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# Defect-Controlled $^{40}\text{Ar}$ Diffusion-Domain Structure of White Micas from High-resolution $^{40}\text{Ar}/^{39}\text{Ar}$ Crystal-Mapping in Slowly-Cooled Muscovite

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Defect-Controlled  $^{40}\text{Ar}$  Diffusion-Domain Structure of White Micas from High-resolution  $^{40}\text{Ar}/^{39}\text{Ar}$  Crystal-Mapping in Slowly-Cooled Muscovite

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1 Defect-Controlled  $^{40}\text{Ar}$  Diffusion-Domain Structure of White Micas  
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3 Muscovite

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15 **Abstract**

16 Using target-matching techniques combining  $^{40}\text{Ar}/^{39}\text{Ar}$  crystal-mapping with elemental  
17 mapping and high-resolution electron microscopy, this study investigates the  $^{40}\text{Ar}$  behavior  
18 in very-slowly cooled muscovite from the Harney Peak Granite (HPG, South Dakota, USA).  
19 Detailed age mapping along (001) in single crystals from different localities of the HPG docu-  
20 ments age gradients in excess of  $\sim 300\text{--}400$  m.y., with conspicuous internal  $^{40}\text{Ar}/^{39}\text{Ar}$  zoning.  
21 This suggests (001) layer-parallel  $^{40}\text{Ar}$  transport driven by diffusion, consistent with previous  
22  $^{40}\text{Ar}/^{39}\text{Ar}$  crystal-mapping studies. The age distribution pattern is complex, however, and  
23 defines a mosaic of sub-grain domains with more retentive core zones, broadly  $\sim 250\text{--}300$   
24  $\mu\text{m}$  across, separated by zones of high diffusivity varying in shape and extent. The maximum  
25 ages preserved in the core domains are independent of their size but vary linearly with the  
26 bulk areal extent of the peripheral (or surrounding) high-diffusivity zones. Spatial  $^{40}\text{Ar}/^{39}\text{Ar}$   
27 relationships inside each grain point to a mechanism of multipath continuum-diffusion inter-  
28 action between subdomains across the whole crystal, rather than via discrete non-interacting  
29 domains such as in K-feldspars. A close spatial correlation exists between younger ages, Na-  
30 depleted (K-enriched) zones, and density of microstructural defects. These defects, identified  
31 as lenticular voids and basal partings ( $< 100$  nm-long), are developed in response to inward

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32 K  $\leftrightarrow$  Na interdiffusion during late-magmatic stages, in the absence of deformation. Coupled  
33 variations in density of microstructural defects and Na–K interchange are inferred to control  
34 the bulk diffusion-domain structure of HPG muscovite. Quantitative diffusion modeling of  
35 coupled compositional–defect–isotopic variations indicates that  $^{40}\text{Ar}$  diffusivity may be en-  
36 hanced by up to six orders of magnitude in defect-controlled high-diffusivity zones relative to  
37 less defective (pristine) domains. On the other hand, empirical diffusivity estimates required  
38 to preserve the core ages are commensurate with diffusion estimates independently derived  
39 from recent atomistic simulations.

40 *Key words:*  $^{40}\text{Ar}$  diffusion, domain structure, multipath diffusion, muscovite,  
41 (001)–parallel age–mapping, FIB-STEM/TEM, Harney Peak granite

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## 42 1. INTRODUCTION

43 Since the first laser-based  $^{40}\text{Ar}/^{39}\text{Ar}$  age-mapping of white micas (Scaillet et al., 1990),  
44 the technique has been rarely used to map internal (within-grain)  $^{40}\text{Ar}$  variations along the  
45 (001) direction in muscovite (Scaillet et al., 1992; de Jong et al., 1992; Hames and Hodges,  
46 1993; Hames and Bowring, 1994; Hodges et al., 1994; Boundy et al., 1997; Hames and  
47 Cheney, 1997; Laurent et al., 2021). Most *in situ*  $^{40}\text{Ar}/^{39}\text{Ar}$  laser work so far has been  
48 focused instead on studying textural *vs.*  $^{40}\text{Ar}$  retention relationships to explore the role of  
49 deformation on  $^{40}\text{Ar}$  redistribution and resetting at the grain-scale (e.g., Di Vincenzo et al.,  
50 2001, 2004, 2006; Kramar et al., 2001, 2003; Mulch et al., 2002, 2005, 2006; Mulch and  
51 Cosca, 2004; Putlitz et al., 2005; Hames et al., 2008; Wells et al., 2008; Wiederkehr et al.,  
52 2009; Rosenbaum et al., 2012; Schneider et al., 2013; Scharf et al., 2016; Fornash et al.,  
53 2016; Kellett et al., 2016; Beaudoin et al., 2020). Such relationships are commonly studied  
54 on samples cut parallel to the  $XZ$ –plane of maximum deformation and tectonic transport  
55 of the deformation ellipsoid, hence normal to the average flattening  $XY$ –plane containing  
56 the mica basal section (001). Because  $^{40}\text{Ar}$  diffusion in mica preferentially occurs along  
57 (001) (Nteme et al., 2022, and references below), such perpendicular cuts strongly minimize  
58 the likelihood of capturing the full travel path of argon from the core to the rim in case  
59 of transport dominated by volume (lattice) diffusion. Also, this approach compromises the  
60 overall ability to resolve near-edge effects hidden under the surface cut due to shallow or

61 contorted grain contacts, especially in the case of complex, interlocked, textural fabrics with  
62 low-angle oblique cuts. More importantly still,  $^{40}\text{Ar}/^{39}\text{Ar}$  gradients in fabric or foliation-  
63 forming micas may be locally affected by internal defects at conditions unlikely to reflect  
64 diffusion-dominated transport (Kramar et al., 2001).

65 The best option to study first-order argon diffusive patterns is by  $^{40}\text{Ar}/^{39}\text{Ar}$  mapping  
66 along (001) in magmatic micas. Micas in plutonic rocks are early-crystallizing phases that  
67 commonly develop mm-size sub-automorphic shapes at magmatic temperatures, often with  
68 little subsequent disruption of the original grain boundaries as the host pluton cools down  
69 and crystallizes unaffected by deformation. Detailed internal 2D mapping along (001) under  
70 such auspices essentially appeared in the early 1990's at a time when the resolving power, ex-  
71 traction wavelength, and instrumental sensitivity and throughput did not match the current  
72 technology for within-crystal  $^{40}\text{Ar}/^{39}\text{Ar}$  mapping (Phillips and Onstott, 1988; Scaillet et al.,  
73 1990, 1992; Onstott et al., 1991; Phillips, 1991; de Jong et al., 1992; Hames and Hodges, 1993;  
74 Hames and Bowring, 1994; Hodges et al., 1994; Hodges and Bowring, 1995; Kelley et al.,  
75 1994; Hames and Cheney, 1997). Despite their limitations, these studies clearly established  
76 that  $^{40}\text{Ar}$  diffusion in micas indeed proceeds along (001) with the effective diffusion length  
77 controlled to first-order by the physical grain size. They also showed that the geometry of  
78 diffusion may be far from perfect, possibly involving internal defects such as Guinier-Preston  
79 zones in biotite and phlogopite (Onstott et al., 1991; Phillips, 1991).

80 Except for one occasion (Hodges et al., 1994), magmatic muscovite largely eluded the  
81 attention of early  $^{40}\text{Ar}/^{39}\text{Ar}$  crystal-mapping investigations, leaving our current perception  
82 of the typology of  $^{40}\text{Ar}$  diffusion in white micas largely shaped by tectono-metamorphic  
83 studies where primary diffusion-driven patterns are invariably obscured by deformation and  
84 recrystallization (e.g., Hames and Cheney, 1997; Kramar et al., 2001, 2003; Mulch et al.,  
85 2002, 2004, 2005, 2006; Putlitz et al., 2005; Hames et al., 2008; Beaudoin et al., 2020).  
86 Purely diffusion-driven (i.e., deformation-free) natural  $^{40}\text{Ar}$  gradients in muscovite remain  
87 inadequately characterized today, raising the question of how to relate  $^{40}\text{Ar}/^{39}\text{Ar}$  age varia-  
88 tions documented in complex field situations to  $^{40}\text{Ar}$  diffusivities derived from experimental  
89 (Robbins, 1972; Harrison et al., 2009), empirical (Hames and Bowring, 1994; Kirschner et  
90 al., 1996), and theoretical (Nteme et al., 2022) studies. These studies differ substantially

91 in terms of kinetic rates, diffusion-domain structure and geometry, with considerable uncer-  
92 tainty surrounding the thermal-kinetic significance one can attach to muscovite  $^{40}\text{Ar}/^{39}\text{Ar}$   
93 data in terms of cooling *vs.* (re)crystallization ages in natural settings.

94 In a previous work (Nteme et al., 2022), we addressed the problem of the quantitative  
95 characterization of  $^{40}\text{Ar}$  kinetics in white micas from lattice-based Molecular Dynamics (MD)  
96 and Transition State theories (TST) and concluded that  $^{40}\text{Ar}$  diffusion in ideal (i.e., defect-  
97 free and stoichiometrically stable) muscovite is orders of magnitude slower than predicted by  
98 experiments and field-based calibrations. In this work, we bring the study a step ahead and  
99 address the case of  $^{40}\text{Ar}$  diffusion in natural igneous muscovite grains that fulfil the condition  
100 of not having been at all or significantly deformed. Inspired by the few precedents of 2D  
101 mapping of igneous micas (Hames and Hodges, 1993; Hames and Bowring, 1994; Hodges et  
102 al., 1994; Hodges and Bowring, 1995), we selected as natural target the Harney Peak Granite  
103 in the Paleoproterozoic Black Hills of South Dakota, USA, for which prior  $^{40}\text{Ar}/^{39}\text{Ar}$  regional  
104 data document protracted cooling over hundreds of million years both in the pluton and  
105 its aureole as a result of long-term stagnation in the mid-crust and progressive exhumation  
106 between  $\sim 1600$ - $1250$  Ma (Holm et al. 1997; Dahl and Foland, 2008).

107 Very slow ( $\sim 0.5$  °C/Myr) subsolidus cooling across this interval produced mm-size age  
108 gradients along (001) within individual mica crystals, in a context akin to a “natural” dif-  
109 fusion experiment optimal for investigating the  $^{40}\text{Ar}$  diffusion mechanisms in undeformed  
110 muscovite with a resolution never approached before. Using target-matching techniques com-  
111 bining extensive  $^{40}\text{Ar}/^{39}\text{Ar}$  crystal-mapping with high resolution electron microscopy imag-  
112 ing and elemental mapping, our study documents fundamental compositional and crystal-  
113 structural effects controlling the defect and diffusion-domain structure of muscovite. These  
114 are described and quantitatively integrated in a numerical model of defect-controlled multi-  
115 path  $^{40}\text{Ar}$  diffusion-domain behavior that is applicable to other settings as well.

## 116 2. GEOLOGICAL SETTING

117 The Harney Peak granite (HPG) is a peraluminous leucogranite located in the south-  
118 central portion of the Proterozoic core of the Black Hills, South Dakota (Fig. 1). It is hosted  
119 by regionally metamorphosed sedimentary rocks affected by staurolite to sillimanite-grade

120 metamorphism. The HPG consists of a large central pluton with smaller satellite granitic  
121 and pegmatitic plutons. The main pluton and the satellite intrusions have domal structures  
122 consisting of hundreds of sills. According to [Duke et al. \(1988\)](#), the HPG grew upward  
123 and outward by successive intrusions of new sills at the periphery of earlier intrusions. The  
124 magma injected during each pulse was initially homogeneous and underwent differentiation  
125 into 0.1 to 2.0 m-thick layers of Na-rich aplites and K-rich pegmatites. The mineralogy of  
126 the HPG is composed dominantly of albite, orthoclase or microcline, quartz and muscovite.  
127 Accessory minerals include biotite, tourmaline and garnet. Biotite and tourmaline are mostly  
128 mutually exclusive, the first being dominant in the core of the main pluton and the latter at  
129 the periphery and in satellite plutons.

130 The HPG pluton was emplaced at the culmination of the Yavapai (N-S compression) and  
131 Black Hills (E-W compression) orogenic sequence, the latter from collision of the Superior  
132 and Wyoming cratons at the southeastern extent of the earlier Trans-Hudson Orogen ([Fig. 1](#);  
133 [Dahl et al., 1999](#); [Chamberlain et al., 2003](#); [Dahl and Foland, 2008](#)). The Black Hills orogeny  
134 resulted in N-S directed foliation that dominates the structural fabric of the Black Hills. The  
135 beginning of the collision is dated at  $\sim 1750$  Ma (U-Th-Pb on monazite inclusions within  
136 metamorphic garnet; [Dahl et al., 2005](#)). A range of ages is associated to the formation of the  
137 HPG:  $1728 \pm 4$  Ma (two highly discordant U/Pb zircon ages; [Redden et al., 1990](#)),  $1715 \pm 3$   
138 Ma (concordant U/Pb monazite age from a thin granite sill in metamorphic rocks; [Redden](#)  
139 [et al., 1990](#)),  $1711 \pm 21$  Ma (Rb-Sr whole-rock age, recalculated by [Krogstad and Walker](#)  
140 [\(1994\)](#) from [Riley \(1970\)](#)), and 1704 to 1700 Ma (U/Pb apatite ages from the Tin Mountain  
141 pegmatite, west of the HPG; [Krogstad and Walker, 1994](#)). This range either reflects variable  
142 discordance with U/Pb re-equilibration or mineral-specific post-crystallization cooling (mon-  
143 azite), in any case placing the most probable range of intrusion-crystallization ages between  
144 1700–1720 Ma, possibly including overlapping of multiple intrusions in this interval as well.  
145 Collectively, the range of published ages indicates that intrusion of the HPG was the termi-  
146 nal stage of the  $\sim 50$  Myr long Yavapai - Black Hills orogenic sequence, consistent with its  
147 undeformed state.

148 HPG liquidus temperature from stable isotope oxygen equilibria in magmatic phases is  
149 estimated at  $\sim 800$  °C ([Nabelek et al., 1992b](#)). Intrusion probably occurred during uplift

150 (Nabelek and Chen, 2014) and continued until final emplacement pressure around 3.5 - 4  
151 kbar. Post-intrusion cooling is constrained by muscovite Rb/Sr ages in the granite (Riley,  
152 1970; Ratté, 1986; Krogstad and Walker, 1994), and  $^{40}\text{Ar}/^{39}\text{Ar}$  ages on hornblende, biotite  
153 and muscovite mostly across the regional contact aureole (Berry et al., 1994; Dahl et al.,  
154 1999; Holm et al., 1997; Dahl and Foland, 2008). These data indicate relatively rapid pluton  
155 cooling through 500 °C isotherm, followed by extremely slow ( $< 0.5$  °C/Myr) sub-solidus  
156 regional cooling characterized by hundreds of millions of years of tectonic stability in the  
157 midcrust (Holm et al., 1997; Dahl and Foland, 2008). The granite and its country rocks were  
158 ultimately uplifted during the 80–50 Ma Laramide orogeny (Lisenbee, 1978).

### 159 3. SAMPLE SELECTION AND DESCRIPTION

160 Muscovite crystals were obtained from five samples collected from different parts of the  
161 intrusive complex (Fig. 1). The samples were originally described in Nabelek et al. (1992a).  
162 A summary of the salient petrographic and mineralogic features is given in Table 1. Samples  
163 HP-10D and HP-13A were collected from the central pluton while HP-34C, HP-45B, and HP-  
164 2A are peripherally located in three distinct western, eastern, and northern satellite plutons,  
165 respectively. This choice was dictated by the need to account for potential age variations  
166 inside the composite pluton (Scaillet et al., 1996).

167 The selected samples show a common mineral assemblage dominated by quartz, K-  
168 feldspar, muscovite, and tourmaline. A few rare garnet crystals occur in HP-2A and HP-45B.  
169 In general, samples from the central facies display fine to coarse-grained granitic textures,  
170 while those of the peripheral plutons show textures ranging from aplitic to pegmatitic. Sam-  
171 ples from the central pluton (HP-10D and HP-13A) consist of mm-size grains (Fig. 2a, b,  
172 d, g). Quartz is sub-rounded and evenly distributed. Albite and K-feldspar occur as sub-  
173 automorphic crystals, generally devoid of inclusions (Fig. 2g). Tourmaline is mm-size but  
174 can be locally larger. Muscovite often occurs as single isolated crystals, but locally forms  
175 monomineralic aggregates (Fig. 2b). While most of the muscovite grains are automorphic,  
176 some show concave edges and symplectitic texture probably due to magmatic resorption  
177 (Fig. 2d).

178 Sample HP-34C (peripheral pluton) contains mm- to cm-size grains. The paragenesis is



179 dominated by K-feldspars and quartz. Muscovite is present but with low modal proportions  
180 compared to centrally located samples. K-feldspar is also distinct from the central facies by  
181 being richer in inclusions (mainly muscovite, Fig. 2h). As in the central pluton, muscovite  
182 is often resorbed (Fig. 2e). Sample HP-45B (eastern peripheral pluton) exhibits a coarse-  
183 grained texture. Feldspars are rich in muscovite inclusions. Primary muscovite occurs as  
184 single isolated crystals displaying similar resorption characteristics. Sample HP-2A (northern  
185 satellite pluton) displays a porphyritic texture dominated by feldspar megacrysts set in a  
186 medium-grained quartz mesostasis. Muscovite often occurs as aggregates (Fig. 2c) locally  
187 exhibiting resorption patterns (Fig. 2f).

## 188 4. ANALYTICAL TECHNIQUES

### 189 4.1. *In situ* $^{40}\text{Ar}/^{39}\text{Ar}$ dating

190 After gentle crushing with a hand-held hammer, individual muscovite grains ( $\geq 1$  mm)  
191 were hand-picked under a binocular microscope based on automorphic shape, lack of visible  
192 alteration, and sharpness of grain edges. This last criterion was not met by all crystals  
193 with some grains exhibiting broken cleavage planes indicated by minor delamination locally  
194 affecting the crystal rims (Fig. 3). The selected grains were ultrasonically bathed in ethanol  
195 and deionized water for 30 s and 60 s, successively, then dried in a 50 °C oven. After  
196 microscopic examination and imaging, they were wrapped in aluminum foil, stacked in an  
197 irradiation can with sanidine monitor FCS ( $28.02 \pm 0.28$  Ma, Renne et al., 1998) interspersed  
198 every five samples and irradiated for 20 h in the CLICIT position of the Oregon State  
199 University Radiation Center (USA). After irradiation, the grains were loaded into an ultra-  
200 high vacuum laser port and baked for  $\sim 60$  hours at  $\sim 200$  °C to remove absorbed atmospheric  
201 Ar and reduce the blanks.

202  $^{40}\text{Ar}/^{39}\text{Ar}$  *in situ* ages were measured along the (001) cleavage plane, identified as the  
203 preferential plane of  $^{40}\text{Ar}$  diffusion in mica (biotite and phlogopite: Giletti et al., 1974; Phillips  
204 and Onstott, 1988; Hodges and Bowring, 1995; white mica: Scaillet et al., 1990; Hames and  
205 Bowring, 1994; Nteme et al., 2022). A high-resolution deep 213-UV laserprobe (Teledyne<sup>®</sup>  
206 CETAC Technologies LSX-213G2+) was used to excavate 35  $\mu\text{m}$  wide cone-shaped ablation  
207 pits about 30-40  $\mu\text{m}$  deep (Fig. 4) at a repetition rate of 20 Hz and 4-5 mJ/pulse. Thirty-

208 four to more than one hundred fifty-six ablation spots were excavated per grain to ensure  
209 reasonably well resolved intracrystalline  $^{40}\text{Ar}/^{39}\text{Ar}$  gradients in the range of the age variations  
210 recorded. The extracted gases were purified for 6 min using two air-cooled GP50 SAES getters  
211 at 250 °C equipped with two Ta-filaments held at 1500 °C, and a thermoregulated cold trap  
212 held at -127 °C before admission into one of the three static noble gas Helix-SFT (Thermo  
213 Scientific<sup>®</sup>) mass-spectrometers operated at ISTO with a mass resolution in excess of 750.  
214 Ar isotopes were measured along with  $^{35}\text{Cl}$  by peak jumping in 10 cycles of 70 s duration  
215 with an electron multiplier ( $^{35}\text{Cl}$ ,  $^{36,37,38,39,40}\text{Ar}$ ) and a  $10^{12} \Omega$  feedback resistor-fitted Faraday  
216 cup ( $^{40}\text{Ar}$  only). Gas handling and mass-spectrometer operations are fully automated using  
217 LabView<sup>®</sup>-based in-house software. Procedural blanks were monitored before every sample  
218 gas admission in the same conditions as the unknowns. Typical values were 0.1-0.05 fA  
219 and  $\sim 0.001$  fA for  $m/e = 40$  and  $m/e = 39, 38, 37, 36$ , respectively. Data regression and  
220 age calculations were applied following Scaillet (2000). Regressed  $^{40}\text{Ar}/^{39}\text{Ar}$  isotopic data  
221 are tabulated in **Supplementary Material A**. Individual age errors are quoted at  $\pm 1\sigma$   
222 and include propagation of all instrumental and procedural uncertainties. Further technical  
223 details can be found in Beaudoin et al. (2020) and Laurent et al. (2021).

