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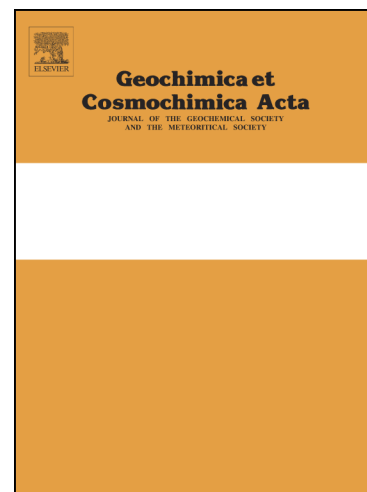
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1 Atomistic Simulations of  $^{40}\text{Ar}$  Diffusion in Muscovite2 Jehiel Nteme<sup>a,b,\*</sup>, Stéphane Scaillet<sup>a</sup>, Pascal Brault<sup>b</sup>, Laurent Tassan-Got<sup>c,d</sup>3 <sup>a</sup>*Univ. Orléans, CNRS, BRGM, Institut des Sciences de la Terre d'Orléans (ISTO), UMR 7327, F-45071,*  
4 *Orléans, France*5 <sup>b</sup>*Univ. Orléans, CNRS, Groupe de Recherches sur l'Energétique des Milieux Ionisés (GREMI), UMR 7344,*  
6 *45067 Orléans, France*7 <sup>c</sup>*Université Paris-Saclay, CNRS, IN2P3, Laboratoire de Physique des deux infinis Irène Joliot-Curie*  
8 *(IJCLab), 91405 Orsay, France*9 <sup>d</sup>*Conseil Européen pour la Recherche Nucléaire (CERN), Espl. des Particules 1, 1211 Meyrin, Geneva,*  
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  $^{40}\text{Ar}$  diffusional behavior. In this contribution, we investigate  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  recoil dynamics in  $2M_1$  muscovite reveal that  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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:**  $^{40}\text{Ar}$  diffusion, Muscovite, Molecular Dynamics, Transition State Theory,  
31 Thermochronology

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\*Corresponding authorEmail address: [jehiel.nteme-mukonzo@univ-orleans.fr](mailto:jehiel.nteme-mukonzo@univ-orleans.fr) (Jehiel Nteme)

## 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  $^{40}\text{Ar}$ -bearing minerals (McDougall and Harrison, 1999). Being non bonded,  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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):

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

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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $\text{kcal.mol}^{-1}$  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  $^{40}\text{Ar}$ -closure temperatures lower than  $500 \text{ }^{\circ}\text{C}$  (Harri-  
73 son et al. 2009). However, cases of effective  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  diffusional behavior in muscovite with respect to  
90 temperature. Unlike previous studies that investigated the  $^{40}\text{Ar}$  diffusivity in muscovite  
91 experimentally and empirically, we re-evaluate the  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  diffusion in muscovite by combining MD with TST. Our results reveal  $^{40}\text{Ar}$  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  ${}^{\text{IV}}\text{Al}-\text{O}-{}^{\text{IV}}\text{Al}$  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  $\text{Si}_4\text{Al}_2$  ring and one  $\text{Si}_5\text{Al}_1$  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  $\epsilon_0$   
 147 is the permittivity of vacuum. The Lennard-Jones parameters  $\sigma_{ij}$  and  $\epsilon_{ij}$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $\gamma$  as:

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

179 where  $\nu$  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  $\nu_i^{init}$  corresponds to the modal vibrational frequencies at the stable site and  $\nu_i^*$  rep-  
183 resents the non-imaginary modal frequencies at the saddle point (Vineyard, 1957). For most  
184 solids, the attempt frequency is comprised between  $10^{12} \text{ s}^{-1}$  and  $10^{13} \text{ s}^{-1}$ . 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  $\alpha$ ,  $\beta$ ,  $\gamma$  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. <sup>40</sup>Ar initial position from interlayer recoil dynamics

207 The investigation of <sup>40</sup>Ar diffusion at the atomic scale requires the determination of its  
208 insertion site within the muscovite structure. Since <sup>40</sup>Ar is produced with a kinetic energy  
209 of 660 kcal.mol<sup>-1</sup> corresponding to a velocity of 0.11765 Å.fs<sup>-1</sup> (Dong et al., 1995; Szczerba  
210 et al., 2015), the <sup>40</sup>Ar insertion site can be determined by modelling the natural <sup>40</sup>Ar recoil  
211 via MD simulations. Such simulations have been performed by Szczerba et al. (2015), who  
212 investigated the natural recoil of <sup>40</sup>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 <sup>40</sup>Ar had the same initial velocity (0.11765 Å.fs<sup>-1</sup>) but varying recoil angles to cover all  
215 possible values within a hemisphere. They identified four possible final positions of <sup>40</sup>Ar. For  
216 recoil vectors subparallel to the (001) plane, <sup>40</sup>Ar systematically remained in the interlayer  
217 region, occupying either the initial site of the parent <sup>40</sup>K or a neighboring vacancy. For recoil  
218 vectors pointing towards the T–O–T sheet, <sup>40</sup>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 <sup>40</sup>Ar recoil in muscovite using the same  
223 methodology as Szczerba et al. (2015). Since the penetration of <sup>40</sup>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 <sup>40</sup>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  $\phi$  as the angle between the  
229 crystallographic direction  $a$  and the recoil vector. The simulations were carried out for recoil  
230 angles from  $0^\circ$  to  $360^\circ$  with a step of  $20^\circ$ . In order to simulate a system under geological  
231 conditions, we equilibrated first the system in the NPT ensemble, at a temperature of  $500^\circ\text{C}$   
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  $^{40}\text{K}$  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  $240^\circ$ ) the radiogenic  $^{40}\text{Ar}$  bounces back from that  
237 neighboring  $\text{K}^+$  and returns to its initial interlayer position. For the other recoil angles,  $^{40}\text{Ar}$   
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  $\text{K}^+$  which is in turn pushed into  
240 the  $^{40}\text{Ar}$  initial site. Along with [Szczerba et al. \(2015\)](#), this is the first theoretical verification  
241 that radiogenic  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  is propelled into  
244 the interstitial site was computed relative to the mean energy of the system when  $^{40}\text{Ar}$  resides  
245 in a regular interlayer site. The simulations reveal that when  $^{40}\text{Ar}$  is in the interstitial site,  
246 i.e., during the first 50 ps, the system has a mean total energy of about  $100\text{ kcal.mol}^{-1}$  higher  
247 than when  $^{40}\text{Ar}$  occupies a regular interlayer site ([Fig. 2](#)). This energy increase is due to the  
248 distortion that  $^{40}\text{Ar}$  causes to the muscovite structure because of its large size. Simulation  
249 snapshots (not shown) reveal that when  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  residence in  
252 the interstitial site and making unlikely a reincorporation of  $^{40}\text{Ar}$  into the interstitial sites  
253 once it has lost its initial recoil velocity. This rules out interstitial mechanism as a viable  
254 mechanism for  $^{40}\text{Ar}$  diffusion in muscovite on geologic timescales.

## 255 5. Pathways and $^{40}\text{Ar}$ diffusion barriers in muscovite

256 The foregoing simulations suggest that the easiest way for  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  in an  
 266 interlayer  $\text{K}^+$  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  $^{40}\text{Ar}$  nor  $\text{K}^+$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$   
 280 site, a motion of potassium atoms along the interlayer region is required for a vacancy to end  
 281 next to  $^{40}\text{Ar}$  so the  $\text{K}^+$  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; Mehler, 2007), we considered the  
 284 migration barriers for these two configurations, i.e., the migration energies of  $^{40}\text{Ar}$  and  $\text{K}^+$

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  $^{40}\text{Ar}$  and  $\text{K}^+$ .  
290 We positioned thus the  $^{40}\text{Ar}$  and  $\text{K}^+$  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  $^{40}\text{Ar}$  and vacancies into the interlayer region was compensated by  
293 substituting Al atoms for Si in tetrahedral sites far from the  $^{40}\text{Ar}$  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. $^{40}\text{Ar}$ migration barriers

300 The energy barriers associated with the interlayer migration of  $^{40}\text{Ar}$  towards neighboring  
301 vacancies display wide distributions (Fig. 4a, b). The migration barriers associated with the  
302 monovacancy mechanism yield a mean value of  $71 \pm 5 \text{ kcal.mol}^{-1}$  ( $1\sigma$ ), while those related to  
303 the divacancy mechanism show a slightly lower but statistically indistinguishable mean value  
304 of  $69 \pm 6 \text{ kcal.mol}^{-1}$  ( $1\sigma$ ). These values are similar to the energy barrier of  $69 \text{ kcal.mol}^{-1}$   
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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  towards a single vacancy is  $65 \text{ kcal.mol}^{-1}$  while that associated with  
311 the jump of  $^{40}\text{Ar}$  into a pair of vacancies is  $61 \text{ kcal.mol}^{-1}$ . 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  $^{40}\text{Ar}$  during these jumps (Fig. 4d) reveal that when  
314 jumping into a single vacancy,  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $\text{K}^+$  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  $\text{K}^+$  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 ( $\text{K}^+$ ) 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  $^{40}\text{Ar}$  within the interlayer region, as suggested by  
337 previous observations and empirical predictions (Scaillet et al., 1992; Dahl, 1996).

### 338 5.2. $\text{K}^+$ migration barriers

339 As with  $^{40}\text{Ar}$ , the  $\text{K}^+$  migration barriers define wide distributions (Fig. 5a, b). Migrations  
340 energies towards monovacancies show a mean value of  $79 \pm 9 \text{ kcal.mol}^{-1}$  ( $1\sigma$ ). Using DFT  
341 simulations, Yu et al. (2016) computed energy barriers associated with the migration of  
342  $\text{K}^+$  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)  $82 \text{ kcal.mol}^{-1}$  for the Al–Al model which contains Al

atoms in the two tetrahedral layers adjacent to the interlayer region; (ii) 146 kcal.mol<sup>-1</sup> for the Al–Si model in which Al atoms are present only in one of the tetrahedral layers, and (iii) 227 kcal.mol<sup>-1</sup> 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<sup>+</sup> energy barriers in illite computed via ClayFF and DFT. They get mean values of 54 ± 12 kcal.mol<sup>-1</sup> for ClayFF energy barriers and 75 ± 8 kcal.mol<sup>-1</sup> 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<sup>+</sup> energy barriers computed using ClayFF after prior equilibration of the muscovite structure are in the range of their DFT-computed barriers.

The K<sup>+</sup> energy barriers associated with the divacancy mechanism yield a mean value of 66 ± 10 kcal.mol<sup>-1</sup> (1σ). This value is significantly lower than the mean energy barrier related to the migration of K<sup>+</sup> into a single vacancy. This pronounced difference is illustrated by the variation of the potential energy along the K<sup>+</sup> migration path between two adjacent stable sites (Fig. 5c). In this example, the K<sup>+</sup> energy barrier associated with the monovacancy mechanism is 70 kcal.mol<sup>-1</sup> and the K<sup>+</sup> energy barrier related to the divacancy mechanism is 55 kcal.mol<sup>-1</sup>. The minimum energy paths followed by K<sup>+</sup> 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<sup>+</sup> ions to minimize interactions with the oxygen atoms lying on their path. Moreover, while <sup>40</sup>Ar 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 <sup>40</sup>Ar (neutral). Despite these structural-charge differences, the K<sup>+</sup> and <sup>40</sup>Ar energy barriers are positively correlated (Fig. 5e), suggesting a similar influence

375 of the local environment on the migration energy landscape.

## 376 6. $^{40}\text{Ar}$ diffusion coefficients

377 In this section, we calculate the  $^{40}\text{Ar}$  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,  $E_{\text{eff}}$ , 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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  via the monovacancy mechanism requires the presence of a vacancy  
 408 in one of its neighboring sites. As long as no vacancies are available,  $^{40}\text{Ar}$  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  $K^+ \leftrightarrow \Box$ ),  $\nu$  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. <sup>40</sup>Ar diffusion in a monovacancy flux

427 Each time a vacancy gets next to a <sup>40</sup>Ar atom it is surrounded by five K<sup>+</sup> ions. Interchange  
 428 between the <sup>40</sup>Ar and vacancy positions (noted <sup>40</sup>Ar ⇌ □) occurs due to thermal agitation  
 429 and the lower barrier potential of <sup>40</sup>Ar ⇌ □ relative to K<sup>+</sup> ⇌ □. The average duration of  
 430 these Ar-vacancy oscillations is therefore:

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

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 <sup>40</sup>Ar into the  
 434 vacancy. The oscillations stop when one of the five K<sup>+</sup> neighbors jumps into the vacancy.  
 435 For three of these K<sup>+</sup>, a successful jump will remove the vacancy away from <sup>40</sup>Ar, stopping  
 436 the <sup>40</sup>Ar ⇌ □ oscillations. For the other two, the vacancy stays in the vicinity of <sup>40</sup>Ar and  
 437 the oscillations can resume among the newly created Ar-vacancy pair.

438 Summing up, when a vacancy gets close to <sup>40</sup>Ar, after an average time  $\Delta t_{\text{osc}}$ , four different  
 439 configurations are possible:

- 440 - The vacancy has gone away leaving <sup>40</sup>Ar in its initial position with a probability of 3/10.
- 441 - The vacancy has moved into one of the two neighboring positions of <sup>40</sup>Ar with a probability  
 442 of 2/10. Oscillations resume among the newly-created <sup>40</sup>Ar-vacancy pair.
- 443 - The <sup>40</sup>Ar ⇌ □ interchange is successful and the vacancy moves further away by more than  
 444 one lattice position with probability of 3/10.
- 445 - The <sup>40</sup>Ar ⇌ □ interchange has occurred but leaving the vacancy next to <sup>40</sup>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 <sup>40</sup>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 <sup>40</sup>Ar  
 451 (the timelife of this configuration) is:

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

453 During this time interval, several trains of oscillations will have occurred. The calculation  
 454 of the variance of the mean displacement of  $^{40}\text{Ar}$  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  $\text{K}^+$  via the  $\text{K}^+ \rightleftharpoons \square$  interchange (vacancy diffusion), not the mobility of  $^{40}\text{Ar}$   
 464 with respect to the vacancy. The vibrational motion of  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$   
 470 through the muscovite interlayer. Consider a portion of lattice containing  $N$  regular interlayer  
 471 sites with a single  $^{40}\text{Ar}$  atom and a density of vacancies  $\rho$ . 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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  (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  $^{40}\text{Ar}$  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  $5.76 \times 10^{-20}$  cm<sup>2</sup>.s<sup>-1</sup>. The diffusion parameters associated with the monovacancy mechanism  
 497 are  $E = 75$  kcal.mol<sup>-1</sup> and  $D_0 = 4 \times 10^{-3}$  cm<sup>2</sup>.s<sup>-1</sup>.

## 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<sup>-1</sup>) 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<sup>-1</sup>). 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  $0^\circ$  (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  $0^\circ$  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  $60^\circ$ , 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  $-60^\circ$  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  $3.89 \times 10^{-16}$  cm<sup>2</sup>.s<sup>-1</sup>, three orders of magnitude faster than the monovacancy mechanism.

### 550 6.2.2. <sup>40</sup>Ar diffusion in a divacancy flux

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

556 divacancy is:

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

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

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

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

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

565 As before, Eq. (39) simplifies to

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

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

569 Denote by  $\rho'$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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,  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$ :

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

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  $\rho'$ . It can be expressed with the density  
590 of monovacancies  $\rho$ . 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  $\text{K}^+$  (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  $\rho$ , 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  $\rho \ll 1$ :

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

At  $T = 700$  °C and for  $\rho = 0.1$ , the  $^{40}\text{Ar}$  diffusion coefficient associated with the divacancy mechanism is  $D_{\text{Ar}\square\square} = 1.16 \times 10^{-18}$  cm<sup>2</sup>.s<sup>-1</sup>, two orders of magnitude higher than the diffusivity of the monovacancy mechanism. The  $^{40}\text{Ar}$  diffusion parameters deduced from the Arrhenius diagram (Fig. 6) are  $E = 66$  kcal.mol<sup>-1</sup> and  $D_0 = 6 \times 10^{-4}$  cm<sup>2</sup>.s<sup>-1</sup>. A summary listing of the final estimates is provided in Table 3.

## 7. Discussion

### 7.1. Comparison with previous $^{40}\text{Ar}$ diffusion estimates

As mentioned above, only a handful of studies have attempted to quantify  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  in muscovite (Harrison et al., 2009) would enhance the disparity even further.

Hydrothermal experiments have been suspected to overestimate  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  kinetics in natural muscovite is more the norm than currently  
 630 acknowledged by existing experimental data.

631 Field-based calibration of  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$   
 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 km<sup>2</sup> 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<sup>-1</sup> 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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  to be diffusively lost from  
 695 muscovite during the experiments, the difference may also reflect  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $\text{H}^+$ , 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  $^{40}\text{Ar}$  migration barrier, thereby accelerating its diffusion. All these mecha-  
 713 nisms suggests that  $^{40}\text{Ar}$  diffusivity measured under hydrothermal conditions provides only  
 714 an upper limit to actual  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  initially  
 719 present in recrystallized (or dissolved) muscovite may be released in the free fluid phase,  
 720 locally enhancing or disrupting  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $\text{Si}^{4+}$ -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 ( $\text{Na}^+$ ,  
 739  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ) 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  $^{40}\text{Ar}$ , 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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  kinetics in natural muscovite. Further empirical and  
 758 theoretical work is required to clarify kinetic interactions between crystal-chemical disequi-  
 759 librium and effective  $^{40}\text{Ar}$  diffusion across such  $D-T$  space.

## 760 8. Conclusions

761 A lattice-based study of  $^{40}\text{Ar}$  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 •  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$   
 767 atom more than a lattice spacing away from its production site from  $^{40}\text{K}$ .
- 768
- 769 • Systematic energy-barrier mapping by NEB coupled with TST allows to identify the most  
 770 probable diffusion pathway and barrier potential for  $^{40}\text{Ar}$  motion along the (001) interlayer;  
 771  $^{40}\text{Ar}$  transport via a divacancy mechanism is shown to be the more energetically favor-  
 772 able pathway for  $^{40}\text{Ar}$  migration along (001) with characteristic diffusion parameters  $E =$   
 773  $66 \text{ kcal.mol}^{-1}$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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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792 the findings" under the 2021 AAPG call "Planétologie, structure et histoire de la Terre".

### 793 **Appendix A. Supplementary Material**

794 Supplementary data associated with this article can be found, in the online version, at  
795 <http://dx.doi.org/xx.xxx/xxxxxxxxxxxxxx>.

796 **References**

- 797 Aagaard P. and Helgeson H. C. (1983) Activity/composition relations among silicates and aqueous  
798 solutions: II. Chemical and thermodynamic consequences of ideal mixing of atoms on homo-  
799 logical sites in montmorillonites, illites, and mixed-layer clays. *Clays and Clay Miner.* **31**,  
800 207-217.
- 801 Allaz, J., Engi, M., Berger, A. and Villa I. M. (2011) The effects of retrograde reactions and of  
802 diffusion on  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  ages of micas. *J. Petrol.*, **52**, 691-716.
- 803 Althaus E., Karotke E., Nitsch K. and Winkler H. (1970) An experimental re-examination of the  
804 upper stability limit of muscovite plus quartz. *Neues Jahrb Miner. Monatsh* **7**, 325–336.
- 805 Amouric M. (1987) Growth and deformation defects in phyllosilicates as seen by HRTEM. *Acta*  
806 *Crystal. B* **43**, 57-63.
- 807 Argyris D., Ho T., Cole D. R. and Striolo A. (2011a) Molecular dynamics studies of interfacial water  
808 at the alumina surface. *J. Phys. Chem. C* **15**, 2038-2046.
- 809 Argyris D., Ashby P. D. and Striolo A. (2011b) Structure and orientation of interfacial water  
810 determine atomic force microscopy results: insights from molecular dynamics simulations.  
811 *ACS nano* **5**, 2215-2223.
- 812 Armstrong R. L. (1966) K-Ar dating of plutonic and volcanic rocks in orogenic belts. In *Potassium*  
813 *Argon dating* (eds. O.A. Schaeffer and J. Zähringer). Springer-Verlag, Berlin, p 117-133.
- 814 Arnaud N. and Kelley S. P. (1995) Evidence for excess argon during high pressure metamorphism in  
815 the Dora Maira Massif (western Alps, Italy), using an ultra-violet laser ablation microprobe  
816  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  technique. *Contrib. Miner. Petrol.* **121**, 1-11.
- 817 Bailey S. W. (1984) Classification and structures of the Micas. In *Micas* (ed. S.W. Bailey). Rev.  
818 *Miner.* **13**, 1-12.
- 819 Baldelli C., Franceschelli M., Leoni L. and Memmi I. (1989) Ferrimuscovite and celadonite substi-  
820 tutions in muscovite from  $\text{Fe}^{3+}$ -rich low-grade psammitic rocks (Northern Apennines, Italy).



- 821 *Lithos* **23**, 201-208.
- 822 Balogh K. and Dunkl I. (2005) Argon and fission track dating of Alpine metamorphism and base-  
823 ment exhumation in the Sopron Mts.(Eastern Alps, Hungary): thermochronology or mineral  
824 growth? *Miner. Petrol.* **83**, 191-218.
- 825 Balout H., Roques J., Gautheron C., Tassan-Got L. and Mbongo-Djimbi D. (2017a) Helium diffusion  
826 in pure hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) for thermochronometric applications: A theoretical multi-scale  
827 study. *Comput. Theor. Chem.* **1099**, 21-28.
- 828 Balout H., Roques J., Gautheron C. and Tassan-Got L. (2017b) Computational investigation of  
829 interstitial neon diffusion in pure hematite. *Comput. Mater. Sci.* **128**, 67-74.
- 830 Bassal F., Roques J. and Gautheron C. (2020) Neon diffusion in goethite,  $\alpha$ -FeO(OH): a theoretical  
831 multi-scale study. *Phys. Chem. Miner.* **47**, 1-14.
- 832 Beaudoin A., Scaillet S., Mora N., Jolivet L. and Augier R. (2020) In Situ and Step-Heating  
833 <sup>40</sup>Ar/<sup>39</sup>Ar Dating of White Mica in Low-Temperature Shear Zones (Tenda Massif, Alpine  
834 Corsica, France). *Tectonics* **39**, e2020TC006246.
- 835 Bell I. A. and Wilson C. (1977) Growth defects in metamorphic biotite. *Phys. Chem. Miner.* **2**,  
836 153-169.
- 837 Bell I. A. and Wilson C. (1981) Deformation of biotite and muscovite: TEM microstructure and  
838 deformation model. *Tectonophysics* **78**, 201-228.
- 839 Beltrando M., Di Vincenzo G. and Ferraris C. (2013) Preservation of sub-microscopic structural  
840 relicts in micas from the Gran Paradiso Massif (Western Alps): Implications for <sup>40</sup>Ar-<sup>39</sup>Ar  
841 geochronology. *Geochim. Cosmochim. Acta* **119**, 359-380.
- 842 Bengtson A., Ewing R. C. and Becker U. (2012) He diffusion and closure temperatures in apatite and  
843 zircon: A density functional theory investigation. *Geochim. Cosmochim. Acta* **86**, 228-238.
- 844 Blanckenburg F. v., Villa I., Baur H., Morteani G. and Steiger R. (1989) Time calibration of a PT-  
845 path from the Western Tauern Window, Eastern Alps: the problem of closure temperatures.

- 846 *Contrib. Miner. Petrol.* **101**, 1-11.
- 847 Bosse V., Féraud G., Ballèvre M., Peucat J. J. and Corsini M. (2005) Rb-Sr and  $^{40}\text{Ar}/^{39}\text{Ar}$  ages  
848 in blueschists from the Ile de Groix (Armorican Massif, France): Implications for closure  
849 mechanisms in isotopic systems. *Chem. Geol.* **220**, 21-45.
- 850 Boundy T. M., Hall C. M., Li G., Essene E. J. and Halliday A. (1997) Fine-scale isotopic hetero-  
851 geneities and fluids in the deep crust: a  $^{40}\text{Ar}/^{39}\text{Ar}$  laser ablation and TEM study of muscovites  
852 from a granulite-eclogite transition zone. *Earth Planet. Sci. Lett.* **148**, 223-242.
- 853 Bröcker M., Baldwin S. and Arkudas R. (2013) The geological significance of  $^{40}\text{Ar}/^{39}\text{Ar}$  and Rb-Sr  
854 white mica ages from Syros and Sifnos, Greece: a record of continuous (re)crystallization  
855 during exhumation? *J. Metam. Geol.* **31**, 629-646.
- 856 Catti M., Ferraris G. and Ivaldi G. (1989) Thermal strain analysis in the crystal structure of  
857 muscovite at 700 °C. *Eur. J. Mineral.*, 625-632.
- 858 Churakov S. V. (2013) Mobility of Na and Cs on montmorillonite surface under partially saturated  
859 conditions. *Environ. sci. technol.* **47**, 9816-9823.
- 860 Cliff R., Bond C., Butler R. and Dixon J. (2017) Geochronological challenges posed by continuously  
861 developing tectonometamorphic systems: insights from Rb/Sr mica ages from the Cycladic  
862 Blueschist Belt, Syros (Greece). *J. Metam. Geol.* **35**, 197-211.
- 863 Cole D. R. and Chakraborty S. (2001) Rates and mechanisms of isotopic exchange. *Rev. Mineral.*  
864 *Geochem.* **43**, 83-223.
- 865 Cosca M., Stunitz H., Bourgeix A. L. and Lee J. P. (2011)  $^{40}\text{Ar}^*$  loss in experimentally deformed  
866 muscovite and biotite with implications for  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology of naturally deformed  
867 rocks. *Geochim. Cosmochim. Acta* **75**, 7759-7778.
- 868 Cygan R. T., Liang J. J. and Kalinichev A. G. (2004) Molecular models of hydroxide, oxyhydroxide,  
869 and clay phases and the development of a general force field. *J. Phys. Chem. B* **108**, 1255-  
870 1266.

- 871 Cygan R. T., Greathouse J. A., Heinz H. and Kalinichev A. G. (2009) Molecular models and  
872 simulations of layered materials. *J. Mater. Chem.* **19**, 2470-2481.
- 873 Dahl P. S. (1996) The crystal-chemical basis for Ar retention in micas: inferences from interlayer  
874 partitioning and implications for geochronology. *Contrib. Miner. Petrol.* **123**, 22-39.
- 875 Di Vincenzo G., Ghiribelli B., Giorgetti G. and Palmeri R. (2001) Evidence of a close link between  
876 petrology and isotope records: constraints from SEM, EMP, TEM and in situ  $^{40}\text{Ar}$ - $^{39}\text{Ar}$   
877 laser analyses on multiple generations of white micas (Lantermann Range, Antarctica). *Earth  
878 Planet. Sci. Lett.* **192**, 389-405.
- 879 Di Vincenzo G., Carosi R. and Palmeri R. (2004) The relationship between tectono-metamorphic  
880 evolution and argon isotope records in white mica: constraints from in situ  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  laser  
881 analysis of the Variscan basement of Sardinia. *J. Petrol.* **45**, 1013-1043.
- 882 Di Vincenzo G., Tonarini S., Lombardo B., Castelli D. and Ottolini L. (2006) Comparison of  $^{40}\text{Ar}$ -  
883  $^{39}\text{Ar}$  and Rb-Sr data on phengites from the UHP Brossasco-Isasca Unit (Dora Maira Massif,  
884 Italy): implications for dating white mica. *J. Petrol.* **47**, 1439-1465.
- 885 Djimbi D. M., Gautheron C., Roques J., Tassan-Got L., Gerin C. and Simoni E. (2015) Impact of  
886 apatite chemical composition on (U-Th)/He thermochronometry: An atomistic point of view.  
887 *Geochim. Cosmochim. Acta* **167**, 162-176.
- 888 Dodson M. H. (1973) Closure temperature in cooling geochronological and petrological systems.  
889 *Contrib. Miner. Petrol.* **40**, 259-274.
- 890 Domingos R., Tremblay M. M., Shuster D. L. and Militzer B. (2020) Simulations and Experiments  
891 Reveal Effect of Nanopores on Helium Diffusion in Quartz. *ACS Earth Space Chem.* **4**,  
892 1906-1912.
- 893 Dong H., Hall C. M., Peacor D. R. and Halliday A. N. (1995) Mechanisms of argon retention in  
894 clays revealed by laser  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  dating. *Science* **267**, 355-359.
- 895 Dunlap W. (1997) Neocrystallization or cooling?  $^{40}\text{Ar}/^{39}\text{Ar}$  ages of white micas from low-grade  
896 mylonites. *Chem. Geol.* **143**, 181-203.

- 897 Dunlap W. and Kronenberg A. (2001) Argon loss during deformation of micas: constraints from  
898 laboratory deformation experiments. *Contrib. Miner. Petrol.* **141**, 174-185.
- 899 Elphick S. and Graham C. (1988) The effect of hydrogen on oxygen diffusion in quartz: evidence  
900 for fast proton transients? *Nature* **335**, 243-245.
- 901 Farver J. R. and Yund R. A. (1990) The effect of hydrogen, oxygen, and water fugacity on oxygen  
902 diffusion in alkali feldspar. *Geochim. Cosmochim. Acta* **54**, 2953-2964.
- 903 Ferrage E., Lanson B., Michot L. J. and Robert J.-L. (2010) Hydration properties and interlayer  
904 organization of water and ions in synthetic Na-smectite with tetrahedral layer charge. Part  
905 1. Results from X-ray diffraction profile modeling. *J. Phys. Chem. C* **114**, 4515-4526.
- 906 Frenkel D. and Smit B. (2002) *Understanding Mol. Simul.: from algorithms to applications. Second*  
907 *edition*. Academic Press, San Diego.
- 908 Forster M. A. and Lister G. S. (2014)  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology and the diffusion of  $^{39}\text{Ar}$  in phen-  
909 gite-muscovite intergrowths during step-heating experiments in vacuo. *Geol. Soc., Lond.,*  
910 *Spec. Publ.* **378**, 117-135.
- 911 Fortier S. M. and Giletti B. J. (1991) Volume self-diffusion of oxygen in biotite, muscovite, and  
912 phlogopite micas. *Geochim. Cosmochim. Acta* **55**, 1319-1330.
- 913 Gautheron C., Djimbi D. M., Roques J., Balout H., Ketcham R. A., Simoni E., Pik R., Seydoux-  
914 Guillaume A.-M. and Tassan-Got L. (2020) A multi-method, multi-scale theoretical study of  
915 He and Ne diffusion in zircon. *Geochim. Cosmochim. Acta* **268**, 348-367.
- 916 Gerin C., Gautheron C., Oliviero E., Bachelet C., Djimbi D. M., Seydoux-Guillaume A.-M., Tassan-  
917 Got L., Sarda P., Roques J. and Garrido F. (2017) Influence of vacancy damage on He diffusion  
918 in apatite, investigated at atomic to mineralogical scales. *Geochim. Cosmochim. Acta* **197**,  
919 87-103.
- 920 Glodny J., Bingen B., Austrheim H., Molina J. F. and Rusin A. (2002) Precise eclogitization ages  
921 deduced from Rb/Sr mineral systematics: the Maksyutov complex, Southern Urals, Russia.  
922 *Geochim. Cosmochim. Acta* **66**, 1221-1235.

- 923 Glodny J., Kühn A. and Austrheim H. (2008) Geochronology of fluid-induced eclogite and amphi-  
924 bolite facies metamorphic reactions in a subduction-collision system, Bergen Arcs, Norway.  
925 *Contrib. Miner. Petrol.* **156**, 27-48.
- 926 Greathouse J. A. and Cygan R. T. (2005) Molecular dynamics simulation of uranyl (VI) adsorption  
927 equilibria onto an external montmorillonite surface. *Phys. Chem. Chem. Phys.* **7**, 3580-3586.
- 928 Greathouse J. A. and Cygan R. T. (2006) Water structure and aqueous uranyl (VI) adsorption  
929 equilibria onto external surfaces of beidellite, montmorillonite, and pyrophyllite: Results from  
930 Mol. Simul.s. *Environ. sci. technol.* **40**, 3865-3871.
- 931 Halama R., Konrad-Schmolke M., Sudo M., Marschall H. R. and Wiedenbeck M. (2014) Effects of  
932 fluid-rock interaction on  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology in high-pressure rocks (Sesia-Lanzo Zone,  
933 Western Alps). *Geochim. Cosmochim. Acta* **126**, 475-494.
- 934 Hames W. and Bowring S. (1994) An empirical evaluation of the argon diffusion geometry in mus-  
935 covite. *Earth Planet. Sci. Lett.* **124**, 161-169.
- 936 Hames W. E. and Cheney J. (1997) On the loss of  $^{40}\text{Ar}^*$  from muscovite during polymetamorphism.  
937 *Geochim. Cosmochim. Acta* **61**, 3863-3872.
- 938 Hames W. and Hodges K. (1993) Laser  $^{40}\text{Ar}/^{39}\text{Ar}$  evaluation of slow cooling and episodic loss of  
939  $^{40}\text{Ar}$  from a sample of polymetamorphic muscovite. *Science* **261**, 1721-1723.
- 940 Hames W. E., Cheney J. T. and Tracy R. J. (2008) Single-crystal  $^{40}\text{Ar}/^{39}\text{Ar}$  age variation in  
941 muscovite of the Gassetts Schist and associated gneiss, Vermont Appalachians. *Am. Mineral.*  
942 **93**, 384-395.
- 943 Hammouda T. and Cherniak D. (2000) Diffusion of Sr in fluorophlogopite determined by Rutherford  
944 backscattering spectrometry. *Earth Planet. Sci. Lett.* **178**, 339-349.
- 945 Harrison T. M., Célérier J., Aikman A. B., Hermann J. and Heizler M. T. (2009) Diffusion of  $^{40}\text{Ar}$   
946 in muscovite. *Geochim. Cosmochim. Acta* **73**, 1039-1051.
- 947 Hart S. R. (1960) Mineral ages and metamorphism. Ph. D. thesis, Massachusetts Institute of

948 Technology.

949 Helgeson H. C. and Aagaard P. (1985) Activity/composition relations among silicates and aque-  
950 ous solutions; I, Thermodynamics of intrasite mixing and substitutional order/disorder in  
951 minerals. *Am. J. Sci.* **285**, 769-844.

952 Herrero C., Sanz J. and Serratos J. (1985) Si, Al distribution in micas; analysis by high-resolution  
953  $^{29}\text{Si}$  NMR spectroscopy. *J. Phys. C* **18**, 13.

954 Herrero C., Gregorkiewitz M., Sanz J. and Serratos J. (1987)  $^{29}\text{Si}$  MAS-NMR spectroscopy of  
955 mica-type silicates: Observed and predicted distribution of tetrahedral Al-Si. *Phys. Chem.*  
956 *Miner.* **15**, 84-90.

957 Hess J., Lippolt H. and Wirth R. (1987) Interpretation of  $^{40}\text{Ar}/^{39}\text{Ar}$  spectra of biotites: Evidence  
958 from hydrothermal degassing experiments and TEM studies. *Chem. Geol. (Isotope Geo-*  
959 *science section)* **66**, 137-149.

960 Hodges K. and Bowring S. (1995)  $^{40}\text{Ar}/^{39}\text{Ar}$  thermochronology of isotopically zoned micas: Insights  
961 from the southwestern USA proterozoic orogen. *Geochim. Cosmochim. Acta* **59**, 3205-3220.

962 Hodges K. V., Harries W. E. and Bowring S. A. (1994)  $^{40}\text{Ar}/^{39}\text{Ar}$  age gradients in micas from  
963 a high-temperature-low-pressure metamorphic terrain: Evidence for very slow cooling and  
964 implications for the interpretation of age spectra. *Geology* **22**, 55-58.

965 Ho T. A., Argyris D., Papavassiliou D. V., Striolo A., Lee L. L. and Cole D. R. (2011) Interfacial  
966 water on crystalline silica: a comparative molecular dynamics simulation study. *Mol. Simul.*  
967 **37**, 172-195.

968 Itaya T., Hyodo H., Tsujimori T., Wallis S., Aoya M., Kawakami T. and Gouzu C. (2009) Regional-  
969 Scale Excess Ar wave in a Barrovian type metamorphic belt, eastern Tibetan Plateau. *Island*  
970 *Arc* **18**, 293-305.

971 Jónsson H., Mills G. and Jacobsen K. W. (1998) Nudged elastic band method for finding minimum  
972 energy paths of transitions. In *Classical and Quantum Dynamics in Condensed Phase Sim-*  
973 *ulations* (eds B. J. Berne, G. Ciccotti, and D. F. Coker). World Scientific, Singapore, pp.

974 385-404.

975 Kalinichev A. G., Padma Kumar P. and James Kirkpatrick R. (2010) Molecular dynamics computer  
976 simulations of the effects of hydrogen bonding on the properties of layered double hydroxides  
977 intercalated with organic acids. *Phil. Mag.* **90**, 2475-2488.

978 Kerisit S., Liu C. and Ilton E. S. (2008) Molecular dynamics simulations of the orthoclase (001)-and  
979 (010)-water interfaces. *Geochim. Cosmochim. Acta* **72**, 1481-1497.

980 Kirkpatrick R., Kalinichev A. and Wang J. (2005) Molecular dynamics modelling of hydrated min-  
981 eral interlayers and surfaces: structure and dynamics. *Mineral. Mag.* **69**, 289-308.

982 Kirschner D. L., Cosca M. A., Masson H. and Hunziker J. C. (1996) Staircase  $^{40}\text{Ar}/^{39}\text{Ar}$  spectra  
983 of fine-grained white mica: Timing and duration of deformation and empirical constraints on  
984 argon diffusion. *Geology* **24**, 747-750.

985 Kramar N., Cosca M. A. and Hunziker J. C. (2001) Heterogeneous  $^{40}\text{Ar}^*$  distributions in natu-  
986 rally deformed muscovite: in situ UV-laser ablation evidence for microstructurally controlled  
987 intragrain diffusion. *Earth Planet. Sci. Lett.* **192**, 377-388.

988 Kramar N., Cosca M. A., Buffat P. A. and Baumgartner L. P. (2003) Stacking fault-enhanced argon  
989 diffusion in naturally deformed muscovite. *Geol. Soc., Lond., Spec. Publ.* **220**, 249-260.

990 Kronenberg A. K., Kirby S. H. and Pinkston J. (1990) Basal slip and mechanical anisotropy of  
991 biotite. *J. Geophys. Res. Solid Earth* **95**, 19257-19278.

992 Larentzos J. P., Greathouse J. A. and Cygan R. T. (2007) An ab initio and classical molecular  
993 dynamics investigation of the structural and vibrational properties of talc and pyrophyllite.  
994 *J. Phys. Chem. C* **111**, 12752-12759.

995 Laurent V., Scaillet S., Jolivet L., Augier R. and Roche V. (2021)  $^{40}\text{Ar}$  behaviour and exhuma-  
996 tion dynamics in a subduction channel from multi-scale  $^{40}\text{Ar}/^{39}\text{Ar}$  systematics in phengite.  
997 *Geochim. Cosmochim. Acta* **311**, 141-173.

998 Lee J. K. (1995) Multipath diffusion in geochronology. *Contrib. Miner. Petrol.* **120**, 60-82.

- 999 Lister G. S. and Baldwin S. L. (1996) Modelling the effect of arbitrary PTt histories on argon  
1000 diffusion in minerals using the MacArgon program for the Apple Macintosh. *Tectonophysics*  
1001 **253**, 83–109.
- 1002 Lister G. and Forster M. (2016) White mica  $^{40}\text{Ar}/^{39}\text{Ar}$  age spectra and the timing of multiple  
1003 episodes of high-P metamorphic mineral growth in the Cycladic eclogite–blueschist belt, Syros,  
1004 Aegean Sea, Greece. *J. Metam. Geol.* **34**, 401–421.
- 1005 Liu H., Wang L., Li S., Yang Y., Tian H., Sun F., Liu L., Li Y., Cui Y. and others (2021) A first-  
1006 principles study of helium diffusion in quartz and coesite under high pressure up to 12GPa.  
1007 *Geosci. Front.* **12**, 1001-1009.
- 1008 Liu X., Lu X., Wang R., Zhou H. and Xu S. (2007) Interlayer structure and dynamics of alky-  
1009 lammonium-intercalated smectites with and without water: A molecular dynamics study.  
1010 *Clays and Clay Miner.* **55**, 554-564.
- 1011 Liu X., Lu X., Wang R. and Zhou H. (2008) Effects of layer-charge distribution on the thermody-  
1012 namic and microscopic properties of Cs-smectite. *Geochim. Cosmochim. Acta* **72**, 1837-1847.
- 1013 Livi K. J., Christidis G. E., Árkai P. and Veblen D. R. (2008) White mica domain formation: A  
1014 model for paragonite, margarite, and muscovite formation during prograde metamorphism.  
1015 *Am. Mineral.* **93**, 520-527.
- 1016 Loewenstein W. (1954) The distribution of aluminum in the tetrahedra of silicates and aluminates.  
1017 *Am. Mineral.: J. Earth Planet. Mater.* **39**, 92-96.
- 1018 Loganathan N. and Kalinichev A. G. (2013) On the hydrogen bonding structure at the aqueous  
1019 interface of ammonium-substituted mica: A molecular dynamics simulation. *Zeitschrift für*  
1020 *Naturforschung A* **68**, 91-100.
- 1021 Malani A., Ayappa K. and Murad S. (2009) Influence of hydrophilic surface specificity on the  
1022 structural properties of confined water. *J. Phys. Chem. B* **113**, 13825-13839.
- 1023 Massonne H. J. and Schreyer W. (1987) Phengite geobarometry based on the limiting assemblage  
1024 with K-feldspar, phlogopite, and quartz. *Contrib. Miner. Petrol.* **96**, 212-224.



- 1025 Massonne H. J. and Schreyer W. (1989) Stability field of the high-pressure assemblage, talc +  
1026 phengite and two new phengite barometers. *Eur. J. Mineral.* **1**, 391-410.
- 1027 McDougall I. and Harrison T. M. (1999) *Geochronology and Thermochronology by the  $^{40}\text{Ar}/^{39}\text{Ar}$*   
1028 *Method.*, Oxford University Press, New York.
- 1029 Mehrer H. (2007) *Diffusion in solids: fundamentals, methods, materials, diffusion-controlled pro-*  
1030 *cesses.*, Springer Science & Business Media.
- 1031 Meleshyn A. (2008) Two-dimensional ordering of water adsorbed on a mica surface at room tem-  
1032 perature. *J. Phys. Chem. C* **112**, 14495-14500.
- 1033 Mellini M. (1982) The crystal structure of lizardite 1T: hydrogen bonds and polytypism. *Am.*  
1034 *Mineral.* **67**, 587-598.
- 1035 Momma K. and Izumi F. (2011) VESTA 3 for three-dimensional visualization of crystal, volumetric  
1036 and morphology data. *J. appl. crystal.* **44**, 1272-1276.
- 1037 Monié, P. (1990) Preservation of Hercynian  $^{40}\text{Ar}/^{39}\text{Ar}$  ages through high-pressure low-temperature  
1038 Alpine metamorphism in the Western Alps. *Eur. J. Mineral.*, 343-361.
- 1039 Monié P. and Chopin C. (1991)  $^{40}\text{Ar}/^{39}\text{Ar}$  dating in coesite-bearing and associated units of the  
1040 Dora Maira massif, Western Alps. *Eur. J. Mineral.*, 239-262.
- 1041 Morrow C. P., Yazaydin A. Ö., Krishnan M., Bowers G. M., Kalinichev A. G. and Kirkpatrick R. J.  
1042 (2013) Structure, energetics, and dynamics of smectite clay interlayer hydration: Molecular  
1043 dynamics and metadynamics investigation of Na-hectorite. *J. Phys. Chem. C* **117**, 5172-  
1044 5187.
- 1045 Mulch A., Cosca M. and Handy M. (2002) In-situ UV-laser  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology of a micaceous  
1046 mylonite: an example of defect-enhanced argon loss. *Contrib. Miner. Petrol.* **142**, 738-752.
- 1047 Padma Kumar P., Kalinichev A. G. and Kirkpatrick R. J. (2006) Hydration, swelling, interlayer  
1048 structure, and hydrogen bonding in organolayered double hydroxides: Insights from molecular  
1049 dynamics simulation of citrate-intercalated hydrotalcite. *J. Phys. Chem. B* **110**, 3841-3844.

- 1050 Purdy J. and Jäger E. (1976) K-Ar ages on rock forming minerals from the Central Alps. *Mem.*  
1051 *1st. Geol. Min. Univ. Padova* **30**, 31.
- 1052 Putlitz B., Cosca M. and Schumacher J. (2005) Prograde mica  $^{40}\text{Ar}/^{39}\text{Ar}$  growth ages recorded in  
1053 high pressure rocks (Syros, Cyclades, Greece). *Chem. Geol.* **214**, 79-98.
- 1054 Putnis A. (2009) Mineral replacement reactions. *Rev. Mineral. Geochem.* **70**, 87-124.
- 1055 Rapaport D. C. (2004) *The art of molecular dynamics simulation.*, Cambridge university press.
- 1056 Robbins C. (1972) Radiogenic argon diffusion in muscovite under hydrothermal conditions. M.S.  
1057 Thesis, Brown University, Providence, RI.
- 1058 Ruiz Pestana L., Kolluri K., Head-Gordon T. and Lammers L. N. (2017) Direct exchange mechanism  
1059 for interlayer ions in non-swelling clays. *Environ. sci. technol.* **51**, 393-400.
- 1060 Saadouné I., Purton J. A. and de Leeuw N. H. (2009) He incorporation and diffusion pathways  
1061 in pure and defective zircon  $\text{ZrSiO}_4$ : A density functional theory study. *Chem. Geol.* **258**,  
1062 182-196.
- 1063 Scaillet S. (1996) Excess  $^{40}\text{Ar}$  transport scale and mechanism in high-pressure phengites: A case  
1064 study from an eclogitized metabasite of the Dora-Maira nappe, western Alps. *Geochim.*  
1065 *Cosmochim. Acta* **60**, 1075-1090.
- 1066 Scaillet S. (1998) K-Ar ( $^{40}\text{Ar}/^{39}\text{Ar}$ ) geochronology of ultrahigh pressure rocks. In *When continents*  
1067 *collide: Geodynamics and geochemistry of ultrahigh-pressure rocks*. Springer. pp. 161-201.
- 1068 Scaillet S., Féraud G., Lagabriele Y., Ballèvre M. and Ruffet G. (1990)  $^{40}\text{Ar}/^{39}\text{Ar}$  laser-probe dating  
1069 by step heating and spot fusion of phengites from the Dora Maira nappe of the Western Alps,  
1070 Italy. *Geology* **18**, 741-744.
- 1071 Scaillet S., Féraud G., Ballèvre M. and Amouric M. (1992) Mg/Fe and [(Mg,Fe)Si-Al<sub>2</sub>] compo-  
1072 sitional control on argon behaviour in high-pressure white micas: A  $^{40}\text{Ar}/^{39}\text{Ar}$  continuous  
1073 laser-probe study from the Dora-Maira nappe of the internal Western Alps, Italy. *Geochim.*  
1074 *Cosmochim. Acta* **56**, 2851-2872.

- 1075 Schertl H. P. and Hammerschmidt K. (2016) Tracking the incidence of excess argon in white mica  
1076 Ar-Ar data from UHP conditions to upper crustal levels in the Dora-Maira Massif, Western  
1077 Alps. *Eur. J. Mineral.* **28**, 1255-1275.
- 1078 Scibiorski E., Jourdan F., Mezger K., Tohver E. and Vollstaedt H. (2021) Cryptic excess argon  
1079 in metamorphic biotite: Anomalously old  $^{40}\text{Ar}/^{39}\text{Ar}$  plateau dates tested with Rb/Sr ther-  
1080 mochronology and Ar diffusion modelling. *Geochim. Cosmochim. Acta* **315**, 1–23.
- 1081 Shau Y.-H., Feather M. E., Essene E. J. and Peacor D. R. (1991) Genesis and solvus relations of sub-  
1082 microscopically intergrown paragonite and phengite in a blueschist from northern California.  
1083 *Contrib. Miner. Petrol.* **106**, 367-378.
- 1084 Shea W. T. and Kronenberg A. K. (1992) Rheology and deformation mechanisms of an isotropic  
1085 mica schist. *J. Geophys. Res. Solid Earth* **97**, 15201-15237.
- 1086 Spencer K., Hacker B., Kylander-Clark A., Andersen T., Cottle J., Stearns M., Poletti J. and  
1087 Seward G. (2013) Campaign-style titanite U-Pb dating by laser-ablation ICP: Implications  
1088 for crustal flow, phase transformations and titanite closure. *Chem. Geol.* **341**, 84-101.
- 1089 Szczerba M., Derkowski A., Kalinichev A. G. and Środoń J. (2015) Molecular modeling of the effects  
1090 of  $^{40}\text{Ar}$  recoil in illite particles on their K-Ar isotope dating. *Geochim. Cosmochim. Acta*  
1091 **159**, 162-176.
- 1092 Tao L., Xiao-Feng T., Yu Z. and Tao G. (2010) Swelling of  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{Ca}^{2+}$ -montmorillonites  
1093 and hydration of interlayer cations: a molecular dynamics simulation. *Chin. Phys. B* **19**,  
1094 109101.
- 1095 Tardy Y. and Fritz B. (1981) An ideal solid solution model for calculating solubility of Clay miner..  
1096 *Clay miner.* **16**, 361-373.
- 1097 Teich-McGoldrick S. L., Greathouse J. A. and Cygan R. T. (2012) Molecular dynamics simulations  
1098 of structural and mechanical properties of muscovite: pressure and temperature effects. *J.*  
1099 *Phys. Chem. C* **116**, 15099-15107.
- 1100 Thompson A. P., Aktulga H. M., Berger R., Bolintineanu D. S., Brown W. M., Crozier P. S.,

- 1101 in 't Veld P. J., Kohlmeyer A., Moore S. G., Nguyen T. D. and others (2021) LAMMPS  
1102 – a flexible simulation tool for particle-based materials modeling at the atomic, meso, and  
1103 continuum scales. *Comput. Phys. Com.* **271**, 108171.
- 1104 Villa I. M. (2021) The in vacuo release of Ar from minerals: 1. Hydrous minerals. *Chem. Geol.*  
1105 **564**, 120076.
- 1106 Villa I. M. and Puxeddu M. (1994) Geochronology of the Larderello geothermal field: new data and  
1107 the “closure temperature” issue. *Contrib. Miner. Petrol.* **115**, 415-426.
- 1108 Vineyard G. H. (1957) Frequency factors and isotope effects in solid state rate processes. *J. Phys.*  
1109 *Chem. Sol.* **3**, 121-127.
- 1110 Wander M. C. and Clark A. E. (2008) Structural and dielectric properties of quartz- water interfaces.  
1111 *J. Phys. Chem. C* **112**, 19986-19994.
- 1112 Wang G. F. and Banno S. (1987) Non-stoichiometry of interlayer cations in micas from low-to  
1113 middle-grade metamorphic rocks in the Ryoke and the Sanbagawa belts, Japan. *Contrib.*  
1114 *Miner. Petrol.* **97**, 313-319.
- 1115 Wang K., Brodholt J. and Lu X. (2015) Helium diffusion in olivine based on first principles calcu-  
1116 lations. *Geochim. Cosmochim. Acta* **156**, 145-153.
- 1117 Wang K., Lu X. and Brodholt J. P. (2020) Diffusion of noble gases in subduction zone hydrous  
1118 minerals. *Geochim. Cosmochim. Acta* **291**, 50-61.
- 1119 White, J. A. (1999) Lennard-Jones as a model for argon and test of extended renormalization group  
1120 calculations. *J. Chem. Phys.* **111**(20), 9352-9356.
- 1121 Wijbrans J. R. and McDougall I. (1986)  $^{40}\text{Ar}/^{39}\text{Ar}$  dating of white micas from an Alpine high-  
1122 pressure metamorphic belt on Naxos (Greece): the resetting of the argon isotopic system.  
1123 *Contrib. Miner. Petrol.* **93**, 187-194.
- 1124 Wijbrans J. and McDougall I. (1988) Metamorphic evolution of the Attic Cycladic Metamorphic  
1125 Belt on Naxos (Cyclades, Greece) utilizing  $^{40}\text{Ar}/^{39}\text{Ar}$  age spectrum measurements. *J. Metam.*

1126 *Geol.* **6**, 571–594.

1127 Wunder B. and Melzer S. (2002) Interlayer vacancy characterization of synthetic phlogopitic micas  
1128 by IR spectroscopy. *Eur. J. Mineral.* **14**, 1129-1138.

1129 Yu C. J., Choe S. H., Jang Y. M., Jang G. H. and Pae Y. H. (2016) First-principles study of  
1130 organically modified muscovite mica with ammonium ( $\text{NH}_4^+$ ) or methylammonium ( $\text{CH}_3\text{NH}_3^+$ )  
1131 ion. *J. Mater. Sci.* **51**, 10806-10818.

Table 1: Interaction parameters used in the simulations

Nonbonded parameters			
Atoms	Charge (e)	$\sigma$ (Å)	$\epsilon$ (kcal.mol <sup>-1</sup> )
H (hydroxyl) <sup>a</sup>	0.4250	-	-
O1 (hydroxyl) <sup>a</sup>	-0.9500	3.1655	0.1554
O2 (bridging Oxygen) <sup>a</sup>	-1.0500	3.1655	0.1554
O3 (Oxygen bonded to tetrahedral Al) <sup>a</sup>	-1.1688	3.1655	0.1554
Al (octahedral) <sup>a</sup>	1.5750	4.2712	$1.3298 \times 10^{-6}$
Al2 (tetrahedral) <sup>a</sup>	1.5750	3.3020	$1.8405 \times 10^{-6}$
Si <sup>a</sup>	2.1000	3.3020	$1.8405 \times 10^{-6}$
K <sup>a</sup>	1.0000	3.3340	0.1000
Ar <sup>b</sup>	0.0000	3.4010	0.2304
<sup>a</sup> Cygan et al. (2004) <sup>b</sup> White (1999)			
Bonded parameters			
Atom 1	Atom 2	$k_1$ (kcal.mol <sup>-1</sup> .Å <sup>-2</sup> )	$r_0$ (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
$\alpha$ ( $^\circ$ )	90.000	89.787	-0.24
$\beta$ ( $^\circ$ )	95.770	95.936	+0.17
$\gamma$ ( $^\circ$ )	90.000	90.175	+0.19
Interlayer sep. (Å)	3.396	3.368	-0.88

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

	Mean energy barriers		Effective energy barriers		$^{40}\text{Ar}$ 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 $^{-1}$ )
$\square$	$71 \pm 5$	$79 \pm 9$	69	75	75	$4 \times 10^{-3}$
$\square\square$	$69 \pm 6$	$66 \pm 10$	65	58	66	$6 \times 10^{-4}$

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  $^{40}\text{Ar}$  recoil with respect to the mean  
 1143 energy of a system in which  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $\text{K}^+$  and  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  along its path towards a monovacancy (black) and towards a vacancy pair (blue).  
 1156 d) Trajectories followed by  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  migration barriers and the  
 1159 total electrostatic energy of the structure.

1161 **Fig. 5.** Results of NEB calculations of  $\text{K}^+$  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  $^{40}\text{Ar}$  and  $K^+$  migration barriers.

1168  
1169 **Fig. 6.** Arrhenius plot of  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$ –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

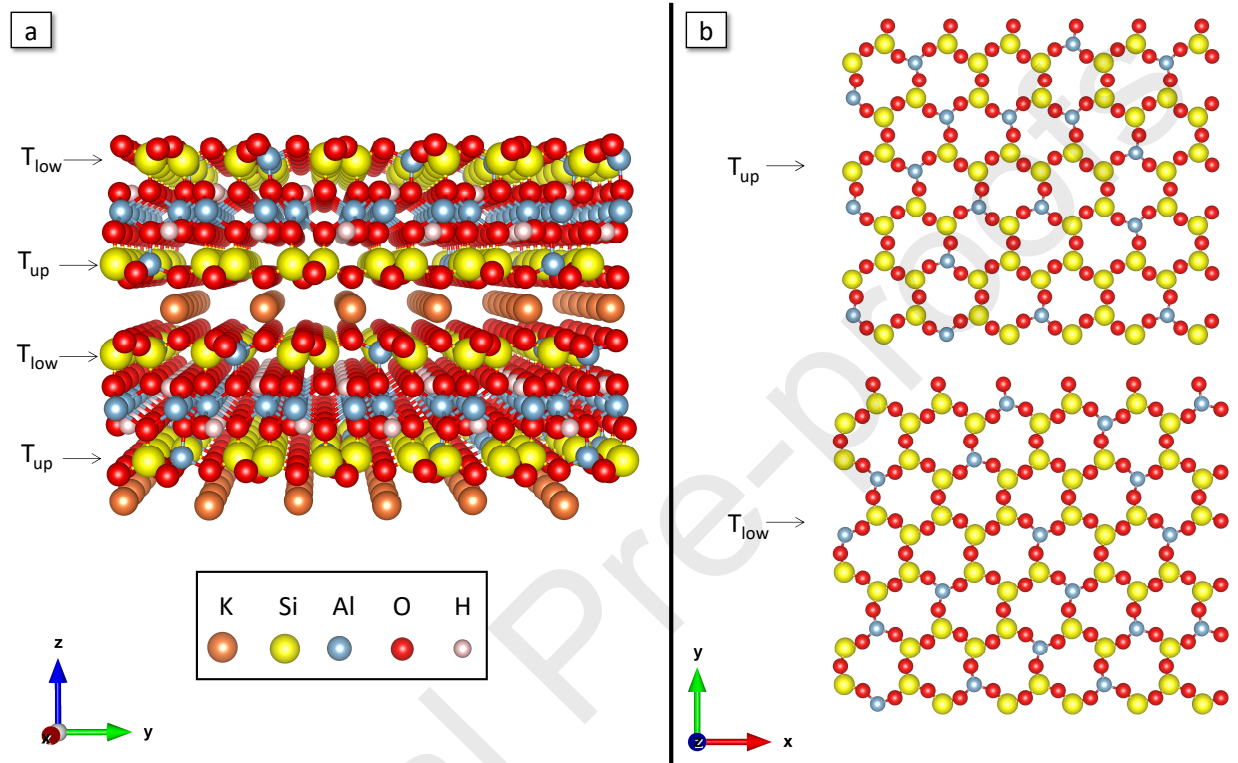


Fig. 2

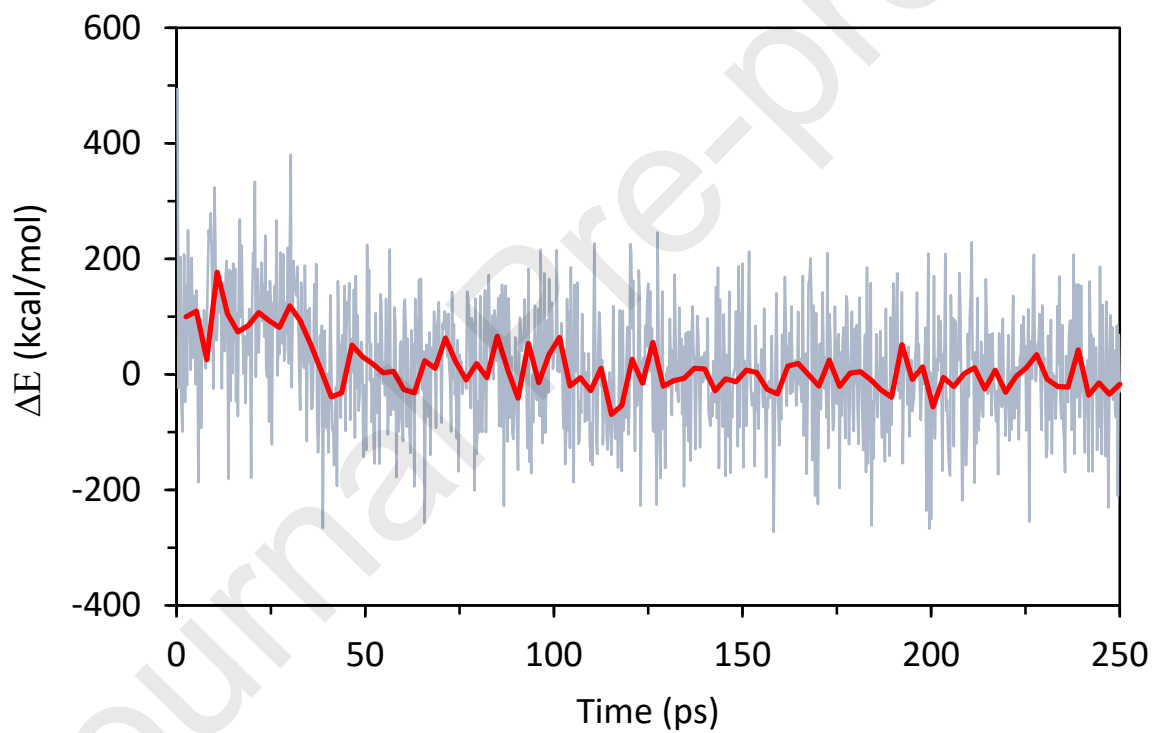


Fig. 3

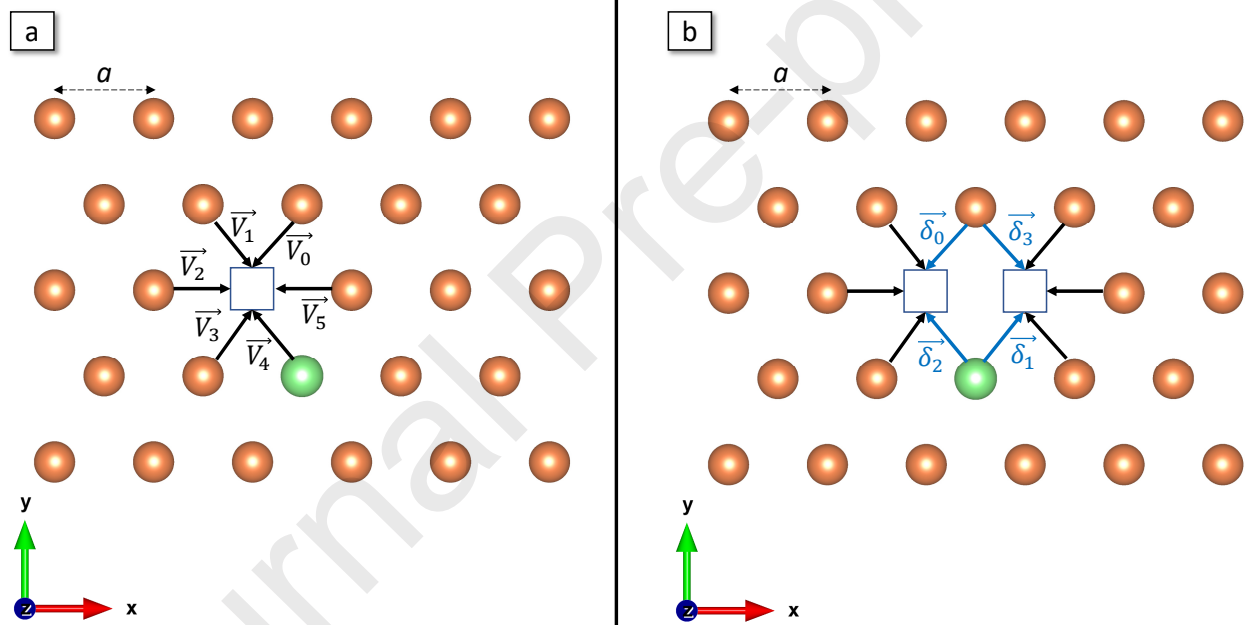


Fig. 4

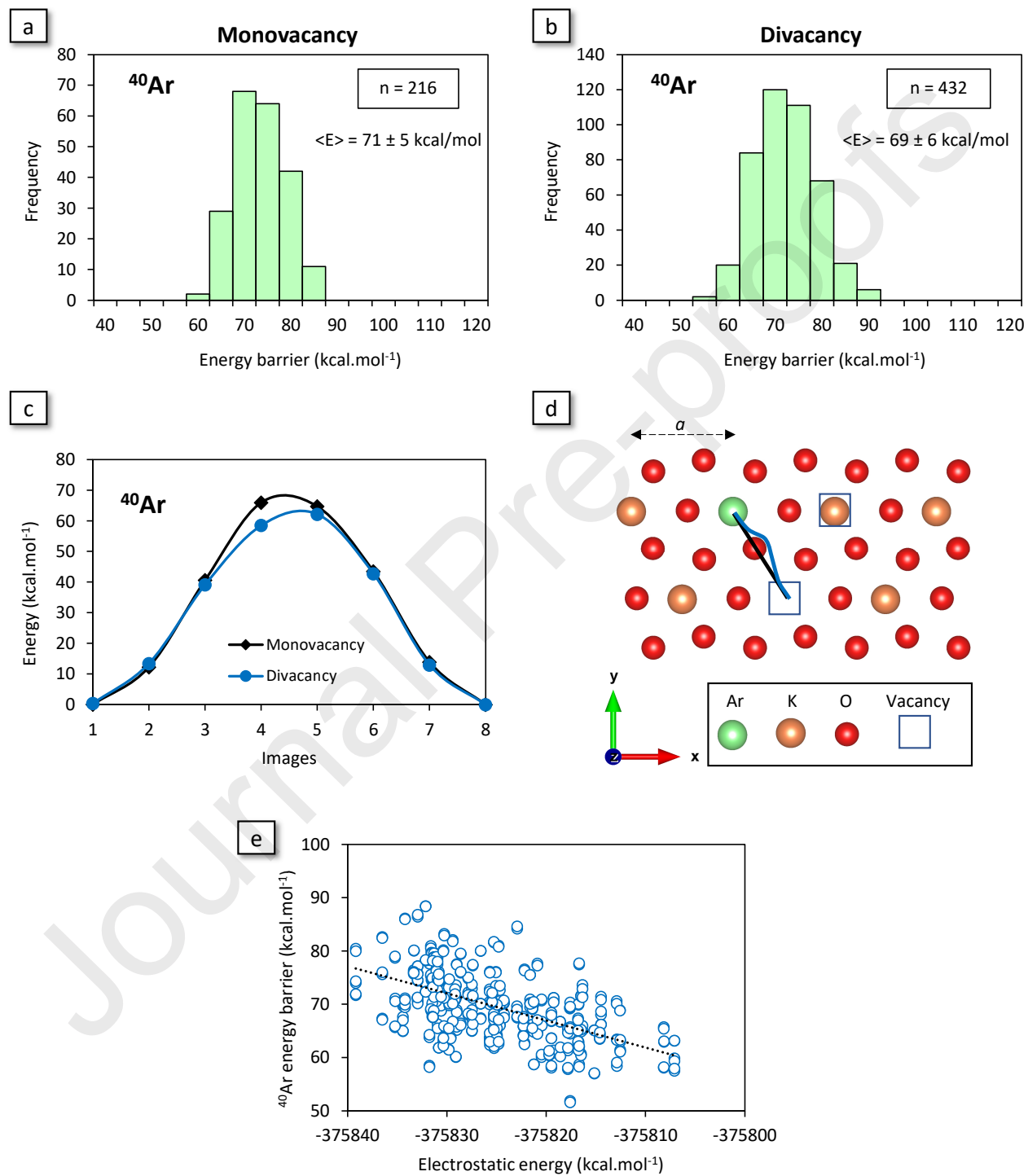


Fig. 5

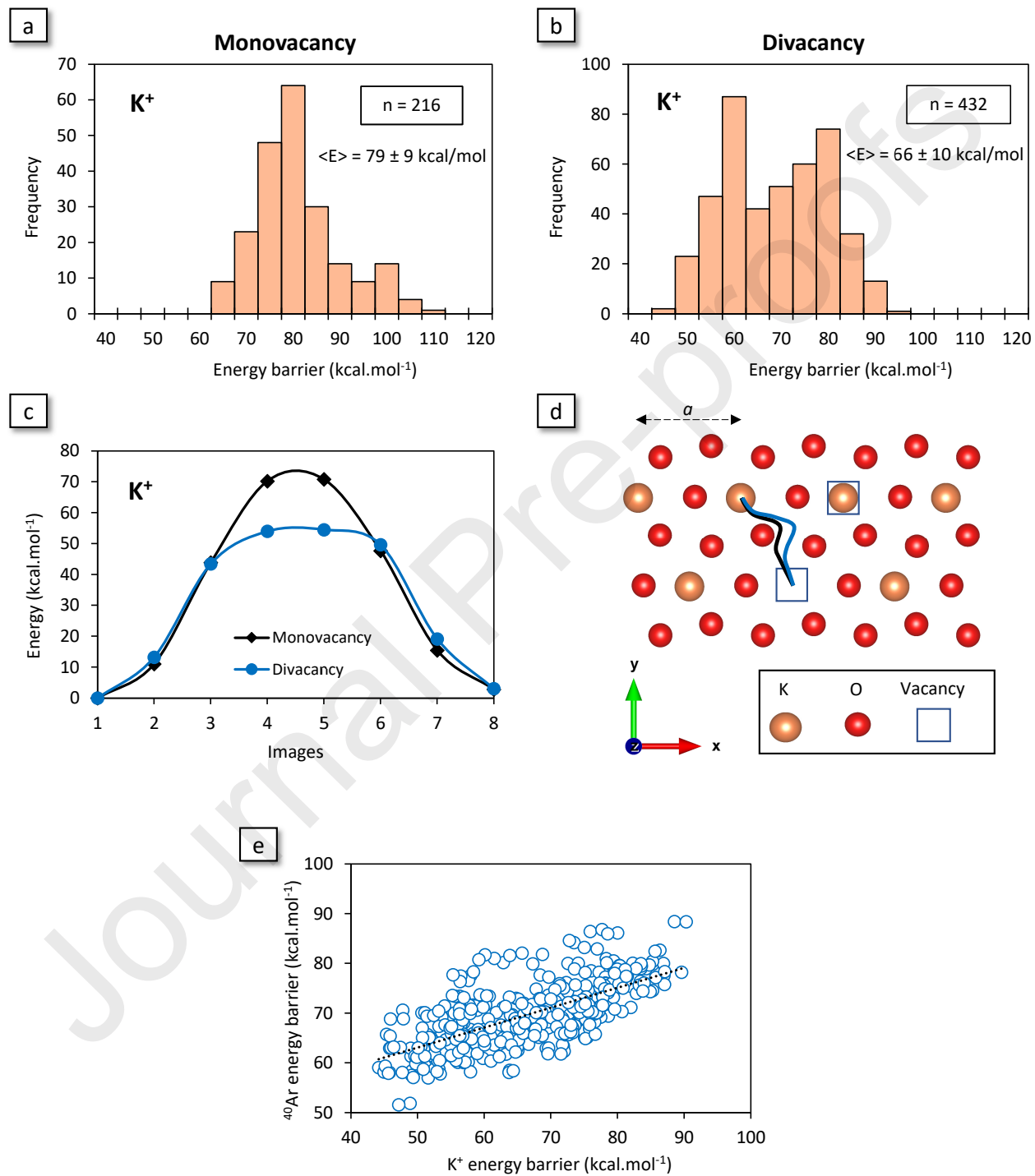


Fig. 6

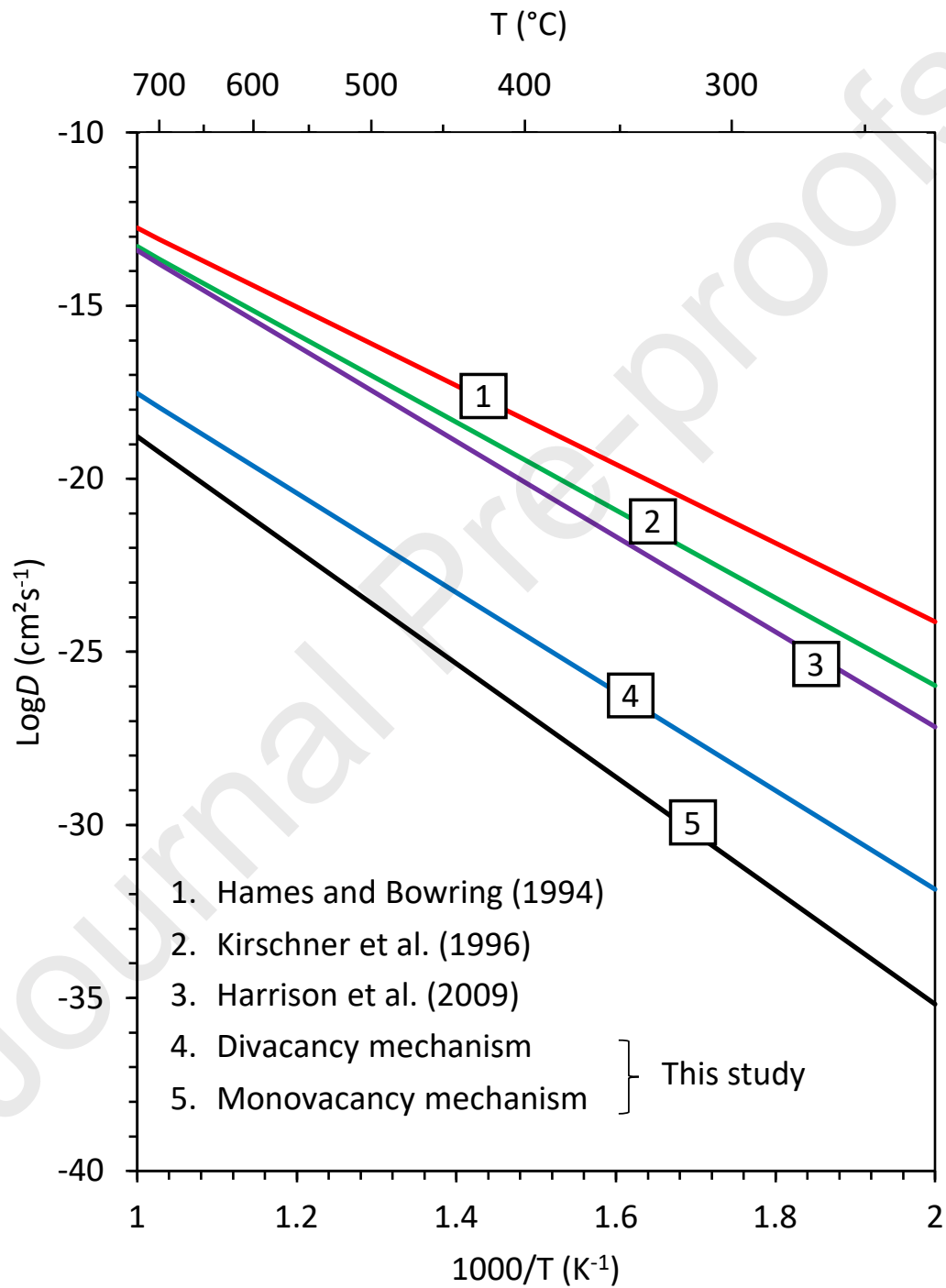
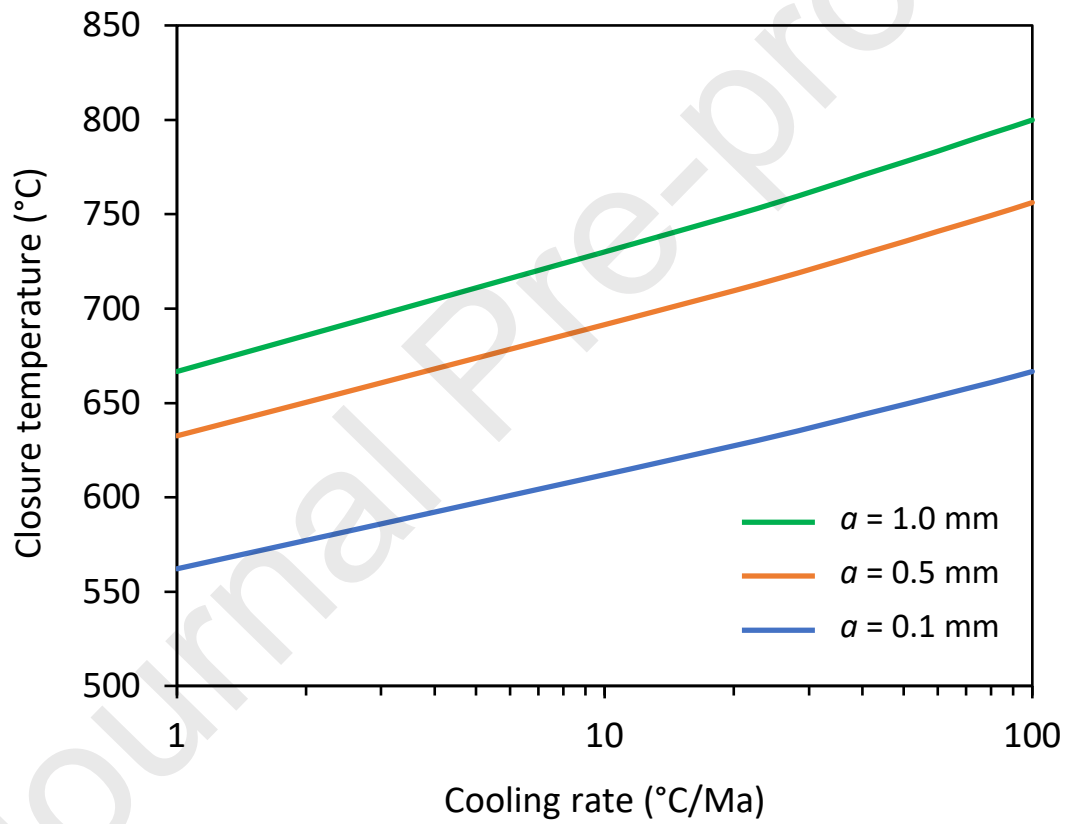


Fig. 7





**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: