is not very tightly constrained, but provides a reasonable, illustrative first estimate of He 670 retention.

671 If our modeling is correct, it is possible to make some predictions. First, for He and Ne, 672 a quite high trapping energy is necessary to reproduce closure temperatures inferred from 673 natural samples (Figure 8 and Figure 10B), and we predict maximum possible trapping energies 674 with  $\Delta Ea_T$  of 140 kJ/mol (E<sub>mig</sub>=1.46 eV) and 300 kJ/mol (E<sub>mig</sub>=3.10 eV) for He and Ne respectively. These trapping energies ( $\Delta Ea_T$ ) are within the limits provided by our DFT 675 676 calculations, as discussed in section 4.2. It means that the total energy needed to go back in the 677 crystal structure will be 164 kJ/mol (Einsertion + Emig=1.7 eV) and 320 kJ/mol (Einsertion + 678  $E_{mig}$ =3.32 eV) for He and Ne respectively. Second, based on published very young volcanic 679 zircon of ZHe ages coherent with other methods (e.g. Farley et al., 2002), we can infer that for low alpha dose (~1-2x10<sup>15</sup>  $\alpha/g$ ), He is retentive to surface temperature implying a Tc of ~60-680 681 100°C (Fig. 10B). Between low damage and the threshold, we could anticipate that Tc may 682 increase following a non-linear (i.e. cubic or exponential) law as is the case for apatite (Flowers 683 et al., 2009), as  $\Delta Ea$  increases until the  $\Delta Ea_T$  threshold (Fig. 10B). As damage fraction 684 increases, clustering increases also and damaged domains with different sizes will form. In this case, the trapping energy can increase as proposed by Recanati et al. (2017) for apatite. It is
interesting to note that the highest closure temperatures obtained by Guenthner et al. (2013) can
be explained by increasing trapping energy when damage dose increases up to a maximum (Fig.
8A). For Ne, the maximum activation energy predicted in this study is similarly very close to
the one reported by van Soest et al. (2013), and we can anticipate a complex relationship of Ne
diffusion with damage dose similar to He.

After some damage threshold, He diffusion increases (Tc decreases), although the Pyrenees samples (Bosch et al., 2016; Vacherat et al., 2016) and work of Johnson et al. (2017) indicate that the threshold dose may be lower than indicated by Guenthner et al. (2013). The source of this discrepancy may be a complex function of damage accumulation and annealing, and more work on this issue is essential. For example, Ginster et al. (2018) document a complicated relationship between damage dose and annealing rate, implying a very complex system.

698 The other implication for a maximum of retentivity located in the vicinity of the no-699 chain alpha damage percolation level (Fig. 9) would be that the dependence of closure 700 temperature on damage fraction increase can be significantly steeper than modeled with Eq. 12 701 (Fig. 10B) if a single  $\Delta Ea_T$  value is assumed. This additional level of complexity will also have 702 implications for developing very precise future quantitative models to predict individual T<sub>C</sub> 703 values for single zircon grains. Such a potential scenario supported by natural data will require 704 new experimental diffusion data to document carefully this key window of alpha-dose in the 705 range of the no-chain percolation level.

706 **5.** Conclusions

In this contribution, we have used a series of computational and theoretical tools to
provide a mechanistic view of the manner in which He and Ne diffuse in zircon. In particular,
we have characterized the undamaged crystalline state and its energy structure at the atomic

710 scale with respect to the diffusing atoms, and how trapping and obstruction as may result from 711 damage or inherent defects affect retention at the grain scale. The set of insights gained can 712 help leverage ongoing analytical efforts to unravel the complex behavior of the (U-Th)/He and 713 (U-Th)/Ne systems in natural settings.

714 Using Density Functional Theory and Transition State theory, we have calculated the 715 insertion energies for He and Ne in ideal zircon, as well as the migration pathways along the 716 a/b and c axes and the migration energies for each jump. For diffusion in the a/b direction, we 717 document the energetics of the rectangular and rhombic pathways to neighboring interstitial 718 sites. Our insertion energies for He are similar to previous work, but our migration energies and 719 their interrelationships are different; notably, our work finds that the relative migration energies 720 along the *c*-axis channel and through the rectangular and rhombic *a/b* gaps are approximately 721 0.24 vs. 0.66 and 2.60 eV for He, and 0.22 vs. 1.53 eV and infinite for Ne. One important 722 finding is that our insertion energies, in combination with our migration energies, predict the 723 maximum activation energies possible for the zircon He and Ne systems, which are consistent 724 with literature values.

725 Our results corroborate previous theoretical and analytical work implying that pristine 726 zircon is non-retentive for He due to low migration energies along the *c*-axis channels in the 727 crystal structure. We also obtain the unexpected result that Ne moves even more freely than He 728 through an unblocked *c*-axis channel, due to the distortion it causes in the insertion site. Both 729 systems therefore require additional factors to explain their natural behavior. Using the Kinetic 730 Monte Carlo method we show that obstruction of *c*-axis pathways forces the migration 731 energetics to become more similar to the slower a/b direction as blockages increase, causing 732 diffusion to become effectively isotropic on the grain scale and characterized by rectangular-733 path-jump energetics. This effect is insufficient to explain slow diffusion of He in zircon, but 734 has a larger impact on Ne, as rectangular *a/b* transitions are much higher-energy, and rhombic

ones are impassable. Of the mechanisms we inspect, we find that trapping is required to explainthe high retention of He and Ne observed in natural zircon.

737 We consider the topology of radiation damage in the context of a data set from Pyrenees 738 granites that indicates a transition from falling to rising diffusivity at a much smaller dose than posed in the Guenthner et al. (2013) diffusivity model, closer to ~2-5×10<sup>17</sup> than 2×10<sup>18</sup>  $\alpha/g$ . 739 740 The transition dose may correspond to the no-chain alpha recoil percolation threshold of 741 Ketcham et al. (2013), suggesting that tip-to-tip recoil track connectivity is not sufficient to 742 form fast diffusion pathways, but more interpenetrative damage intersections can. Increasing 743 track intersections may also create more and deeper traps, and the evolution of not just trap 744 abundance but also trap energetics may be necessary to arrive at a quantitative understanding 745 of rare gas diffusion in natural zircon.

#### 746 Acknowledgment

This project and salary for Duval Mbongo-Djimbi were funded by the Agence National
de la Recherche – grant no. ANR-12-BS06-0005-01. DIM OXYMORE funded by the region
île de France is thanked for salary for Hilal Balout. We thank Christophe Diarra for his precious
help in managing the IPNO cluster GRIF (http:// www.grif.fr). William Guenthner is warmly
thanked for sharing the diffusion data of his 2013 contribution. Daniele Cherniak, Peter Reiners
and Martin Danišík are warmly thanked for their constructive reviews.

## 753 Appendix A and B - Supplementary data

754 Supplementary data associated with this article can be found, in the online version.

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891	Tables captions
892	
893	<b>Table 1:</b> Helium and neon insertion energies in zircon, hematite and apatite crystal structure.
894	
895	Table 2: Migration energies in eV for both helium and neon in zircon compared with the
896	theoretical studies of He diffusion (Bengtson et al., 2012; Reich et al., 2007; Saadoune et al.,
897	2009). Rect. and Rhom. are for the rectangular and rhombic gap.
898	
899	Table 3: Diffusion parameters for He and Ne in ideal lattice.
900	
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902	obstruction, as shown in Figure 8.
903	

905

#### **Figure captions**

906

907 Figure 1: Sequence of computational tools developed and used in this study. Migration 908 energies and attempt frequencies from DFT are used with TST to calculate activation energy 909 *Ea* and frequency factor  $D_0$  at the atomic level for an ideal pristine crystal. Zircon crystal results 910 from this study are used for illustration. These results are used in a KMC code to calculate in 911 3D diffusion paths that accounts for the effects of obstruction and trapping. The example of 912 diffusion in apatite is shown (Djimbi et al., 2015). At the macroscopic level, for anisotropic 913 diffusion and to account for crystal shape, a finite geometry Monte Carlo code (Gautheron and 914 Tassan-Got, 2010) is used to calculate the (U-Th)/He age for a determined thermal history and 915 effective closure temperature. The example of apatite and zircon crystals are shown. Finally, 916 all these data can serve as the basis for a damage model.

917

918Figure 2: Representation of the zircon crystal supercell  $(2\times2\times2)$  showing the channels919along the *c*-axis (A) and along the *a*- and *b*-axes (B). He/Ne insertion sites indicated by square920and circle. Along the diffusion *c*-channel and *a*- and *b*-channel (note that the *a*- and *b*-axes are921identical), the different He/Ne insertion sites S<sub>1</sub> and S<sub>1</sub>' are denoted (A' and B'). Along *a*- and922*b*-channels, He/Ne atoms have to pass through a rhombic (Rhom.) or rectangular (Rect.) gap.923Note that along the *a*-axis the sites are only S1 type whereas along *b*-axis the sites are only S1'924type.

925

Figure 3: Evolution of the minimal energy path (MEP) between insertion site  $S_1$  to  $S_1$ ' along the *c*-channel (A) and (A') and along *a*- and *b*- channels (B) and (B') for He and Ne respectively. Rect. and Rhom. are for the rectangular and rhombic gaps. As with Figure 2, the sites along the *a* and *b*-axes are S1 and S1' respectively. 930

Figure 4: Schematic illustration of the different diffusion pathways in zircon identified with the insertion energies along the three axes (a, b and c). The two sites S<sub>1</sub> and S<sub>1</sub>' are distinguished and the example of different diffusion pathways between those sites are shown.

Figure 5: Correlation of the activation energy  $E_a$  with frequency factor D<sub>0</sub> (A) and closure temperature (B) determined in 3D for He and Ne (green diamonds). Results obtained on natural zircon crystal by Cherniak et al. (2009); Guenthner et al. (2013); Reiners et al. (2004) for He and are reported. A minimal deduced  $E_a$  value for Ne obtained from the closure temperature estimate of Gautheron et al. (2006) is reported in diagram B.

940

941 Figure 6: Schematic representation of mechanisms that may affect diffusivity. (A) He 942 and Ne diffusion pathway depends only on diffusion coefficients between all insertion sites. 943  $Ea_c$ ,  $Ea_{rhom}$  and  $Ea_{rect}$  refer to the activation energies along the c-axis and through the a-axis 944 rhombic and rectangular gaps. The same color codes as in Figure 4 are used for diffusion 945 through rectangular or rhombic gaps. One can note that the energy to diffuse through a rhombic 946 gap is high compare to a rectangular one, and that no diffusion can occur through impassable 947 boundaries (thick black lines). (B) Some pathways are obstructed (blue cross), and He or Ne 948 can only go around the blocked paths. Same diffusion coefficient between insertion sites is 949 taken as in A. (C) Damage represented by the open blue oval can trap atoms, as the needed 950  $\Delta Ea_T$  is much higher than the activation energy between interstitial sites.

951

Figure 7: Evolution of the diffusion coefficient as a function of inverse temperature along a/b-axis (A) and c-axis (B) for various values of obstructed pathways from 1 to 20%. As a reference the diffusion coefficient evolution in 3D and for all axes, and for natural zircon 955 (gray line; Reiners et al., 2004; orange lines with similar dashed lines from Guenthner et al.,
956 2013) are reported in both figures.

957

958 Figure 8: Models of helium and neon closure temperature dependence on alpha dose 959 (A, C) and activation energy (B, D). Closure temperature evolution with dose (A, C, black lines) 960 modeled for a 60-µm radius spherical grain, using the base level diffusion coefficients obtained 961 in this study and equation (12) to estimate the effects of dose and trapping energy.  $\Delta Ea$  values 962 of 40, 80, 100, 120 and  $\Delta Ea_T$  of 140 kJ/mol are modeled for He, and  $\Delta Ea$  values of 160, 200 963 and  $\Delta Ea_T$  of 300 kJ/mol for Ne. Diagram B and D shows the evolution of the modified 964 activation energy as a function of the calculated closure temperature. Data obtained from this 965 study (diamonds), on natural zircon from Guenthner et al. (2013) (red dots; Figures A, B), and 966 data from van Soest et al. (2013) for Ne diffusion are reported for comparison. Black and gray 967 circles same as in Figure 5.

968

**Figure 9:** ZHe age evolution as a function of the equivalent alpha-dose, for two Pyrenean massifs (Bosch et al., 2016; Vacherat et al., 2016). The values for the 6-8-chain, nochain and fission-track percolation thresholds of Ketcham et al. (2013) are reported for comparison. Apatite fission track (AFT) and apatite (U-Th)/He (AHe) ages range from Bosch et al. (2016) and Vacherat et al. (2016) are also shown for comparison.

974

**Figure 10:** (A) Schematic representation of the energetic levels of a diffusion pathway for He; a similar representation can be made for Ne. 1.46 eV is the He insertion energy, and  $E_{mig}$  is the migration energy, that can be for He 0.24, 0.66 eV for regular lattice (24 and 66 kJ/mol respectively). In a damage zone, He insertion can be lower and the resulting trapping energy will increase and can be up to 1.46 eV, resulting in a migration energy of 1.7 eV 980 (E<sub>mig</sub>=164 kJ/mol). In this model, the size of the regular insertion site (a<sub>IS</sub>, black arrow) is 981 smaller than for a damage zone (a<sub>D</sub>, blue arrow) resulting in a different energy level. (B) 982 Evolution of the closure temperature as a function of the alpha dose (black lines). Data from 983 Guenthner et al. (2013) (red circles) and calculated with the DFT results (this study, red square) 984 are reported in addition to the trapping model with trapping energies  $\Delta Ea$  of 100, 120 and  $\Delta Ea_T$ 985 140 kJ/mol, and the blocking pathway model at 1, 5, 10 and 20% of obstruction (details about 986 the calculation are given in Table 4). The calculated damage thresholds from Ketcham et al. 987 (2013) and the one inferred from Pyrenees samples (Fig. 9) are also reported. Inferred closure 988 temperature for very young zircon (<1 Ma; Farley et al., 2002), Pyrenean samples (Bosch et al., 989 2016; Vacherat et al., 2016) and highly damages zircon from Johnson et al. (2017) are also 990 shown. The relation between obstructed pathways with alpha dose is not straightforward, but 991 we estimate the transition from rising to falling closure temperature to be in the 2-5×10<sup>17</sup>  $\alpha/g$ 992 range.

993

Insertion	Zircon, this	Zircon, Saadoune	Hematite, Balout et	Apatite, Djimbi
energy	work	et al. (2009)	al. (2017a, b)	et al. (2015)
He (eV)	1.46	1.45	1.51	1.15 (a,b-plan); 0.66 (c-axis)
Ne (eV)	3.10	-	3.38	-

Table 1. Insertion energies for He and Ne into interstitial sites in this and other studies.

	Helium		Neon			
	<i>c</i> -channel	<i>a and b</i> -channel		c-channel	a and b-channel	
		Rect.	Rhom.	•	Rect.	Rhom.
This work	0.24	0.66	2.60	0.22	1.53	none
Reich et al. (2007)	0.14	0.46	1.05	-	-	-
Saadoune et al. (2009)	0.22	0.44	2.68	-	-	-
Bengtson et al. (2012)	0.44	0.43	2.64	-	-	-

## Table 2. Migration energies (in eV) for He and Ne in zircon.

Migration energies in eV for both helium and neon in zircon compared with the theoretical studies of He diffusion (Bengtson et al., 2012; Reich et al., 2007; Saadoune et al., 2009). Rect. and Rhom. are for the rectangular and rhombic gaps.

		Saddle point	E <sub>mig</sub> (eV)	E <sub>a</sub> (kJ/mol)	v (THz)	a (Å)
		Rect.	0.66	63.7	5.50	3.35
	a and b-channel					
He		Rhom.	2.6	250.9	3.44	3.35
	<i>c</i> -channel		0.24	23.2	7.06	1.5
		Rect.	1.53	147.6	3.90	3.35
	a and b-channel					
Ne		Rhom.	none	none	none	3.35
	<i>c</i> -channel		0.22	21.2	1.36	1.5

## Table 3. Diffusion parameters for He and Ne in ideal lattice.

Table 4: Diffusion coefficients (D<sub>0</sub> and Ea) along a/b and c axes for different percentages of obstruction, as shown in Figure 8.

%	$\mathbf{D}_{0}\left( c ight)$	<b>Ea</b> ( <i>c</i> )	$\mathbf{D}_{0}\left( a/b ight)$	Ea ( <i>a</i> , <i>b</i> )	Tc
obstruction	$(\mathbf{m}^2/\mathbf{s})$	(kJ/mol)	( <b>m</b> <sup>2</sup> / <b>s</b> )	(kJ/mol)	(° <b>C</b> )
0	1.6×10 <sup>-7</sup>	23.1	1.5×10 <sup>-7</sup>	63.6	-193
1	4.6×10 <sup>-4</sup>	61.8	1.5×10 <sup>-7</sup>	63.6	-100
5	1.1×10 <sup>-5</sup>	60.6	1.5×10 <sup>-7</sup>	63.6	-88
10	2.3×10 <sup>-6</sup>	60.1	1.5×10 <sup>-7</sup>	63.6	-83
20	5.6×10 <sup>-7</sup>	61.9	1.1×10 <sup>-7</sup>	54.0	-73

Closure temperature calculated for a  $100 \times 100 \times 200 \ \mu m$  prism, cooling rate of  $10^{\circ}$ C/Ma and no ejection.







Β









D0 (m<sup>2</sup>/s)

# **Closure temperature (°C)**

Figure6 Perfect cell

**Obstruction** 

Trapping

![](_page_52_Figure_3.jpeg)

![](_page_53_Figure_1.jpeg)

# Helium

![](_page_54_Figure_2.jpeg)

Figure9

![](_page_55_Figure_1.jpeg)

maximum possible current dose

# Alpha dose (α/g)

maximum possible dose at estimated time of partial resetting

Figure10

![](_page_56_Figure_1.jpeg)

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