#### 224 4.2. Microchemistry and high-resolution electron microscopy

225 Muscovite composition was investigated in thin sections with an electron microprobe  
226 (EMP) CAMECA<sup>®</sup> SX FIVE using a 15 keV and 6 nA beam at ISTO. The surfaces of  
227 some grains initially analyzed by  $^{40}\text{Ar}/^{39}\text{Ar}$  were mapped with energy-dispersive X-ray spec-  
228 troscopy (EDS) using a 30 keV and 3.2 nA beam in a scanning electron microscope coupled  
229 with focused Ga-ion beam and scanning transmission electron detector (SEM-FIB-STEM)  
230 FEI Helios Nanolab<sup>®</sup> 660 at CIMAP. EDS chemical compositions are computed and inter-  
231 nally calibrated via the proprietary Aztec<sup>®</sup> EDS acquisition and data processing software  
232 (Oxford Instruments).

233 Microstructure was investigated on  $^{40}\text{Ar}/^{39}\text{Ar}$  dated and chemically mapped grains using  
234 transmission electron microscopy. Ion-thinned,  $\sim 100$  nm-thick lamellas (FIB foils) were  
235 extracted perpendicularly to the surface of selected samples, i.e., perpendicularly to (001)  
236 plane, using the SEM-FIB-STEM. They were imaged using the SEM-FIB-STEM operated

237 at 30 keV and via transmission electron microscopy (TEM) with a JEOL 2010F<sup>®</sup> model  
238 operated at 200 keV.

## 239 5. *IN SITU* <sup>40</sup>Ar/<sup>39</sup>Ar MAPPING RESULTS

240 *In situ* <sup>40</sup>Ar/<sup>39</sup>Ar mapping was performed on all individual grains, including two split pairs  
241 obtained by cleaving individual mica flakes (muscovite *M19* and *M21* of HP-13A). This was  
242 done in order to check for intra-sample variations in diffusive behavior at the scale of different  
243 flakes ( $\sim 50 \mu\text{m}$  thick) within the same mica specimen. Ablation pits are not systematically  
244 distributed over the same (topmost) surface layer on all samples. Some analyzes were also  
245 obtained on planes locally exposed underneath due to peripheral delamination (mechanical  
246 splitting) during extraction (cf. Fig. 4). The *in situ* data are presented as apparent age  
247 maps interpolated between ablation pits using the Kriging interpolation option of Surfer<sup>®</sup>  
248 13 software. The overall age distribution at the scale of each individual grain is displayed as  
249 a stacked probability density plot (probability density distribution plot, PDD, or ideogram,  
250 cf. Deino and Potts, 1992) constructed by summing the individual Gaussian densities of each  
251 analysis and normalizing to the total number of spots included. Also, PDD are compared  
252 with the age frequency curve integrated from the <sup>40</sup>Ar/<sup>39</sup>Ar scalar field interpolated across the  
253 pointwise data distribution for each grain and computed over of 100,000 to  $\sim 500,000$  points  
254 according to the crystal size (labelled “IAF”, for Interpolated Age Frequency). Tabulated  
255 data and figures showing the location of the ablation pits inside each crystal are provided in  
256 **Supplementary Material A**. In what follows, individual crystals from the same sample  
257 are designated with their respective label (e.g., muscovite *M3* of sample HP-10D) as reported  
258 in the plots, along with their split number #, where applicable.

### 259 5.1. Sample HP-10D (Central pluton)

260 *HP-10D (M3)*:  $N = 57$  *in situ* <sup>40</sup>Ar/<sup>39</sup>Ar ages were extracted that range from 1.3 to  
261 1.7 Ga. The PDD and the IAF spectra show a dominant mode between 1.60 and 1.65 Ga  
262 and some smaller peaks of younger age (Fig. 5a). The age map reveals two older cores  
263 approximately 350 and 500  $\mu\text{m}$  across surrounded by younger ages ( $< 1.45$  Ga) located  
264 mainly in the lower left corner of the grain in the orientation displayed.

265 *HP-10D (M9)*:  $N = 126$  ages were obtained between 1.28 and 1.73 Ga. These were  
 266 measured mainly on the topmost surface plane, but also include data from layers exposed  
 267 underneath by peripheral delamination. The PDD curve shows a dominant peak at 1.60  
 268 Ga and another at 1.40 Ga (Fig. 5b). The IAF curve shows a similar distribution, with a  
 269 more prominent peak at 1.40 Ga. The age map reveals concentric gradients with a gradual  
 270 core-to-rim younging except for the rightmost crystal side, delineating three broad sub-grain  
 271 domains (coined “sub-domains” for short hereafter).

272 *HP-10D (M10)*:  $N = 104$  ages measured on the same cleavage plane are comprised  
 273 between 1.30 and 1.72 Ga. The PDD curve shows a dominant peak at 1.4 Ga and a secondary  
 274 one between 1.60 and 1.65 Ga (Fig. 5c). The IAF curve reproduces the same peaks with an  
 275 additional one at 1.5 Ga. The age map reveals two broadly concentric core zones preserving  
 276 ages older than 1.55 Ga separated by a relatively narrow zone of younger ages between 1.50  
 277 and 1.45 Ga. Ages younger than 1.40 Ga are mostly located on the rims but also predominate  
 278 over a large area at the top left corner of the grain.

279 *HP-10D (M11)*: The  $N = 93$  data range from 1.30 to 1.73 Ga. The PDD and IAF curves  
 280 reveal an age distribution similar to *HP-10D (M3)* with a dominant peak at 1.65 Ga and  
 281 younger maxima (Fig. 5d). Again, a concentric core-to-rim rejuvenation is seen with the age  
 282 gradient locally disturbed by zones of younger ages delineating two sub-domains, 350 to 500  
 283  $\mu\text{m}$  across.

## 284 5.2. Sample *HP-13A (Central pluton)*

285 *HP-13A (M3)*:  $N = 130$  spots measured on different cleavage planes (levels) range from  
 286 1.20 to 1.70 Ga with similar PDD and IAF curves showing a dominant peak at 1.50 Ga  
 287 (Fig. 6a). A rim-ward rejuvenation pattern is seen with two cores featuring ages older than  
 288 1.55 Ga. Most of the ages younger than 1.45 Ga are from lower layers exposed in peripheral  
 289 (delaminated) areas.

290 *HP-13A (M18)*: The  $N = 128$  spot data range from 1.30 to 1.70 Ga with a more com-  
 291 plex PDD pattern showing a dominant peak at 1.60 Ga followed by a younger one at 1.40  
 292 Ga (Fig. 6b). The IAF curve shows a similar distribution. These are again associated to  
 293 concentric core-to-rim younging gradients with irregularly shaped younger zones ( $< 1.45$  Ga)  
 294 running across the crystal and isolating two sub-domains.

295 *HP-13A (M19)*: Two splits (#1 and #2) were mapped in detail. Split #1 ( $N = 123$ )  
296 covers the range 1.30-1.63 Ga with scattered peaks at 1.40, 1.45, and 1.55 Ga (revealed both  
297 by the PDD and IAF curves; Fig. 6c). Split #2 ( $N = 101$ ) ranges from 1.30 to 1.61 Ga  
298 with two well-resolved peaks at 1.55 and 1.40 Ga (Fig. 6d). Age maps of both splits define a  
299 broadly similar island-and-trough distribution, with younger ages isolating up to three cores  
300 with a characteristic dimension of 400-500  $\mu\text{m}$  (Fig. 6c, d).

301 *HP-13A (M21)*: Two splits (#1 and #2) were mapped in detail. Split #1 ( $N = 102$ )  
302 returned a range between 1.30 and 1.72 Ga. The PDD and the IAF plots show a dominant  
303 peak at 1.65 Ga (Fig. 6e). In Split #2, ages ( $N = 113$ ) range from 1.67 and 1.30 Ga. The  
304 PDD and the IAF spectra reveal two peaks at 1.65 and 1.45 Ga (Fig. 6f). The age maps  
305 show quite markedly different distributions between both splits, with two older concentric  
306 cores in Split #1,  $\sim 500 \mu\text{m}$  across, surrounded by younger ages near the rims. The rightmost  
307 core appears truncated by the rim, presumably as a result of sample comminution during  
308 extraction (Fig. 6e). Split #2 also shows a younging towards the rims but with younger  
309 ages  $< 1.45$  Ga distinctly organized in a channel-shaped zone separating the crystal into two  
310 parallel subdomains (Fig. 6f).

### 311 5.3. Sample *HP-45B* (Eastern peripheral pluton)

312 *HP-45B (M8)* has been mapped in detail with  $N = 119$  spots on different planes exposed  
313 across the external surface. Ages range from 1.25 to 1.73 Ga, the majority being comprised  
314 between 1.30 and 1.60 Ga. The PDD curve displays a broad peak extending from 1.35 to  
315 1.55 Ga (Fig. 7a). The IAF curve shows a dominant peak at 1.35 Ga. The age map shows  
316 a systematic younging towards the rims and a broad central zone of older ages arranged  
317 diagonally across the crystal.

### 318 5.4. Sample *HP-2A* (Northen peripheral pluton)

319  $N = 28$  ablations in crystal *M6* returned ages between 1.25 and 1.55 Ga with a dominant  
320 peak at 1.40 Ga (in both PDD and IAF curves) and a younging pattern towards the rim  
321 (Fig. 7b).

### 322 5.5. Sample HP-34C (Western peripheral pluton)

323 Four grains were mapped:  $M1$  ( $N = 85$ ),  $M3$  ( $N = 72$ ),  $M4$  ( $N = 85$ ) and  $M5$  ( $N = 145$ ),  
 324 all yielding significantly older ages than grains in the other locations, between 1.45–2.00 Ga  
 325 (Fig. 8). All PDD and IAF spectra show a broad unimodal peak centered about 1.65–1.70  
 326 Ga. The PDD curve for grain  $M4$  appears smoother due to larger errors in individual ages.  
 327 Unlike the central pluton samples, the age maps do not show a well-defined geometric pattern  
 328 but instead multiple peaks and troughs of older and younger ages scattered throughout the  
 329 crystals. Despite these much older ages, the youngest ages are all located on the rims.

## 330 6. MUSCOVITE CHEMISTRY AND MICROSTRUCTURE

331 To check for compositional correlations with internal  $^{40}\text{Ar}/^{39}\text{Ar}$  variations, extensive mi-  
 332 crochemical analyzes were carried out on individual crystals and across multiple crystals in  
 333 three critical samples, HP-10D, HP-13A, and HP-34C. Electron microprobe analyses show  
 334 that muscovite crystals from the central pluton (HP-10D and HP-13A) have broadly the same  
 335 chemical composition (Table 2, Fig. 9), with slight inter-facies variations notably illustrated  
 336 by the higher Mg content of HP-10D muscovite (Fig. 9b). Muscovite in the western periph-  
 337 eral facies HP-34C is distinctly enriched in Si but has lower Fe contents than the central  
 338 facies (Fig. 9a,b). Significantly, and despite these differences, all samples show a systematic  
 339 K  $\leftrightarrow$  Na anti-correlation (Fig. 9c). EMP compositional profiles performed along (001) in two  
 340 muscovite grains (one from HP-13A, the other from HP-34C) reveal that the anti-correlation  
 341 K  $\leftrightarrow$  Na is spatially associated to a rim-ward decrease in Na concentration and a concomitant  
 342 increase in K (Fig. 10). Though less pronounced, a Fe  $\leftrightarrow$  Mg anti-correlation is also apparent  
 343 along these profiles with an increase in Fe towards the rims (more apparent in the HP-13A  
 344 grain) and a concomitant decrease in Mg (more visible in the HP-34C grain). The Si content  
 345 appears homogeneous in both samples. The Al content is homogeneous in muscovite HP-13A  
 346 and increases slightly towards a rim in muscovite HP-34C (Fig. 10b).

347 For context with *in situ*  $^{40}\text{Ar}/^{39}\text{Ar}$  variations, SEM maps were performed on the  $^{40}\text{Ar}/^{39}\text{Ar}$   
 348 mapped split #1 and #2 of  $M19$  from HP-13A and split #1 from HP-13A  $M21$  (Fig. 11,  
 349 **Supplementary Material B**). As with the EMP data, while no dominant pattern is ob-  
 350 served for all major elements, Na and K display a marked anti-correlation with a systematic

351 Na decrease towards the rims, locally observed also inside the crystals. The target-matching  
352 approach employed to correlate isotope patterns with elemental patterns reveals that these  
353 antithetical variations are strongly coupled to the apparent  $^{40}\text{Ar}/^{39}\text{Ar}$  variations along (001).  
354 The slight but significant contrast in Na content from EDS maps unambiguously correlates  
355 with the  $^{40}\text{Ar}/^{39}\text{Ar}$  patterns (compare in particular Fig. 11c with Fig. 6f). The correlation  
356 is even more apparent in selected profiles showing sympathetic variations in Na content and  
357 apparent  $^{40}\text{Ar}/^{39}\text{Ar}$  age (Fig. 11). The zones depleted in Na correspond to apparent younger  
358 ages, and vice versa.

359 STEM characterization was carried out to further refine the compositional–isotope cor-  
360 relations in connection with crystal microstructure. Microstructural investigations were per-  
361 formed on two grains of HP-13A (Split #2 of *M19*, Split #2 of *M21*), as well as on grain *M11*  
362 of HP-10D (not chemically analyzed). FIB foils were extracted to compare areas depleted  
363 in Na and corresponding to younger ages, with areas enriched in Na preserving older ages  
364 (Fig. 12). In all foils, STEM images reveal the presence of extended defects parallel to the  
365 basal plane and distributed across the crystals (Fig. 12a-c). However, the density of these  
366 defects differs drastically between zones differing in Na content. Microstructural defects are  
367 much more abundant in Na-depleted zones with younger ages than in Na-rich areas preserving  
368 older ages. High magnification TEM imaging of a FIB foil extracted from a Na-depleted area  
369 of the grain HP-10D (*M11*) reveals the defects to be (001)–parallel lenticular delaminations  
370 10 to a few hundred nm-long and up to 10 nm-wide (Fig. 12d).

## 371 7. DISCUSSION

### 372 7.1. Significance of the $^{40}\text{Ar}/^{39}\text{Ar}$ gradients

373 The intracrystalline concentric age pattern revealed for all HPG micas is consistent with  
374 previous  $^{40}\text{Ar}/^{39}\text{Ar}$  crystal-mapping studies of igneous micas that suggest intra-crystalline  
375  $^{40}\text{Ar}$  transport driven by diffusion along (001) with a strong control of grain boundaries and  
376 internal microstructural defects (Phillips and Onstott, 1988; Onstott et al., 1991; Phillips,  
377 1991; Hames and Hodges, 1993; Hodges et al., 1994; Hodges and Bowring, 1995). Noteworthy,  
378 all micas in the HPG concentrate the youngest ages near the rims around a common value  
379 near 1.30–1.35 Ga. The only exceptions are the grains from the peripheral sample HP-34C.

380 On the other hand, all grains retain one (or more) irregular “core” zone(s) with variably older  
381 ages, from 1.60 Ga up to 1.73 Ga (again excluding HP-34C). Importantly, the oldest recorded  
382 ages ( $1.73 \pm 0.03$  Ga, excluding HP-34C) are strikingly close to the intrusion age estimated  
383 between 1.70 to 1.73 Ga (cf. [section 2](#)). Accordingly, we see these ages as geologically  
384 meaningful and closely matching, within the resolution of individual  $^{40}\text{Ar}/^{39}\text{Ar}$  spot ages ( $\pm$   
385 30 Ma,  $1\sigma$ ), early (magmatic) HPG growth by stepwise coalescence of multiple sills ([Nabelek](#)  
386 [et al., 2010](#)).

387 Standing apart are the older ages recorded by muscovite in HP-34C (western peripheral  
388 pluton). These ages suggest muscovite growth from a melt initially enriched in  $^{40}\text{Ar}$ , with  
389 wholesale incorporation of large amounts of non-radiogenic  $^{40}\text{Ar}$  during or after crystalliza-  
390 tion. The fact that the youngest ages are found at the rims argues for the first hypothesis,  
391 implying subsequent diffusive re-equilibration of the initial excess ([Fig. 8](#)). The much older  
392 ages of this sample compared to the others from the central pluton are also paralleled by a dis-  
393 tinctly higher Si content ([Fig. 9a](#)), suggesting particular compositional-genetic relationships  
394 specific to that peripheral pegmatitic facies.

395 The collective preservation (except for HP-34C) of near-intrusion “core” ages surrounded  
396 by an outward, diffusive-like, younging pattern is consistent with protracted cooling from  
397 initial (magmatic) stages followed by regional (crustal) slow cooling over hundreds of Myr, as  
398 previously inferred from regional-scale concentric biotite + muscovite  $^{40}\text{Ar}/^{39}\text{Ar}$  ages mapped  
399 across the HPG metamorphic aureole ([Dahl and Foland, 2008](#)). Note that the regional  
400  $^{40}\text{Ar}/^{39}\text{Ar}$  pattern excludes diffusive reopening by a later reheating pulse to explain the  
401 common “rim” age at ca. 1.30 Ga in HPG muscovite (see above). Partial diffusive resetting  
402 is not supported either by the lack of any recognized thermal event of this age in the area  
403 ([Dahl and Foland, 2008](#)).

404 *In situ* closure  $^{40}\text{Ar}/^{39}\text{Ar}$  gradients of such an extent have been already documented  
405 in igneous micas from other slowly-cooled intrusives elsewhere in the southwestern United  
406 States Proterozoic orogenic belt (south-central Arizona: Crazy Basin monzogranite, [Hames](#)  
407 [and Bowring, 1994](#); [Hodges et al., 1994](#); Horse Mountain biotite, [Hodges and Bowring, 1995](#)).  
408 Such internal age gradients due to slow cooling were not anticipated here on account of the  
409 dominantly flat  $^{40}\text{Ar}/^{39}\text{Ar}$  release spectra previously documented by step-heating experiments



410 on HPG muscovite (Dahl and Foland, 2008; Holm et al., 1997). As emphasized by Hodges and  
411 Bowring (1995), incremental heating results in dehydroxylation of micas that can homogenize  
412 intracrystalline  $^{40}\text{Ar}$  gradients, as independently shown by Gaber et al. (1988) and Sletten  
413 et al. (1998). Such an artifact is also demonstrated by our new data and most likely explains  
414 why this feature passed undetected in past  $^{40}\text{Ar}/^{39}\text{Ar}$  studies of the HPG and its country  
415 rocks.

#### 416 7.2. $^{40}\text{Ar}$ diffusion-domain structure of HPG muscovite

417 The irregular geometry of the age gradients along (001) in all HPG muscovite grains  
418 indicates that  $^{40}\text{Ar}$  retention during progressive cooling was not strictly controlled by a  
419 single volume-diffusion mechanism. This pattern is reminiscent of the complex  $^{40}\text{Ar}/^{39}\text{Ar}$   
420 closure gradients just mentioned for the slowly-cooled micas analyzed by Hames and Hodges  
421 (1993), Hodges et al. (1994), and Hodges and Bowring (1995). This pattern was explained  
422 by Hodges and Bowring (1995) via a double mechanism involving volume diffusion on a scale  
423 comparable to that of the grain radius with rapid diffusion along discrete zones of high crystal  
424 defect density. Subsequent work by the Lausanne group (notably Kramar et al., 2001, 2003;  
425 Kramar, 2002) indeed showed that internal deformation structures can promote localized  
426 intracrystalline  $^{40}\text{Ar}$  loss in strongly deformed (porphyroclastic) muscovite via a network of  
427 localized defects (unit dislocations and stacking faults bordered with partial dislocations)  
428 cutting across the crystal. The Crazy Basin and Horse Mountain monzogranites cooled  
429 mostly underformed after static crystallization (as the HPG did), which excludes subsolidus  
430 deformation as a major cause for defect-enhanced  $^{40}\text{Ar}$  loss in these texturally simple micas.  
431 Unfortunately, neither Hames and Hodges (1993), Hames and Bowring (1994), Hodges et  
432 al. (1994), nor Hodges and Bowring (1995) could document the intracrystalline structure of  
433 their samples to aid in the identification of the microstructures responsible for the irregular  
434 domain-like  $^{40}\text{Ar}$  loss pattern produced during progressive cooling.

435 Here, the combination of high spatially-resolved *in situ*  $^{40}\text{Ar}/^{39}\text{Ar}$  dating, microchemistry,  
436 and high-resolution electron microscopy data unambiguously document direct coupling be-  
437 tween age, composition and microstructure. In particular, our data show that the  $^{40}\text{Ar}/^{39}\text{Ar}$   
438 gradients and Na/K variations are coupled at the scale of the whole grains, to the point

439 of permitting targeting of critical zones for TEM imaging based on the observed isotope-  
440 elemental patterns. This allows us to address fundamental aspects of the diffusion-domain  
441 structure of muscovite, notably (i) the origin of the observed Na/K zoning, (ii) the relation-  
442 ship to microstructural defects, and (iii) their respective role in the development of the  $^{40}\text{Ar}$   
443 diffusional gradients. These aspects are explored in turn below.

#### 444 7.2.1. Origin of $\text{K} \leftrightarrow \text{Na}$ zonations

445 The dependence of  $^{40}\text{Ar}$  diffusion on the Na/K ratio is obvious from the close spatial  
446 association between domains featuring younger ages and low Na/K ratios, mostly around  
447 the rims but also invading the grain interiors (Section 6). Less apparent is the nature of the  
448 interaction coupling elemental with isotopic transfer at the scale of the whole crystals and  
449 the interlayer proper.

450 The textural Na/K pattern is systematic, both within grains of the same sample and across  
451 the sample suite as a whole. Atomic  $\text{K} \leftrightarrow \text{Na}$  interdiffusion is attested by the near-unity ratio  
452 between the number of atoms lost (Na) to those gained (K) in muscovite from HP-13A and  
453 HP-34C (Fig. 13). Texturally, the Na and K concentration profiles near the muscovite rims  
454 are smooth and distinct from stepped profiles typically associated with overgrowth (Sio et al.,  
455 2013). This implies  $\text{K} \leftrightarrow \text{Na}$  substitutional exchange (sometimes paralleled by a sympathetic  
456  $\text{Fe} \leftrightarrow \text{Mg}$  substitution as well) due to grain-boundary disequilibrium independent of bulk  
457 composition and driven by post-crystallization interaction with either some K-rich residual  
458 magmatic liquid near the solidus (or any exsolved fluid from the magma), or late K-rich  
459 hydrothermal fluids after complete solidification.

460 Disequilibrium interactions with intercumulus residual liquid at near-solidus temperatures  
461 can result either in topotactic overgrowth by a chemically distinct rim, or in crystal dissolu-  
462 tion with replacement by other phases. Petrographic observations show that some muscovite  
463 grains are corroded/embayed and locally replaced by magmatic phases (e.g., quartz; Fig. 2e,  
464 f), effectively indicating local/transient disequilibrium with the residual melt. EMPA tra-  
465 verses show that local Na/K gradients are not truncated by partial dissolution-replacement  
466 textures, and thus post-date (or accompany) resorption at magmatic- $T$  (Fig. 10b). A high-K  
467 residual melt was invoked by Nabelek and Ternes (1997) to explain the chemical and textural

relationships between aplitic and pegmatitic layers in the HPG. They suggest magma evolution characterized by liquidus crystallization of sodic minerals (plagioclase and tourmaline) under low  $H_2O$  activity, followed by crystallization of a relatively potassic residual melt under higher  $H_2O$  activity. Oxygen isotope ratios between quartz and other minerals indicate  $\Delta^{18}O$  equilibration values between 800 and 650 °C, between liquidus and solidus (Nabelek et al., 1992b).  $\delta D$  values in micas are also compatible with magmatic temperatures, except for limited post-crystallization interactions with non-magmatic fluids in the southern part of the HPG (Nabelek et al., 1992b). Coupled with the resorption texture, these high- $T$  estimates are consistent with incongruent dissolution coeval with partial re-equilibration of muscovite to higher Na/K values at the rims locally affected by replacement (and locally reaching into the core as well, Fig. 10b).

Fluid-inclusion microthermometry of HPG quartz and tourmaline provides evidence for two generations of magmatic fluids trapped in at least three types of inclusions (Nabelek and Ternes, 1997; Sirbescu and Nabelek, 2003). Type 1 inclusions are  $H_2O + CO_2$  mixtures trapped as primary inclusions at temperatures above the solidus in magmatic quartz and tourmaline. Type 2 and 3 inclusions are secondary inclusions trapped along healed microfractures in quartz. These are rich in  $H_2O$  and  $CO_2$ , respectively, and are interpreted to have resulted from re-equilibration and unmixing of Type 1 fluids that progressively changed composition and density with decreasing temperature and pressure. They were trapped under subsolidus conditions and are likely candidates for late-stage interaction and exchange with muscovite at subsolidus conditions as well. While the low solubility of alkali chlorides in  $CO_2$ -rich fluids (Webster et al., 1989) precludes the carbonic fraction from causing K enrichment, the abundance of alkalis (including Na, K, and Li) is noted in primary mixed fluid inclusions (Nabelek and Ternes, 1997; Sirbescu and Nabelek, 2003).  $(Na/K)_{\text{musc}}/(Na/K)_{\text{fluid}}$  exchange partitioning strongly favors incorporation of K over Na into muscovite, even at low Na/K fluid-ratios (Volfinger 1976). This may explain the inward K enrichment seen in muscovite, although this is not texturally tied to the muscovite habitus as is the resorption at magmatic temperatures. K-rich aqueous fluids coupled to textural replacement are documented only locally in the contact aureole, but in the reverse sense with staurolite replaced by muscovite (Nabelek et al., 2006).

498 Together, textural, fluid-inclusion thermometry, and stable isotopes relationships argue  
 499 for Na/K interchange occurring either at late-magmatic or subsolidus conditions, in any case  
 500 very early during high- $T$  cooling + solidification of the HPG. Kinetically, the nature of the  
 501 interaction between  $K \leftrightarrow Na$  interdiffusion and  $^{40}\text{Ar}$  diffusion is unlikely to have involved  
 502 dynamic coupling. The inward  $K \leftrightarrow Na$  diffusion profiles are on average 300  $\mu\text{m}$ -long  
 503 (Fig. 10 and Fig. 11). Considering a diffusion coefficient for K of  $6 \times 10^{-17} \text{ cm}^2 \cdot \text{s}^{-1}$  at 650  $^\circ\text{C}$   
 504 (Nteme et al., 2022), a diffusion duration of only  $\sim 0.1$  Myr is required to produce such  
 505 profiles. This is more than three orders of magnitude shorter than the time span of several  
 506 hundreds of Myr recorded by the  $^{40}\text{Ar}/^{39}\text{Ar}$  zoning patterns. These timescales are clearly  
 507 decoupled and indicate that solid-state  $K \leftrightarrow Na$  interdiffusion must have stopped well before  
 508 the development of intracrystalline  $^{40}\text{Ar}/^{39}\text{Ar}$  age gradients.

#### 509 7.2.2. Genetic connection to lenticular defects

510 While direct (dynamic) coupling cannot be invoked between  $^{40}\text{Ar}$  diffusion and  $K \leftrightarrow Na$   
 511 exchange, static-compositional effects can indirectly affect  $^{40}\text{Ar}$  diffusivity via the modifica-  
 512 tions they impart to the mica structure, notably via the  $\text{FeMg}_{-1}$  substitution and Tschermak  
 513 exchange (e.g., Norwood, 1974; Harrison et al., 1985; Scaillet et al., 1992; Dahl, 1996).  $K \leftrightarrow$   
 514  $Na$  substitution along the muscovite-paragonite join similarly involves crystallographic modi-  
 515 fications, in particular the decrease of the interlayer spacing along the  $c$ -axis with increasing  
 516  $Na$  (Guidotti, 1984). This may increase the migration barrier for  $^{40}\text{Ar}$  along the (001) plane,  
 517 potentially lowering diffusivity in  $Na$ -rich domains. However, the overwhelming abundance  
 518 of the interlayer cation  $K$  ( $\sim 0.90$  a.p.f.u) over  $Na$  ( $\sim 0.07$  a.p.f.u) and the relatively modest  
 519 change in  $K/(K+Na)$  ratio between  $Na$ -rich and  $Na$ -poor zones ( $< 1\%$ ) in HPG muscovite  
 520 are unlikely to have induced major variations in effective  $^{40}\text{Ar}$  diffusivity across composition-  
 521 ally distinct zones. This is independently corroborated by Molecular Dynamics simulations  
 522 as well (Nteme, 2021).

523 Coupled variations between  $^{40}\text{Ar}/^{39}\text{Ar}$  age and  $Na/K$  ratio have been already documented  
 524 by Boundy et al. (1997) in muscovite from eclogites of the Holsnøy Island (Norway). Using  
 525 target-matching techniques as here, they found homogeneous *in situ* laser ages around 443  
 526 Ma in crystals with homogeneous  $Na/K$  ratio, in contrast to much older and heterogeneous

527 ages (445–625 Ma) in muscovite exhibiting higher and variable Na/K. Resolved (5–100 nm  
528 scale) analytical electron microscopy (AEM) on the same sample revealed variable Na/K,  
529 but no separate paragonite domains. In contrast, muscovite grains with homogeneous ages  
530 showed little Na/K variability at the microprobe level. A broad, within-crystal, correlation  
531 was suggested between Na-rich zones and older ages inside their sample BA59/89 (grain  
532 1), but the cross-matching coverage is less well-resolved than here. This precluded clear  
533 attribution of compositional effects on internal  $^{40}\text{Ar}/^{39}\text{Ar}$  patterns. Although no discernible  
534 intracrystalline defects were detected, splitting of SAED (00 $l$ ) diffraction patterns indicated  
535 intergrown micas with different basal spacing, most probably muscovite and sodic muscovite  
536 interlayered at the unit cell level (< 5 nm). To explain the irregular  $^{40}\text{Ar}$  distribution, [Boundy  
537 et al. \(1997\)](#) invoked a process of volume-diffusive loss of excess  $^{40}\text{Ar}$  initially incorporated  
538 at eclogite-facies conditions, locally mediated by nanostructural heterogeneities at the scale  
539 of the interlayer.

540 In our case, layer-parallel defects (lenticular voids and basal parting) are seen that directly  
541 correlate in distribution and density with the Na/K maps (and the  $^{40}\text{Ar}/^{39}\text{Ar}$  ages). Identifi-  
542 cation of these nanostructures and their interpretation as primary defects is not unequivocal  
543 however. Lenticular voids parallel to (001) similar to those documented are reported in other  
544 TEM studies of phyllosilicates ([Veblen, 1983](#); [Ahn et al., 1986](#); [Amouric, 1987](#); [Goodwin and  
545 Wenk, 1990](#); [Merriman et al., 1990](#); [Onstott et al., 1991](#); [Phillips, 1991](#); [Shau et al., 1991](#);  
546 [Ahn and Buseck, 1998](#); [Giorgetti et al., 2000](#); [Kramar, 2002](#); [Capitani et al., 2016](#); [Aslin et  
547 al., 2019](#)). They have been variably attributed to Guinier-Preston zones ([Onstott et al., 1991](#);  
548 [Phillips, 1991](#)), deformation ([Amouric, 1987](#); [Kramar, 2002](#); [Aslin et al., 2019](#)), or electron  
549 beam damage ([Veblen, 1983](#); [Ahn et al., 1986](#); [Goodwin and Wenk, 1990](#); [Merriman et al.,  
550 1990](#); [Shau et al., 1991](#); [Ahn and Buseck, 1998](#); [Giorgetti et al., 2000](#); [Capitani et al., 2016](#)).

551 By exposing paragonite to increasing durations and intensities of TEM electron beam,  
552 [Ahn et al. \(1986\)](#) observed a progressive degradation of the crystal structure manifested by  
553 abundant delaminations (lenticular voids) normal to the  $c$ -axis. These were correlated to a  
554 loss of Na leaving Al and Si unaffected. The voids were interpreted as damage zones caused  
555 by Na loss from the interlayer region under the beam, with the collapse of the paragonite  
556 structure to a pyrophyllite-like structure causing volume loss and reduction of basal spacing.

557 Mechanical parting of paragonite layers along (001) was inferred to be caused by the release  
558 of the elastic strain due to local collapse of the structure.

559 Our FIB samples were imaged by STEM at 30 kV. To investigate the effect of extended  
560 exposure to the beam, a succession of three images was gathered over the same area of a FIB  
561 foil from grain *M11* of HP-10D but the defects observed in the first image did not evolve  
562 appreciably further on (see **Supplementary material C**, Fig. S-C-1). Further FIB testing  
563 of another muscovite with similar composition under identical thinning and beam conditions  
564 revealed no visible microstructural defect (muscovite SSY92-9, St. Sylvestre leucogranite,  
565 Massif Central, France; [Scaillet et al., 1996](#)) (**Supplementary material C**, Fig. S-C-2).  
566 Together, both tests rule out beam and thinning artifacts as the primary cause of the observed  
567 defects as they would have equally affected both specimens. Note also that lenticular voids  
568 commonly identified as beam damage in white micas are systematically reported for Na-rich  
569 (paragonite) endmembers ([Ahn et al., 1986](#); [Giorgetti et al., 2000](#)), not for compositionally  
570 intermediate micas with low Na/K as studied here (and in [Boundy et al., 1997](#), who could  
571 not identify beam damage in their moderately Na-enriched muscovite either).

572 These observations strongly argue for the defects being primary. Because the muscovite  
573 samples are undeformed, the critical observation that the density and distribution of defects  
574 correlate with the intracrystalline Na/K zoning ([Fig. 12](#)) suggests a genetic link with the  $K \leftrightarrow$   
575 Na exchange during early (near-solidus) cooling as discussed in Section 7.2.1. Microstructural  
576 defects induced by  $K \leftrightarrow$  Na interdiffusion have not been described as such in micas, but are  
577 known in alkali feldspar ([Neusser et al., 2012](#); [Scheidl et al., 2014](#); [Petrishcheva et al. 2019](#)).  
578 In feldspar, lattice mismatch between Na- and K-rich domains produced by local variations  
579 in  $K \leftrightarrow$  Na exchange can result in tensile stress buildup triggering internal fracturing once  
580 a threshold is exceeded ([Scheidl et al., 2014](#)). In micas, K and Na segregate along the  
581 interlayer plane into immiscible nanodomains of pure muscovite and paragonite due to their  
582 different sizes ([Shau et al., 1991](#); [Livi et al., 2008](#)). The segregation of interlayer cations into  
583 immiscible nanodomains is coupled with the segregation of octahedral cations as well ([Livi](#)  
584 [et al., 2008](#)), so that paragonite domains have higher Al/Si ratio than muscovite domains  
585 (which are more phengitic). Such coupled changes involve rotation and corrugation of the  
586 tetrahedra required to match the smaller Na into the XII site while the octahedra become

587 larger and tend to flatten with increasing phengite content. At some point, the tetrahedral  
588 and octahedral sheets can no longer fit together (Radoslovich, 1960; Guidotti, 1984) and the  
589 stress buildup due to the mismatch at the interface between the muscovite and paragonite  
590 nanodomains may trigger splitting along the interlayer, producing the observed lenticular  
591 defects.

592 To conclude, the higher defect density seen in K-substituted, Na/K intermixed, subdo-  
593 mains of HPG muscovite may be either a direct manifestation of incoherent stress-induced  
594 delamination nucleating between isostructural packets of layers with variable Na/K ratio  
595 (Fig. 12), or the indirect consequence of structural recombination due to Na–K segregation  
596 at the elementary stacking level (nanodomains). Along with the Holsnøy precedent (Boundy  
597 et al., 1997), these observations suggest that  $K \leftrightarrow Na$  exchange materially affects the in-  
598 terlayer  $^{40}\text{Ar}$  diffusivity of white micas. The irregularly depressed non-Fickian profiles seen  
599 near the rims and locally reaching into the core indicate that  $^{40}\text{Ar}$  diffusivity is enhanced  
600 directly by these microstructural defects or via the underlying substitutional-structural mech-  
601 anism(s) affecting the interlayer. This further suggests that these defects, although appearing  
602 isolated, must be interconnected into a network of pathways to provide access to the exter-  
603 nal grain-boundary medium. They do not necessarily act as traps as sometimes suggested  
604 (e.g. Camacho et al., 2012). Importantly, inter-split variations in  $K \leftrightarrow Na$  exchange (Fig. 11  
605 and Fig. 12) and  $^{40}\text{Ar}/^{39}\text{Ar}$  maps (Fig. 6c,d,e,f) show that these channeled, layer-parallel,  
606 defects involve little cross-layer communication beyond  $50\ \mu\text{m}$  (the penetration depth of the  
607 UV–probe).

### 608 7.3. $^{40}\text{Ar}$ diffusion geometry and multipath diffusion

609 Depending on their topology (e.g., crystallographic orientation, spacing, distribution, and  
610 interconnectivity), extended lattice defects can either impart a discrete multi-domain diffu-  
611 sion behavior (MDD model, Lovera et al., 1989), or a wholesale multi-path diffusion regime  
612 where two or more mechanisms continuously interact through the bulk of the crystal (Phillips,  
613 1991; Lee, 1995). Schematically, the MDD model assumes no interaction between sub-crystal  
614 domains with instant (very-high diffusivity) access to the grain boundary network whenever  
615 a domain boundary is reached. In contrast, the multipath model assumes a continuum across  
616 the lattice till the grain boundary.

617 The mapped  $^{40}\text{Ar}/^{39}\text{Ar}$  distributions bear directly on such “continuous *vs.* discrete”  
618 typology of the diffusive network along (001). Rather than the juxtaposition of discrete sub-  
619 domains, the internal age contours and gradients interpolated by kriging reveal a dominantly  
620 fuzzy pattern with a diffusive lengthscale commensurate with the grain size (Figs. 5, 6, 7).  
621 The extent of the age gradients clearly indicates that the interpolated  $^{40}\text{Ar}/^{39}\text{Ar}$  scalar fields  
622 are a fair representation of the true  $^{40}\text{Ar}$  intragrain diffusive network. In parallel, optical and  
623 electron microscopy reveal an array of layer-parallel nano-structural defects disseminated and  
624 correlated to the  $\text{K} \leftrightarrow \text{Na}$  exchange at the scale of the whole crystals (Section 7.2.2), with  
625 no evidence of intragranular cracks, kinks, or segmentation susceptible to cut across (and  
626 reduce) the effective diffusion radius.

627 We tested the continuous *vs.* discrete  $^{40}\text{Ar}$  diffusion-domain typology by plotting the  
628 apparent percentage of defect-rich areas integrated along (001) against the maximum age  
629 recorded by grains of the central pluton (including pits only distributed over the same topmost  
630 surface layer). The percentage of defect-rich areas cannot be assessed directly but may be  
631 approximated by the areal proportion of zones featuring apparent ages younger than 1.5  
632 Ga. This threshold is arbitrary but corresponds to the isopleths in the  $^{40}\text{Ar}/^{39}\text{Ar}$  maps that  
633 most closely match the zones of coupled Na-defect pattern in Fig. 11 and Fig. 12. The plot  
634 (Fig. 14a) reveals a well-defined negative correlation for a collection of grains varying widely  
635 in shape and average radius (note that the correlation remains fairly identical,  $R^2 > 0.8$ ,  
636 for a cut-off between 1.43–1.59 Ga). The internal age variability does not correlate in any  
637 obvious way with the average radius of the crystals (Fig. 14b). In particular, we see no scaled  
638 progression between the maximum age(s) recorded in a crystal and the shortest distance to  
639 the rim or a discrete fast-path drain or grain segmentation hypothetically running nearby  
640 (i.e., the MDD prediction; Fig. 14c). Instead, the negative correlation indicates that, at  
641 any point in the muscovite crystals and irrespective of their dimension, the oldest recorded  
642 age is directly controlled by the overall defect structure integrated throughout the whole  
643 grain, not by discrete extended defects located nearby. This observation strongly argues for  
644 the multipath model and flies in the face of the notion that MDD modeling of muscovite  
645 incremental heating data is an adequate description of the processes taking place in real  
646 samples.



647 A multipath model accounting for the presence of layer-parallel defects was already sug-  
 648 gested for muscovite by Kramar and co-workers (Kramar et al., 2001, 2003) to explain prefer-  
 649 ential  $^{40}\text{Ar}$  loss along stacking faults developed along (001) by basal slip during intragranular  
 650 shear. Basal slip by partial dislocation glide along (001) leads to localized repulsive forces  
 651 with a net dilation (and enhanced  $^{40}\text{Ar}$  mobility) along the interlayer. While transient, the  
 652 transport efficiency along these defects can be much greater than pipe diffusion because the  
 653 volume fraction of the lattice swept over by moving dislocations during ongoing deformation  
 654 is orders of magnitude higher (Kramar et al., 2003). In the HPG case there is clearly no such  
 655 a deformation drive. This role is played by the irreversible modifications brought about by  
 656 the  $\text{K} \leftrightarrow \text{Na}$  exchange that locally served as a guide for enhanced  $^{40}\text{Ar}$  diffusion along (001).

657 Summing up, the spatial continuum inferred from the  $^{40}\text{Ar}$  concentration gradients calls  
 658 for a model combining multi-path diffusion with spatially variable domains characterized by  
 659 distinct bulk diffusivities. These are internally controlled by their own defect density leading  
 660 to a mosaic of high-diffusivity *zones* (rather than *pathways*) coexisting with (or transitioning  
 661 smoothly into) low-defect zones preserving near-regular lattice diffusion constants.

#### 662 7.4. Quantitative modeling of the $^{40}\text{Ar}$ diffusion-domain structure

663 To contrast quantitatively the diffusion rates in defect-poor (slow-diffusing) domains with  
 664 those prevailing in defect-rich (fast-diffusing) domains, we devise a simple 2D diffusion model  
 665 along (001) according to:

$$666 \quad \frac{\partial C}{\partial t} = D(t) \left( \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} \right) + S(t) \quad (1)$$

667 where  $C$  is the  $^{40}\text{Ar}$  concentration,  $D(t)$  its time-varying diffusivity, and  $S(t)$  the production  
 668 term due to spontaneous  $^{40}\text{K}$  decay:

$$669 \quad S(t) = \lambda_e {}^{40}\text{K}_0 \exp(-\lambda t) \quad (2)$$

670 with  $\lambda_e = 0.581 \times 10^{-1} \text{ Ga}^{-1}$  and  $\lambda = 5.543 \times 10^{-1} \text{ Ga}^{-1}$  (Steiger and Jäger, 1977).  ${}^{40}\text{K}_0$   
 671 is the initial K concentration at  $t_0$ . We consider a cooling model deduced from independent  
 672  $T-t$  couples reviewed in Dahl and Foland (2008) and parametrized as (cf. Fig. 15):

$$673 \quad T_{\text{mid}}(t) = 272 \exp(-0.04t) - 0.409t + 751 \quad (3)$$

674 with  $T_{\text{mid}}$  in Kelvin and  $t$  in Ga. The exponential term accounts for conductive cooling *in situ*  
 675 in the country rocks, followed by steady-state (linear) cooling of the crust (+ intrusion) during  
 676 progressive exhumation (see discussion in [Dahl and Foland, 2008](#)). Bounding curves  $T_{\text{min}}(t)$   
 677 and  $T_{\text{max}}(t)$  are defined to bracket the cooling curve arbitrarily within  $\pm 50$  °C ([Dahl and](#)  
 678 [Foland, 2008](#)). Homogeneous initial and boundary conditions are assumed at  $t_0 = 1.715$  Ga,  
 679 along with spatially uniform  $^{40}\text{K}_0$  and  $S(t)$  across all crystals during cooling. Since the HPG  
 680 was emplaced at shallow depths with protracted cooling during tectonic quiescence (very  
 681 slow exhumation; [Holm et al., 1997](#); cf. Section 2), the pressure effect on  $D(t)$  is neglected  
 682 in the model. The loss-production Eq. (1) is solved by a finite-element scheme accounting  
 683 for the specific grain geometry in 2D along (001) under MATLAB<sup>®</sup>. The computed 2D  $^{40}\text{Ar}$   
 684 concentration field is converted into a map of apparent ages,  $t_{\text{app}}$ , via:

$$685 \quad t_{\text{app}} = \frac{1}{\lambda} \ln \left( 1 + \frac{\lambda}{\lambda_e} \frac{C(t)}{K(t)} \right) \quad (4)$$

686 where  $C(t)$  and  $K(t)$  are the concentration of  $^{40}\text{Ar}$  and  $^{40}\text{K}$  at time  $t$ , respectively.

#### 687 7.4.1. Defect-free $^{40}\text{Ar}$ diffusion kinetics

688 Our goal here is to model  $^{40}\text{Ar}$  volume diffusion in grains that preserve regular concentric  
 689 gradients with core values approaching or overlapping the HPG intrusion age ( $\geq 1.70$  Ga).  
 690 This age is found in four grains from the central pluton (HP-10D (*M9*), HP-10D (*M10*),  
 691 HP-10D (*M11*) and HP-13A (*M21-#1*), [Fig. 5](#) and [Fig. 6e](#)), indicating that diffusive loss  
 692 out from the core of these grains became inefficient very early during subsolidus cooling.  
 693 An estimate of the maximum diffusivity preserving these core ages would provide an upper  
 694 empirical bound on  $^{40}\text{Ar}$  diffusivity.

695 We focused on muscovite *M11* of HP-10D ([Fig. 5d](#)). In addition to exhibiting regular  
 696 concentric age gradients centered on an intrusion-like age of  $1.73 \pm 0.03$  Ga, this grain  
 697 retains original pristine edges with dimensions representative of most other grains. Assuming  
 698 a spatially homogeneous volume-diffusion coefficient  $D_v$  given by:

$$699 \quad D_v(t) = D_0^v \exp \left( - \frac{E_v}{RT(t)} \right) \quad (5)$$

700 we use Eq. (1) along with the cooling models of [Fig. 15](#) to find the maximum frequency factor  
 701  $D_0^v$  reproducing the core age for a range of exploratory activation energies typical of micas

702 (including biotite and phlogopite:  $E_v = 40\text{--}70 \text{ kcal.mol}^{-1}$ ; Robbins, 1972; Giletti, 1974;  
 703 Harrison et al., 1985; Hames and Bowring, 1994; Grove and Harrison, 1996; Kirschner et al.,  
 704 1996; Harrison et al., 2009; Forster and Lister, 2014; Nteme et al., 2022). The  $E_v\text{--}D_0^v$  pairs  
 705 empirically found to fit the core retention age trade-off in Arrhenian space with a single well-  
 706 defined cross-over point for each model considered (Table 3). In an Arrhenius plot (Fig. 16a),  
 707 these collectively define a diffusivity domain (orange field) delineating an upper bound below  
 708 which any  $E_v\text{--}D_0^v$  couple would preserve the core age as well. Experimental and empirical  
 709 diffusion estimates (Hames and Bowring, 1994; Kirschner et al., 1996; Harrison et al., 2009)  
 710 plot up to two orders of magnitude above this upper bound. In contrast, the Arrhenian  
 711 relationship derived from atomistic simulations by Nteme et al. (2022) plots within the  
 712 domain, independently supporting the sluggish  $^{40}\text{Ar}$  diffusion behavior theoretically predicted  
 713 for undefective muscovite. Remarkably, while reproducing the target core age, the modeled  
 714  $E_v\text{--}D_0^v$  pairs all predict a rather flat core-to-rim profile, at odds with the depressed gradients  
 715 empirically revealed by  $^{40}\text{Ar}/^{39}\text{Ar}$  crystal-mapping (Fig. 16b). Such a mismatch clearly  
 716 indicates that the observed age distribution should be approximated with a composite model  
 717 allowing for substantially higher diffusion rates than those preserving the core age.

#### 718 7.4.2. Defect-enhanced $^{40}\text{Ar}$ diffusion rates

719 We now test a spatially-variable diffusion model in which  $^{40}\text{Ar}$  migrates simultaneously  
 720 along defect-poor and defect-rich paths with different diffusivities. This case has been already  
 721 treated by Kramar et al. (2003) to account for extended intracrystalline defects affecting the  
 722 internal diffusion-domain structure of deformed porphyroclastic muscovite in a mylonite. The  
 723 diffusion coefficient in Eq. (1) is replaced by an effective diffusion coefficient defined as (Hart,  
 724 1957):

$$725 \quad D_{\text{eff}}(t) = f_d D_d(t) + (1 - f_d) D_v(t) \quad (6)$$

726 where  $f_d$  is the volume fraction of defects in the considered domain and  $D_d$  the limiting  
 727 diffusivity along the defective path. Eq. (6) provides an upper limit for  $D_{\text{eff}}$  in the case of  
 728 diffusivity along parallel pathways, which amounts to neglect tortuosity. The defect density  
 729 (here  $f_d$ ) is assumed to be low on account of STEM observations. On the other hand, the  
 730 contrast between  $D_v$  and  $D_d$  should be high to allow strongly depressed  $^{40}\text{Ar}/^{39}\text{Ar}$  gradients

731 to develop away from the cores (Fig. 16b). In the limit  $f_d \ll 1$  and  $D_v \ll D_d$ , Eq. (6)  
 732 simplifies to its first term that we assume to follow the Arrhenian form:

$$733 \quad D_{\text{eff}}(t) = f_d D_d(t) = f_d D_0^d \exp\left(-\frac{E_d}{RT(t)}\right) \quad (7)$$

734 A mean-field approximation making no assumption of specific diffusive anisotropy (the  
 735 Maxwell approximation) would reduce this estimate by a factor of 2/3 (Mehrer, 2007), which  
 736 is immaterial in terms of order-of-magnitude characterization of the process.  $^{40}\text{Ar}$  diffusivity  
 737 in microstructural defects is poorly constrained, but an activation energy between 40–45  
 738 kcal.mol $^{-1}$  is commonly assumed (Lee, 1993; Kramar, 2002). In the following, we take  $E_d =$   
 739 45 kcal.mol $^{-1}$ .

740 We focused again on muscovite *M11* of HP-10D, including also the splits of grains *M21* and  
 741 *M19* from HP-13A (Fig. 5d and Fig. 6c,d,f). The crystals were subdivided into several sub-  
 742 grain domains mimicking the Na/K and/or age zoning and the lumped parameter  $\psi_d = f_d D_0^d$   
 743 was then adjusted by trial and error for each domain to match the internal 2D age pattern.  
 744 Best-matching  $\psi_d$  values adjusted for each domain in each grain are listed in Table 4. The  
 745 geometry and extent of the modeled domains are displayed for each grain in Fig. 17 along with  
 746 the empirical  $^{40}\text{Ar}/^{39}\text{Ar}$  age map, the simulated age map, and a selected profile comparing  
 747 observations with predictions. For a fair comparison, the simulation maps were interpolated  
 748 via Surfer<sup>®</sup> 13 based on the nodes strictly coinciding with the *in situ* position of the ablation  
 749 pits across the crystals. Fig. 17 shows that the 2D  $^{40}\text{Ar}/^{39}\text{Ar}$  grain-scale patterns are fairly  
 750 well reproduced by this relatively simple model. Core-to-rim  $^{40}\text{Ar}/^{39}\text{Ar}$  age profiles broadly  
 751 agree between observations and model, although in some cases the oldest age is not well  
 752 reproduced (e.g., *M11* grain of HP-10D, Fig. 17a).

753 Diffusivity estimates empirically inferred for defect-rich sub-domains in the four modeled  
 754 grains define a broad domain in Arrhenian space (blue field in Fig. 18). These are enhanced  
 755 by a factor of up to 6 or 10 orders of magnitude (between 700–300 °C) compared to the  
 756 ideal, defect-free, lattice diffusion model (Nteme et al., 2022, trend labelled “4” in Fig. 18).  
 757 This enhancement accounts for an overall “extra” loss around 15 % as estimated from the  
 758 mean age of each individual muscovite grain relative to the intrusion age (1.715 Ga). Along  
 759 with previous studies (Kramar et al., 2001, 2003), these results show that microstructural

760 defects can considerably affect  $^{40}\text{Ar}$  retention properties of muscovite, including undeformed  
 761 primary magmatic specimens. Interestingly, all previous experimental and empirical diffusion  
 762 estimates (Hames and Bowring, 1994; Kirschner et al., 1996; Harrison et al., 2009) plot within  
 763 the domain of enhanced diffusivity defined in Fig. 18, suggesting they likely derive from  
 764 muscovite containing microstructural defects as well. Combined with theoretical predictions  
 765 (Nteme et al., 2022) and the present results, these field and laboratory-based estimates  
 766 collectively define the  $D$ – $T$  field probably spanned by  $^{40}\text{Ar}$  kinetics in natural muscovite  
 767 (dashed domain in Fig. 18).

768 Implicit in Eq. (7) is that the limiting diffusivity  $D_d(t)$  is the same for all defective  
 769 domains, and that the inferred variations in  $\psi_d$  (Fig. 17 and Table 4) directly correlate to  
 770 spatial variations in  $f_d$  (and the implied orders-of-magnitude variations in relative defect  
 771 densities). If, as is more likely,  $f_d$  and  $D_0^d$  are not directly (linearly) coupled,  $\psi_d$  variations  
 772 cannot be tied to defect density variations. This is the main issue still to be resolved. Further  
 773 characterization by dedicated FIB-STEM/TEM imaging and MD modeling is clearly required  
 774 to understand how  $D_0^d$  and  $f_d$  are coupled in terms of defect structure and enhanced atomic-  
 775 scale  $^{40}\text{Ar}$  mobility.

## 776 8. SUMMARY AND CONCLUSIONS

777  $^{40}\text{Ar}$  diffusion in slowly cooled muscovite from the HPG pluton has been investigated  
 778 using target-matching techniques combining extensive  $^{40}\text{Ar}/^{39}\text{Ar}$  *in situ* mapping ( $> 1,600$   
 779 individual measurements) with elemental mapping and high resolution electron microscopy.  
 780 The main results can be summarized as follows.

781  
 782 •  $^{40}\text{Ar}/^{39}\text{Ar}$  crystal-mapping reveals irregular, mm-size, concentric age patterns due to pro-  
 783 tracted cooling across the  $^{40}\text{Ar}$  retention interval of muscovite; these define a mosaic-like  
 784 structure with sub-domains, broadly  $\sim 250$ – $300 \mu\text{m}$  across, separated by zones of high dif-  
 785 fusivity varying in shape and extent along (001).

786  
 787 • Each grain is unique, with splits of the same crystal recording themselves widely vary-  
 788 ing internal  $^{40}\text{Ar}/^{39}\text{Ar}$  patterns and extent of retentivity. The maximum ages preserved in

789 the core(s) are unrelated to either the size of the specific subdomain or the overall dimension  
790 of the host crystal; they vary primarily in connection with the areal extent of high-diffusivity  
791 zones distributed all over (001) across the micas. Inter-split variations in  $^{40}\text{Ar}$  diffusion  
792 pattern indicate strong diffusion anisotropy with little communication (if at all) across the  
793 interlayer beyond  $50\ \mu\text{m}$  (the penetration depth of the UV-probe).

794

795 • A striking spatial association is documented between sub-domains with younger ages,  
796 low Na/K ratios, and high density of microstructural defects (basal parting) seen through  
797 FIB-STEM/TEM. These defects are argued to have formed in response to inward  $\text{K} \leftrightarrow$   
798 Na interdiffusion during late magmatic stages and prior to protracted crustal cooling. The  
799 diffusion-domain structure of HPG muscovite thus appears passively controlled by elemental  
800 substitutions and their consequences at the level of the interlayer in terms of structural sta-  
801 bility and chemical reactivity.

802

803 • The diffusion-domain structure along (001) in white micas is documented as a spatial  
804 continuum at the scale of the whole grains down to the UV-probe lateral resolution ( $\sim$   
805  $35\ \mu\text{m}$ ). Grain-scale internal  $^{40}\text{Ar}/^{39}\text{Ar}$  diffusion gradients cannot be reproduced with 2D  
806 Fickian-type profiles assuming homogeneous diffusion under protracted cooling. The mecha-  
807 nism invoked is one of continuous grain-scale interactions between subdomains with different  
808 diffusivity along (001), and is fundamentally distinct from domain-like segmentation pro-  
809 duced by discrete high-diffusivity linear or planar defects cutting across the cleavage plane.

810

811 • Quantitative modeling shows that  $^{40}\text{Ar}$  diffusivity through defect-poor subdomains is very  
812 sluggish, at least two orders of magnitude lower than existing experimental and empirical es-  
813 timates, but consistent with Molecular Dynamics estimates for undefective muscovite (Nteme  
814 et al., 2022). In contrast, defect-rich domains are characterized by  $^{40}\text{Ar}$  diffusivities up to 6  
815 to 10 orders of magnitude faster between  $700\text{--}300\ \text{°C}$ . No matter how approximate, these  
816 estimates quantitatively constrain the range of  $^{40}\text{Ar}$  transport rates in natural, undeformed,  
817 muscovite affected by coupled chemical-nanostructural transformations of the interlayer.

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## 1090 TABLES

Table 1: Location and mineralogy of dated samples. Mineral abbreviations after [Whitney and Evans \(2010\)](#).

Samples	Location	Mineralogy							GPS coordinate (WGS 84)	
		Qz	Ab	Mc	Ms	Bt	Tur	Grt	Latitude	Longitude
HP-10D	Central pluton	x	x	x	x		x		44.100000	-103.7555556
HP-13A	Central pluton	x	x	x	x		x		43.988889	-103.5888889
HP-45B	E. Sat. pluton	x	x	x	x		x	x	43.897500	-103.6102778
HP-2A	N. Sat. pluton	x	x	x	x		x	x	43.994444	-103.7388889
HP-34C	W. Sat. pluton	x	x	x	x		x		44.022778	-103.8044444

Table 2: HPG muscovite composition

Sample	HP-10D	HP-13A	HP-34C
SiO <sub>2</sub>	46.17	46.54	48.19
TiO <sub>2</sub>	0.19	0.11	0.18
Al <sub>2</sub> O <sub>3</sub>	34.23	34.61	34.78
FeO	1.7	1.67	1.42
MnO	0.04	0.02	0.03
MgO	0.63	0.54	0.65
Na <sub>2</sub> O	0.43	0.56	0.53
K <sub>2</sub> O	10.71	10.47	10.52
F	0.05	0.07	0.00
Total	94.15	94.59	96.29
<i>Formula Basis 11 oxygens</i>			
Si	3.12	3.13	3.17
Al(IV)	0.88	0.87	0.83
Al(VI)	1.85	1.86	1.85
Ti	0.01	0.01	0.01
Fe	0.10	0.09	0.08
Mg	0.06	0.05	0.06
Mn	0.00	0.00	0.00
K	0.92	0.90	0.88
Na	0.06	0.07	0.07

Table 3: Cross-over ( $1000/T_{xo}$ ;  $\log D_{xo}$ ) point in Arrhenian space of best-fitting  $E_v-D_0^v$  solution pairs matching the core age in muscovite *M11* of HP-10D (Fig. 16b) for the three thermal models considered in Fig. 15 assuming a range of activation energies between  $E_v = 40-70$  kcal.mol<sup>-1</sup>. Last columns block: examples of characteristic  $E_v-D_0^v$  couples for the three cross-over families.

Thermal model	$1000/T_{xo}$ (K <sup>-1</sup> )	$\log D_{xo}$ (cm <sup>2</sup> .s <sup>-1</sup> )	$D_0^v$ (cm <sup>2</sup> .s <sup>-1</sup> )			
			40*	50*	60*	70*
$T_{min}$	1.261	-18.70	$2 \times 10^{-8}$	$1 \times 10^{-5}$	$7 \times 10^{-3}$	3
$T_{mid}$	1.147	-18.14	$8 \times 10^{-9}$	$3 \times 10^{-6}$	$6 \times 10^{-4}$	$3 \times 10^{-1}$
$T_{max}$	1.097	-18.30	$2 \times 10^{-9}$	$6 \times 10^{-7}$	$1 \times 10^{-4}$	$3 \times 10^{-2}$

\* Activation energies (in kcal.mol<sup>-1</sup>)

Table 4: Empirical diffusion-domainal structure and diffusivities used in 2D modeling of defect-enhanced  $^{40}\text{Ar}$  diffusion gradients (Fig. 17).

Grain	Domain	$\psi_d = f_d D_0^d$ ( $\text{cm}^2 \cdot \text{s}^{-1}$ )
HP-10D ( <i>M11</i> )	1	$3 \times 10^{-5}$
	2	$1 \times 10^{-6}$
	3	$2 \times 10^{-4}$
	4	$6 \times 10^{-5}$
	5	$2 \times 10^{-5}$
HP-13A ( <i>M19</i> , split #1)	1	$6 \times 10^{-4}$
	2	$6 \times 10^{-6}$
	3	$1 \times 10^{-3}$
	4	$3 \times 10^{-3}$
	5	$2 \times 10^{-3}$
HP-13A ( <i>M19</i> , split #2)	1	$3 \times 10^{-4}$
	2	$6 \times 10^{-6}$
	3	$5 \times 10^{-4}$
	4	$5 \times 10^{-4}$
HP-13A ( <i>M21</i> , split #2)	1	$3 \times 10^{-4}$
	2	$2 \times 10^{-6}$
	3	$2 \times 10^{-2}$
	4	$6 \times 10^{-6}$
	5	$2 \times 10^{-4}$
	6	$6 \times 10^{-6}$

1091 **FIGURES CAPTIONS**

1092 **Fig. 1.** Geological map of the southern part of the Black Hills (South Dakota, USA). Inset  
 1093 shows location of the mostly Proterozoic core of the Black Hills relative to regional  
 1094 lithotectonic domains. Abbreviations: WC and SC = Wyoming and Superior cratons;  
 1095 CPO/YAV = Central Plains (Yavapai) orogen; THO and BHO = Trans-Hudson and  
 1096 Black Hills orogens; BMD and HPD = Bear Mountain and Harney Peak domes; MT,  
 1097 WY, NE, ND, and SD = Montana, Wyoming, Nebraska, North and South Dakota,  
 1098 respectively. Modified from [Dahl and Foland \(2008\)](#).

1099  
 1100 **Fig. 2.** Thin section photomicrographs of selected samples. Automorphic muscovite crystals  
 1101 in samples HP-10D (a) and HP-13A (b). Muscovite aggregates in the sample HP-2A  
 1102 (c). Resorbed muscovite rims in samples HP-13A (d), HP-34C (e) and HP-2A (f). (g)  
 1103 Feldspars crystals devoid of inclusions (HP-13A). (h) Feldspars rich in inclusions (HP-  
 1104 34C).

1105  
 1106 **Fig. 3.** Optical microphotographs under crossed polars of muscovite grains selected for this  
 1107 study. Scale bar is 1 mm.

1108  
 1109 **Fig. 4.** SEM photograph of typical cone-shaped morphology and distribution of 35  $\mu\text{m}$  wide  
 1110 213-UV ablation pit along (001) in muscovite (sample HP-13A (*M19*) - #2).

1111  
 1112 **Fig. 5.** In situ  $^{40}\text{Ar}/^{39}\text{Ar}$  mapping data in muscovite grains from HP-10D. Age contour maps  
 1113 reveal a conspicuous but irregular internal zoning, characterized by a consistent core-  
 1114 to-rim rejuvenation and the presence of a few isolated sub-cores retaining ages  $> 1.60$   
 1115 Ga. The dashed red line delimits peripheral delaminations. PDD curves plotted along  
 1116 with the IAF curves (see text for definitions). Both show consistent distributions. Scale  
 1117 bar is 1 mm. Age scale (color bar) with HPG intrusion age indicated.

1118  
 1119 **Fig. 6.** In situ  $^{40}\text{Ar}/^{39}\text{Ar}$  mapping data in muscovite from HP-13A. All grains show a con-  
 1120 sistent age decrease towards the rims and the presence of a few sub-domains retaining

1121 ages > 1.60 Ga. The dashed red line delimits peripheral delaminations. PDD and  
 1122 IAF curves show consistent distributions. Scale bar is 1 mm. Age scale (color bar) with  
 1123 HPG intrusion age indicated.

1124

1125 **Fig. 7.** In situ  $^{40}\text{Ar}/^{39}\text{Ar}$  mapping data in muscovite from HP-45B (a) and HP-2A (b). Both  
 1126 grains show a rejuvenation towards the rims. The dashed red line delimits peripheral  
 1127 delaminations. PDD and IAF curves show consistent distributions. Scale bar is 1 mm.  
 1128 Age scale (color bar) with HPG intrusion age indicated.

1129

1130 **Fig. 8.** In situ  $^{40}\text{Ar}/^{39}\text{Ar}$  mapping data in muscovite from HP-34C. All grains preserve ages  
 1131 older than the HPG crystallization age and show complex zoning patterns with younger  
 1132 zones all located on the rims. The dashed red line delimits peripheral delaminations.  
 1133 PDD and IAF curves show consistent distributions, except for grain *M4*. Scale bar is 1  
 1134 mm. Age scale (color bar) with HPG intrusion age indicated.

1135

1136 **Fig. 9.** Compositional diagrams for three representative samples (HP-10D, HP-13A, HP-  
 1137 34C). Data from EMP analyses on thin sections. Notice marked  $\text{Na}_2\text{O}$  vs.  $\text{K}_2\text{O}$  anti-  
 1138 correlation for all three samples.

1139

1140 **Fig. 10.** EMP chemical profiles along (001) plane showing characteristic spatial compositional  
 1141 variations in representative samples (HP-13A and HP-34C). Observe anti-correlative  
 1142 variations of Na and K towards the rims.

1143

1144 **Fig. 11.** EDS chemical maps showing the spatial distribution of Na in HP-13A muscovite  
 1145 grains. Profiles A–B show a systematic core-to-rim decrease in Na content and an  
 1146 anti-correlative trend in K. Na profiles coincide in shape and first-order features with  
 1147 grain-scale  $^{40}\text{Ar}/^{39}\text{Ar}$  variations extracted from *in situ* mapping (see age maps in **Fig. 6**).

1148

1149 **Fig. 12.** Microstructural TEM imaging of crystal zones selected based on  $^{40}\text{Ar}/^{39}\text{Ar}$  distri-  
 1150 bution patterns. (a-c) STEM of FIB foils extracted perpendicular to (001) at locations



1151 shown (stars) on the age contour and Na compositional maps. Notice the greater abun-  
 1152 dance of microstructural defects in Na-poor areas corresponding to younger  $^{40}\text{Ar}/^{39}\text{Ar}$   
 1153 ages. (d) Close-up TEM image (HP-10D, *M11*) revealing the defects as localized basal  
 1154 parting and delaminations (lenticular voids) up to 100–nm long parallel to (001); pack-  
 1155 ets of layers sandwiched between planar defects display a characteristic mottled con-  
 1156 trast.

1157  
 1158 **Fig. 13.** Substitutional relationship between Na and K in HPG muscovite. Red line: one-  
 1159 to-one (stoichiometric) exchange vector.  $\Delta\text{K}$  and  $\Delta\text{Na}$  calculated from data in profiles  
 1160 A–B shown in **Fig. 10**.

1161  
 1162 **Fig. 14.** Plot showing  $^{40}\text{Ar}/^{39}\text{Ar}$  internal relationships in terms of age range and grain size.  
 1163 (a) Maximum recorded age versus percentage of defective zones (arbitrarily equated  
 1164 to age-map areas featuring ages younger than 1.5 Ga). Negative correlation suggests  
 1165 a continuum-diffusive scalar field interconnecting the cores with the edges. (b) Grain  
 1166 radius versus mean ages showing no correlation. (c) Maximum recorded ages ver-  
 1167 sus shortest distance to rim showing lack of apparent correlation and suggesting  $^{40}\text{Ar}$   
 1168 transport through a non-uniform diffusive field.

1169  
 1170 **Fig. 15.** Model cooling curves used in numerical simulations. Data from **Dahl and Foland**  
 1171 **(2008)**.

1172  
 1173 **Fig. 16.** Diffusion modeling results. (a) Arrhenian display of  $^{40}\text{Ar}$  diffusion parameters  
 1174 allowing preservation of the intrusion age in the core of muscovite *M11* of HP-10D.  
 1175 Orange field contains all  $E-D_0$  possible pairs, setting an upper bound to permissible  
 1176  $^{40}\text{Ar}$  diffusion rates in the absence of microstructural defects. Solid circles indicate  
 1177 cross-over points for the three thermal models  $T_{\text{min}}$  (blue),  $T_{\text{mid}}$  (red) and  $T_{\text{max}}$  (green).  
 1178 Line labeled “4”: Arrhenian relationship derived from atomistic simulations for ideal  
 1179 muscovite (**Nteme et al., 2022**). Empirical and experimental estimates of **Hames and**  
 1180 **Bowring (1994)**, **Kirschner et al. (1996)** and **Harrison et al. (2009)** as indicated. (b)

1181 Core-to-rim profile (orange line) predicted from spatially-uniform 2D–diffusive model-  
1182 ing under the cooling displayed in Fig. 15 using the best-fitting  $E-D_0$  pair in (a); note  
1183 strong disparity with actual profile (purple line) measured across the grain (upper age  
1184 map panel).

1185

1186 Fig. 17. Multi-path diffusion modeling results. Displayed for each grain are: i) the inter-  
1187 polated age map, ii) the diffusion-domain structure featuring the outline and number  
1188 label referring to the domains reported in Table 4, iii) the synthetic age map, iv) a  
1189 selected profile across (001) comparing theoretical 2D predictions with observed varia-  
1190 tions across (001).

1191

1192 Fig. 18. Arrhenius space of effective  $^{40}\text{Ar}$  diffusion coefficient in HPG muscovite grains. The  
1193 field in blue delimits  $^{40}\text{Ar}$  diffusivity in the presence of microstructural defects. Pub-  
1194 lished empirical and experimental diffusion estimates plot within this field, suggesting  
1195 the presence of microstructural defects in the studied material. Stippled field: likely  
1196  $D-T$  space spanned by  $^{40}\text{Ar}$  kinetics in natural muscovite.

Fig. 1

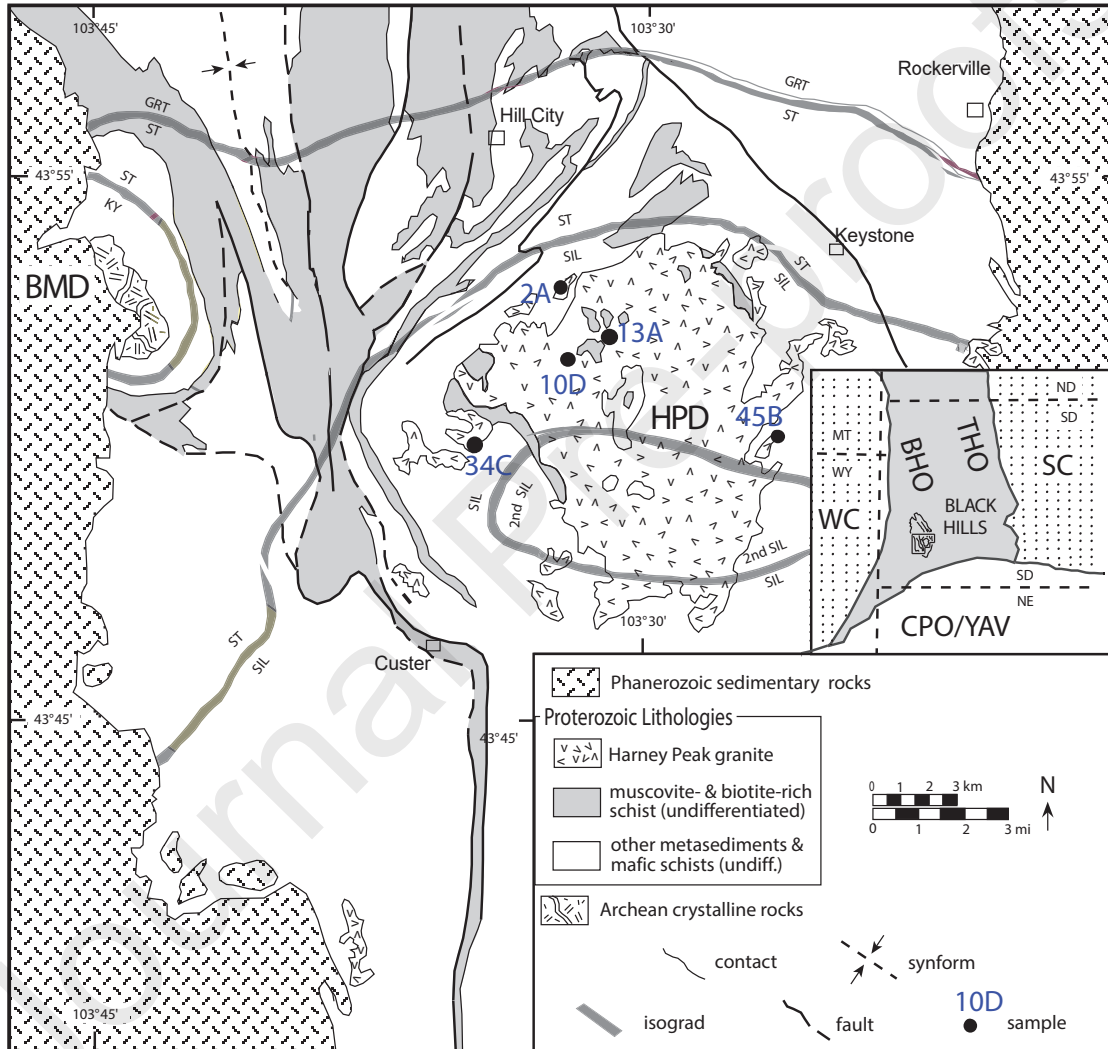


Fig. 2

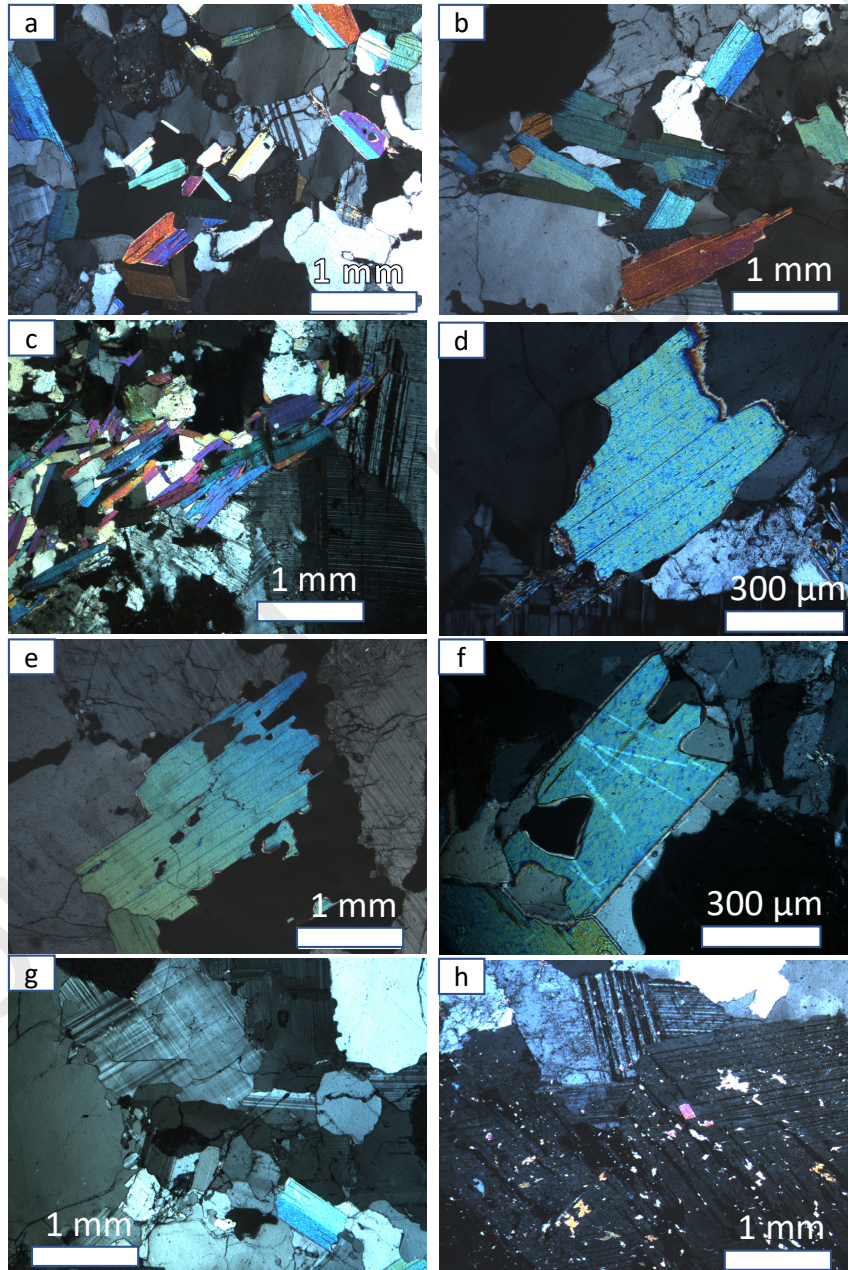


Fig. 3

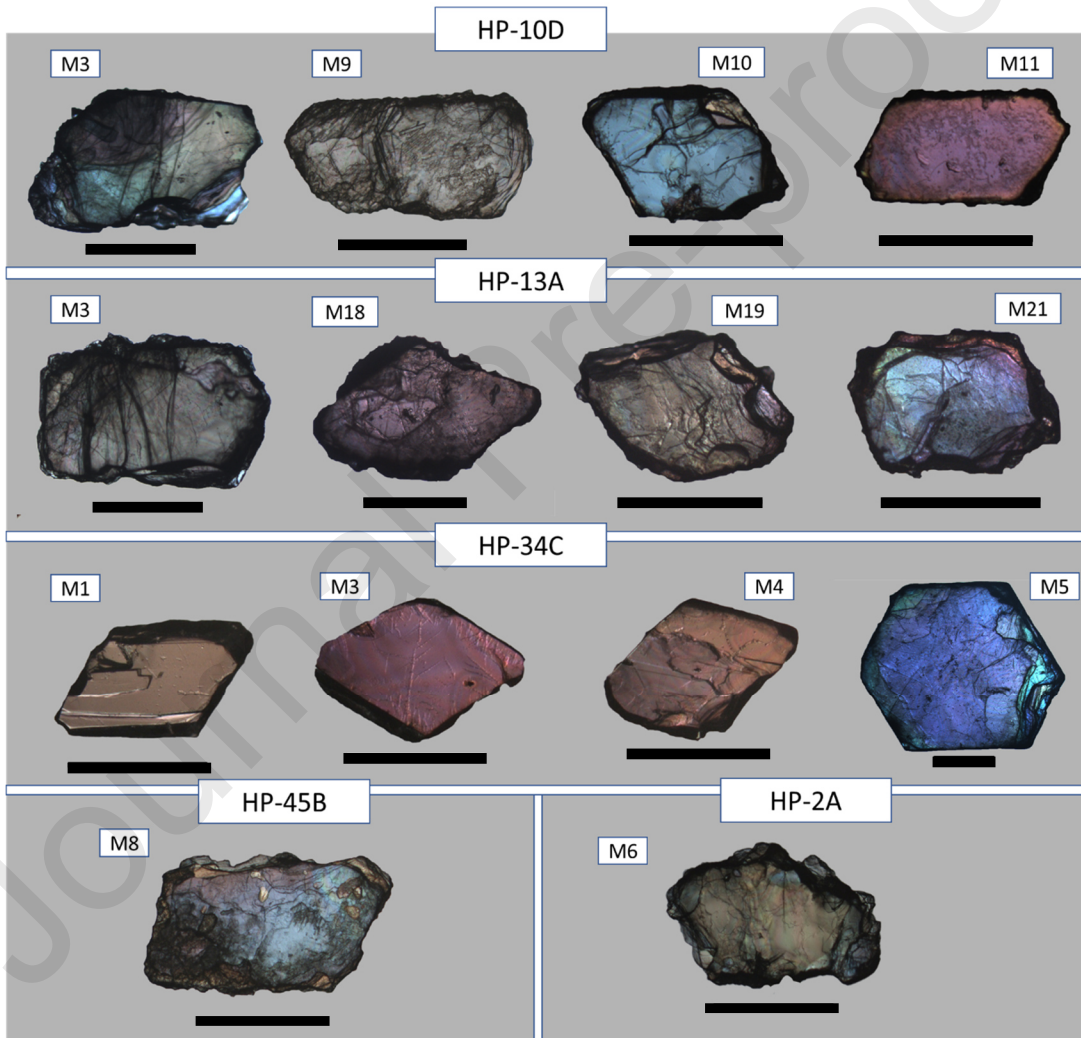


Fig. 4

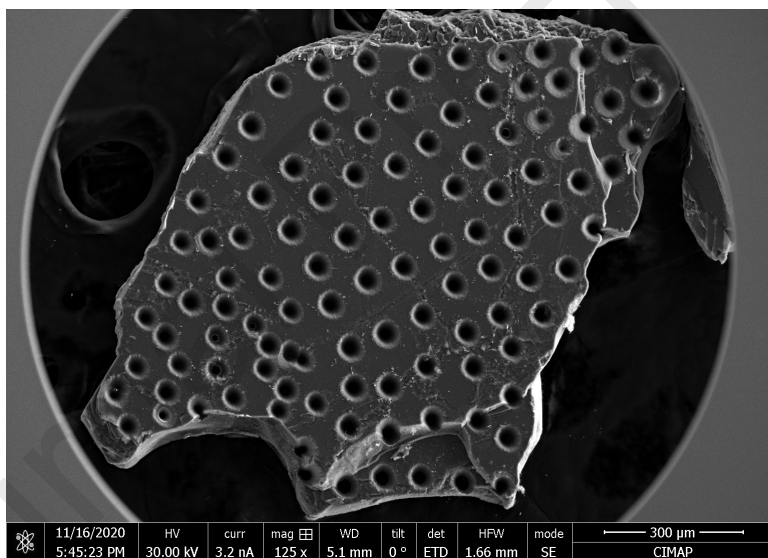


Fig. 5

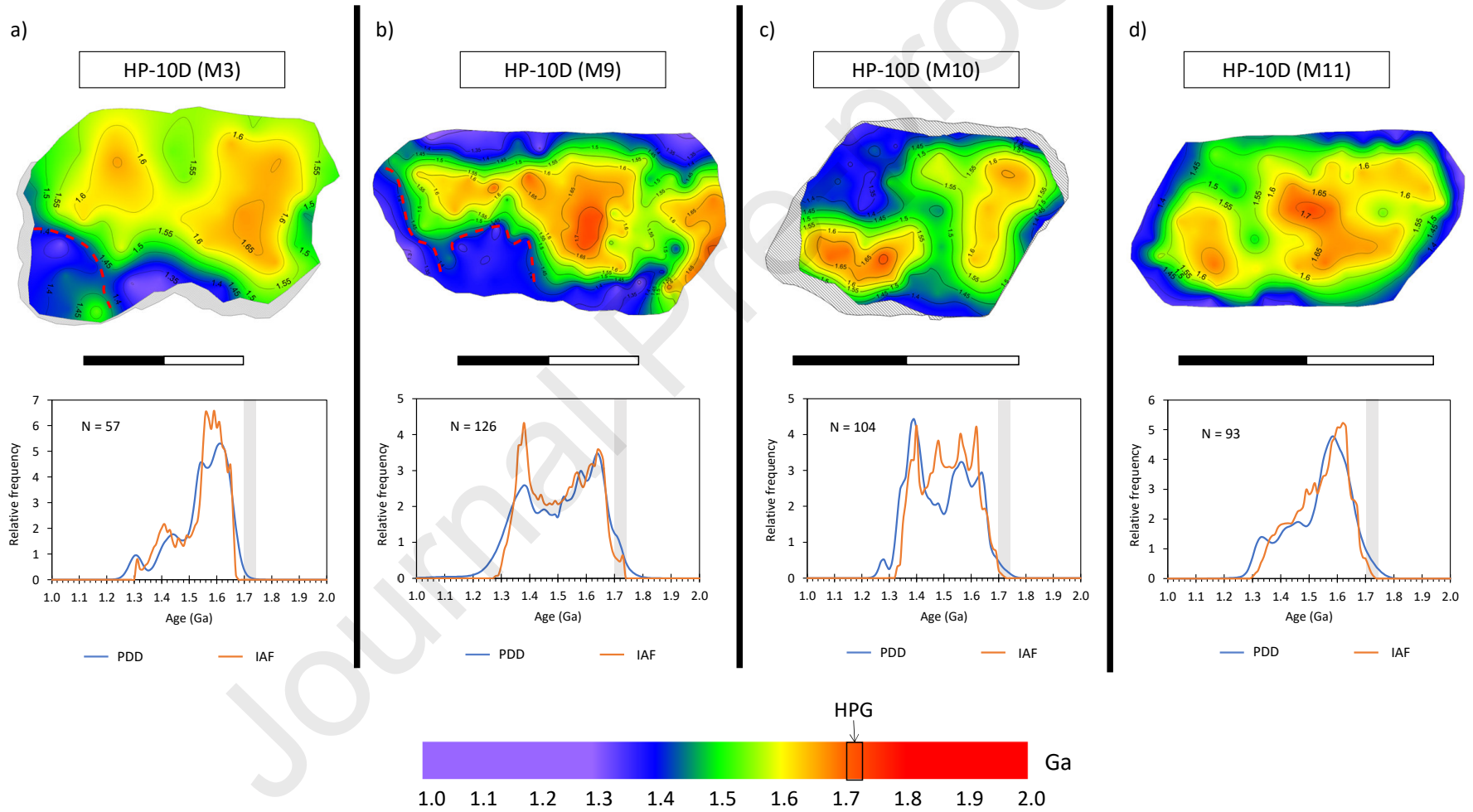


Fig. 6

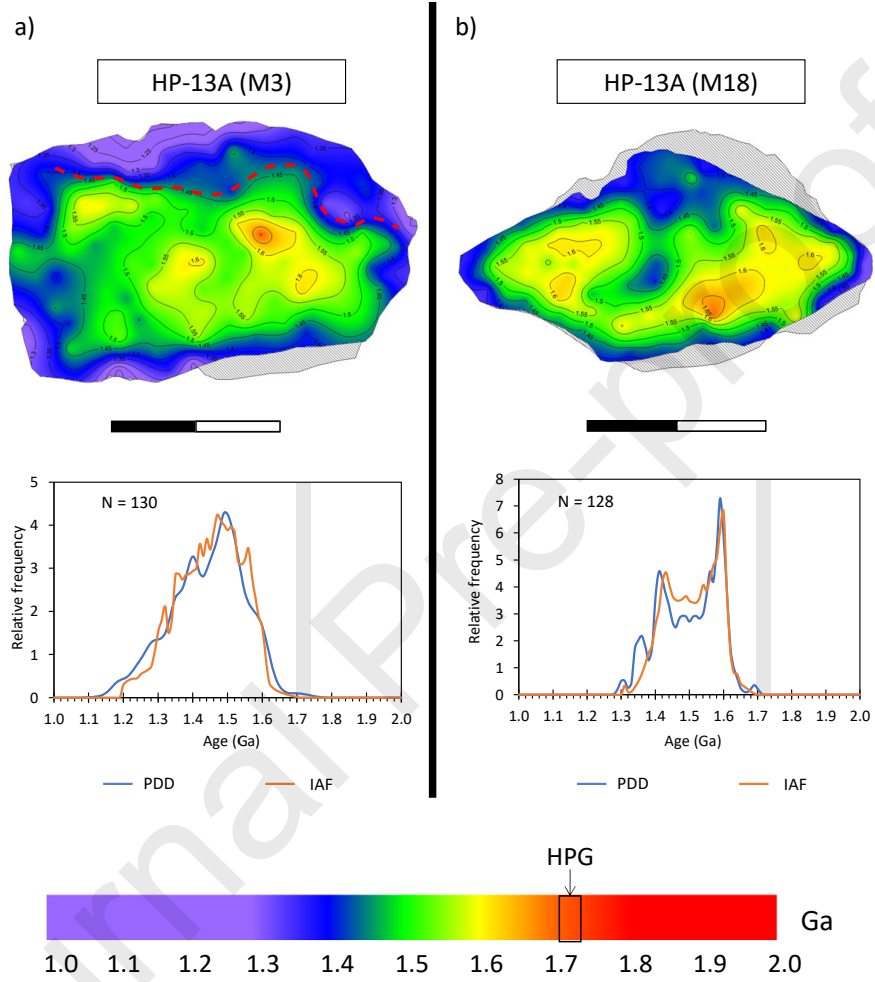




Fig. 6: (continued)

55

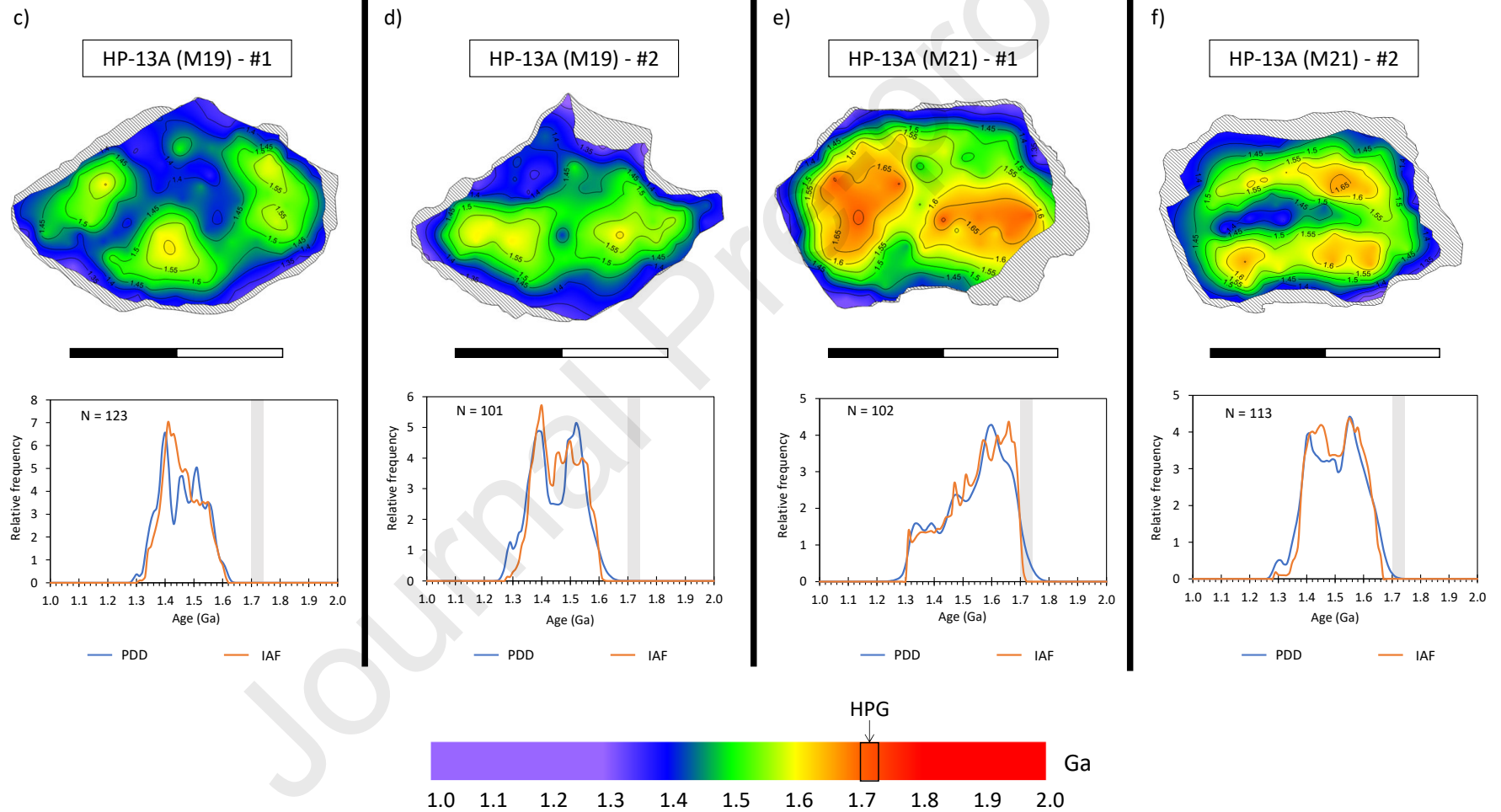


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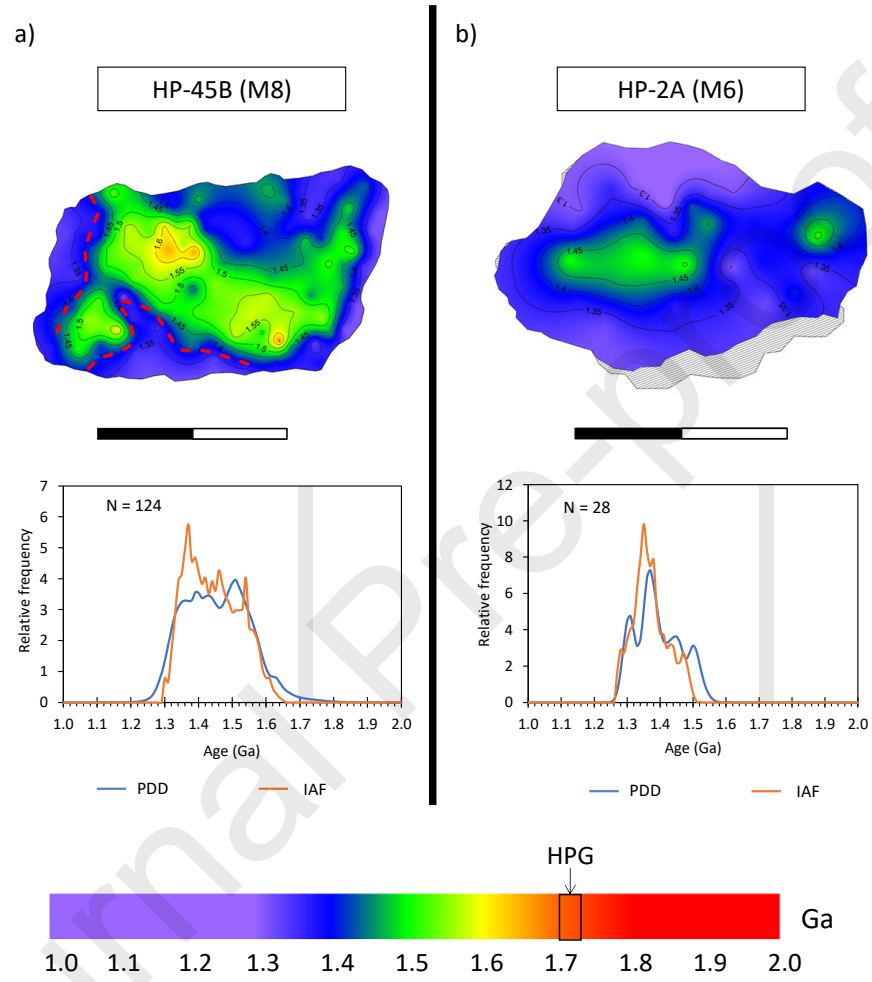


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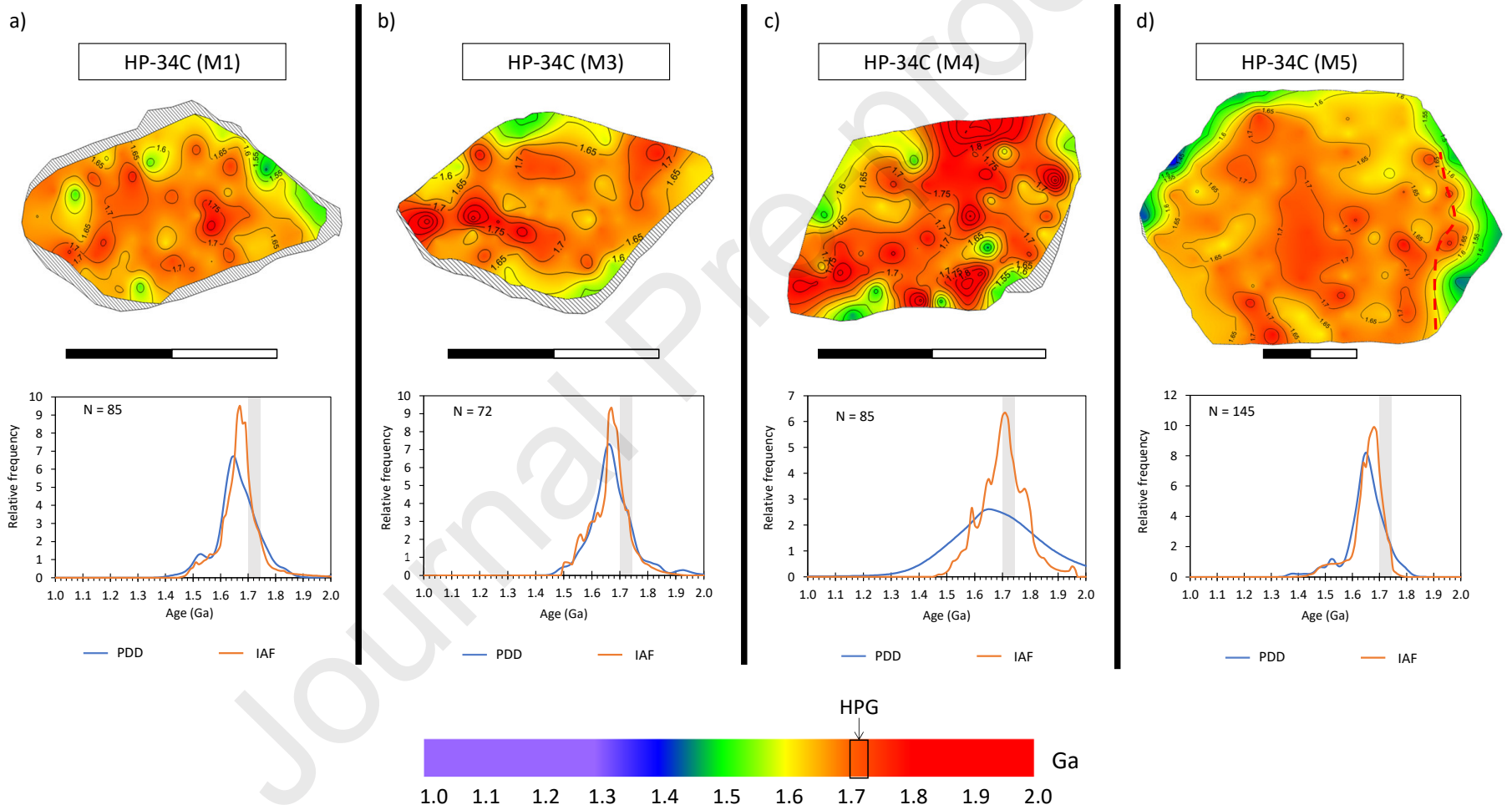


Fig. 9

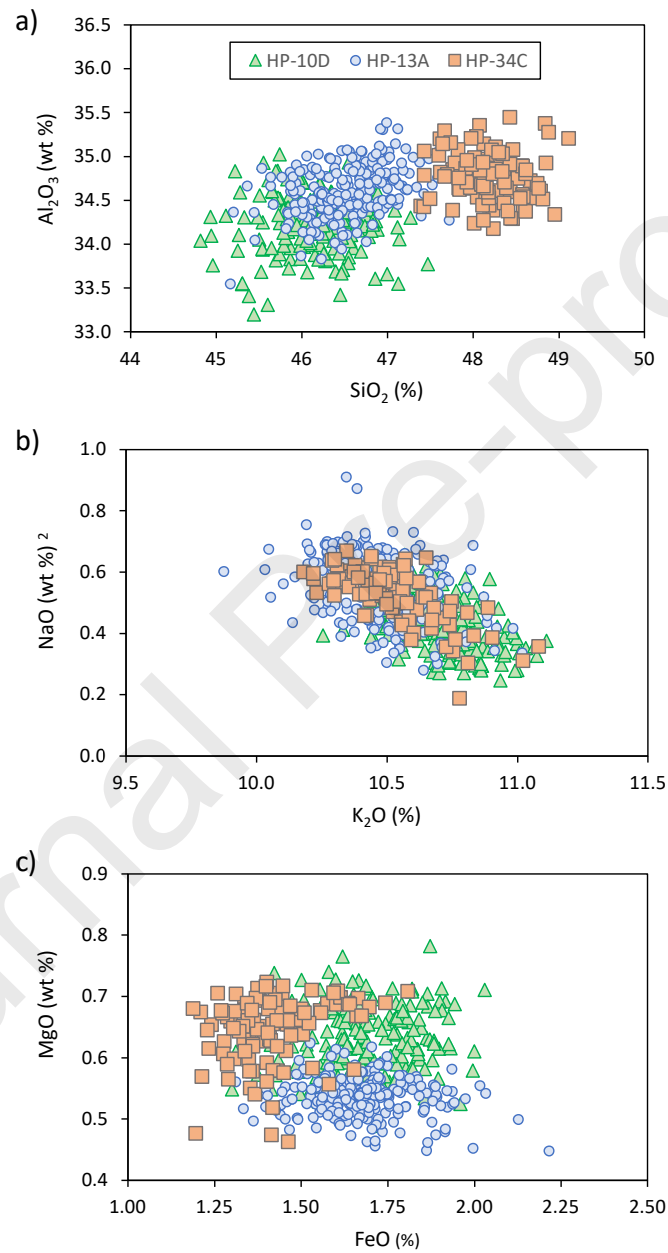


Fig. 10

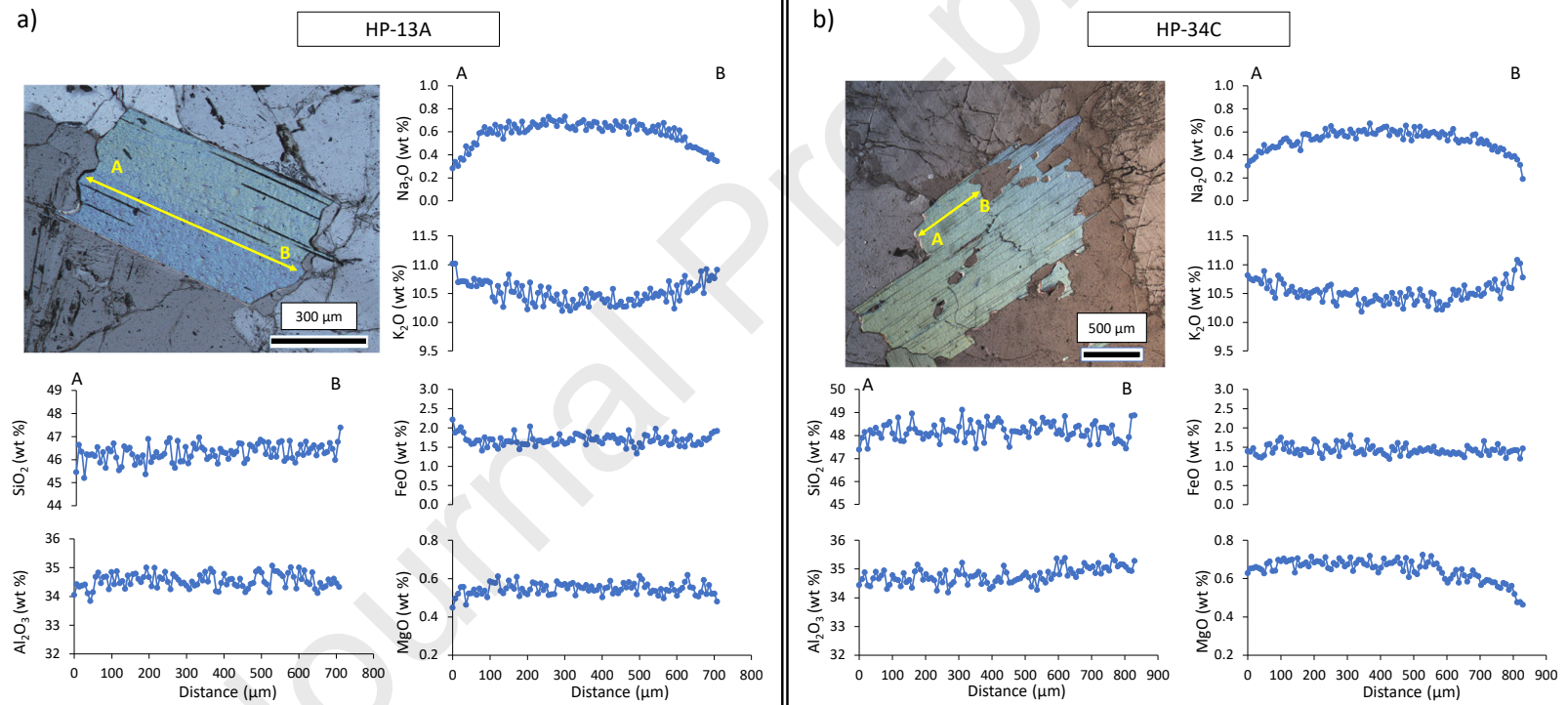


Fig. 11

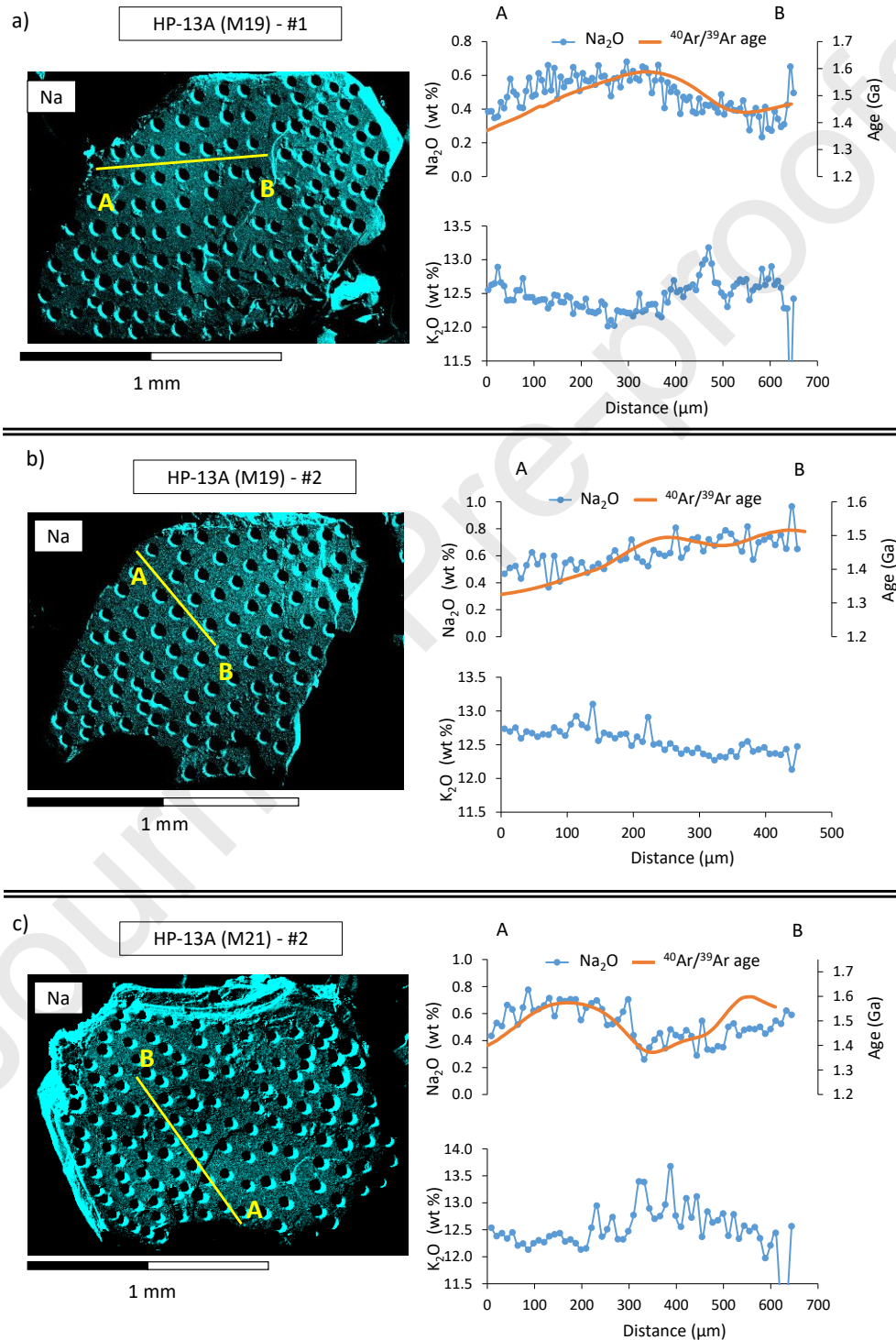
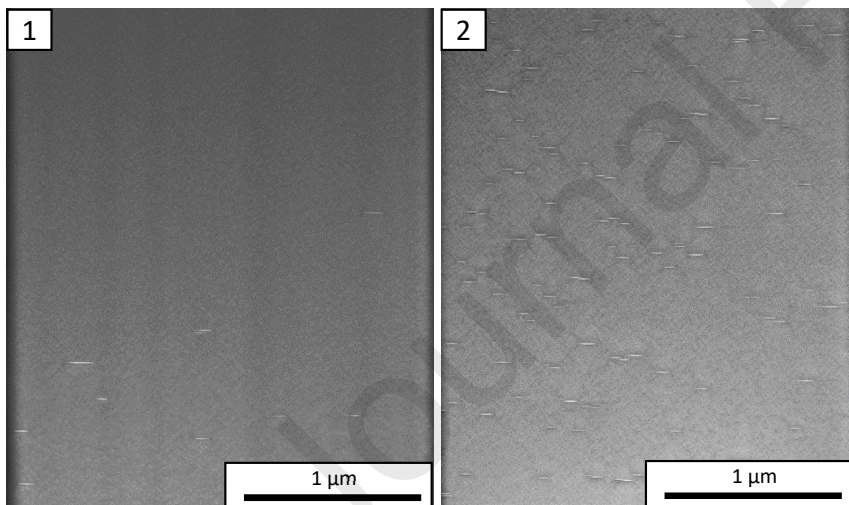
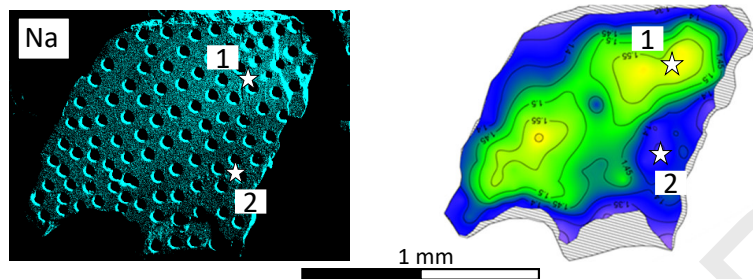


Fig. 12

a) HP-13A (M19) - #2



b) HP-13A (M21) - #2

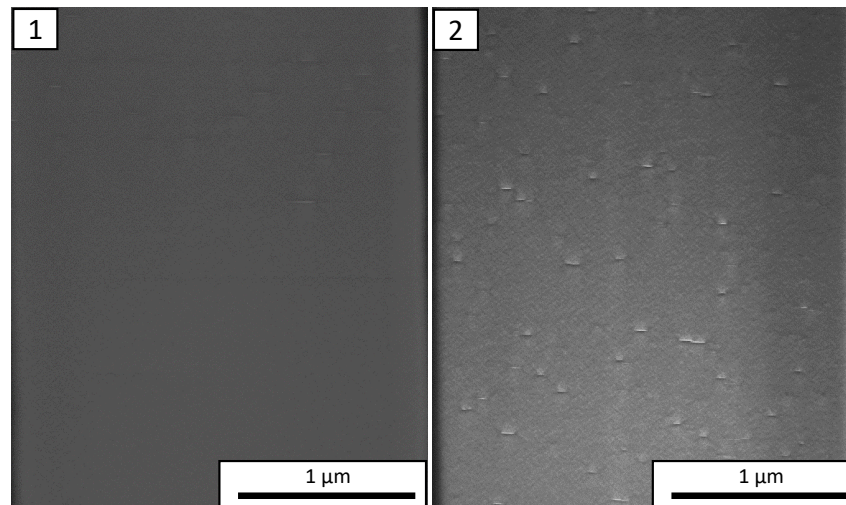
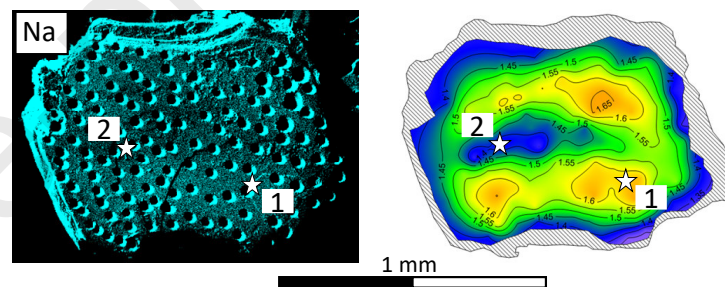


Fig. 12: (Continued)

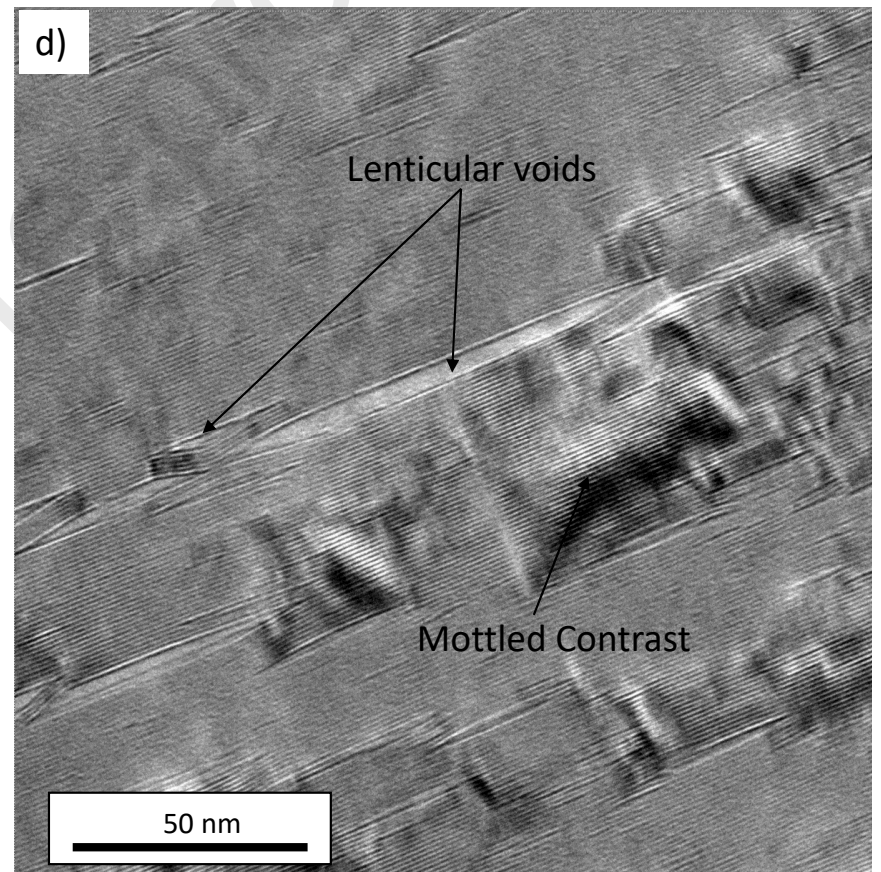
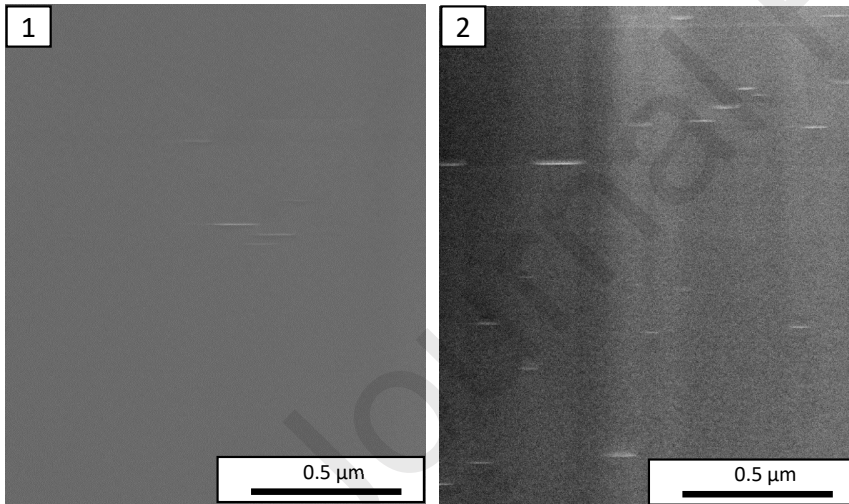
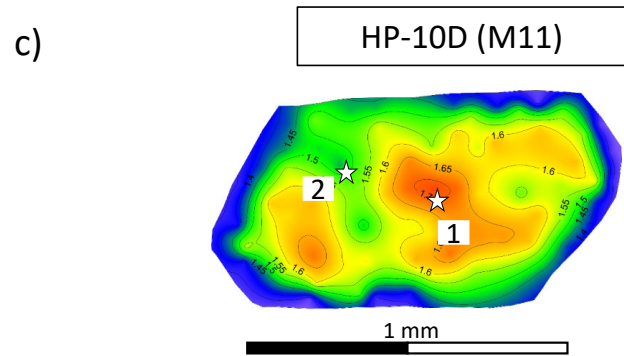




Fig. 13

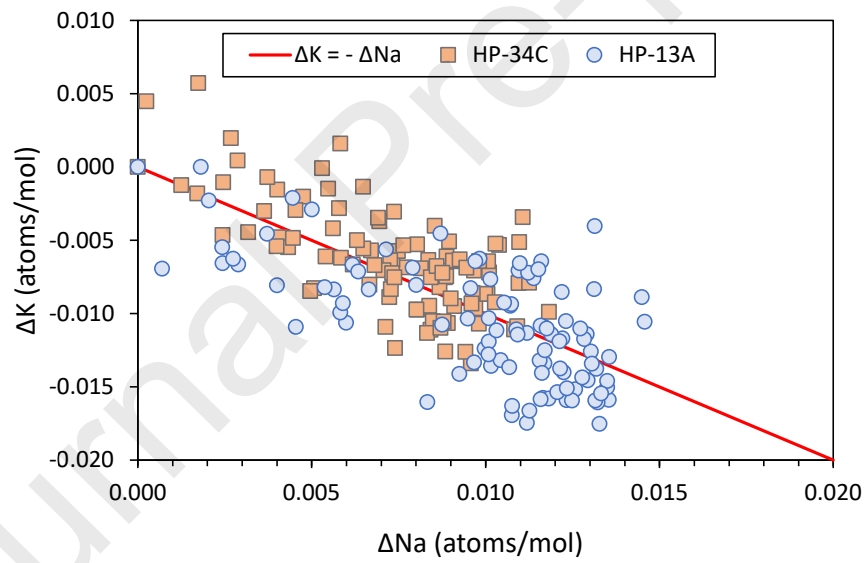


Fig. 14

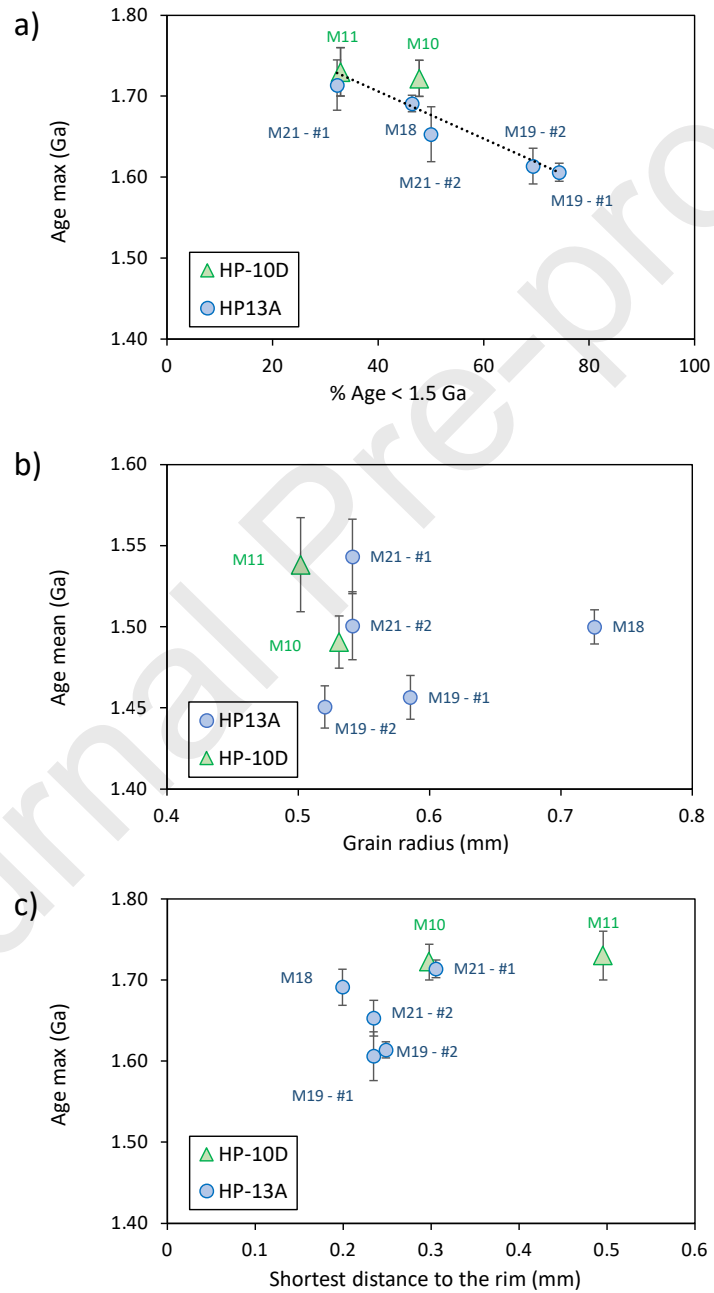


Fig. 15

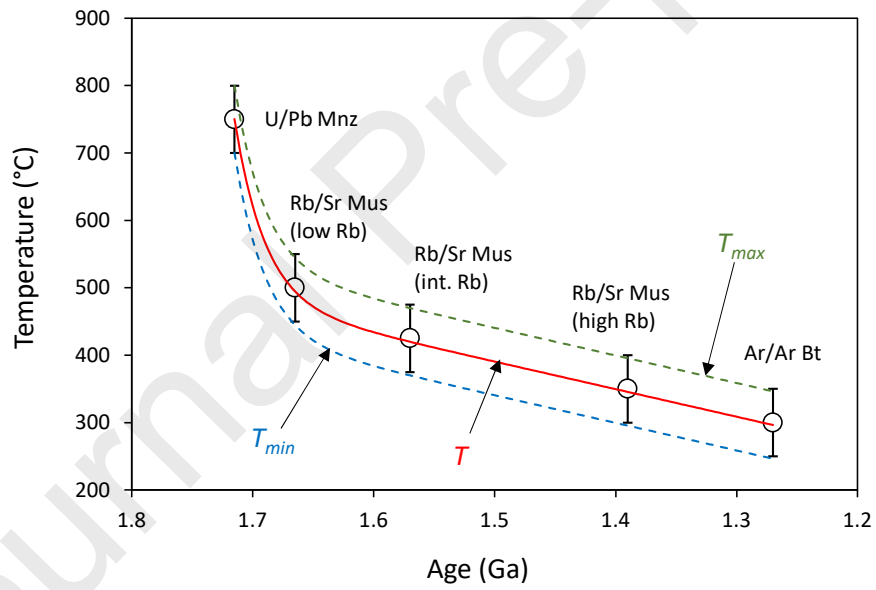
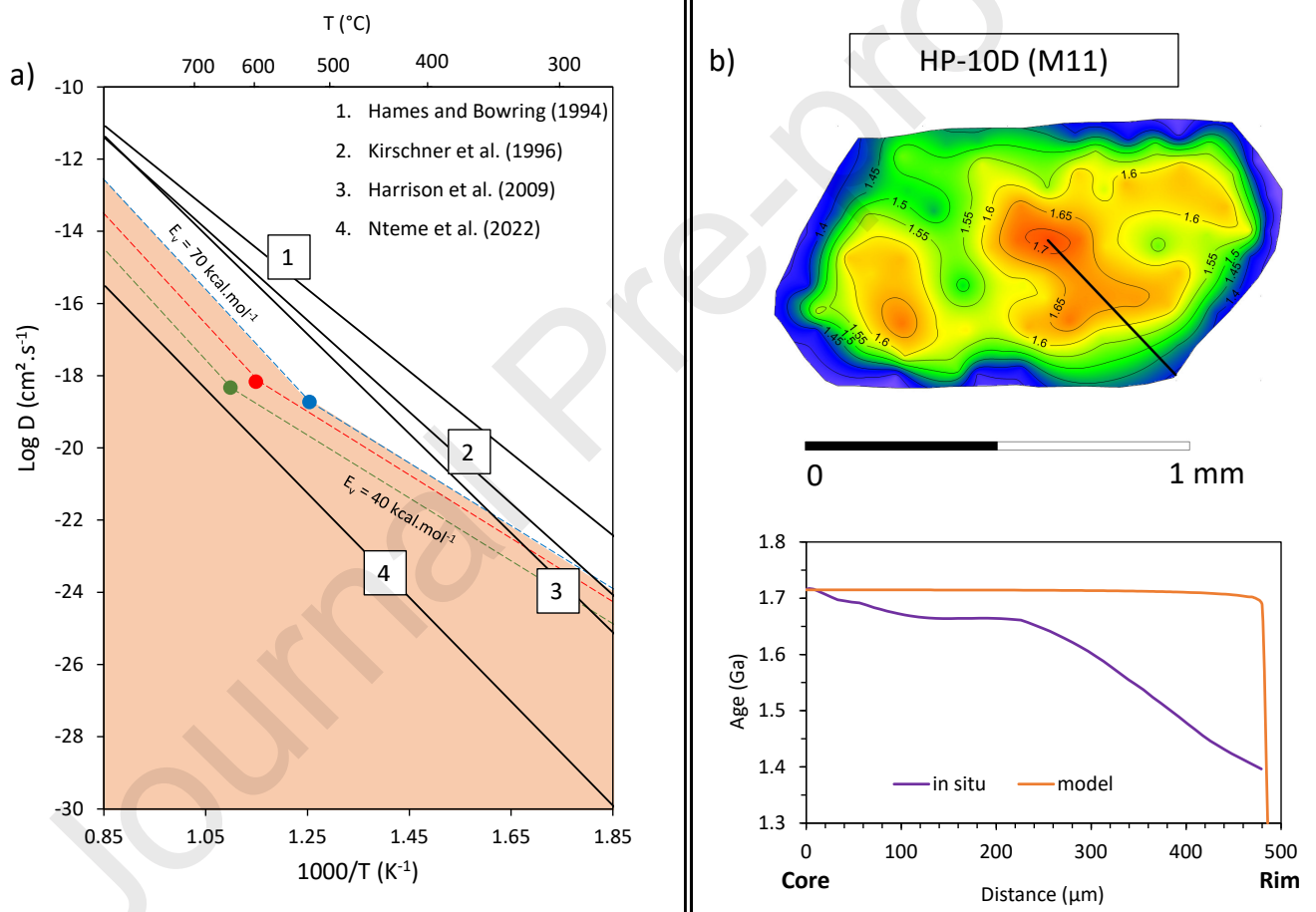


Fig. 16



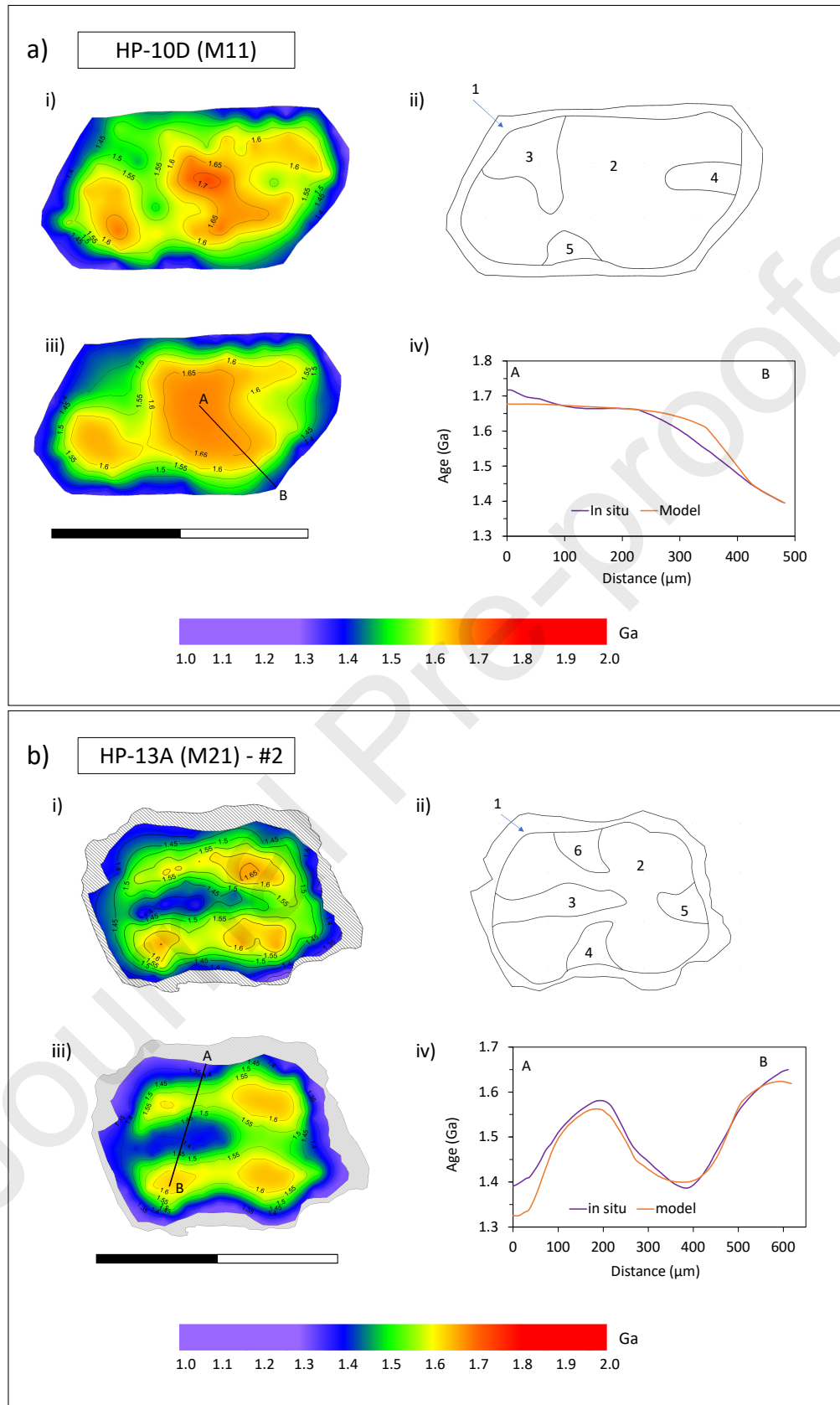


Fig. 17  
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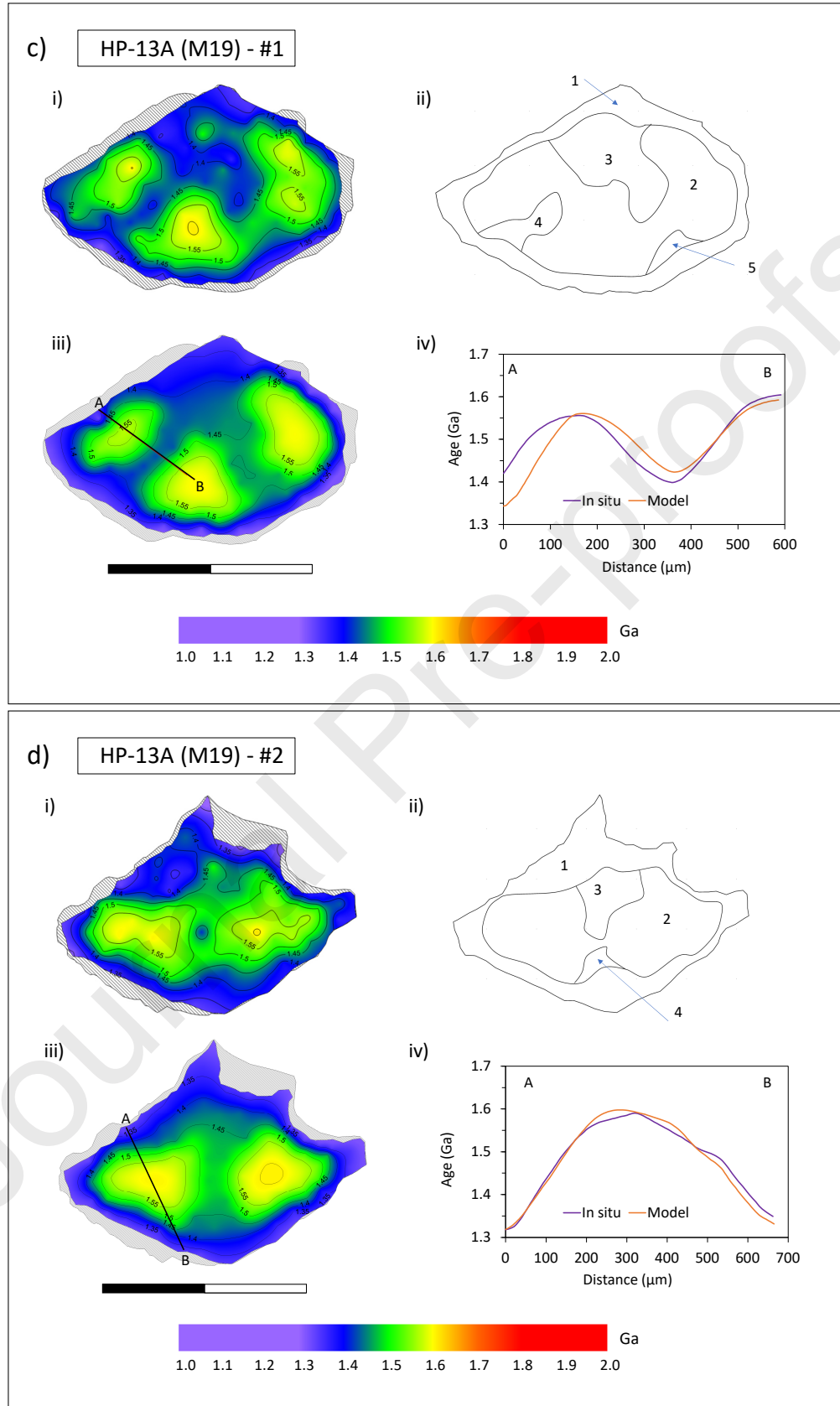
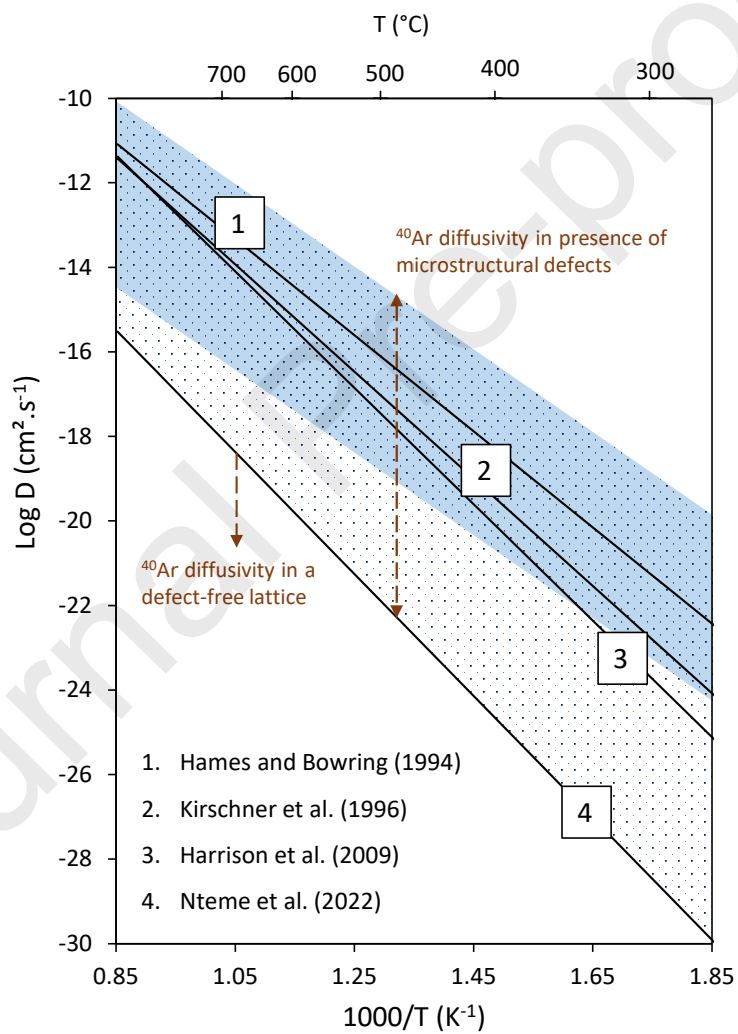


Fig. 17: (Continued)  
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Fig. 18



**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: