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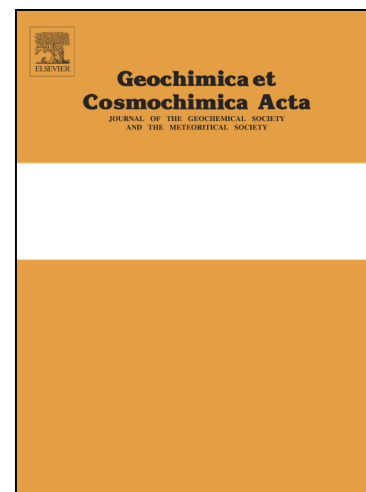
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1 Atomistic Simulations of ^{40}Ar Diffusion in Muscovite2 Jehiel Nteme^{a,b,*}, Stéphane Scaillet^a, Pascal Brault^b, Laurent Tassan-Got^{c,d}3 ^a*Univ. Orléans, CNRS, BRGM, Institut des Sciences de la Terre d'Orléans (ISTO), UMR 7327, F-45071,*
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10 *Switzerland*11 **Abstract**

12 Muscovite ranks among the most commonly dated minerals in $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology. Yet,
13 its use in thermochronological reconstructions is hampered by the lack of reliable data on
14 its ^{40}Ar diffusional behavior. In this contribution, we investigate ^{40}Ar lattice diffusion in
15 muscovite at the atomic scale using Molecular Dynamics (MD) simulations combined with
16 Nudged Elastic Band (NEB) and Transition State Theory (TST). Classical MD simulations
17 of ^{40}Ar recoil dynamics in $2M_1$ muscovite reveal that ^{40}Ar initially resides predominantly
18 in the interlayer region, close to its production site. Systematic computations of migration
19 barriers coupling NEB with TST identify the divacancy mechanism as the more energetically
20 favorable pathway for ^{40}Ar diffusion in the interlayer region, with characteristic enthalpy
21 of motion $E = 66 \text{ kcal.mol}^{-1}$ and vibrational entropy term $D_0 = 6 \times 10^{-4} \text{ cm}^2.\text{s}^{-1}$. For
22 typical cooling rates between $1\text{--}100 \text{ }^\circ\text{C.Ma}^{-1}$ and grain size varying from 0.1 and 1 mm,
23 these parameters predict closure temperatures significantly higher ($\sim 200 \text{ }^\circ\text{C}$) than currently
24 accepted maximum estimates ($\sim 500 \text{ }^\circ\text{C}$). Consistent with long-standing empirical evidence,
25 our theoretical results downplay the role of purely thermally activated diffusion in promoting
26 efficient ^{40}Ar transport in ideal (stoichiometrically stable and undefective) muscovite. Along
27 with experimental and field-based evidence, they call for more complex physics to explain the
28 ^{40}Ar retention properties of natural muscovite, most notably by considering crystal-chemical
29 disequilibrium interactions and the reactivity of the interlayer with the external medium.

30 **Keywords:** ^{40}Ar diffusion, Muscovite, Molecular Dynamics, Transition State Theory,
31 Thermochronology

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1. Introduction

Diffusion is the main mechanism governing atomic transport in minerals. It is fundamental to the understanding of many geological processes in terms of kinetics of metamorphic transformations and closure behavior of radio-isotopic systems (Dodson, 1973). Among these, the $^{40}\text{Ar}/^{39}\text{Ar}$ dating technique has been widely applied for studying Earth processes in the thermal range controlling the retention behavior of ^{40}Ar -bearing minerals (McDougall and Harrison, 1999). Being non bonded, ^{40}Ar is expected to be much more mobile than silicate-forming elements and therefore much more sensitive to thermal effects. The commonly observed discordance between for example $^{40}\text{Ar}/^{39}\text{Ar}$ and U/Pb ages has been attributed to the fact that common minerals lose their ^{40}Ar at crustal medium to moderate temperatures, giving apparent $^{40}\text{Ar}/^{39}\text{Ar}$ ages that do not reflect the time of crystallization but the time when the mineral was sufficiently cold to become effectively closed to ^{40}Ar loss by diffusion (Hart, 1960; Armstrong, 1966). Such a closed-system behavior has been theoretized in terms of a physically defined closure temperature (T_c) taking into account the Arrhenian dependence of intracrystalline (lattice) diffusion to temperature according to (Dodson, 1973):

$$T_c = \frac{E}{R \ln \left(\frac{AR T_c^2 D_0 / a^2}{E dT/dt} \right)} \quad (1)$$

in which E is the activation energy and D_0 the pre-exponential factor. dT/dt is the cooling rate, a the diffusion radius, A a numerical constant appropriate for the chosen geometry for diffusion, and R the gas constant. This expression emphasizes the importance of the diffusion parameters E and D_0 in any quantitative interpretation of $^{40}\text{Ar}/^{39}\text{Ar}$ metamorphic ages in terms of thermal-kinetic crustal processes.

Among those minerals commonly dated by $^{40}\text{Ar}/^{39}\text{Ar}$, muscovite stands apart due to its high potassium content and ubiquity in most crustal lithologies, all the way down from the epizone to subduction-zone metamorphic conditions (McDougall and Harrison, 1999). However, the ^{40}Ar diffusion behavior in muscovite remains poorly understood. Early on, maximum retention temperatures of ca. 350 °C to as high as 400 °C (or greater) were inferred from field calibration of apparent ages vs. metamorphic grade (Purdy and Jäger, 1976)

59 and pioneering diffusion experiments (Hart, 1960). Other ^{40}Ar diffusivity estimates were
60 later proposed by Hames and Bowring (1994), Lister and Baldwin (1996) and Kirschner
61 et al. (1996). Hames and Bowring (1994) and Lister and Baldwin (1996) re-evaluated
62 the early thermal-hydrothermal experimental data of Robbins (1972) to suggest the values
63 $E = 52 \text{ kcal.mol}^{-1}$ and $D_0 = 0.04 \text{ cm}^2.\text{s}^{-1}$ (Hames and Bowring, 1994), and $E = 41.8$
64 kcal.mol^{-1} and $D_0 = 3.352 \times 10^{-7} \text{ cm}^2.\text{s}^{-1}$ (Lister and Baldwin, 1996). Kirschner et al.
65 (1996) inferred an activation energy of $E = 58 \text{ kcal.mol}^{-1}$ with $D_0 = 0.24 \text{ cm}^2.\text{s}^{-1}$ from
66 an empirical thermal model binned to $^{40}\text{Ar}/^{39}\text{Ar}$ ages in muscovites grown during nappe
67 thrusting in the Western Alps. Nowadays, commonly adopted values are those determined
68 by Harrison et al. (2009) from hydrothermal experiments conducted in the range 730-600
69 $^{\circ}\text{C}$ and $P = 10, 20 \text{ kbar}$ ($E = 63 \text{ kcal.mol}^{-1}$; $D_0 = 2.3 \text{ cm}^2.\text{s}^{-1}$). Some other estimates
70 were inferred by Forster and Lister (2014) and Lister and Forster (2016) using in vacuo
71 experiments ($E = 67 \text{ kcal.mol}^{-1}$ and $D_0/a^2 = 1.2 \times 10^9 \text{ s}^{-1}$).

72 These parameters imply theoretical ^{40}Ar -closure temperatures lower than $500 \text{ }^{\circ}\text{C}$ (Harri-
73 son et al. 2009). However, cases of effective ^{40}Ar retention have been consistently reported for
74 muscovites exposed to temperatures in excess of this value (Monié, 1990; Scaillet et al., 1990,
75 1992; Monié and Chopin, 1991; Arnaud and Kelley, 1995; Scaillet, 1996; Di Vincenzo et al.,
76 2001, 2004, 2006; Balogh and Dunkl, 2005; Hames et al., 2008; Itaya et al., 2009; Allaz et al.,
77 2011; Beltrando et al., 2013; Halama et al., 2014; Schertl and Hammerschmidt, 2016; Laurent
78 et al., 2021). While most of these studies relate to high-pressure phengites from eclogite-
79 facies rocks for which the combined effect of pressure and composition (e.g., Tschermak sub-
80 stitution) may have influenced the ^{40}Ar diffusion behavior (Wijbrans and McDougall, 1986;
81 Scaillet et al., 1992; Scaillet, 1998), a high retentivity has also been suggested in other set-
82 tings for which compositional and pressure effects are not prevalent (Di Vincenzo et al., 2004;
83 Hames et al., 2008; Itaya et al., 2009; Allaz et al., 2011). The discordance between experi-
84 mental predictions and geologic evidence raises the fundamental question as to the meaning
85 of such $^{40}\text{Ar}/^{39}\text{Ar}$ ages: Do they reflect cooling or (re)crystallization? The answer requires
86 a better understanding of the ^{40}Ar diffusion behavior in muscovite as a function of several
87 parameters including temperature, chemical composition, and other intensive variables such
88 as pressure.

89 In this work, we focus on the ^{40}Ar diffusional behavior in muscovite with respect to
90 temperature. Unlike previous studies that investigated the ^{40}Ar diffusivity in muscovite
91 experimentally and empirically, we re-evaluate the ^{40}Ar diffusion dependence to temperature
92 via atomistic simulations. These simulations, which include various methods (e.g., Density
93 Functional Theory – DFT, Molecular Dynamics – MD, Kinetic Monte-Carlo – KMC, etc.),
94 show many advantages over laboratory experiments. While the determination of rare-gas
95 diffusivities in hydrothermal experiments is based on finite-state observables (fractional loss),
96 atomistic simulations investigate the diffusion behavior at the atomic scale, allowing the
97 identification and characterization of the diffusion mechanism (e.g., interstitial vs. vacancy
98 mechanism) apt to explain the bulk migration of the diffusing species across the crystal. Also,
99 atomistic simulations permit to analyze the diffusion process in a perfect lattice structure,
100 unlike laboratory experiments that use natural crystals which commonly contain impurities
101 and microstructural defects.

102 Atomistic simulations have been widely applied to the study of solid-state diffusion in the
103 field of Material Science. Quite recently, they have been used for the theoretical characteri-
104 zation of low-temperature (fast-diffusing) thermochronometers like He and Ne in hematite,
105 goethite, zircon, apatite and quartz via a multi-scale approach combining DFT with KMC
106 (Saadoune et al., 2009; Bengston et al., 2012; Djimbi et al., 2015; Balout et al., 2017a,b;
107 Gerin et al., 2017; Bassal et al., 2020; Domingos et al., 2020; Gautheron et al., 2020). DFT
108 simulations of rare-gas (He, Ne, Ar, Kr, Xe) diffusion in hydrated minerals have further been
109 applied to quantify the efficiency of noble gas recycling in subduction zones (Wang et al.,
110 2020). DFT has also been successfully used to constrain He diffusion in olivine, quartz and
111 coesite at mantle pressures (Wang et al., 2015; Liu et al., 2021). In this paper, we investigate
112 ^{40}Ar diffusion in muscovite by combining MD with TST. Our results reveal ^{40}Ar diffusion
113 kinetics several orders of magnitude slower than current estimates.

114 2. Methods

115 2.1. Crystal structure model

116 The crystal structure of muscovite $[\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2]$ consists of a stacking of tetra-
117 hedral - octahedral - tetrahedral (T–O–T) layers held together across the interlayer space

118 by K^+ ions, which compensate the negative structural charge resulting from the substitution
 119 of Al for Si (Bailey, 1984). Tetrahedral silicon layers and dioctahedral aluminum layers are
 120 connected through bridging oxygens. In this work, we use a $2M_1$ muscovite atomic model
 121 based on the structural data of Catti et al. (1989). The model consists of a periodic supercell
 122 of $6 \times 3 \times 1$ unit cells along the crystallographic directions a , b , and c , respectively (Fig. 1a).
 123 Tetrahedral Al atoms are distributed in an irregular pattern while obeying the short range
 124 Lowenstein rule (Loewenstein, 1954) and the principle of local charge balance (Herrero et
 125 al., 1985, 1987). Accordingly, no ${}^{IV}Al-O-{}^{IV}Al$ bond was allowed and each hexagonal tetra-
 126 hedral ring contains either one or two Al atoms (Fig. 1b). Each K^+ is located between one
 127 Si_4Al_2 ring and one Si_5Al_1 ring to ensure an equitable charge distribution.

128 2.2. Computational details

129 Classical Molecular dynamics (MD) consists in simulating the trajectory of a system of
 130 interacting particles (atoms and/or molecules) over time by solving Newton's equations of
 131 motion (Frenkel and Smith, 2002; Rapaport, 2004). Interatomic interactions are computed
 132 based on force fields, which are parameterized using experimental results or *ab initio* simu-
 133 lations. We performed MD simulations using the simulation package LAMMPS (Thompson
 134 et al., 2021). The interatomic interactions were computed using ClayFF, a non-reactive
 135 force field that describes hydrated mineral systems through essentially nonbonded potentials
 136 (Cygan et al., 2004). Since its development, this force field has been widely used in MD
 137 simulations of phyllosilicates and other common minerals for which it has been shown to
 138 faithfully reproduce the structure and many thermodynamic properties (Greathouse et al.,
 139 2005, 2006; Kirkpatrick et al., 2005; Padma et al., 2006; Larentzos et al., 2007; Liu et al.,
 140 2007, 2008; Kerisit et al., 2008; Meleshyn, 2008; Wander and Clark, 2008; Cygan et al., 2009;
 141 Malani et al., 2009; Ferrage et al., 2010; Kalinichev et al., 2010; Tao et al., 2010; Argyris
 142 et al., 2011a,b; Ho et al., 2011; Teich-McGoldrick et al., 2012; Churakov, 2013; Loganathan
 143 and Kalinichev, 2013; Morrow et al., 2013). The pairwise energy for atoms i and j separated
 144 by a distance r_{ij} is given by

$$145 E_{ij} = \frac{e^2 q_i q_j}{4\pi\epsilon_0 r_{ij}} + 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (2)$$

146 where e is the fundamental charge of an electron, q_i and q_j are partial atomic charges and ϵ_0
 147 is the permittivity of vacuum. The Lennard-Jones parameters σ_{ij} and ϵ_{ij} correspond to the
 148 zero-crossing distance for the energy and the depth of the potential energy well, respectively.
 149 Interaction between hydroxyl atoms are computed with a bonded potential that describes
 150 the bond stretch energy by a simple harmonic term:

$$151 \quad E_{ij}^{\text{bond}} = k_1(r_{ij} - r_0)^2 \quad (3)$$

152 where k_1 is a force constant and r_0 the equilibrium bond length. Interaction parameters
 153 used in this study are provided in [Table 1](#). As there are no parameters for Ar in ClayFF,
 154 we assigned it a zero charge and Lennard-Jones parameters as reported by [White \(1999\)](#).
 155 The nonbonded parameters are given for interactions between identical atom types ($i =$
 156 j). Interaction parameters between unlike atoms ($i \neq j$) are calculated using the Lorentz-
 157 Berthelot mixing rules:

$$158 \quad \sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \quad (4)$$

$$159 \quad \epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \quad (5)$$

161
 162 The muscovite atomic model was optimized in a series of preliminary calculations consist-
 163 ing of energy minimization followed by 250 ps MD runs performed in the isobaric-isothermal
 164 (NPT) ensemble using the Nosé-Hoover thermostat and barostat, with damping parameters
 165 for temperature and pressure of 0.01 and 1 ps, respectively, and a time step of 0.001 ps.
 166 Short-range interactions were evaluated with a cut-off distance of 10 Å whereas long-range
 167 interactions were treated using the Ewald summation. The ^{40}Ar diffusion energy barriers
 168 were quantified using the Nudged Elastic Band (NEB) method ([Jónsson et al., 1998](#)), which
 169 determines the minimum energy path (MEP) between two stable sites by solving simultane-
 170 ously independent system images, each one containing one ^{40}Ar atom located on the path
 171 connecting the stable sites. Images are linked by a spring force to ensure the continuity of
 172 the path and the equal spacing between images along the MEP. The migration energy is
 173 obtained by taking the difference in energy between the saddle point and the initial stable
 174 site. In this study, eight images were generated and all the NEB calculations were performed
 175 with a spring constant of 23 kcal.mol $^{-1}$.Å $^{-2}$.

176 The transport rate based on those migration barriers was evaluated using the Transition
177 State Theory (TST) that expresses the jump probability γ as:

$$178 \quad \gamma = \nu \exp\left(\frac{-E}{RT}\right) \quad (6)$$

179 where ν is the attempt frequency, E the migration barrier, R the gas constant, and T the
180 temperature of the system (in Kelvin). The attempt frequency is given by:

$$181 \quad \nu = \frac{\prod_{i=1}^{3N} \nu_i^{init}}{\prod_{i=1}^{3N-1} \nu_i^*} \quad (7)$$

182 in which ν_i^{init} corresponds to the modal vibrational frequencies at the stable site and ν_i^* rep-
183 resents the non-imaginary modal frequencies at the saddle point (Vineyard, 1957). For most
184 solids, the attempt frequency is comprised between 10^{12} s^{-1} and 10^{13} s^{-1} . This parameter
185 is usually approximated by a fixed value within this interval to avoid the computationally
186 expensive determination of modal frequencies. In this work, we used $\nu = 5 \times 10^{12} \text{ s}^{-1}$, which
187 is close to the attempt frequency of $4.61 \times 10^{12} \text{ s}^{-1}$ computed via DFT for Ar in lizardite
188 (Wang et al., 2020). The diffusion coefficient is related to the transition rate via:

$$189 \quad D = ga^2\gamma = ga^2\nu \exp\left(\frac{-E}{RT}\right) \quad (8)$$

190 where g is a numerical constant depending on the geometry of the lattice and a is the distance
191 between two neighboring stable sites. The frequency factor D_0 is given by:

$$192 \quad D_0 = ga^2\nu \quad (9)$$

193 3. Force field validation

194 To validate the application of the ClayFF force field to the study of muscovite, we com-
195 pared the lattice parameters computed at ambient conditions ($P = 0.001 \text{ kbar}$ and $T =$
196 $25 \text{ }^\circ\text{C}$) for our muscovite atomic model with experimental data (Catti et al., 1989). The
197 results (Table 2) show that ClayFF reproduces the experimental crystal structure well. The
198 lattice parameters a , b , c and the angles α , β , γ are all within 2 % (and in most cases 0.5 %)

199 of the experimental values. The interlayer separation is also well reproduced (within 1 % of
200 experimental determinations). Moreover, ClayFF also faithfully reproduces the stacking of
201 adjacent T–O–T layers. In the interlayer region, the basal oxygens of one T–O–T layer
202 are directly above those of the adjacent layer, in keeping with experimental determinations.
203 Each potassium atom is located at the center of the upper and lower tetrahedral rings. As
204 expected for a di-octahedral mica, the hydroxyl groups point towards the vacant octahedral
205 site and remain subparallel to the (001) plane.

206 4. ^{40}Ar initial position from interlayer recoil dynamics

207 The investigation of ^{40}Ar diffusion at the atomic scale requires the determination of its
208 insertion site within the muscovite structure. Since ^{40}Ar is produced with a kinetic energy
209 of $660 \text{ kcal.mol}^{-1}$ corresponding to a velocity of $0.11765 \text{ \AA.fs}^{-1}$ (Dong et al., 1995; Szczerba
210 et al., 2015), the ^{40}Ar insertion site can be determined by modelling the natural ^{40}Ar recoil
211 via MD simulations. Such simulations have been performed by Szczerba et al. (2015), who
212 investigated the natural recoil of ^{40}Ar in illite, a clay mineral structurally similar to muscovite.
213 Using both REAXFF and ClayFF force fields, they performed several simulations in which
214 ^{40}Ar had the same initial velocity ($0.11765 \text{ \AA.fs}^{-1}$) but varying recoil angles to cover all
215 possible values within a hemisphere. They identified four possible final positions of ^{40}Ar . For
216 recoil vectors subparallel to the (001) plane, ^{40}Ar systematically remained in the interlayer
217 region, occupying either the initial site of the parent ^{40}K or a neighboring vacancy. For recoil
218 vectors pointing towards the T–O–T sheet, ^{40}Ar remained mainly in the interlayer region
219 (79.5 %) but also penetrated into the T–O–T layer (20.5 %), where it ended up either in
220 the tetrahedral layer adjacent to the interlayer region (16.5 %), or in the octahedral layer
221 (1.5 %) or in the opposite tetrahedral layer (2.5 %).

222 In this work, we simulate the trajectory of the ^{40}Ar recoil in muscovite using the same
223 methodology as Szczerba et al. (2015). Since the penetration of ^{40}Ar into the T–O–T layer
224 induces deformations in the crystal structure (Szczerba et al., 2015), and ClayFF being a
225 non-reactive force field designed to model undeformed structures (Cygan et al., 2004), we
226 investigated recoil trajectories parallel to the interlayer region only. We consider that ^{40}Ar
227 penetrates into the muscovite T–O–T layer in the same proportions as in illite, due to

228 the similarity of their structures. We define the recoil angle ϕ as the angle between the
229 crystallographic direction a and the recoil vector. The simulations were carried out for recoil
230 angles from 0° to 360° with a step of 20° . In order to simulate a system under geological
231 conditions, we equilibrated first the system in the NPT ensemble, at a temperature of 500°C
232 and a pressure of 5 kbar. The recoil simulations were then carried out in the NVT ensemble,
233 for a duration of 250 ps with a time step of 1 fs.

234 The simulations reveal that, in the absence of vacancies in the immediate vicinity of the
235 parent ^{40}K initial site, when the recoil vector is oriented towards a neighboring potassium
236 atom (i.e. for $\phi = 0^\circ, 60^\circ, 120^\circ, 180^\circ$ and 240°) the radiogenic ^{40}Ar bounces back from that
237 neighboring K^+ and returns to its initial interlayer position. For the other recoil angles, ^{40}Ar
238 is first propelled into an interstitial position where it remains for about 50 ps, before either
239 returning in its initial position or replacing a neighboring K^+ which is in turn pushed into
240 the ^{40}Ar initial site. Along with [Szczerba et al. \(2015\)](#), this is the first theoretical verification
241 that radiogenic ^{40}Ar initially resides predominantly close to its production site in K-bearing
242 phyllosilicates ([Dong et al., 1995](#)), and not many unit cells away as sometimes suggested.

243 The variation of the total energy of the system when the radiogenic ^{40}Ar is propelled into
244 the interstitial site was computed relative to the mean energy of the system when ^{40}Ar resides
245 in a regular interlayer site. The simulations reveal that when ^{40}Ar is in the interstitial site,
246 i.e., during the first 50 ps, the system has a mean total energy of about 100 kcal.mol^{-1} higher
247 than when ^{40}Ar occupies a regular interlayer site ([Fig. 2](#)). This energy increase is due to the
248 distortion that ^{40}Ar causes to the muscovite structure because of its large size. Simulation
249 snapshots (not shown) reveal that when ^{40}Ar is located in the interstitial position, it repels
250 its neighboring basal oxygens, increasing locally the interlayer spacing by ca. 15 %. This
251 is a highly unfavourable configuration energetically, precluding protracted ^{40}Ar residence in
252 the interstitial site and making unlikely a reincorporation of ^{40}Ar into the interstitial sites
253 once it has lost its initial recoil velocity. This rules out interstitial mechanism as a viable
254 mechanism for ^{40}Ar diffusion in muscovite on geologic timescales.

255 5. Pathways and ^{40}Ar diffusion barriers in muscovite

256 The foregoing simulations suggest that the easiest way for ^{40}Ar to move within the mus-
 257 covite structure without causing major distortions is by jumping into neighboring interlayer
 258 vacancies. Vacancies are always present in minerals. They form at high temperature to
 259 reduce the Gibbs free energy of the crystal (Mehrer, 2007). Beside those intrinsic vacancies,
 260 additional vacancies can be introduced in the mica interlayer region via the pyrophyllitic sub-
 261 stitution $\text{Si} + \square \rightarrow \text{IVAl} + \text{K}$ (Tardy and Fritz, 1981; Aagaard and Helgeson, 1983; Helgeson
 262 and Aagaard, 1985; Wang and Banno, 1987; Baldelli et al., 1989; Wunder and Melzer, 2002).
 263 Their abundance estimated from the commonly measured stoichiometric deficit of interlayers
 264 cations (up to ca. 10 %) suggests that they can be involved in the motion of interlayer
 265 atoms. Therefore, we performed MD simulations in which we initially positioned ^{40}Ar in an
 266 interlayer K^+ site and added interlayer vacancies in its vicinity. Simulations were performed
 267 in the NPT ensemble at temperatures of 650 to 750 °C and $P = 5$ kbar, for time durations
 268 up to 25 ns. No migration could be observed; neither ^{40}Ar nor K^+ atoms jumped into the
 269 vacancies. This immobility suggests high migration energy barriers, making diffusion through
 270 a vacancy mechanism an infrequent event, unobservable on the timescales of classical MD.

271 To overcome the timescale limitation, we studied ^{40}Ar diffusion using TST. This requires
 272 the migration paths and the migration energies of diffusing atom to be determined first, unlike
 273 classical MD simulations which only require initial positions and velocities of atoms. The
 274 ^{40}Ar migration energies from its interlayer sites to neighboring vacancies were computed using
 275 the NEB method. Since the value of the migration energy in Eqs. (6) and (8) corresponds
 276 to the migration barrier of a system at the absolute zero, we first equilibrated the system via
 277 NPT simulations at $P = 0$ kbar and $T = -273.1$ °C (i.e., 0.5 K since there is no dynamics
 278 at 0 K). The migration of ^{40}Ar in the muscovite interlayer region depends on the presence
 279 of a vacancy in its immediate vicinity. Since vacancies can initially form far from the ^{40}Ar
 280 site, a motion of potassium atoms along the interlayer region is required for a vacancy to end
 281 next to ^{40}Ar so the K^+ migration barriers must be also determined. Furthermore, because
 282 vacancies move essentially either individually or by pairs (vacancy clusters involving more
 283 than two vacancies being thermodynamically less stable; Mehre, 2007), we considered the
 284 migration barriers for these two configurations, i.e., the migration energies of ^{40}Ar and K^+

285 from their sites towards a simple vacancy (monovacancy mechanism, labelled "□"; Fig. 3a),
286 or towards a vacancy adjacent to another vacancy (divacancy mechanism, labelled "□□";
287 Fig. 3b). As the environment around each interlayer site is variable, in particular because
288 of the irregular distribution of Al in the tetrahedral layers, the statistical (probabilistic)
289 calculations must take into account the configuration of atoms in the vicinity of ^{40}Ar and K^+ .
290 We positioned thus the ^{40}Ar and K^+ in all the interlayer sites of the model and computed
291 the migrations energies towards all possible neighboring sites. The charge deficit induced
292 by the incorporation of ^{40}Ar and vacancies into the interlayer region was compensated by
293 substituting Al atoms for Si in tetrahedral sites far from the ^{40}Ar migration path (some unit
294 cells away). Our results show that, in the case of the divacancy mechanism, the migration
295 barriers related to the "black" jumps (Fig. 3b) are identical to the energy barriers associated
296 with the monovacancy mechanism. Therefore, we report below 216 migration energies for the
297 monovacancy mechanism (all possible combinations), and 432 for the divacancy mechanism
298 (corresponding only to the "blue" jumps).

299 5.1. ^{40}Ar migration barriers

300 The energy barriers associated with the interlayer migration of ^{40}Ar towards neighboring
301 vacancies display wide distributions (Fig. 4a, b). The migration barriers associated with the
302 monovacancy mechanism yield a mean value of $71 \pm 5 \text{ kcal.mol}^{-1}$ (1σ), while those related to
303 the divacancy mechanism show a slightly lower but statistically indistinguishable mean value
304 of $69 \pm 6 \text{ kcal.mol}^{-1}$ (1σ). These values are similar to the energy barrier of 69 kcal.mol^{-1}
305 computed using DFT for the migration of Ar in lizardite (Wang et al., 2020), which consists of
306 a stacking of tetrahedral and octahedral layers like muscovite (Mellini, 1982). The similarity
307 between the migration barriers related to both mechanisms is illustrated by the variation
308 of the ^{40}Ar potential energy along its migration path between two neighboring stable sites
309 (corresponding to images "1" and "8"; Fig. 4c). In this example, the energy barrier related
310 to the migration of ^{40}Ar towards a single vacancy is 65 kcal.mol^{-1} while that associated with
311 the jump of ^{40}Ar into a pair of vacancies is 61 kcal.mol^{-1} . In both cases, the forward and
312 backward migration barriers are similar, and this has been observed for all computed paths.
313 The minimum energy paths followed by ^{40}Ar during these jumps (Fig. 4d) reveal that when
314 jumping into a single vacancy, ^{40}Ar follows an almost rectilinear trajectory, passing directly

315 below the basal oxygens crossed along the path. When it migrates into a pair of vacancies,
316 ^{40}Ar follows a similar trajectory but avoids the basal oxygens, passing quite closer to the
317 vacancy not involved in the migration path. The slight difference in trajectories shows that
318 the difference in magnitude between the respective migration barriers is directly related to
319 the presence or not of a K^+ around the pathway.

320 The migration barriers are anticorrelated to the total electrostatic energies calculated for
321 each Ar-vacancy configuration in the muscovite model (Fig. 4e). Ruiz Pestana et al. (2017)
322 also report such anticorrelation between the potassium migration energies and the cohesive
323 energies of K^+ at stable sites in illite. These observations suggest that the observed variability
324 in the magnitude of the energy barriers in our model is related to the nonuniform distribution
325 of electrostatic charges around the migration paths, which results from the irregular distri-
326 bution of Al atoms in the tetrahedral layers. The highest migration barriers are related to
327 paths with less tetrahedral Al around, in contrast to the lowest energies obtained for those
328 surrounded by more tetrahedral Al. In addition to the irregular distribution of tetrahedral
329 Al atoms, variations in the magnitude of migrations barriers also depend to some extent on
330 the relative position of the octahedral vacancies with respect to the migration path. In $2M_1$
331 muscovite, the projection of octahedral cations and interlayer atoms (K^+) on the (001) plane
332 shows that the octahedral vacancies are located directly above the migration paths forming
333 angles of $\pm 60^\circ$ and $\pm 120^\circ$ with the a axis. We observe that for migration paths with
334 the same number of surrounding tetrahedral Al, migration energies are systematically higher
335 for paths parallel to the a axis. These observations suggest a non-negligible effect of the
336 mica structure on the intrinsic diffusion of ^{40}Ar within the interlayer region, as suggested by
337 previous observations and empirical predictions (Scaillet et al., 1992; Dahl, 1996).

338 5.2. K^+ migration barriers

339 As with ^{40}Ar , the K^+ migration barriers define wide distributions (Fig. 5a, b). Migrations
340 energies towards monovacancies show a mean value of $79 \pm 9 \text{ kcal.mol}^{-1}$ (1σ). Using DFT
341 simulations, Yu et al. (2016) computed energy barriers associated with the migration of
342 K^+ towards a single vacancy in muscovite, for atomic models differing in their number of
343 tetrahedral Al surrounding the interlayer region where the migrating potassium is located.
344 They report energy barriers of (i) 82 kcal.mol^{-1} for the Al–Al model which contains Al

atoms in the two tetrahedral layers adjacent to the interlayer region; (ii) 146 kcal.mol⁻¹ for the Al–Si model in which Al atoms are present only in one of the tetrahedral layers, and (iii) 227 kcal.mol⁻¹ for the Si–Si model with tetrahedral layer adjacent to the considered interlayer layer region fully occupied by Si atoms. Noteworthy, the energy barrier reported for their Al–Al model, which is equivalent to ours, is within the range of values computed in our study with ClayFF. Ruiz Pestana et al. (2017) report a distribution of K⁺ energy barriers in illite computed via ClayFF and DFT. They get mean values of 54 ± 12 kcal.mol⁻¹ for ClayFF energy barriers and 75 ± 8 kcal.mol⁻¹ for those computed using DFT. They conclude that ClayFF underestimates energy barriers due to the non-bonded nature of the force field which makes structures excessively deformable. However, this apparent discordance between ClayFF and DFT is probably related to the fact that Ruiz Pestana et al. (2017) performed their ClayFF simulations without prior equilibration of their illite structure. In our study, the K⁺ energy barriers computed using ClayFF after prior equilibration of the muscovite structure are in the range of their DFT-computed barriers.

The K⁺ energy barriers associated with the divacancy mechanism yield a mean value of 66 ± 10 kcal.mol⁻¹ (1σ). This value is significantly lower than the mean energy barrier related to the migration of K⁺ into a single vacancy. This pronounced difference is illustrated by the variation of the potential energy along the K⁺ migration path between two adjacent stable sites (Fig. 5c). In this example, the K⁺ energy barrier associated with the monovacancy mechanism is 70 kcal.mol⁻¹ and the K⁺ energy barrier related to the divacancy mechanism is 55 kcal.mol⁻¹. The minimum energy paths followed by K⁺ during these migrations show that, in both cases, the potassium atom follows a curvilinear trajectory avoiding the basal oxygen atoms along the path (Fig. 5d). However, in the case of the divacancy mechanism, potassium passes further away from the oxygen atoms than in the monovacancy mechanism. This suggests that the decrease in the migration energy is due to the ability of K⁺ ions to minimize interactions with the oxygen atoms lying on their path. Moreover, while ⁴⁰Ar is at the same energy level in two neighboring vacancies, potassium shows an energy difference between the two sites (Fig. 5c). This is because potassium (charged) is more sensitive to the local charge distribution than ⁴⁰Ar (neutral). Despite these structural-charge differences, the K⁺ and ⁴⁰Ar energy barriers are positively correlated (Fig. 5e), suggesting a similar influence

375 of the local environment on the migration energy landscape.

376 6. ^{40}Ar diffusion coefficients

377 In this section, we calculate the ^{40}Ar diffusion coefficients in muscovite for both the
 378 monovacancy and the divacancy mechanisms by TST (Eq. (8)). Since the investigated
 379 migrations occur along the interlayer region, we perform calculations for 2D diffusion in a
 380 hexagonal lattice. As given above, Eq. (8) allows the analytical derivation of the diffusion
 381 coefficient for a pristine and homogenous crystal, i.e., a crystal in which the migration barrier
 382 is the same for all equivalent jumps. In our case, because of the irregular distribution of Al
 383 atoms in the tetrahedral layers, the energy barriers of interlayer atoms vary from one direction
 384 to another, and from one interlayer site to another. To take into account the spatial variation
 385 of the migration barrier, we consider for each diffusing atom an overall effective migration
 386 energy, E_{eff} , defined as:

$$387 \exp\left(\frac{E_{\text{eff}}}{RT}\right) = \sum_{i=1}^n \frac{1}{n} \exp\left(\frac{E_i}{RT}\right) \quad (10)$$

388 where E_i is the effective energy barrier required for an atom to leave an interlayer site i and
 389 n is the total number of stable sites in the interlayer region. The effective energy barrier for
 390 each site (E_i) is derived from:

$$391 \exp\left(\frac{-E_i}{RT}\right) = \sum_{j=1}^m \frac{1}{m} \exp\left(\frac{-E_{ij}}{RT}\right) \quad (11)$$

392 in which E_{ij} is the migration energy for leaving the interlayer site i in the direction j , and
 393 m is the number of all possible directions ($m = 6$ in a hexagonal lattice).

394 Eqs (10) and (11) are justified by making an analogy with an electric circuit. When
 395 different paths from a given site are possible, the conductances of the paths add up. As the
 396 conductance is proportional to the Boltzmann factor, this leads to Eq. (11). A consequence
 397 is that the path having the lowest migration energy dominates. When considering a set of
 398 sites, they are travelled in sequence so that the resistances add up as expressed by Eq. (10).
 399 In particular a site having a high migration energy will slow down the entire diffusion process,
 400 this is the trapping effect. Using the energy barriers calculated in [section 5](#), we obtain effective
 401 ^{40}Ar migration energy barriers $E_{\text{eff}}^{\text{Ar}\square} = 69 \text{ kcal.mol}^{-1}$ and $E_{\text{eff}}^{\text{Ar}\square\square} = 65 \text{ kcal.mol}^{-1}$ for the

402 monovacancy and the divacancy mechanism, respectively. For K^+ (or vacancy) migration,
 403 the calculated effective barriers are $E_{\text{eff}}^{K\Box} = 75 \text{ kcal.mol}^{-1}$ (monovacancy mechanism) and
 404 $E_{\text{eff}}^{K\Box\Box} = 58 \text{ kcal.mol}^{-1}$ (divacancy mechanism).

405 6.1. Monovacancy mechanism

406 6.1.1. Diffusion of monovacancies in a hexagonal lattice of K^+

407 The diffusion of ^{40}Ar via the monovacancy mechanism requires the presence of a vacancy
 408 in one of its neighboring sites. As long as no vacancies are available, ^{40}Ar cannot move,
 409 requiring first to study the diffusivity of the vacancies in the interlayer region. When a
 410 vacancy is present in the interlayer region, it is filled by the jump of a neighboring K^+ which,
 411 in turn, releases a vacancy in its initial site (Fig. 3a). The displacement vectors have as
 412 components:

$$413 \quad \vec{V}_0 = \begin{pmatrix} \frac{1}{2}a \\ \frac{\sqrt{3}}{2}a \end{pmatrix} \quad \vec{V}_1 = \begin{pmatrix} -\frac{1}{2}a \\ \frac{\sqrt{3}}{2}a \end{pmatrix} \quad \vec{V}_2 = \begin{pmatrix} -a \\ 0 \end{pmatrix} \quad \vec{V}_3 = \begin{pmatrix} -\frac{1}{2}a \\ -\frac{\sqrt{3}}{2}a \end{pmatrix} \quad \vec{V}_4 = \begin{pmatrix} \frac{1}{2}a \\ -\frac{\sqrt{3}}{2}a \end{pmatrix} \quad \vec{V}_5 = \begin{pmatrix} a \\ 0 \end{pmatrix} \quad (12)$$

414 and the variance of the displacement of the vacancy is:

$$415 \quad \Delta x^2 = \Delta y^2 = \frac{a^2}{2} \quad (13)$$

416 We denote by $\gamma_{K\Box}$ the frequency of the jump of one of the neighbouring K^+ towards a
 417 monovacancy (noted $K^+ \leftrightarrow \Box$), ν the attempt frequency, and $E_{\text{eff}}^{K\Box}$ the migration barrier of
 418 K^+ . According to TST, the jump frequency is given by:

$$419 \quad \gamma_{K\Box} = \nu \exp\left(-\frac{E_{\text{eff}}^{K\Box}}{RT}\right) \quad (14)$$

420 The timelife of the vacancy (i.e., the average time for a successful displacement) is:

$$421 \quad \Delta t_K = \frac{1}{6\gamma_{K\Box}} \quad (15)$$

422 and the 2D diffusion coefficient of the vacancy is:

$$423 \quad D_{\Box} = \frac{\Delta x^2 + \Delta y^2}{4\Delta t_K} = \frac{3}{2}a^2\nu \exp\left(-\frac{E_{\text{eff}}^{K\Box}}{RT}\right) \quad (16)$$

424 where a is the distance between two neighboring interlayer sites ($a = 5.2 \text{ \AA}$). At $T = 700 \text{ }^\circ\text{C}$,
 425 the diffusion coefficient of a single vacancy is $D_{\Box} = 2.88 \times 10^{-19} \text{ cm}^2.\text{s}^{-1}$.

426 6.1.2. ^{40}Ar diffusion in a monovacancy flux

427 Each time a vacancy gets next to a ^{40}Ar atom it is surrounded by five K^+ ions. Interchange
 428 between the ^{40}Ar and vacancy positions (noted $^{40}\text{Ar} \rightleftharpoons \square$) occurs due to thermal agitation
 429 and the lower barrier potential of $^{40}\text{Ar} \rightleftharpoons \square$ relative to $\text{K}^+ \rightleftharpoons \square$. The average duration of
 430 these Ar-vacancy oscillations is therefore:

$$431 \quad \Delta t_{\text{osc}} = \frac{1}{5\gamma_{\text{K}\square}} \quad (17)$$

432 During this time, many oscillations will have occurred with equal probability 0.5 of ending
 433 up either in the initial configuration (no exchange) or in effective migration of ^{40}Ar into the
 434 vacancy. The oscillations stop when one of the five K^+ neighbors jumps into the vacancy.
 435 For three of these K^+ , a successful jump will remove the vacancy away from ^{40}Ar , stopping
 436 the $^{40}\text{Ar} \rightleftharpoons \square$ oscillations. For the other two, the vacancy stays in the vicinity of ^{40}Ar and
 437 the oscillations can resume among the newly created Ar-vacancy pair.

438 Summing up, when a vacancy gets close to ^{40}Ar , after an average time Δt_{osc} , four different
 439 configurations are possible:

- 440 - The vacancy has gone away leaving ^{40}Ar in its initial position with a probability of 3/10.
- 441 - The vacancy has moved into one of the two neighboring positions of ^{40}Ar with a probability
 442 of 2/10. Oscillations resume among the newly-created ^{40}Ar -vacancy pair.
- 443 - The $^{40}\text{Ar} \rightleftharpoons \square$ interchange is successful and the vacancy moves further away by more than
 444 one lattice position with probability of 3/10.
- 445 - The $^{40}\text{Ar} \rightleftharpoons \square$ interchange has occurred but leaving the vacancy next to ^{40}Ar with proba-
 446 bility of 2/10. Oscillations resume again among the new Ar-vacancy pair.

447 The average number of jumps $\langle n_s \rangle$ needed to move the vacancy away from ^{40}Ar can be
 448 calculated by combining the respective probabilities:

$$449 \quad \langle n_s \rangle = \frac{3}{5} \sum_{n=1}^{\infty} n \left(\frac{2}{5} \right)^{n-1} = \frac{5}{3} \frac{1}{(1 - 2/5)^2} = \frac{5}{3} \quad (18)$$

450 According to Eq. (18), the average residence time of the vacancy in the vicinity of ^{40}Ar
 451 (the timelife of this configuration) is:

$$452 \quad \Delta t_o = \frac{5}{3} \Delta t_{\text{osc}} = \frac{1}{3\gamma_{\text{K}\square}} \quad (19)$$

453 During this time interval, several trains of oscillations will have occurred. The calculation
 454 of the variance of the mean displacement of ^{40}Ar is complicated by the fact the successive
 455 displacements are correlated. However, KMC simulations show that the positional variance
 456 of the displacement of \square along either \vec{x} or \vec{y} is completely defined by the number of jumps
 457 n_s of the vacancy remaining in the neighborhood:

$$458 \quad \langle \Delta x^2 \rangle = \langle \Delta y^2 \rangle = \frac{n_s + 1}{8} a^2 \quad (20)$$

459 By summing over the n_s probabilities, we obtain the average variance resulting in the nearest-
 460 neighbor vacancy configuration:

$$461 \quad \langle \Delta x^2 \rangle = \langle \Delta y^2 \rangle = \frac{a^2}{3} \quad (21)$$

462 Note that, despite its higher energy barrier, the variance is stochastically dominated by the
 463 bulk motion of K^+ via the $\text{K}^+ \rightleftharpoons \square$ interchange (vacancy diffusion), not the mobility of ^{40}Ar
 464 with respect to the vacancy. The vibrational motion of ^{40}Ar just ensures that it will take
 465 (with probability 0.5) a quantum step away from its initial position when the vacancy passes
 466 close by. Note also that this is the variance induced by the proximity of a vacancy. Most of
 467 the time, no vacancy hangs around ^{40}Ar which cannot move then (the time goes on with the
 468 variance remaining unchanged).

469 We now inquire into the bulk vacancy flux that governs the overall mobility of ^{40}Ar
 470 through the muscovite interlayer. Consider a portion of lattice containing N regular interlayer
 471 sites with a single ^{40}Ar atom and a density of vacancies ρ . The number of neighboring
 472 sites around a vacancy is six and the number of vacancies $N\rho$. At each vacancy jump, the
 473 probability of starting from either a normal “bulk” position or next to ^{40}Ar is proportional
 474 to their respective populations. The probability of starting from a neighboring site must
 475 be weighted by a factor of 5/6 because only five directions allow it to be reached, instead
 476 of six for a normal site. This quantitative reduction has been tested by KMC simulation
 477 ([Appendix A](#)). Finally, during a vacancy jump the probability of starting from a bulk site is
 478 $P_b = (N - 6)/N$ while that of jumping from the vicinity of ^{40}Ar is $P_v = 6/N(5/6) = 5/N$.

479 Consider now a trajectory of m jumps of the $N\rho$ vacancies. Among these m jumps
 480 mP_b will start from a bulk site whose lifetime is $t_b = 1/(6\gamma_{\text{K}\square})$ and mP_v will come from

481 neighboring sites with lifetime $t_v = 1/(5\gamma_{K_\square})$. The total duration of these trajectories of m
 482 jumps is therefore:

$$483 \quad t = m \left(1 - \frac{6}{N}\right) \frac{1}{6\gamma_{K_\square}} + m \frac{5}{N} \frac{1}{5\gamma_{K_\square}} = \frac{m}{6\gamma_{K_\square}} \quad (22)$$

484 The average number of vacancy jumps ending next to ^{40}Ar is:

$$485 \quad m_v = m \frac{5}{N} N \rho = 5\rho m \quad (23)$$

486 We have seen that in the direct-neighbor configuration (Fig. 3a), on average 5/3 jumps move
 487 the vacancy away from ^{40}Ar (Eq. (18)). The number of such moves in a bulk vacancy flux
 488 is:

$$489 \quad m'_v = 3\rho m \quad (24)$$

490 According to Eq. (21), each of these moves has variance $a^2/3$ so that on average:

$$491 \quad \langle \Delta x^2 \rangle = \langle \Delta y^2 \rangle = \rho a^2 m = 6\rho\gamma_{K_\square} a^2 t \quad (25)$$

492 The diffusion coefficient for ^{40}Ar is thus:

$$493 \quad D_{\text{Ar}\square} = \frac{\langle x^2 \rangle + \langle y^2 \rangle}{4t} = 3a^2 \gamma_{K_\square} \rho = 3a^2 \nu \rho \exp\left(-\frac{E_{\text{eff}}^{K_\square}}{RT}\right) \quad (26)$$

494 The temperature dependence of this diffusion mechanism is reported in the Arrhenius
 495 diagram (Fig. 6). For example, at $T = 700$ °C and $\rho = 0.1$, the diffusion coefficient is $D_{\text{Ar}\square} =$
 496 5.76×10^{-20} cm².s⁻¹. The diffusion parameters associated with the monovacancy mechanism
 497 are $E = 75$ kcal.mol⁻¹ and $D_0 = 4 \times 10^{-3}$ cm².s⁻¹.

498 6.2. Divacancy mechanism

499 6.2.1. Diffusion of divacancies in a hexagonal lattice of K^+

500 In the case of a divacancy mechanism, K^+ atoms are adjacent either to only one vacancy
 501 or both (Fig. 3b). In the latter configuration, the jumps (blue arrows) have a lower effective
 502 energy barrier (58 kcal.mol⁻¹) and therefore a higher probability of occurrence than those of
 503 the first configuration (in black), whose migration barriers are identical to those associated
 504 with the monovacancy mechanism (75 kcal.mol⁻¹). When one of these “blue” migrations
 505 occurs, a K^+ atom fills one vacancy and a new vacancy is created in its initial position.
 506 This new vacancy lies in one of the sites neighboring the unoccupied vacancy of the initial

507 pair, and both form a new vacancy pair. Therefore, one can expect a correlated mobility of
 508 divacancies along the interlayer region.

509 The two pertinent quantities to calculate here are the diffusion coefficient of the divacancy
 510 and its lifetime. The divacancy is characterized by its position (barycenter of the vacancy
 511 pair), the direction passing through the vacancy pair, and the angle made by the direction
 512 with the x -axis which can be 0° (Fig. 3b) or $\pm 60^\circ$. Each atom jump filling a vacancy
 513 produces a virtual displacement and the apparent rotation of the divacancy direction. Let
 514 us calculate the average variance of such a displacement.

515 When the starting angle is 0° the jumps $\vec{\delta}_0, \vec{\delta}_1, \vec{\delta}_2, \vec{\delta}_3$ produce respectively the angles
 516 $60^\circ, 60^\circ, -60^\circ, -60^\circ$, and the divacancy displacement vectors:

$$517 \quad \vec{V}_0 = \begin{pmatrix} \frac{1}{4}a \\ \frac{\sqrt{3}}{4}a \end{pmatrix} \quad \vec{V}_1 = \begin{pmatrix} -\frac{1}{4}a \\ -\frac{\sqrt{3}}{4}a \end{pmatrix} \quad \vec{V}_2 = \begin{pmatrix} \frac{1}{4}a \\ -\frac{\sqrt{3}}{4}a \end{pmatrix} \quad \vec{V}_3 = \begin{pmatrix} -\frac{1}{4}a \\ \frac{\sqrt{3}}{4}a \end{pmatrix} \quad (27)$$

518 By symmetry, these jumps are equiprobable.

519 For a starting angle of 60° , the divacancy displacement vectors \vec{V}_i are just rotated by this
 520 angle :

$$521 \quad \vec{V}'_i = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix} \vec{V}_i \quad (28)$$

522 and:

$$523 \quad \vec{V}'_0 = \begin{pmatrix} -\frac{1}{4}a \\ \frac{\sqrt{3}}{4}a \end{pmatrix} \quad \vec{V}'_1 = \begin{pmatrix} \frac{1}{4}a \\ -\frac{\sqrt{3}}{4}a \end{pmatrix} \quad \vec{V}'_2 = \begin{pmatrix} \frac{1}{2}a \\ 0 \end{pmatrix} \quad \vec{V}'_3 = \begin{pmatrix} -\frac{1}{2}a \\ 0 \end{pmatrix} \quad (29)$$

524 For the -60° configuration, the corresponding rotation is:

$$525 \quad \vec{V}''_0 = \begin{pmatrix} \frac{1}{2}a \\ 0 \end{pmatrix} \quad \vec{V}''_1 = \begin{pmatrix} -\frac{1}{2}a \\ 0 \end{pmatrix} \quad \vec{V}''_2 = \begin{pmatrix} -\frac{1}{4}a \\ -\frac{\sqrt{3}}{4}a \end{pmatrix} \quad \vec{V}''_3 = \begin{pmatrix} \frac{1}{4}a \\ \frac{\sqrt{3}}{4}a \end{pmatrix} \quad (30)$$

526 Whatever the starting configuration, it can be shown that $\langle x \rangle = \langle y \rangle = 0$. For a given tra-
 527 jectory, the orientations are equiprobable. For all jumps keeping the vacancy pair connected
 528 the displacements \vec{V}_i, \vec{V}'_i and \vec{V}''_i occur with equal probability of $1/12$. One may verify that
 529 $\langle x \cdot y \rangle = 0$, indicating that the displacements along either x or y are uncorrelated which is a
 530 consequence of hexagonal symmetry. In terms of variance of displacements we have:

$$531 \quad \langle x^2 \rangle = \langle y^2 \rangle = \frac{1}{8}a^2 \quad (31)$$

532 due again to the symmetry in x and y .

533 Denote by $\gamma_{K_{\square}}$ the jump frequency corresponding to a “black” migration and $\gamma_{K_{\square\square}}$ for
534 the “blue” migration (Fig. 3b). The residence time of the divacancy at any given position is:

$$535 \quad t_r = \frac{1}{4\gamma_{K_{\square\square}} + 6\gamma_{K_{\square}}} \quad (32)$$

536 The average migration time after m jumps is:

$$537 \quad \langle t \rangle = m t_r = \frac{m}{4\gamma_{K_{\square\square}} + 6\gamma_{K_{\square}}} \quad (33)$$

538 and the variance of the displacement:

$$539 \quad \langle x^2 \rangle = \langle y^2 \rangle = m \frac{a^2}{8} \quad (34)$$

540 From these, we deduce the divacancy diffusion coefficient:

$$541 \quad D_{\square\square} = \frac{1}{4} a^2 \left(\gamma_{K_{\square\square}} + \frac{3}{2} \gamma_{K_{\square}} \right)$$

$$542 \quad D_{\square\square} = \frac{1}{4} a^2 \nu \exp \left(- \frac{E_{\text{eff}}^{K_{\square\square}}}{RT} \right) \left[1 + \frac{3}{2} \exp \left(\frac{E_{\text{eff}}^{K_{\square\square}} - E_{\text{eff}}^{K_{\square}}}{RT} \right) \right] \quad (35)$$

544 where $E_{\text{eff}}^{K_{\square\square}}$ is the K^+ migration barrier towards a divacancy. The second exponential in
545 parentheses (rightmost term) is much smaller than unity and the diffusion coefficient reduces
546 to:

$$547 \quad D_{\square\square} = \frac{1}{4} a^2 \nu \exp \left(- \frac{E_{\text{eff}}^{K_{\square\square}}}{RT} \right) \quad (36)$$

548 At $T = 700$ °C, the diffusion coefficient associated with the divacancy migration is $D_{\square\square} =$
549 3.89×10^{-16} cm².s⁻¹, three orders of magnitude faster than the monovacancy mechanism.

550 6.2.2. ⁴⁰Ar diffusion in a divacancy flux

551 When a divacancy lies in the vicinity of ⁴⁰Ar, the latter can be adjacent to either one
552 or both vacancies and the probability that one is filled by ⁴⁰Ar depends on the specific
553 nearest-neighbor configuration. Denote by $E_{\text{eff}}^{\text{Ar}_{\square}}$ the ⁴⁰Ar energy barrier faced by the “black”
554 transitions and by $E_{\text{eff}}^{\text{Ar}_{\square\square}}$ that associated with “blue” migrations. When the ⁴⁰Ar is adjacent
555 to only one of the two vacancies (Fig. 3b) the probability of jump before a move of the

556 divacancy is:

$$\begin{aligned}
 557 \quad P_{\text{Ar}\square} &= \frac{\exp\left(-\frac{E_{\text{eff}}^{\text{Ar}\square}}{RT}\right)}{\exp\left(-\frac{E_{\text{eff}}^{\text{Ar}\square}}{RT}\right) + 5 \exp\left(-\frac{E_{\text{eff}}^{\text{K}\square}}{RT}\right) + 2 \exp\left(-\frac{E_{\text{eff}}^{\text{K}\square\square}}{RT}\right)} \\
 558 \quad &= \frac{\exp\left(-\frac{E_{\text{eff}}^{\text{Ar}\square} - E_{\text{eff}}^{\text{K}\square\square}}{RT}\right)}{\exp\left(-\frac{E_{\text{eff}}^{\text{Ar}\square} - E_{\text{eff}}^{\text{K}\square\square}}{RT}\right) + 5 \exp\left(-\frac{E_{\text{eff}}^{\text{K}\square} - E_{\text{eff}}^{\text{K}\square\square}}{RT}\right) + 2} \quad (37)
 \end{aligned}$$

559 The exponentials in the denominator are much smaller than one because of the difference in
 560 the energy barriers, and Eq. (37) simplifies to

$$561 \quad P_{\text{Ar}\square} = \frac{1}{2} \exp\left(-\frac{E_{\text{eff}}^{\text{Ar}\square} - E_{\text{eff}}^{\text{K}\square\square}}{RT}\right) \quad (38)$$

562 On the other hand, there are two positions where the ^{40}Ar is close to both vacancies
 563 (Fig. 3b) and the probability of jumping into one of them before the divacancy move is:

$$564 \quad P_{\text{Ar}\square\square} = \frac{\exp\left(-\frac{E_{\text{eff}}^{\text{Ar}\square\square}}{RT}\right)}{\exp\left(-\frac{E_{\text{eff}}^{\text{Ar}\square}}{RT}\right) + 6 \exp\left(-\frac{E_{\text{eff}}^{\text{K}\square}}{RT}\right) + \exp\left(-\frac{E_{\text{eff}}^{\text{K}\square\square}}{RT}\right)} \quad (39)$$

565 As before, Eq. (39) simplifies to

$$566 \quad P_{\text{Ar}\square\square} = \exp\left(-\frac{E_{\text{eff}}^{\text{Ar}\square\square} - E_{\text{eff}}^{\text{K}\square\square}}{RT}\right) \quad (40)$$

567 The relative importance of the probabilities Eqs. (38) and (40) depends on the frequency of
 568 each configuration.

569 Denote by ρ' the density of divacancies in the interlayer region, defined as the number of
 570 divacancies divided by the number of interlayer sites in the lattice. Consider a trajectory of
 571 m jumps of the divacancies. For $6m\rho'$ positions the ^{40}Ar will be close to one only vacancy,
 572 and for $m\rho'$ it will be close to both vacancies. The above expressions can be deduced by
 573 weighing the different orientations and by observing that the double-vicinity of the ^{40}Ar can

574 be reached only from one side, and they have been confirmed by running dedicated KMC
575 simulations (Appendix A).

576 In the bulk divacancy flux, the residence time of a divacancy is given by Eq. (32) in which
577 $\gamma_{K_{\square}}$ can be neglected. This residence time is nearly the same when a ^{40}Ar is close to only
578 one vacancy, but it doubles when it neighbors the two vacancies. Therefore the time for a
579 trajectory of m jumps is:

$$580 \quad t = \frac{m}{4\gamma_{K_{\square}}}(1 + \rho') = \frac{m}{4\nu}(1 + \rho') \exp\left(\frac{E_{\text{eff}}^{K_{\square\square}}}{RT}\right) \quad (41)$$

581 For $6m\rho'$ configurations, ^{40}Ar sees only one vacancy and the jump probability is given by Eq.
582 (38). For $m\rho'$ configurations it neighbors the two vacancies and has a jump probability given
583 by Eq. (40). For any jump the variance in coordinates is given by Eq. (13). In the end, for
584 m jumps the variance is:

$$585 \quad \langle x^2 \rangle = \langle y^2 \rangle = m\rho' \frac{a^2}{2} \left[3 \exp\left(-\frac{E_{\text{eff}}^{\text{Ar}_{\square}} - E_{\text{eff}}^{K_{\square\square}}}{RT}\right) + \exp\left(-\frac{E_{\text{eff}}^{\text{Ar}_{\square\square}} - E_{\text{eff}}^{K_{\square\square}}}{RT}\right) \right] \quad (42)$$

586 From Eq. (41) and (42) we can deduce the diffusion coefficient for ^{40}Ar :

$$587 \quad D_{\text{Ar}_{\square\square}} = \frac{\rho'}{1 + \rho'} a^2 \nu \left[3 \exp\left(-\frac{E_{\text{eff}}^{\text{Ar}_{\square}}}{RT}\right) + \exp\left(-\frac{E_{\text{eff}}^{\text{Ar}_{\square\square}}}{RT}\right) \right] \quad (43)$$

588 in which the first term inside the brackets is small compared to the last one.

589 It remains to determine the density of divacancies ρ' . It can be expressed with the density
590 of monovacancies ρ . The divacancies are produced when two monovacancies hit each other,
591 because their coherent motion is energetically favored. On the other hand they decay when
592 one of its vacancies is filled by a neighboring K^+ (black jumps; Fig. 3). This is a dynamical
593 equilibrium reached when the rate of production equates the rate of decay.

594 Consider N regular interlayer sites. The number of monovacancies is $N\rho$. At any jump
595 of a vacancy, the probability to make a collision (i.e. to reach the neighborhood of another
596 vacancy) is proportional to ρ , so that the number of produced divacancies is $kN\rho^2$, where k
597 is a number to be determined. A dedicated random walk simulation shows that $k = 2.5$. The
598 duration of each step is $1/(6\gamma_{K_{\square}})$ giving a production rate of $15N\rho^2\gamma_{K_{\square}}$. The decay rate is
599 $6N\rho'\gamma_{K_{\square}}$. By equating the two rates one gets $\rho' = 2.5\rho^2$.

After replacement of this value in Eq. (43) and taking into account that $\rho \ll 1$:

$$D_{\text{Ar}\square} = \frac{5}{2}\rho^2 a^2 \nu \left[3 \exp\left(-\frac{E_{\text{eff}}^{\text{Ar}\square}}{RT}\right) + \exp\left(-\frac{E_{\text{eff}}^{\text{Ar}\square\square}}{RT}\right) \right] \quad (44)$$

At $T = 700$ °C and for $\rho = 0.1$, the ^{40}Ar diffusion coefficient associated with the divacancy mechanism is $D_{\text{Ar}\square} = 1.16 \times 10^{-18}$ cm².s⁻¹, two orders of magnitude higher than the diffusivity of the monovacancy mechanism. The ^{40}Ar diffusion parameters deduced from the Arrhenius diagram (Fig. 6) are $E = 66$ kcal.mol⁻¹ and $D_0 = 6 \times 10^{-4}$ cm².s⁻¹. A summary listing of the final estimates is provided in Table 3.

7. Discussion

7.1. Comparison with previous ^{40}Ar diffusion estimates

As mentioned above, only a handful of studies have attempted to quantify ^{40}Ar diffusion in muscovite (Robbins, 1972; Hames and Bowring, 1994; Kirschner et al., 1996; Lister and Baldwin, 1996, 2016; Harrison et al., 2009; Forster and Lister, 2014). While ^{40}Ar diffusivity estimates inferred by these studies are broadly consistent, they considerably differ from the present results. Our MD and TST estimates are up to five orders of magnitude lower than the corresponding Arrhenian laws (Fig. 6). Note that our results are calculated for muscovite at $P = 0$ kbar. Assuming a pressure effect on diffusivity of ^{40}Ar in muscovite (Harrison et al., 2009) would enhance the disparity even further.

Hydrothermal experiments have been suspected to overestimate ^{40}Ar diffusivity in natural muscovite for quite a while now (Monié, 1990; Scaillet et al., 1990, 1992; Monié and Chopin, 1991; Arnaud and Kelley, 1995; Scaillet, 1996; Di Vincenzo et al., 2001, 2004, 2006; Balogh and Dunkl, 2005; Hames et al., 2008; Itaya et al., 2009; Allaz et al., 2011; Beltrando et al., 2013; Halama et al., 2014; Schertl and Hammerschmidt, 2016; Laurent et al., 2021). As emphasized before, most of these studies relate to high-pressure (phengitic) muscovite. The high retentivity (i.e., low ^{40}Ar diffusivity) of muscovite in these conditions has long been traced to crystal-structural effects suspected to affect the interlayer at increasingly higher pressure (Scaillet et al., 1992; Scaillet, 1998). It is also supported by the diffusion data of Harrison et al. (2009) which predict lower diffusivities at high pressure. Evidence for a pronounced ^{40}Ar retentivity in muscovite has been also reported in other settings as well

628 (e.g. Di Vincenzo et al., 2004; Hames et al., 2008; Itaya et al., 2009; Allaz et al., 2011),
 629 suggesting that sluggish ^{40}Ar kinetics in natural muscovite is more the norm than currently
 630 acknowledged by existing experimental data.

631 Field-based calibration of ^{40}Ar retention kinetics in muscovite is scarce and highly context-
 632 specific (e.g., Wijbrans and McDougall, 1986, 1988; Blanckenburg et al., 1989; Kirschner et
 633 al., 1996). So far, such efforts have been taken to indicate moderate or intermediate ^{40}Ar
 634 retention properties of muscovite relative to other isotope-mineral pairs (by order of decreas-
 635 ing retentivity: U/Pb–zircon > Rb/Sr–muscovite > K/Ar–amphibole > K/Ar–muscovite
 636 > K/Ar–biotite \approx K/Ar–alkali feldspar). Mounting evidence, in particular from grain-
 637 scale Rb/Sr and laser-based $^{40}\text{Ar}/^{39}\text{Ar}$ disequilibrium data (e.g. Bröcker et al., 2013; Cliff
 638 et al., 2017; Laurent et al., 2021), shows that Ar-Rb-Sr retention systematics in natu-
 639 ral muscovite are actually quite similar (Glodny et al., 2002; 2008; Bosse et al., 2005;
 640 Scibiorski et al., 2021), pointing to otherwise more sluggish kinetics than suggested by the
 641 above trend for elements that are either ionically bonded (Rb, Sr) and/or simply too big (Ar)
 642 to easily jump from a lattice position to the next. This is most clearly illustrated by peak-
 643 metamorphic $^{40}\text{Ar}/^{39}\text{Ar}$ retention ages commonly preserved in muscovite despite deformation
 644 and overprinting (Putlitz et al., 2005; Beaudoin et al., 2020, Laurent et al., 2021). This is also
 645 emphasized by congruent $^{40}\text{Ar}/^{39}\text{Ar}$ muscovite and U/Pb titanite ages metastably preserved
 646 over map-scales in excess of 450-750 km² in dry granulite-amphibolite crust exposed to $T \geq$
 647 700 °C for tens of Myr (Spencer et al., 2013).

648 Using the diffusion data retrieved from our modeling ($E = 66 \text{ kcal.mol}^{-1}$ and $D_0 =$
 649 $6 \times 10^{-4} \text{ cm}^2.\text{s}^{-1}$), nominal closure temperatures can be calculated via Eq. (1) for various
 650 cooling rates and grain sizes. For cooling rates ranging from 1 to 100 °C.Ma⁻¹ and grain
 651 size varying between 0.1-1.0 mm, this returns closure temperatures in the range 560-800 °C
 652 (Fig. 7). These are significantly (up to 200 °C) higher than predicted by current experimental
 653 estimates (Hames and Bowring, 1994; Kirschner et al., 1996; Harrison et al., 2009) and close
 654 to the upper stability limit of muscovite ($\sim 700 \text{ °C}$; Massonne and Schreyer, 1987, 1989),
 655 which by the way is significantly lower in presence of quartz (Althaus et al., 1970). This
 656 opens up the prospect that crystallization ages may be more likely than cooling ages in
 657 natural muscovite.

658 However, empirical evidence also abounds to suggest that intracrystalline ^{40}Ar mobility
659 may be enhanced by other factors beyond purely diffusion-driven rates such as predicted by
660 our model. Our model calculations apply to ideal (undefective) muscovite. Natural micas
661 are far from perfect and always contain microstructural defects such as dislocations, stacking
662 faults, microcleavages, etc., which can develop during crystal growth, or more commonly, in
663 response to deformation (e.g. [Bell and Wilson, 1977, 1981](#); [Amouric, 1987](#); [Kronenberg et al., 1990](#);
664 [Shea and Kronenberg, 1992](#); [Dunlap, 1997](#); [Beaudoin et al., 2020](#)). Such extended
665 microstructural defects act as high diffusivity pathways that can considerably enhance the
666 mobility of diffusing atoms ([Lee, 1995](#)). Sizeable extents of ^{40}Ar loss have been documented in
667 naturally and experimentally deformed muscovite in connection with microstructural defects
668 ([Kramar et al., 2001, 2003](#); [Mulch et al., 2002](#); [Cosca et al., 2011](#)). Ascribing the observed
669 losses in such cases to diffusion only is bound to overestimate ^{40}Ar diffusion rates, but to a
670 largely unknown extent if the crystal-defective structure of the mica is not properly quantified
671 ([Kramar et al., 2001, 2003](#)). A case in point are the diffusion rates empirically derived from
672 the muscovites studied by [Kirschner et al. \(1996\)](#). These crystallized during deformation by
673 thrusting and most likely contain microstructural defects as well.

674 The same caveat applies to diffusion experiments performed under hydrothermal condi-
675 tions ([Dunlap, 1997](#)). To optimize the fractional loss of their starting material, [Harrison et al. \(2009\)](#)
676 used fine-grained muscovite fractions ($< 100 \mu\text{m}$ across) obtained by mechanical
677 grinding of larger grains. Such grinding is likely to have produced extended intracrystalline
678 defects in their samples, a problem already raised by [Dunlap \(1997\)](#) for the early thermal-
679 hydrothermal experiments conducted by [Robbins \(1972\)](#). While these defects may have little
680 effect on the effective loss of ^{40}Ar in vacuum ($< 0.5\%$; [Dunlap and Kronenberg, 2001](#)), their
681 impact under hydrothermal conditions may be vastly underestimated because of the longer
682 duration of these experiments. Incidentally, [Harrison et al. \(2009\)](#) used a multi-domain
683 diffusion model in an attempt to fit their hydrothermal-loss data to complex *in vacuo* gen-
684 erated $^{40}\text{Ar}/^{39}\text{Ar}$ spectrum patterns. Such a non-ideal behavior may to some extent reflect
685 the complex defective structure artificially induced during sample preparation.

686 An additional complication is the presence of reactive fluids, both in Nature and exper-
687 iments. When out of equilibrium with the solid phase, fluid-phase dissolution-precipitation

688 may lead to partial destabilization depending on fluid-solid equilibria, crystal boundary struc-
689 ture and width, and exchange duration (Cole and Chakraborty, 2001; Putnis, 2009). Fluid-
690 phase dissolution kinetics are much faster than solid-state intracrystalline diffusion (Scaillet,
691 1998; Putnis, 2009), potentially enhancing ^{40}Ar loss well beyond lattice diffusion rates in
692 hydrothermal experiments. Harrison et al. (2009) report a fractional loss 10 % higher for
693 a hydrothermal run compared to the same P – T run under dry conditions. Although the
694 authors infer that a fluid phase is a necessary reservoir for ^{40}Ar to be diffusively lost from
695 muscovite during the experiments, the difference may also reflect ^{40}Ar diffusion enhanced
696 in the presence of water. Harrison et al. (2009) also report an Al enrichment of their run
697 products compared to the starting material. As discussed by Villa (2021), this may hint
698 at dissolution–precipitation transformations during the runs, potentially compromising (i.e.,
699 overestimating) the diffusion rates derived from the observed losses. Evidence of recrystal-
700 lization of micas during hydrothermal experiments is also reported by Hess et al. (1987) and
701 Villa and Puxeddu (1994).

702 Although not dealing with ^{40}Ar diffusion in muscovite proper, studies of Sr diffusion in
703 biotite (Hammouda and Cherniak, 2000) have revealed four orders magnitude difference in
704 diffusion rates between hydrothermally treated biotite (faster-diffusing) and dry F-phlogopite
705 (slower-diffusing). These authors rule out F-substitutional effects in favor of the weaken-
706 ing effect of water on the mica structure to explain this behavior, possibly enhanced by
707 dissolution–recrystallization processes during the hydrothermal treatment. Water molecules
708 can also act as source of H^+ , which weaken Si–O and Al–O bonds and consequently en-
709 hance the diffusion of oxygen in minerals such as quartz (Elphick and Graham, 1988), al-
710 kali feldspar (Farver and Yund, 1990) and micas (Fortier and Giletti, 1991). Hydrolysis of
711 K–O bonds in muscovite, similar to that of Si–O and Al–O in other common silicates,
712 could lower the ^{40}Ar migration barrier, thereby accelerating its diffusion. All these mecha-
713 nisms suggests that ^{40}Ar diffusivity measured under hydrothermal conditions provides only
714 an upper limit to actual ^{40}Ar transport rates across the mica lattice.

715 7.2. Applicability to natural systems and implications for $^{40}\text{Ar}/^{39}\text{Ar}$ thermochronology

716 All the above processes work the same in Nature, but with even more free thermodynamic
717 variables (e.g., multiphase equilibria, transient fluids) and much longer durations than in hy-

718 drothermal diffusion cells. In fluid-assisted metamorphic transformations, the ^{40}Ar initially
 719 present in recrystallized (or dissolved) muscovite may be released in the free fluid phase,
 720 locally enhancing or disrupting ^{40}Ar concentration gradients pre-existing in the original crys-
 721 tals (e.g. Hames and Cheney, 1997; Scaillet, 1998; Di Vincenzo et al., 2001, 2004; Hames
 722 et al., 2008; Beltrando et al., 2013; Beaudoin et al., 2020; Laurent et al., 2021). Partial to
 723 complete ^{40}Ar resetting with intracrystalline $^{40}\text{Ar}/^{39}\text{Ar}$ gradients do exist however, as doc-
 724 umented *in situ* in natural muscovite (e.g., Scaillet et al., 1990, 1992; Hames and Hodges,
 725 1993; Hodges et al., 1994; Hodges and Bowring, 1995; Scaillet, 1996; Boundy et al., 1997).
 726 The mere existence of these spatial gradients is indication that bulk (volume) diffusive mo-
 727 tion is effectively operating in Nature, but not with the rate constants and barrier potentials
 728 theoretically predicted for ideal (undefective) muscovite. The empirical Ar-Rb-Sr parallel
 729 drawn above and the highly disparate ^{40}Ar diffusion rates documented both experimentally
 730 and in the field clearly indicate that $^{40}\text{Ar}/^{39}\text{Ar}$ systematics in natural systems are not fully
 731 captured yet in terms of lattice-scale processes.

732 Our findings point to a fundamental, yet largely unexplored, crystal-structural thread
 733 connecting the Ar isotopic record with mixed-scale diffusional \pm compositional \pm struc-
 734 tural *disequilibrium interactions* during the natural "growth \rightarrow closure" cycle of muscovite.
 735 During metamorphic $P-T$ changes, white micas react via segregation and re-organization
 736 of Si^{4+} -rich domains involving the cooperative interdiffusion of several components such as
 737 $2\text{Na}^+ + \text{Al}^{3+} = \text{K}^+ + \text{Si}^{4+} + \square$ that progressively produce discrete compositional domains dur-
 738 ing re-equilibration (Shau et al., 1991), analogous to segregation of interlayer cations (Na^+ ,
 739 Ca^{2+} , K^+) into nanodomains (Livi et al., 2008; Beltrando et al., 2013). Crystal-structural ev-
 740 idence above suggests that such modifications are decoupled kinetically across the interlayer
 741 hosting radiogenic ^{40}Ar , especially in the presence of grain-scale chemical potential and stress
 742 gradients (Scaillet et al., 1992; Scaillet, 1996, 1998), severely impairing the interpretation of
 743 microscale $^{40}\text{Ar}/^{39}\text{Ar}$ patterns in terms of either diffusion or (re)crystallization (Beaudoin et
 744 al., 2020; Laurent et al., 2021).

745 Hence, the reason why empirical ^{40}Ar diffusion rates are so distinct from DFT and MD es-
 746 timates is not failure of these approaches in describing fundamental lattice-based processes.
 747 Rather, it is the manifestation of atomic-scale kinetics combining diffusion with (as yet)

748 largely unmodeled physics, most notably those controlling reactivity of the interlayer with
749 the external medium. Thermodynamic equilibrium is the common-denominator assumption
750 of both experimental and theoretical diffusion modeling. So far, fulfilling this condition has
751 proven elusive in the hydrothermal treatment of muscovite (Villa, 2021). In contrast, equilib-
752 rium is a built-in condition in theoretical models ensuring, as here, full control on boundary
753 conditions along with a test that the system indeed remains thermodynamically stable. As
754 such, our MD and TST diffusion estimates provide the first reliable benchmark against which
755 to gauge first-order ^{40}Ar diffusion kinetics in a stoichiometrically stable muscovite structure.
756 Combined with hydrothermal predictions (Fig. 6), they collectively define the probable $D-T$
757 space spanned by intracrystalline ^{40}Ar kinetics in natural muscovite. Further empirical and
758 theoretical work is required to clarify kinetic interactions between crystal-chemical disequi-
759 librium and effective ^{40}Ar diffusion across such $D-T$ space.

760 8. Conclusions

761 A lattice-based study of ^{40}Ar diffusion in muscovite has been attempted for the first time
762 via Molecular Dynamics simulations coupled with Nudged Elastic Band and Transition State
763 Theory. The main results lead to the following conclusions:

- 764
- 765 • ^{40}Ar diffusion in $2M_1$ muscovite predominantly occurs along the (001) interlayer with
766 recoil energies too low to permit extensive or systematic implantation of the radiogenic ^{40}Ar
767 atom more than a lattice spacing away from its production site from ^{40}K .
- 768
- 769 • Systematic energy-barrier mapping by NEB coupled with TST allows to identify the most
770 probable diffusion pathway and barrier potential for ^{40}Ar motion along the (001) interlayer;
771 ^{40}Ar transport via a divacancy mechanism is shown to be the more energetically favor-
772 able pathway for ^{40}Ar migration along (001) with characteristic diffusion parameters $E =$
773 66 kcal.mol^{-1} and $D_0 = 6 \times 10^{-4} \text{ cm}^2.\text{s}^{-1}$.
- 774
- 775 • These theoretical estimates suggest that purely diffusion-driven (Brownian) motion is not
776 an efficient mechanism for ^{40}Ar intracrystalline transport in a stoichiometrically pure and

777 stable muscovite structure.

778

779 • Along with hydrothermal and field-based evidence, they call for more complex (multi-scale
780 and multi-process) physics to explain ^{40}Ar exchange and retention properties of natural mus-
781 covite, most notably by considering the chemical-stoichiometric reactivity of the interlayer
782 with the external medium.

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793 **Appendix A. Supplementary Material**

794 Supplementary data associated with this article can be found, in the online version, at
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Table 1: Interaction parameters used in the simulations

| Nonbonded parameters | | | |
|--|--------------|--|--------------------------------------|
| Atoms | Charge (e) | σ (Å) | ϵ (kcal.mol ⁻¹) |
| H (hydroxyl) ^a | 0.4250 | - | - |
| O1 (hydroxyl) ^a | -0.9500 | 3.1655 | 0.1554 |
| O2 (bridging Oxygen) ^a | -1.0500 | 3.1655 | 0.1554 |
| O3 (Oxygen bonded to tetrahedral Al) ^a | -1.1688 | 3.1655 | 0.1554 |
| Al (octahedral) ^a | 1.5750 | 4.2712 | 1.3298×10^{-6} |
| Al2 (tetrahedral) ^a | 1.5750 | 3.3020 | 1.8405×10^{-6} |
| Si ^a | 2.1000 | 3.3020 | 1.8405×10^{-6} |
| K ^a | 1.0000 | 3.3340 | 0.1000 |
| Ar ^b | 0.0000 | 3.4010 | 0.2304 |
| ^a Cygan et al. (2004) ^b White (1999) | | | |
| Bonded parameters | | | |
| Atom 1 | Atom 2 | k_1 (kcal.mol ⁻¹ .Å ⁻²) | r_0 (Å) |
| O1 (hydroxyl) | H (hydroxyl) | 554.1349 | 1.0000 |

Table 2: Comparison of experimental and simulated crystallographic parameters of $2M_1$ Muscovite

| | Experiment | MD simulations (CLAYFF) | Deviation (\pm %) |
|-----------------------|------------|-------------------------|----------------------|
| a (Å) | 5.191 | 5.182 | -0.17 |
| b (Å) | 9.006 | 8.944 | -0.69 |
| c (Å) | 20.068 | 19.697 | -1.85 |
| α ($^\circ$) | 90.000 | 89.787 | -0.24 |
| β ($^\circ$) | 95.770 | 95.936 | +0.17 |
| γ ($^\circ$) | 90.000 | 90.175 | +0.19 |
| Interlayer sep. (Å) | 3.396 | 3.368 | -0.88 |

Table 3: Computed migration barriers and ^{40}Ar diffusion parameters for the monovacancy (\square) and divacancy ($\square\square$) mechanisms.

| | Mean energy barriers | | Effective energy barriers | | ^{40}Ar Diffusion parameters | |
|------------------|--|---|---|--|---------------------------------------|--------------------------------|
| | $\langle E^{\text{Ar}} \rangle$ (kcal.mol $^{-1}$) | $\langle E^{\text{K}} \rangle$ (kcal.mol $^{-1}$) | $E_{\text{eff}}^{\text{Ar}}$ (kcal.mol $^{-1}$) | $E_{\text{eff}}^{\text{K}}$ (kcal.mol $^{-1}$) | E (kcal.mol $^{-1}$) | D_0 (cm 2 .s $^{-1}$) |
| \square | 71 ± 5 | 79 ± 9 | 69 | 75 | 75 | 4×10^{-3} |
| $\square\square$ | 69 ± 6 | 66 ± 10 | 65 | 58 | 66 | 6×10^{-4} |

1133 **Figure captions**

1134 **Fig. 1.** The crystal structure atomic model of muscovite imaged with VESTA (Momma and
 1135 Izumi, 2011). The system ($n = 1512$ atoms) consists of a supercell ($6 \times 3 \times 1$ unit cells)
 1136 of initial dimensions $L_x = 31.146 \text{ \AA}$, $L_y = 27.018 \text{ \AA}$ and $L_z = 19.966 \text{ \AA}$. a) Perspective
 1137 view down the a axis. b) Tetrahedral layers (as labelled in (a)) showing the irregular
 1138 distribution of Al atoms. Atoms are drawn with their Van der Waals radii. T_{up} and
 1139 T_{low} indicate the upper and the lower tetrahedral layers with respect to the interlayer
 1140 region, respectively.

1142 **Fig. 2.** Variation of the energy of the system during ^{40}Ar recoil with respect to the mean
 1143 energy of a system in which ^{40}Ar occupies an regular interlayer site. The red line is
 1144 the running mean energy averaged over 2.5 ps. The decrease of the energy at 50 ps
 1145 corresponds to the move of ^{40}Ar from the interstitial site to the lattice stable site.

1147 **Fig. 3.** Geometry of diffusion in the muscovite interlayer plane. a) Monovacancy mechanism.
 1148 b) Divacancy mechanism. Orange and green circles correspond to K^+ and ^{40}Ar atoms
 1149 respectively. \square represents the vacancy, \vec{V}_i are the displacement vectors and $\vec{\delta}_i$ indicate
 1150 atomic jumps preserving the divacancy. See text for discussion.

1152 **Fig. 4.** Results of NEB calculations of ^{40}Ar migration in muscovite. a) Histogram of migra-
 1153 tion barriers associated with a monovacancy mechanism. b) Histogram of migration
 1154 barriers associated with a divacancy mechanism. c) Variation of the potential energy of
 1155 ^{40}Ar along its path towards a monovacancy (black) and towards a vacancy pair (blue).
 1156 d) Trajectories followed by ^{40}Ar as it migrates from a stable site towards a single va-
 1157 cancy (black) and towards a vacancy pair (blue). Red circles represent basal oxygens.
 1158 e) Diagram showing the anticorrelation between the ^{40}Ar migration barriers and the
 1159 total electrostatic energy of the structure.

1161 **Fig. 5.** Results of NEB calculations of K^+ migration in muscovite. a) Histogram of migration
 1162 barriers associated with a monovacancy mechanism. b) Histogram of migration barri-

1163 ers associated with a divacancy mechanism. c) Variation of the potential energy of K^+
1164 along its path towards a monovacancy (black) and towards a vacancy pair (blue). d)
1165 Trajectories followed by K^+ as it migrates from a stable site towards a single vacancy
1166 (black) and towards a vacancy pair (blue). Red circles represent basal oxygens. e)
1167 Diagram showing the positive correlation between the ^{40}Ar and K^+ migration barriers.

1168
1169 **Fig. 6.** Arrhenius plot of ^{40}Ar diffusion coefficients calculated for the monovacancy and the
1170 divacancy mechanisms. Results of previous studies are also reported for comparison.

1171
1172 **Fig. 7.** Nominal variations in ^{40}Ar –muscovite closure temperature (Eq (1) in text) with
1173 cooling rate and grain size. T_c are calculated for a cylindrical geometry ($A = 27$), using
1174 diffusion parameters deduced from Molecular Dynamics and Transition State Theory
1175 ($E = 66 \text{ kcal.mol}^{-1}$; $D_0 = 6 \times 10^{-4} \text{ cm}^2.\text{s}^{-1}$). See text for discussion.

1176

Fig. 1

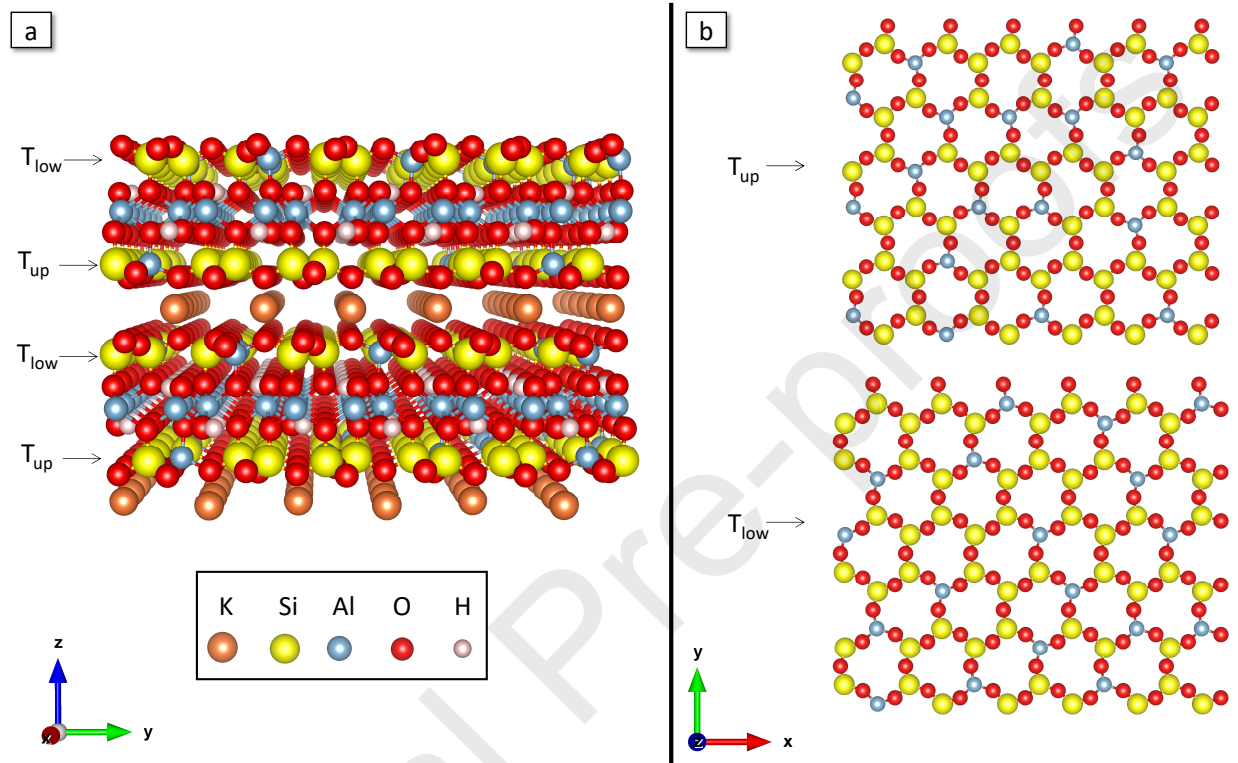


Fig. 2

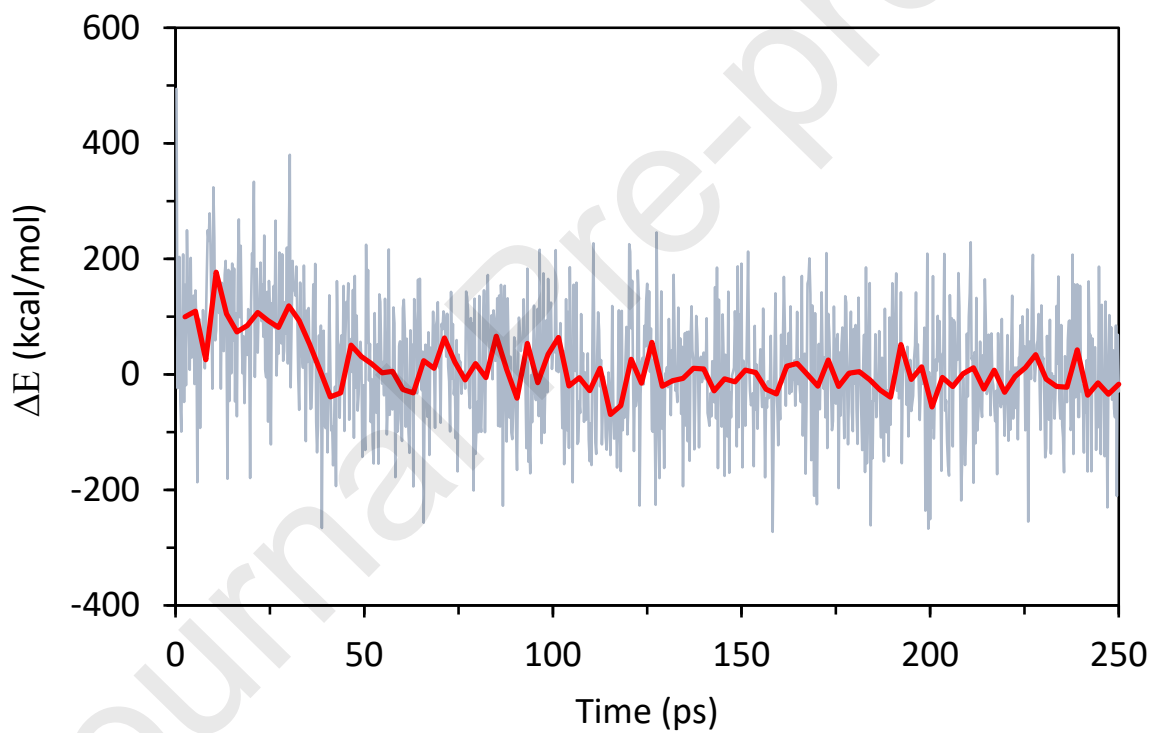


Fig. 3

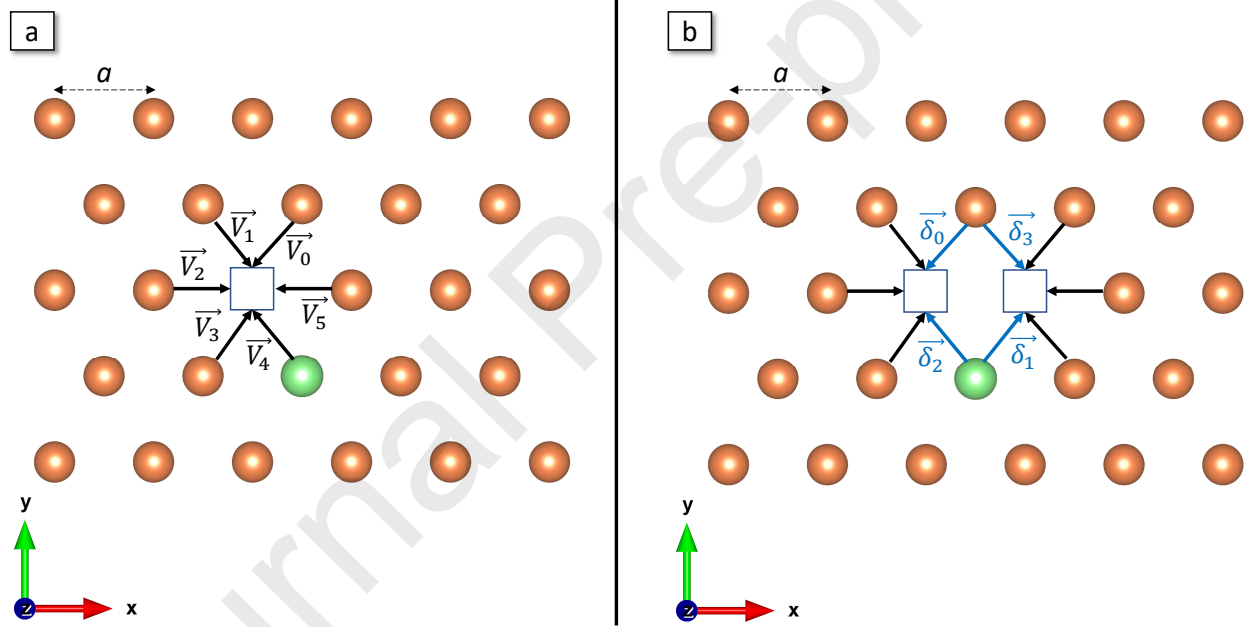


Fig. 4

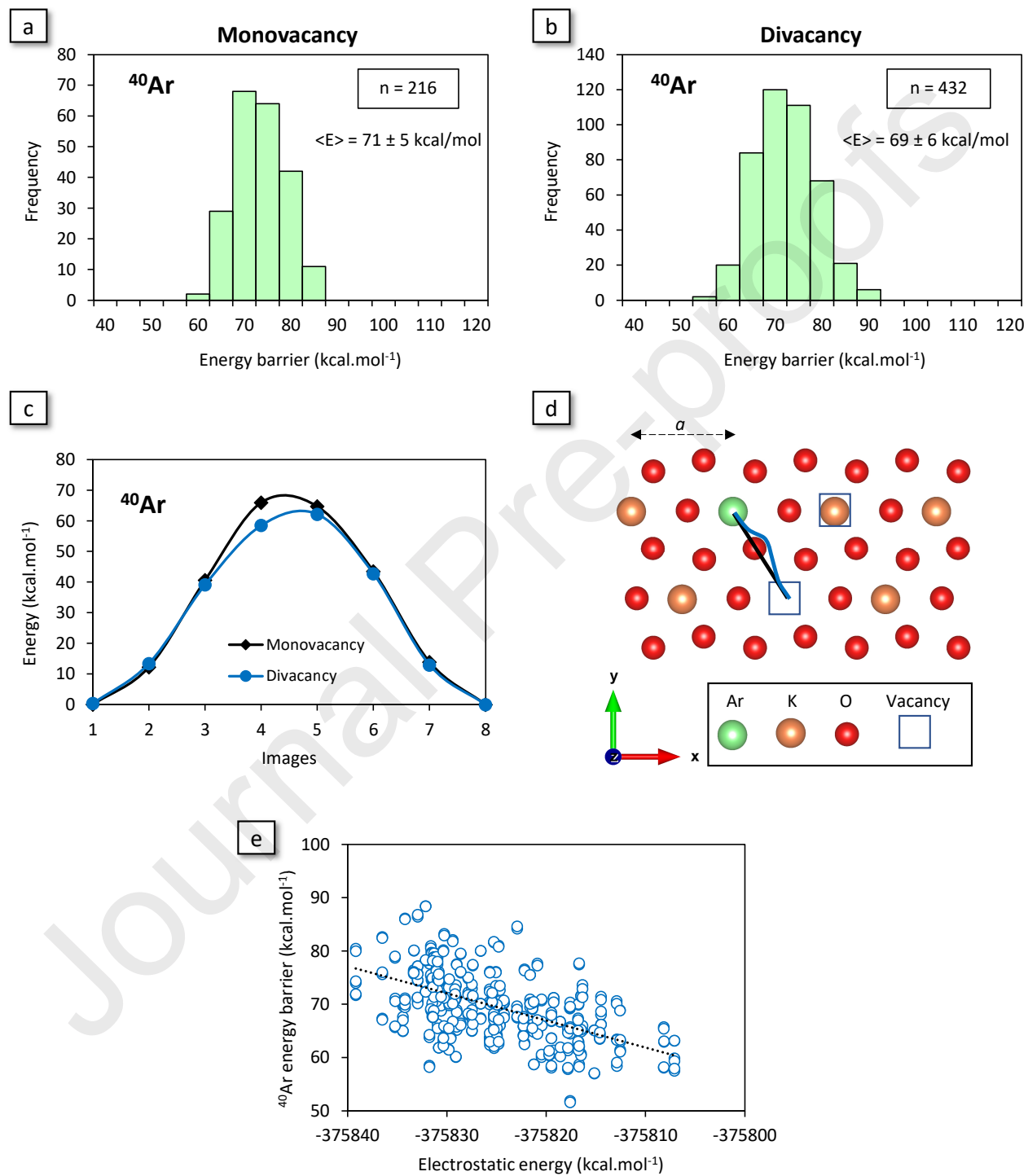


Fig. 5

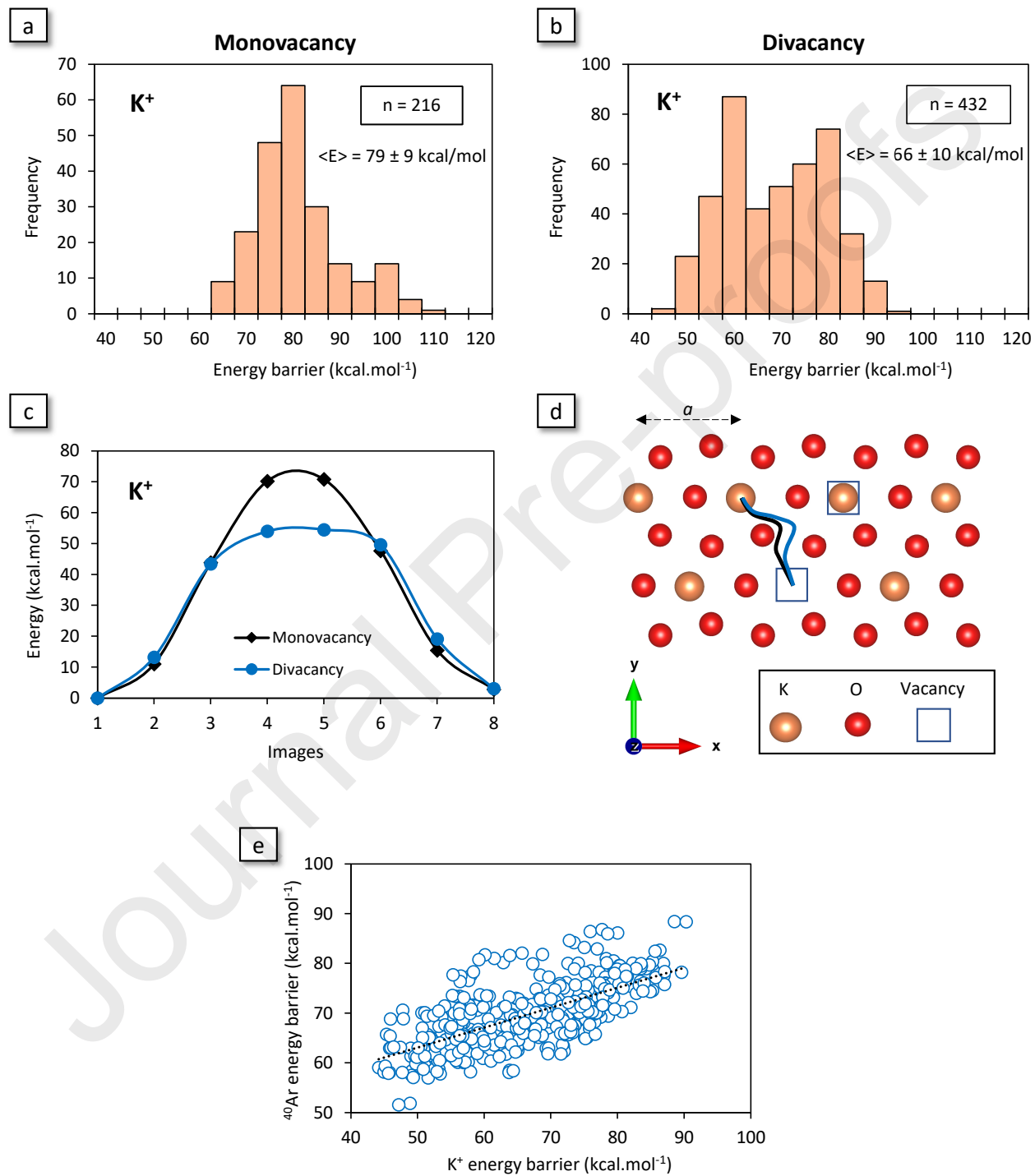


Fig. 6

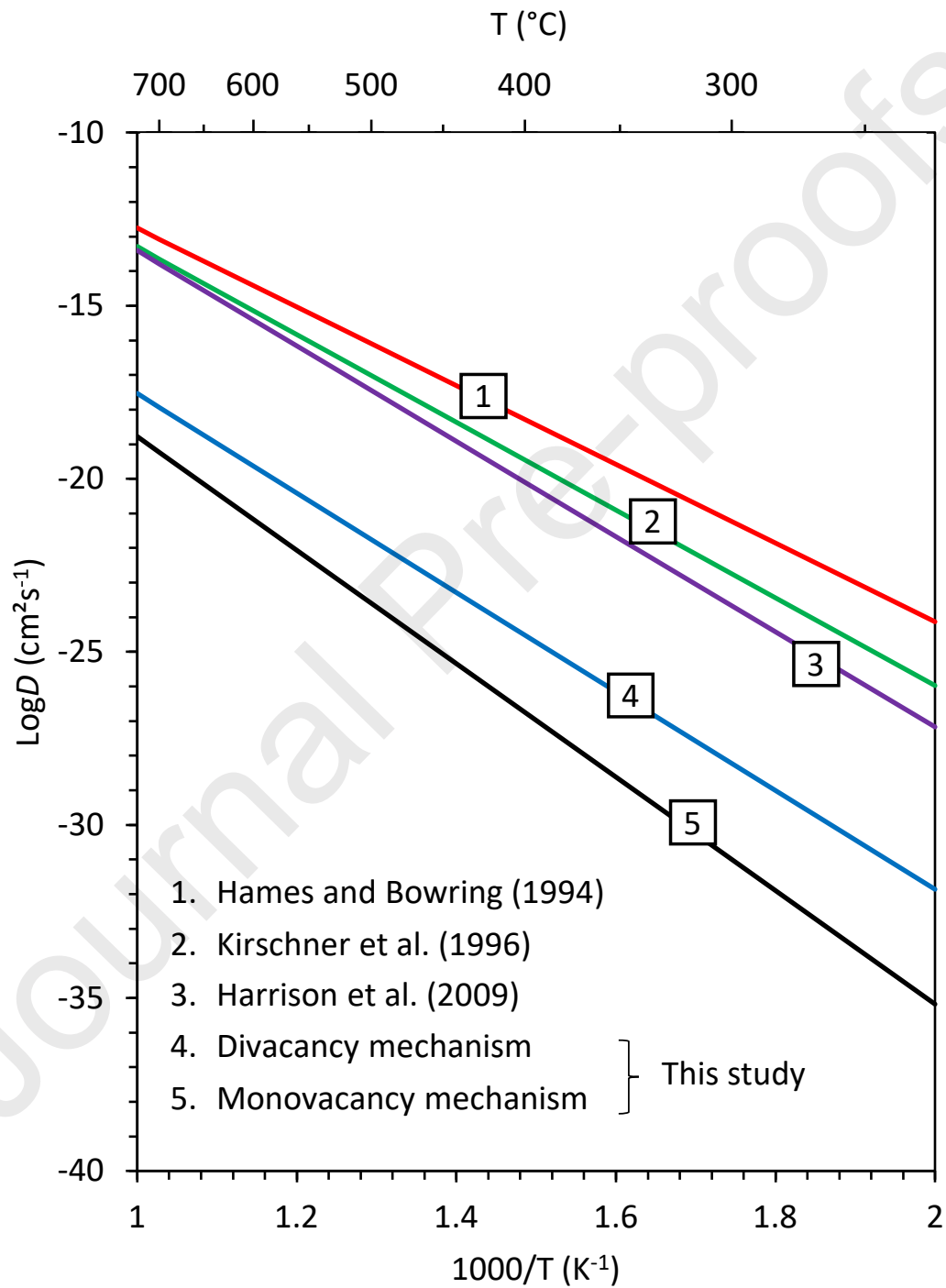
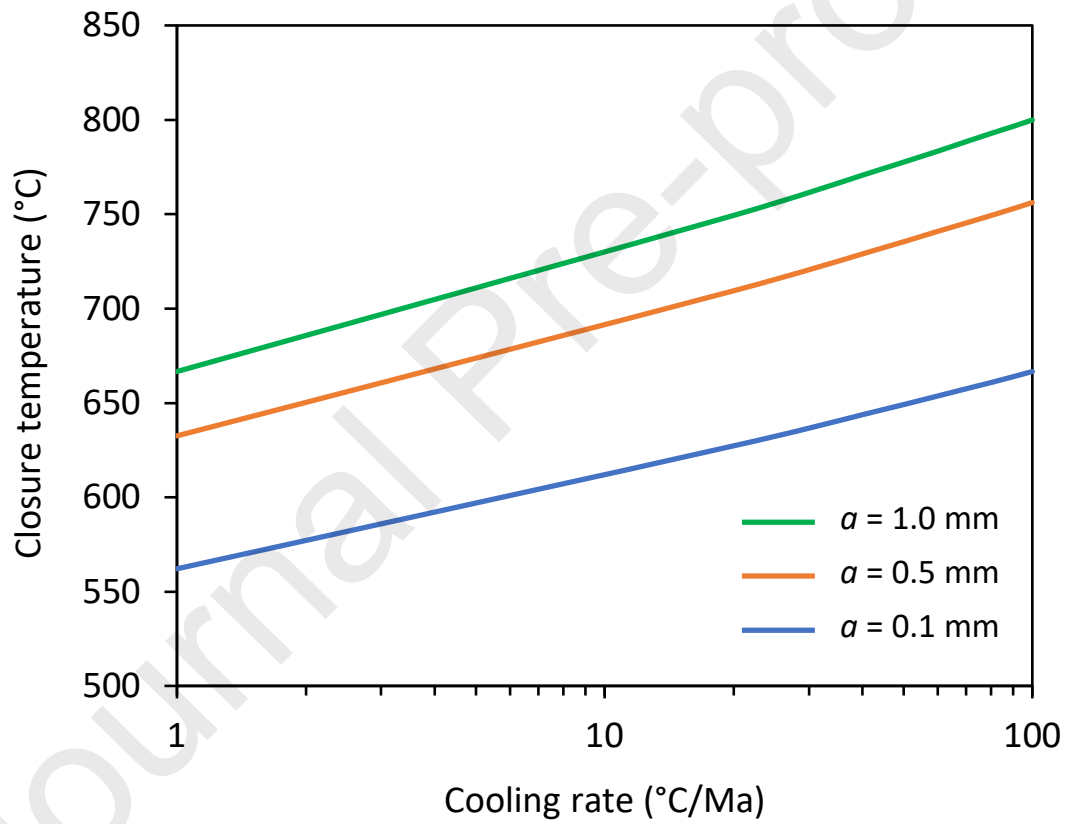


Fig. 7



Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: