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Ar-Ar dating of authigenic K-feldspar: quantitative modelling of radiogenic argon-loss through subgrain boundary networks

D. F. Mark^{1,2*}, S. P. Kelley³, M. R. Lee⁴, J. Parnell¹, S. C. Sherlock³ & D. Brown⁴

¹ Department of Geology & Petroleum Geology, Meston Building, Meston Walk, University of Aberdeen, Aberdeen, AB24 3UE

² NERC Argon Isotope Facility, Scottish Universities Environmental Research Centre, Rankine Avenue, Scottish Enterprise Technology Park, East Kilbride, G75 0QF, Scotland, UK

³ Centre for Earth, Planetary, Space and Astronomical Research (CEPSAR), Department of Earth Sciences, Open University, Walton Hall, Milton Keynes, MK7 6AA

⁴ Department of Geographical and Earth Sciences, University of Glasgow, Gregory Building, Lilybank Gardens, Glasgow, G12 8QQ

ABSTRACT

We have analysed two distinct generations of authigenic K-feldspar in Fucoïd Bed sandstones from An-t-Sron and Skiag Bridge, NW Highlands, Scotland, which have experienced post-growth heating to levels in excess of the predicted Ar closure temperature. Authigenic K-feldspars show microtextural similarities to patch perthites; that is subgrains separated by dislocation rich boundary networks that potentially act as fast diffusion pathways for radiogenic argon.

The two generations of authigenic K-feldspar in the Fucoïd Bed sandstones can be distinguished by different microtextural zones, bulk mineral compositions, fluid inclusion populations, and inferred temperatures and chemistries of parent fluids. Ar-Ar age data obtained using high-resolution ultraviolet laser ablation, show that the

* Corresponding author (d.mark@suerc.gla.ac.uk)

first cementing generation is Ordovician and the second cementing generation is Silurian.

Modelling of Ar-diffusion using subgrain size as the effective diffusion dimension and a simplified tectono-thermal thrust model assuming transient heating of the Fucoid Beds is inconsistent with observed data. Removal of heat from the thrust zone through rapid flushing of heated fluids rather than transient heating can be invoked to explain the observed Ar-Ar ages for both generations of cement. Alternatively, Ar-diffusion modelling using overgrowth thickness as the effective diffusion dimension instead of subgrain size also yields models that are consistent with both the Fucoid Bed palaeothermal maxima and determined Ar-Ar age ages for the two generations of K-feldspar cement. Based on this alternate explanation, we propose a theoretical microtextural model that highlights fundamental differences between the microtextures of deuterically formed patch perthites and authigenic K-feldspars, explaining the apparent robustness of authigenic K-feldspar with respect to Ar-retention.

KEYWORDS

Authigenic K-feldspar, Ar diffusion, FIB-TEM, Ar-Ar, subgrain, microtexture

1. INTRODUCTION

1.1 Alkali K-feldspar

55 The abundance of K-feldspar in igneous rocks and its occurrence as detrital and
56 authigenic constituents in sedimentary rocks, has ensured its extensive use in Ar-Ar
57 dating (McDougall & Harrison, 1999). Step heating experiments (Burgess *et al.*,
58 1992; Parsons, 1994) show that Ar-Ar dates obtained from plutonic and detrital K-
59 feldspars reflect the age of cooling below the Ar closure temperature (T_c). T_c is simply
60 one temperature range in a range of temperatures (a closure 'interval') in the cooling
61 history of a rock that corresponds to its apparent age (Lee, 1995).

62

63 Patch perthite microtextures are key indicators of interaction of alkali feldspar with
64 deuteritic fluids and are characterised by mosaics of slightly misaligned submicron- to
65 micron-sized incoherent subgrains with abundant dislocations along their boundaries
66 and are also typically associated with micropores (Foland, 1994; Parsons & Lee,
67 2005; Walker *et al.*, 1995: Fig. 1). Combined Ar-Ar geochronology and transmission
68 electron microscope (TEM) studies suggest that Ar-loss from alkali feldspar is
69 controlled directly by subgrain microtextures (Parsons, 1978; Worden *et al.*, 1990;
70 Burgess *et al.*, 1992; Parsons & Lee, 2000; Lee & Parsons, 2003; Parsons & Lee.,
71 2005).

72

73 1.2 Authigenic K-feldspar

74

75 Although step heating experiments originally designed to determine the age of
76 authigenic K-feldspar overgrowths (Hearn & Sutter, 1985; Hearn *et al.*, 1987; Girard
77 *et al.*, 1988; Spotl *et al.*, 1996; Warnock & van der Kamp, 1999; Liu *et al.*, 2003)
78 have not directly enabled the distinction between detrital and authigenic generations,
79 the data suggest that authigenic K-feldspar may record isotopic information relating to

80 diagenetic events. The introduction of laserprobe isotope extraction techniques has
81 offered higher-spatial resolution than conventional methods, permitting Ar-extraction
82 from individual grains and potentially eliminating problems of contamination from
83 detrital feldspar. Initial laserprobe studies used Ar-ion and infrared laser systems for
84 analysis of authigenic K-feldspar (Walgenwitz *et al.*, 1990). Laser absorption by
85 feldspar at such wavelengths is poor, however, and extensive heating occurred outside
86 the site of laser-mineral interaction, resulting not only in the extraction of Ar from the
87 overgrowth, but also from the detrital grain and surrounding minerals. The ultraviolet
88 (UV, 266 nm) laserprobe (Kelley *et al.*, 1994) has a greater spatial resolution than the
89 Ar-ion and infrared laser systems (UV laser can achieve a spot resolution of 12 μm)
90 and the wavelengths are absorbed strongly by the feldspar. As a consequence the UV
91 laser does not heat the sample beyond the point of laser-sample interaction and
92 therefore only extracts Ar from the desired locations. Investigations dating K-feldspar
93 overgrowths using the UV laserprobe have yielded meaningful Ar-Ar growth ages
94 (Hagen *et al.*, 2001; Mark *et al.*, 2005, 2008; Sherlock *et al.*, 2005).

95
96 Authigenic K-feldspar overgrowths within sedimentary rocks from the Permo-Triassic
97 of Elgin (Worden & Rushton, 1992), the Jurassic Humber Group of the North Sea
98 (Lee & Parsons, 2003) and the Cretaceous Atlantic Margin Victory Formation (Mark
99 *et al.*, 2005), all show mineralogical and microtextural similarities. These overgrowths
100 comprise mosaics of slightly misaligned submicron- to micron-sized subgrains,
101 intercalated micropores, and nanometre growth bands orientated parallel to
102 dislocation-rich subgrain boundaries. Overgrowths from Elgin and the Victory
103 Formation have a regular subgrain size and well-developed crystal faces dominated by
104 the {110} adularia habit. Subgrain boundaries of overgrowths from the Humber

105 Group are slightly curved with the {110} adularia habit. Subgrain size also increases
106 with distance from the detrital grain-overgrowth interface. The presence of illite along
107 subgrain boundaries at interfaces was noted in two studies (Worden & Rushton, 1992;
108 Lee & Parsons, 2003).

109

110 Ar-Ar dating of authigenic K-feldspar is contentious because subgrain microtextures
111 are superficially similar to those of deuterically formed patch perthites (Lee &
112 Parsons, 2003) which quantitatively leak Ar at low temperatures (Burgess *et al.*,
113 1992). However, because subgrains can be equated to spherical Ar diffusion domains
114 it is possible to model Ar-loss (Wheeler, 1996) by assuming that Ar diffuses out of the
115 subgrains via lattice volume diffusion to an infinite zero concentration reservoir. The
116 effective diffusion domain (sphere diameter) is directly related to T_c ; the larger the
117 diffusion domain the higher the T_c (Dodson, 1973). Therefore, because authigenic K-
118 feldspar microtextures are superficially similar to those of patch perthites, it has been
119 logically suggested that authigenic K-feldspar will leak Ar at relatively low
120 temperatures, with the initial temperature of Ar-loss being related directly to the
121 radius of the smallest subgrain (Lee & Parsons, 2003).

122

123 Sherlock *et al.* (2005) modelled the thermal response of authigenic K-feldspar to an
124 episode of tectonically induced heating. Because TEM was not used to characterise
125 microtextures, the model was generic and covered a wide range of subgrain sizes but
126 demonstrated that authigenic K-feldspar can potentially retain Ar. The first fully
127 quantitative study of authigenic K-feldspar incorporating Ar diffusion modelling, Ar-
128 Ar geochronology and TEM (Mark *et al.*, 2005), modelled subgrain response in terms
129 of Ar-loss against a thermal burial history that was reconstructed using apatite fission

track analysis, fluid inclusion microthermometry and vitrinite reflectance. The model showed that 3 to 5 μm subgrains exposed to a maximum temperature of 125 °C for ~ 10 Ma, yielded meaningful Ar-Ar growth ages. Predicted closure temperature estimates for sugrains of such sizes range from ~ 150 to 175 °C (Foland, 1974, 1994).

A key question which this study aims to address is the difference between the Ar-retention properties of deuterically formed patch perthites within alkali feldspars (Fig. 1) and authigenic K-feldspar overgrowths. As these microtextures are superficially similar, how do their Ar-diffusion properties compare?

1.3 Study aims

This study attempts to determine if Ar is quantitatively retained by authigenic K-feldspar overgrowths when exposed to temperatures in excess of predicted T_c determined from the calculations of Dodson (1973) and Foland (1974, 1994). Ar-Ar geochronology, TEM imaging and electron diffraction and Ar-diffusion modelling were employed to constrain the subgrain response of authigenic K-feldspar to temperatures in the order of 200 °C. A Focused Ion Beam (FIB) technique (Lee *et al.*, 2003) was used to cut electron-transparent foils from precisely located areas of K-feldspar crystals within polished thin sections. Comparison of subgrain microtexture revealed by TEM with Ar-Ar data enabled the simulation of Ar-diffusion domains and subsequently, the data were modelled against a post-crystallization, orogenesis-driven tectono-thermal episode, hence constraining the reliability of the Ar-Ar ages. Fine-grained sandstone samples were collected from Fucoid Bed outcrops at An-t-Sron and Skiaig Bridge, NW Highlands, two sites that are geographically 30 km apart (Fig. 2).

155 A documented enrichment of K-feldspar, up to 12 wt. % K₂O (Bowie *et al.*, 1966) has
156 been reported in the lower part of the Lower Cambrian An-t-Sron Formation (Furoid
157 Beds) thus providing an ideal geological context for assessing the retentiveness of
158 authigenic K-feldspar with respect to Ar. This manuscript should be considered as a
159 companion to Mark *et al.* (2007).

160

161 2. GEOLOGICAL SETTING

162

163 The Furoid Beds were deposited between 518 and 510 Ma (Gradstein *et al.*, 2004) on
164 the Laurentian Platform, and consist of up to 27 m of siltstones with interbedded
165 sandstones and dolostones. These rocks crop out along the Moine Thrust Zone and
166 were a focus for deformation during closure of the Iapetus Ocean. The Moine
167 Supergroup was thrust onto the Cambrian-Ordovician succession during the Scandian
168 episode (435-420 Ma; Dewey, 2005) of the Caledonian Orogeny (a continent-
169 continent collision that produced a mountain range of similar scale to the active
170 Himalaya; Johnson *et al.*, 1985). Thrusting disturbed the geothermal gradient of this
171 region and equilibrium was restored by conductive heat transport from the thrust sheet
172 to the underlying Cambrian-Ordovician sequence (Oxburgh & Turcotte, 1974). It has
173 been estimated from acritarch coloration index (Downie, 1982), fluid inclusion studies
174 (Baron *et al.*, 2003; Mark *et al.*, 2007) and illite crystallinity analyses (Johnson *et al.*,
175 1985) that temperatures in the sampled sections of the Furoid Beds reached a
176 temperature of 200 °C, the sampled regions palaeothermal maxima.

177

178 3. METHODS (SMALL TEXT IN MANUSCRIPT)

179

180 3.1 Excision of electron transparent foils using the focused ion beam technique

181

182 Sites within the K-feldspar overgrowths to be sampled for TEM work were selected by
183 backscattered electron imaging of carbon coated polished thin sections using a FEI Quanta
184 200 field-emission scanning electron microscope (SEM) operated at 20 kV in high vacuum
185 mode. Qualitative X-ray analyses of micrometer-sized spots were also obtained using an
186 EDAX Pegasus 2000 energy dispersive spectrometer (EDS) microanalysis system attached
187 to the Quanta SEM. Prior to cutting the electron-transparent foils using the Focused Ion Beam
188 (FIB) instrument the thin sections were sputter coated with ~40 nm of gold to alleviate
189 charging. The FIB work used a FEI 200 TEM operated at 30 kV. The milling process is
190 described briefly below but in more detail by Heaney *et al.* (2001) and Lee *et al.* (2003). Prior
191 to cutting of each foil a 1 μm thick platinum strip was deposited over the area of interest to
192 protect it from damage by the Ga^+ ion beam. A pair of parallel trenches ~10 to 15 μm in length
193 by ~ 5 μm in depth were then excavated on either side of the strip to eventually leave a ~ 110
194 nm thick slice of feldspar remaining between them (Fig. 3). This electron-transparent foil of
195 the K-feldspar overgrowth (Fig. 3C, D) was then extracted from the grain using an *ex-situ*
196 micromanipulator and placed on a 3.05 mm diameter perforated carbon film for TEM study
197 (Fig. 3E).

198

199 3.2 High-resolution petrography

200

201 Each of the FIB-produced foils was examined initially using the Quanta SEM equipped with a
202 secondary transmission electron microscope (STEM) detector (Fig. 3E), which enables
203 images to be formed using electrons that have been transmitted through the thin sample
204 (Smith *et al.*, 2006). Bright-field STEM images are formed from un-scattered electrons using
205 an electron detector positioned directly beneath the thin slice whereas dark-field images are
206 formed from high angle scattered electrons using an offset detector. Diffraction-contrast TEM
207 images were subsequently acquired using a FEI T20 instrument operated at 200 kV and
208 equipped with a charge-coupled device (CCD) camera for digital image capture.

209

210 3.3 Ar-Ar ultra-violet laser ablation dating

211
212 Prior to irradiation, the two 100 µm thick doubly polished fluid inclusion wafers were cleaned
213 ultrasonically in methanol and deionised water. Samples were cadmium shielded and
214 irradiated for 25 (An-t-Sron) and 33 (Skiag Bridge) hours in the Canadian McMaster reactor.
215 Neutron flux was monitored with biotite standard GA1550 ($\sim 98.8 \pm 0.5$ Ma; Renne *et al.*,
216 1998); calculated J values of 0.00639 ± 0.000032 (An-t-Sron) and 0.01398 ± 0.00007 (Skiag
217 Bridge) were used. A New Wave Research UP-213 nm pulsed Nd-YAG laser with a 12 µm
218 spot size was used for Ar extraction. Due to their small size entire K-feldspar overgrowths had
219 to be ablated in order to extract approximately ten times the blank ^{40}Ar levels. Extracted
220 gases were cleaned using three SAES AP10 getters, two operated at 450 °C and one at room
221 temperature. A Map 215-50 noble gas mass spectrometer analysed Ar isotope compositions.
222 The data were corrected for blanks, mass spectrometric discrimination, ^{37}Ar decay and
223 reactor induced interferences. Quoted Ar-Ar errors are 2σ and include a 0.5 % error (including
224 lateral variation in the flux gradient) assigned to the J value. Reactor induced correction
225 factors used were: $(^{39}\text{Ar}/^{37}\text{Ar})_{\text{Ca}} = 0.00065$, $(^{36}\text{Ar}/^{37}\text{Ar})_{\text{Ca}} = 0.000264$, $(^{40}\text{Ar}/^{39}\text{Ar})_{\text{K}} = 0.0085$.
226 Mark *et al.* (2006) provides details concerning the integration of fluid inclusion and Ar-Ar data.

227

228 3.4 Ar-diffusion modelling

229

230 Thermal history data was input into a finite element diffusion model DIFFARG (Wheeler,
231 1996) which works with MATLAB® software. The programme allows modelling of a precise
232 thermal history. Effective diffusion domain size can be inputted for a series of geometry
233 shapes and their response to the thermal history over time can be tested. DIFFARG is a
234 forward modelling programme and hence, 0 Ma corresponds to the time of K-feldspar
235 authigenesis. The model yields the amount of age resetting in Ma from which we determined
236 by re-arrangement of the Ar-Ar age equation how much radiogenic Ar has been lost.

237

238 4. RESULTS

239

240 4.1 Generations of authigenic K-feldspar

241

242 Mark *et al.* (2007) show that the two generations of authigenic K-feldspar within the
243 Fucoid Beds can be resolved (prior to Ar-Ar dating) by optical and scanning electron
244 microscopy, quantitative mineral compositions, fluid inclusion petrography and parent
245 fluid temperature and chemistry throughout the whole 180 km Fucoid Bed outcrop.
246 Generation 1 cements (P1_C) comprise 10 to 40 µm sized overgrowths that envelop
247 detrital alkali feldspar grains whereas generation 2 cements (P2_C) enclose P1_C and
248 occlude remaining porosity (Fig. 3A).

249

250 4.2 Authigenic K-feldspar microtextures

251

252 Foils for TEM study were cut (in samples from both An-t-Sron and Skiag Bridge)
253 using the FIB from the detrital grain-P1_C interface, P1_C cement, and P2_C cement (Fig.
254 3B; the fourth foil removed from trench 1 in Fig. 3B was destroyed during extraction).
255 P1_C and P2_C are microtexturally distinct, in line with the contrasting properties of
256 their fluid inclusion populations (Mark *et al.*, 2007). The microtexture of P1_C feldspar
257 changes with distance from its interface with the detrital grain (Fig. 4). Proximal to
258 the interface (trench 2), the feldspar is free of subgrains and micropores and has a low
259 defect density (Fig. 4A). Further from the interface in trench 3 the P1_C feldspar
260 contains 2 to 3 µm sized subgrains whose boundaries are delineated by long and
261 narrow micropores (Fig. 4B). Aggregates of a very fine (< 0.2 µm) and poorly
262 crystalline mineral occur within the micropores along subgrain boundaries, but could
263 not be identified unambiguously; their habit is suggestive of illite (Fig. 4c). By
264 contrast, the P2_C feldspar (trench 4) comprises a mosaic of 0.5-1 µm sized subhedral
265 to euhedral subgrains elongate approximately parallel to b* and the euhedral

subgrains have the {110} adularia habit (Fig. 4D). Subgrain boundaries are decorated with dislocations that have an average spacing along the boundary of ~30 nm (Fig. 4E, F) and associated with micropores whose outlines are again parallel to {110} (Fig. 4E) and whose origins are inferred to be related to crystal nucleation and growth (Worden & Rushton, 1992). All of the K-feldspar has a diffuse mottling (Fig. 4F) that is characteristic of adularia. Measurements from selected area electron diffraction (SAED) patterns show that the reciprocal cell angle of this cement (γ^* , or ‘triclinicity’, which is sensitive to Si, Al order-disorder) is 90.7° and value of d_{010}/d_{100} (which is sensitive to composition) is 1.72. These values are similar to those of overgrowths in Permo-Triassic sandstones studied by Worden and Rushton (1992). $P1_C$ and $P2_C$ from both An-t-Sron and Skiag Bridge display comparable microtextures.

4.3 Ar-Ar geochronology

All Ar-Ar data are reported as 2σ throughout this manuscript. Ar-Ar ages (Ar-Ar age data tables presented in Mark *et al.*, 2007) from the detrital alkali feldspars range from 518 ± 19.7 to 926 ± 51.7 Ma ($n = 9$). This variability is potentially a result of a combination of factors including loss of radiogenic Ar ($^{40}\text{Ar}^*$), deuteric alteration during cooling of their parent rock, natural variation in feldspar source regions and diagenetic alteration during burial. Due to these factors it was not possible to accurately constrain the source regions of the detrital K-feldspar grains. The interfaces between detrital grains and the $P1_C$ overgrowths were optically identifiable and avoided during laser ablation by leaving a 10 μm boundary between the interface and

ablation areas. Hence, the older detrital feldspar component did not contaminate the ages of the younger K-feldspar overgrowths.

Ar-Ar ages from optically identified P1_C cement (entire P1_C overgrowths were ablated in an attempt to maximise the extraction of Ar from the sample and minimise Ar-Ar age error) range from 450.3 ± 8.7 to 490.3 ± 14.0 Ma at An-t-Sron (n=24; Fig. 5) and 458.0 ± 26.1 to 490.2 ± 14.8 Ma at Skiag Bridge (n=15; Fig. 5). The interface between P1_C and P2_C cements was also optically identifiable. A 10 μm boundary was left on both sides of the P1_C and P2_C boundary to ensure there was no contamination during laser ablation. Ar-Ar ages from the P2_C cements (entire zones of P2_C cement, on average $\sim 50 \mu\text{m}^2$, were also ablated to minimise Ar-Ar age error) are 413.1 ± 15.0 to 450.4 ± 14.4 Ma at An-t-Sron (n=10; Fig. 5) and 403.2 ± 24.5 to 455.0 ± 25.7 Ma at Skiag Bridge (n=32; Fig. 5). Fig. 5 shows a summary of the Ar-Ar data for the authigenic K-feldspar and a probability density diagram for both cement generations.

Scatter within the Ar-Ar data for each generation of cement may potentially be attributed to geological variation. For example, if you consider that K-feldspar overgrowths from the Victory Formation (UK Atlantic Margin) were precipitated over a 30 Ma period (Mark *et al.*, 2005), then some Ar-Ar age variation for P1_C and P2_C is expected. The two ages for P1_C and P2_C authigenesis broadly correspond with the Grampian (475 to 467 Ma; Dewey, 2005) and Scandian (435 to 420 Ma; Johnson *et al.*, 1985) episodes of the Caledonian Orogeny (Mark *et al.*, 2007).

5. DISCUSSION

315 5.1 Resolution of different generations of cement

316

317 Bimodal distributions for minimum fluid entrapment temperatures and salinities
318 corresponding to both P1_C and P2_C at both An-t-Sron and Skiag Bridge, supported by
319 mineral compositional differences (Ba in P2_C; Mark *et al.*, 2007), show that the Ar-Ar
320 ages from P2_C represent a second episode of authigenesis. If only a single fluid
321 inclusion population were present within both cement generations and there was no
322 change in parent fluid composition (Mark *et al.*, 2007), then we would have to
323 consider Ar-loss from P1_C and contamination of zone P1_C with excess Ar as potential
324 mechanisms of producing the observed Ar-Ar age differences between P1_C and P2_C.
325 Due to differing parent fluid data and compositions for both generations we can
326 discount these mechanisms.

327

328 5.2 Clay content

329

330 Aggregates of 20 by 100 nm sized crystals are present along subgrain boundaries
331 within P1_C (Fig. 4). These crystals are inferred to be illite from their habit and the
332 findings of illite in two previous TEM studies of K-feldspar overgrowths from the UK
333 (Worden & Rushton, 1992; Lee & Parsons, 2003). The replacement of K-feldspar by
334 illite, or passive precipitation of illite within pores (processes which occur post-
335 precipitation of the authigenic K-feldspar; Lee & Parsons, 2003) may potentially
336 affect Ar-Ar ages because illite also contains ⁴⁰K that will radiogenically decay to
337 ⁴⁰Ar*. However, considering the amount of illite present along subgrain boundaries,
338 the K-ratio between illite and K-feldspar and placing both of these factors in context
339 with the amount of material ablated in order to obtain a single P1_C Ar-Ar age (whole

overgrowths), the input of $^{40}\text{Ar}^*$ from clay ($< 0.1\%$) would have had a minimal effect on the Ar-Ar data relative to the error range determined for each individual Ar-Ar age (see Ar-Ar tables in Mark *et al.*, 2007).

343

5.3 Excess Ar and fluid inclusions

345

We have to consider if excess Ar within fluid inclusions which were ablated during Ar-Ar age determination could have influenced the true age of the two cementing generations. We did not directly analyse fluid inclusions for the presence of excess Ar, we used basic modelling.

350

Inclusions containing fluids of deep crustal origin often contain between 0.1 and 10 ppm excess Ar (Kelley, 2002). Therefore, ablation of fluid inclusions within authigenic K-feldspar overgrowths may have had varying effects upon the final isotopic Ar-Ar age of the mineral, depending on the volume fraction of the inclusions that have been ablated. Fluid inclusions within P1_C and P2_C at Skiag Bridge and An-t-Sron are sparse and range in size from 3-6 μm and 4-9 μm , respectively (Mark *et al.*, 2007). Calculations show that if the fluid content of the ablation areas was 1 volume %, and parent fluids contained 0.1 ppm excess Ar, then K-feldspar would exhibit an Ar-Ar age increase of 0.35 Ma. If the same 1 volume % parent fluids contained 10 ppm excess Ar, the associated Ar-Ar age increase would be 35 Ma. However, because fluid inclusion volumes, their occurrence and distributions varies between different K-feldspar overgrowths within both samples, and the Ar-Ar ages for each cement generation remain consistent, we suggest that excess Ar within fluid inclusions is not a significant contributing factor. Furthermore, the two samples come from sites that

are 30 km apart and it seems highly unlikely that the two samples could have experienced identical excess Ar histories thereby producing similar Ar-Ar ages for both generations of K-feldspar. Additionally, variations in $^{38}\text{Ar}_{\text{Cl}}/^{39}\text{Ar}_{\text{K}}$ which is a proxy for Cl/K ratio and used as an indicator of brine-borne excess Ar (Harrison *et al.*, 1994), show no correlation with Ar-Ar age (Mark *et al.*, 2007).

5.4 ^{39}Ar recoil and sample heating during irradiation

Recoil loss of ^{39}Ar during irradiation has to be eliminated as a potential process that could result in scattering of the Ar-Ar ages for both P1_C and P2_C. ^{39}Ar has a recoil distance of $\sim 0.1 \mu\text{m}$ (Onstott *et al.*, 1995; Villa, 1997). With respect to subgrain sizes for the P1_C microtexture, 15 and 2-3 μm , recoil loss of ^{39}Ar would not be sufficient to explain Ar-Ar age distributions. In P2_C microtextures that contain 0.5-1 μm subgrains, ^{39}Ar recoil is potentially a problematic issue. However, as the ablation areas were maximised (a minimum $50 \mu\text{m}^2$), any potential effect of ^{39}Ar movement by $\sim 0.1 \mu\text{m}$ was negated by the analytical process.

Sample heating during irradiation of cadmium shielded samples can potentially induce significant Ar-loss. Both wafers were irradiated at different times for different durations in different positions of the McMaster reactor. If heating had induced significant Ar-loss in one or both samples, then we would not have obtained comparable data from both samples.

5.5 Thermally induced Ar-loss and Ar-Ar age resetting

In order to test the Ar-Ar ages for resetting, Ar-loss from subgrains was modelled through a series of tectono-thermal histories (Wheeler, 1996). To model this data we have assumed weighted means for the different cementing phases using v. 3.00 of the isoplot/Ex program (Ludwig, 2003). $P1_C$ at An-t-Sron has a weighted mean of 472.3 ± 5.1 Ma (mean square weighted deviation [MSWD] 3.9) and at Skiag Bridge a weighted mean of 467.0 ± 6.0 Ma (MSWD 2.6). $P2_C$ at An-t-Sron has a weighted mean of 435.9 ± 7.3 Ma (MSWD 1.8) and at Skiag Bridge a weighted mean of 430.2 ± 5.1 Ma (MSWD 4.0). Although the data do not conform to a normal distribution (Fig. 5), with the implication there exists scatter due to geological causes, the weighted means represent a first-order acceptable approximations for the ages of the two episodes of authigenesis for use in Ar diffusion modelling.

The temperatures experienced by the Fucoid Beds during Moine emplacement (which occurred at ~ 430 to 422 Ma; Dewey, 2005), have been reconstructed using evidence from acritarch coloration index (Downie, 1982), illite crystallinity (Johnson *et al.*, 1985) and fluid inclusion analysis (Baron *et al.*, 2003; Mark *et al.*, 2007). Minimum temperatures experienced by the sampled sections of the Fucoid Beds during Moine emplacement are ~ 200 °C. The thermal data was entered into a simplified tectono-thermal thrust model (Oxburgh & Turcotte, 1974). A simplified thrust model is sufficient to model Ar-diffusion and the maximum palaeotemperature and duration of heating (along with the effective diffusion dimension) are the main controls on Ar diffusion.

5.5.1 Ar-diffusion model

415 The Ar-diffusion model uses forward projection to test the Ar-Ar ages by establishing
416 a thermal history (Wheeler, 1996) against which assumed Ar-Ar ‘growth ages’ can be
417 evaluated in terms of Ar-loss. In the model, 0 Ma corresponds to ages of authigenesis
418 for both generations of authigenic K-feldspar (~470 and 432 Ma for P1_C and P2_C,
419 respectively), and 470 and 432 Ma in the model correspond to the present day for P1_C
420 and P2_C, respectively. Prior to thrust sheet emplacement at 430 Ma, the model
421 assumes that the temperature in the Fucoïd Beds is represented by the fluid
422 entrapment temperatures that were determined previously (90 and 128 °C for P1_C and
423 P2_C, respectively; Mark *et al.*, 2007). Note that P2_C is younger and contains smaller
424 subgrains than P1_C. Therefore, although small P2_C subgrains appear have lost less Ar
425 than larger P1_C subgrains in some instances, P1_C was subjected to an extra 30-40 Ma
426 of heating pre-thrusting.

427

428 *5.5.1.1 8 Ma, 200 °C thermal event.* During thrust sheet emplacement (thrusting
429 inferred to start at 430 Ma; Johnson *et al.*, 1985; Kinny *et al.*, 1999), a stepped
430 gradient developed within the footwall and the temperature at the thrust sheet-footwall
431 interface was 0.5T (200 °C), where T is the temperature at the thrust sheet base prior
432 to emplacement (~ 400 °C). Rapid thermal re-equilibration of the footwall occurred as
433 heat was conducted away from the thrust front (Johnson *et al.*, 1985) through the
434 over-thrusted successions. The footwall cooled from palaeo-maximum temperatures
435 (~ 200 °C) in response to syn- and post-uplift erosion. Assuming a standard erosion
436 rate of 1 km/Myr for a continent-continent collision (current Himalaya erosion rates
437 of 2.1 to 2.9 mm/yr; Galy & France-Lanord, 2001) and a geothermal gradient of 30
438 °C/km, the Fucoïd Beds cooled to 150 °C by 422 Ma. We infer a simple linear cooling
439 trend from 422 Ma to present day, and an approximated temperature of 10 °C to

440 represent the current Fucoïd Bed surface temperature. It is important to note that
441 much of the recent Fucoïd Bed temperature-time path has had insignificant effects on
442 the diffusion of Ar in the K-feldspar subgrains (Fig. 6).

443

444 Diffusion domain sizes determined from TEM work were used to represent the
445 effective diffusion dimensions (Dodson, 1973; subgrains equated to spheres and
446 corresponding radii determined from Fig. 4). P1_C is relatively featureless and has
447 large subgrains (~15 µm in diameter) adjacent to the detrital grain-overgrowth
448 boundary and smaller subgrains (~3 µm diameter) further from the boundary (Fig.
449 4A-B). From TEM observations and cooling rates calculated using the tectono-thrust
450 model outline above (Fig. 6; 430-422 Ma = 6.25 °C/Ma; and 422-present day = 0.33
451 °C/Ma), it is possible to calculate the theoretical closure temperatures of the K-
452 feldspar subgrains within the Fucoïd Bed samples (Dodson, 1973). 15 and 3 µm
453 subgrains respectively have theoretical closure temperatures of 200 and 212 °C, and
454 155 and 170 °C for cooling rates of 0.33 and 6.25 °C/Ma. Subgrains are smaller (~1
455 µm) and more abundant, but irregularly distributed within the P2_C cements (Fig. 4D-
456 F). 1 µm subgrains have a T_c of 143 and 154 °C for cooling rates of 0.33 and 6.25
457 °C/Ma. Ar-diffusion models were run to quantitatively determine the amount of Ar-
458 loss from both cement generations.

459

460 The Ar-diffusion model (Fig. 7) indicates that the 3 µm subgrains will have lost 33 %
461 of their initial ⁴⁰Ar* (Table 1), and so will yield Ar-Ar ages 140 Ma younger than the
462 growth age. The 15 µm subgrains will have lost 28 % of their ⁴⁰Ar* and will have
463 yielded Ar-Ar ages 120 Ma younger than the growth age (Table 1). However, because
464 entire P1_C overgrowths were ablated in order to obtain the maximum amount of Ar for

each mass spectrometer measurement, each P1_C Ar-Ar age is a function of variable ratios of 3 µm and 15 µm subgrains. The FIB-TEM method enables examination of only small regions of the authigenic K-feldspar (15x5 µm foils) and as such, it is not possible to give accurate estimates of the proportion of large to small subgrains ablated for any single Ar-Ar age. Assuming a simple subgrain ratio of 1:1 for 15 and 3 µm subgrains, the model estimates that P1_C has lost 30 % of its ⁴⁰Ar* and Ar-Ar ages have been reset by ~ 130 Ma. Therefore, the Ar-diffusion model estimates the actual age of P1_C authigenesis to be ~600 Ma. The same Ar-diffusion thermal model used for P1_C (Fig. 6) indicates that 1 µm P2_C subgrains (which are younger than the P1_C subgrains) have lost 32 % ⁴⁰Ar*, resetting the P2_C Ar-Ar age by 127 Ma and thus indicating a 'model' Ar-Ar age for P2_C authigenesis of 559 Ma (Fig. 7).

Comparison of the modelled Ar-Ar ages for 'modelled crystallization' of P1_C (600 Ma) and P2_C (559 Ma) with the depositional age of the Fucoid Beds (518 to 510 Ma; Gradstein *et al.*, 2004), indicates discrepancies with the Ar diffusion modelling. The subgrain sizes were measured using TEM (Fig. 4) and are consistent with previous observations (Lee and Parsons, 2003). Therefore either the peak palaeotemperature associated with Scandian thrusting or the duration of heating has been overestimated, thereby overestimating Ar-loss from both cement generations. The impact of reducing both the peak palaeotemperature and the duration of the thermal perturbation can be tested by re-running the Ar-diffusion model using new parameters.

5.5.1.2 Reduced palaeothermal maxima. A second series of Ar-diffusion models (still using a thrust-related heating event at 430 Ma for duration of 8 Ma) were run with peak temperatures set at 180, 160 and 140 °C (Fig. 6). The model results are

490 summarised in Fig. 7. The lowest maximum palaeotemperature of 140 °C causes little
491 (4 %) $^{40}\text{Ar}^*$ -loss from 15 μm subgrains and reduces Ar-Ar ages by only ~ 16 Ma.
492 $^{40}\text{Ar}^*$ -loss from 3 μm (7 % $^{40}\text{Ar}^*$ -loss) and 1 μm (9 % $^{40}\text{Ar}^*$ -loss) subgrains, thereby
493 producing widely scattered Ar-Ar ages that are reduced by 27 and 33 Ma, respectively
494 (Table 1).

495

496 Despite a geographical separation of 30 km between the two sampling sites, the two
497 generations of cement in both samples have similar Ar-Ar age distributions, implying
498 that P1_C and P2_C Ar-Ar ages at both sites have lost exactly the same amounts of $^{40}\text{Ar}^*$
499 (i.e. experienced identical thermal histories resulting in equal resetting of both
500 samples). In order for authigenic K-feldspar at both sites to have been reset
501 identically, the thrust induced increase in thermal gradient must have been
502 synchronous and uniform over the 30 km distance between the sites as any variation
503 in temperature or timing, would have resulted in different thermal histories and hence,
504 different Ar-Ar ages. Thermal synchronicity between the two sites is not consistent
505 with field and laboratory data.

506

507 Dewey (2005) showed that the impingement of the colliding landmasses during the
508 Scandian episode of the Caledonian Orogeny occurred first in the south and resulted
509 in the northern sector of the colliding landmass swivelling into the Laurentian margin.
510 Thrusting was not synchronous across the entire 180 km Moine Thrust Zone. Fluid
511 inclusion data (Baron *et al.*, 2003; Mark *et al.*, 2007) also show that thrust induced
512 heat flow within the Caledonian Foreland was neither synchronous nor uniform.
513 During thrust emplacement, sites in the south (close to Skiag Bridge) were 30 to 40
514 °C cooler than those in the north (close to An-t-Sron). Data show that equal resetting

of both P1_C and P2_C in both samples is highly unlikely. Furthermore, we know that temperatures reached a minimum of 200 °C in the Furoid Beds (Downie, 1982; Johnson *et al.*, 2005; Baron *et al.*, 2003; Mark *et al.*, 2007), but modelling of Ar-diffusion in line with a thermal history depicting peak temperatures of 200 °C and transient heating from the hanging wall into the footwall, clearly overestimates Ar-loss thereby dating the first episode of authigenesis as pre-deposition.

The evidence therefore suggests, if it is assumed that: (i) the K-feldspar diffusion coefficients are correct (Foland, 1974), (ii) there was transient heating to 200 °C and, (iii) subgrain size is representative of the effective diffusion dimension, that the Ar-Ar ages are incompatible with the geological context of the rocks. The other parameter in the Ar diffusion model that can be modified to compensate for the Ar-Ar age overestimation is the mechanism by which heat is removed from the thrust zone and hence, the duration of thrust-induced heating.

5.5.1.3 Short term heating. The alternative heat flow model to transient heating would be very short thermal pulsing of large volumes of hot fluids through the rock, a similar mechanism to which has been observed in Himalayan thrust zones (Le Fort, 1981; Copeland *et al.*, 1991). As we know that fluids attained a temperature of 200 °C, the implied periods of fluid flushing removing heat from the thrust zone are short, perhaps in the order of ~10 Ka. The Ar diffusion model was re-run and modified to incorporate short term heating to 200 °C over 10 Ka for P1_C and P2_C (Fig. 8). The model shows that P1_C 15 µm subgrains would lose 4 % ⁴⁰Ar* and 3 µm subgrains would lose 6 % ⁴⁰Ar*, whilst P2_C 1 µm subgrains would lose 4 % ⁴⁰Ar* (Fig. 9). Assuming a 1:1 subgrain ablation ratio for P1_C subgrains (15 and 3 µm), Ar-Ar ages

would have been reset by ~ 20 Ma, and P2_C Ar-Ar ages by 17 Ma. The new model shows that the degree of age resetting due to thermally induced Ar-loss by rapid flushing of fluids is consistent with the observed variability of the authigenic K-feldspar Ar-Ar ages (section 4.3). Although the re-run Ar diffusion model incorporating short term heating by fluids is consistent with the observed Ar-Ar ages for both generations of authigenic K-feldspar at both sites, the simplicity of the thermal model depicting short term heating by fluids in the Himalaya has been questioned. Harrison *et al.* (1997) suggested that other factors may be acting in association with short term heating by fluids to influence heat flow within the Himalayas.

In summary, a tectono-thermal model assuming transient heating to 200 °C is incompatible with the Ar-Ar ages of the two generations of K-feldspar cement relative to the age of deposition for the Fucoid Beds. Transient heating to lower temperatures is inconsistent with the regional geology. A tectono-thermal model invoking rapid removal (in the order of 10 Ka) of heat from the thrust zone via flushing of hot fluids is consistent with the Ar-Ar age data and the regional context of the samples, but the validity of the tectono-thermal model has been questioned (Harrison *et al.*, 1997). We have assumed for all of the above models that subgrain size is indicative of the effective diffusion dimension. This assumption is based on the fact that dislocation rich subgrain boundaries in authigenic K-feldspar act as fast diffusion boundaries (zero Ar concentration) for ⁴⁰Ar* as they do in superficially similar patch perthite (Burgess *et al.*, 1992). What if this is an incorrect assumption?

5.6 Subgrain microtextures and the effective diffusion dimension

565

566 In order to answer fundamental questions regarding the magnitude and mechanisms of
567 Ar-loss from authigenic K-feldspar, what this paper sets out to address, it is pertinent
568 to consider the properties of superficially similar patch perthite microtextures within
569 deuterically altered alkali feldspars from plutonic igneous rocks (Fig. 1). Direct
570 comparisons have been made between the Ar retention properties of these
571 microtextures and authigenic K-feldspar (Lee & Parsons, 2003). Patch perthites form
572 by deuteric/hydrothermal alteration of strain-controlled exsolution microtextures
573 (unzipping reactions; Parsons & Lee., 2005) and are composed of aggregates of sub-
574 μm to μm -sized subgrains. Microporous patch perthites form veins of networks that
575 develop as fluids have penetrated the grain interior (Fig. 1). As a consequence,
576 deuterically altered alkali feldspars are highly permeable in zones where
577 recrystallization has occurred (Worden *et al.*, 1990). Burgess *et al.* (1992) showed that
578 these volumes of recrystallized alkali feldspar lose significant volumes of Ar over
579 time.

580

581 Patch perthite subgrains are typically incoherent and so their boundaries are
582 dislocation-rich (Worden *et al.*, 1990). As a consequence, it has been suggested that
583 short-circuit diffusion, which takes place at a rate 4-5 orders of magnitude greater
584 than lattice volume diffusion (Wartho *et al.*, 1999), must be the principle mechanism
585 of Ar-loss from patch perthites and not volume diffusion (Lee, 1995). Whereas most
586 alkali feldspars from slowly cooled igneous rocks have discrete patches or veins of the
587 subgrain-rich microtexture (Parsons *et al.*, 1999), entire authigenic K-feldspar
588 overgrowths are composed of subgrains (Worden & Rushton, 1992; Lee & Parsons,
589 2003; Mark *et al.*, 2005; Mark *et al.*, 2006). Hence we assume that at very low

temperatures, subgrained authigenic K-feldspar will leak Ar (Lee & Parsons, 2003). Therefore, depending on the thermal history of its parent rock, authigenic K-feldspar Ar-Ar ages may record isotopic closure rather than the crystallization. However, results of previous Ar-Ar studies investigating authigenic K-feldspar (Hagen *et al.*, 2001; Mark *et al.*, 2005; Sherlock *et al.*, 2005), suggest that there must be fundamental differences between patch perthite and authigenic K-feldspar (Fig. 1 & 4) that can account for why the former leaks Ar whereas the latter appears to retain Ar.

Although volumes of patch perthite appear turbid in thin section, K-feldspar overgrowths are typically uniform and glass-clear in transmitted-light, indicating that authigenic feldspar has a lower density of micropores and inclusions. Furthermore, unlike patch perthite subgrains, authigenic K-feldspar subgrains form during crystal growth (not recrystallization), and there is no reason why micropores should be interconnected. Thus, if micropores are not connected, short-circuit Ar diffusion will not operate in the same manner as it does in patch perthite. Furthermore, Fitz Gerald *et al.* (2006) have recently observed networks of even smaller pores within alkali feldspars from igneous rocks which could potentially act as additional pathways for rapid diffusion of Ar. These structures are characteristic of the semicoherent exsolution microtextures of perthitic alkali feldspars and so would not be present within the authigenic K-feldspar.

Given the hypothesised low micropermeability of microporous authigenic K-feldspar, a theoretical model has been formulated to explain why authigenic K-feldspar may (unlike patch perthite) yield meaningful Ar-Ar growth ages. We suggest there is no

615 direct route for the Ar to escape authigenic K-feldspar on the scale of tens or hundreds
616 of microns as micropores are not connected and therefore diffusion cannot operate at
617 enhanced rates in authigenic K-feldspar as it does in microporous/micropervious
618 patch perthite (Fig. 10). Once an approximate equilibrium is established between the
619 concentrations of Ar in the subgrains, the micropores and dislocation-rich boundaries,
620 diffusion from the subgrains into the porous regions of the mineral will be controlled
621 by re-equilibration over time (i.e. the Ar is trapped within dislocations, micropores
622 and subgrain boundaries and therefore violates the assumption that such features act
623 as infinite reservoirs with zero concentrations of Ar). Re-equilibration will occur as
624 further Ar within subgrains is produced by radioactive decay and Ar diffuses out of
625 the K-feldspar subgrains via volume diffusion into dislocations, micropores and
626 subgrain boundaries.

627

628 Although short-circuit diffusion of Ar is potentially restricted within authigenic K-
629 feldspar, thus preventing rapid Ar-loss in comparison to patch perthite, lattice volume
630 diffusion still occurs. Contrary to patch perthite, volume diffusion may be the
631 dominant diffusion mechanism. Ar-loss from the overgrowth boundary will still be
632 occurring by volume diffusion and hence we have to model Ar-Ar age data
633 accordingly (Fig. 10). The implications of this theoretical model are that rather than
634 modelling Ar-loss from K-feldspar overgrowths using subgrain sizes determined from
635 TEM images, Ar-diffusion models should use overgrowth thickness as the effective
636 diffusion dimension (Fig. 10).

637

638 We can quantitatively test the theoretical model by re-running the Ar diffusion models
639 with different effective diffusion dimensions. P1_C overgrowths have a maximum

640 thickness of $\sim 40 \mu\text{m}$ and P2_C overgrowths are up to $\sim 100 \mu\text{m}$ thick (Fig. 3). Using a
641 heating event at 430 Ma with duration of 8 Ma and peak temperature of 200°C (the
642 original Ar-diffusion model; Fig. 6) and effective diffusion dimensions of 40 and 100
643 μm , the Ar-diffusion model was re-run to test the theoretical model outlined in Fig.
644 10. Grains were approximated to spheres (geometry is not a massively significant
645 variable with respect to the effective diffusion dimension and temperature and
646 duration of heating) and no excess Ar was input into the model. Results are shown in
647 Fig. 11. 470 Ma $40 \mu\text{m}$ thick overgrowths have been reset by 13 Ma (lost 3 % $^{40}\text{Ar}^*$)
648 and 432 Ma $100 \mu\text{m}$ thick overgrowths have been reset by 3 Ma (lost $< 1\%$ $^{40}\text{Ar}^*$).
649 The Ar-diffusion model produces data that are consistent (considering that the model
650 used the maximum effective diffusion dimension for P1_C and P2_C and there was a lot
651 of variability in overgrowth thickness) with the determined Ar-Ar ages, thereby
652 supporting a thermal model of transient heating (Fig. 11) that is also consistent with
653 the regional geology.

654
655 It could be argued that the consistency between the model incorporating transient
656 heating to 200°C and overgrowth thickness as the effective diffusion dimension (Fig.
657 11) with the Ar-Ar age data is due to an overestimation of the true effective diffusion
658 dimensions (i.e. use of grain size rather than subgrain size determined from TEM
659 imaging), especially as previous studies successfully modelled Ar diffusion using
660 subgrain diameter as the effective diffusion dimension (Mark *et al.*, 2005). Although
661 Mark *et al.* (2005) successfully modelled Ar diffusion using subgrain size rather than
662 overgrowth thickness, the rocks were only exposed to low post-growth temperatures
663 following authigenesis (125°C). Hence, the variation in effective diffusion dimension

664 is not as significant as it is with respect to the Furoid Bed case study, and had a
665 limited impact on the Ar-loss data.

666

667 **6. CONCLUSION**

668

669 The Ar-Ar ages two generations of Furoid Bed authigenic K-feldspar (P1_C and P2_C)
670 record different stages of mineral growth and have undergone minimal Ar-loss and
671 Ar-Ar age resetting. Two separate models have been proposed, both of which are
672 consistent with the geological context of the samples (heating to a minimum of 200
673 °C) and can account for the apparent robustness of the authigenic K-feldspar with
674 respect to microtextural repetitiveness of Ar: short-term hot fluid flushing (assuming
675 subgrain sizes are appropriate estimations of the effective diffusion dimension) and
676 transient heating (assuming overgrowth thickness as an appropriate estimation of the
677 effective diffusion dimension).

678

679 We highlight that although K-feldspar microtextures appear to be microporous, it is
680 potentially micropermeability that is the critical factor with respect to Ar-loss and the
681 ability of a mineral phase to record meaningful Ar-Ar isotopic data. This project is not
682 intended to be the definitive study of Ar-diffusion within authigenic K-feldspar, but
683 provides a suitable starting point for discussions of factors governing the reliability of
684 Ar-Ar dating using authigenic K-feldspar and the importance of understanding Ar
685 trapping mechanisms within different feldspar microtextures. More experimental
686 work is required to develop and test (prove/disprove) the theoretical model outlined in
687 this paper. The collection of quantitative Ar-Ar data from authigenic K-feldspar that

688 has been exposed to a range of high-temperature settings is required before the
689 validity of the model proposed here can be confirmed.

690

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692

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700

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903 **FIGURE CAPTIONS**

- 904
- 905 Fig.1: Bright-field TEM image of alkali feldspar grain from the Lower Devonian Shap
906 Granite. The image shows a vein of patch perthite cross-cutting otherwise pristine
907 cryptoperthite. Albite exsolution lamellae in the cryptoperthite are oriented SE-NW in

the image and close to (-701) in the corresponding [01-1] SAED pattern. The patch perthite vein comprises a number of subgrains, giving the mottled contrast, and micropores of various sizes (white in the image). Scale bar 1 μm .

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Fig. 2: Simplified geological map of the NW Highlands showing relationship of Caledonian Foreland to Moine Thrust Belt. Sampling sites also shown.

914

Fig. 3: Sample shown from An-t-Sron. (A) Backscattered electron SEM image showing generation 1 ($P1_C$) K-feldspar overgrowths on detrital alkali feldspar grains. Generation 2 K-feldspar cement ($P2_C$) envelops $P1_C$ and has occluded remaining porosity. Dol denotes authigenic dolomite and Qz is detrital quartz (After Mark *et al.*, 2007). (B) Secondary electron FIB image showing the location of pits excavated using the ion beam into the grain in the upper right of (A). (C) Secondary electron FIB image of a trench prior to lifting out of the foil, which lies between the two crosses. (D) Secondary electron FIB image of the trench following foil removal. (E) SEM-STEM image of a slice on a holey carbon film. The slice comprises feldspar that is thicker on the left and right hand sides than in the central portion, above which is a narrow (~50 nm) layer of gold (white) overlain by the thicker (~1 μm) platinum strap.

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Fig. 4: Samples shown from An-t-Sron. Bright-field TEM images of foils that have been cut and extracted from the grain in Figure 3B. Image A is from trench 2, images B and C are from trench 3 and D, E and F are from trench 4. (A) The interface between the detrital alkali feldspar grain and $P1_C$ cement. Mottling in the detrital grain is due to the abundance of dislocations and subgrains and a number of small angular micropores are also present. The authigenic K-feldspar is subgrain-free, has a low

933 defect density and a fine-scale modulated microtexture. The indexed SAED pattern
 934 (from the detrital grain) shows that the electron beam is parallel to [312]. Scale bar 1
 935 μm . (B) Subgrains (2 to 3 μm in size) within P1_C K-feldspar further from the interface
 936 with the detrital grain. Their boundaries (arrowed) have been etched by fluids to form
 937 long and narrow pores (arrowed). Scale bar 500 nm. (C) A subgrain boundary within
 938 P1_C cement along which have formed clumps of fibrous and poorly crystalline
 939 minerals, probably illite. Scale bar 500 nm. (D) P2_c cement that contains a number of
 940 sub- μm to μm -sized subgrains, all of which have dislocation-rich boundaries. The
 941 euhedral subgrains have a {110} adularia habit. Some small micropores have also
 942 formed along one of the subgrain boundaries. Electron beam parallel to [001]. Scale
 943 bar 1 μm . (E) One subgrain in the P2_c cement. Areas of strain contrast highlight
 944 dislocations along subgrain boundaries and sub- μm sized angular micropores also
 945 occur at subgrain boundaries. Electron beam parallel to [001]. Scale bar 100 nm. (F)
 946 Subgrains within P2_c cement with more irregular but still dislocation-rich boundaries.
 947 Bend contours in the foil help highlight a diffuse microtexture with modulations
 948 approximately parallel to a^* and b^* . Electron beam parallel to [001]. Scale bar 500
 949 nm. Note due to a technical failure of the double-tilt axis during TEM examination,
 950 the reciprocal lattice directions are not shown in all images.

951

952 Fig. 5: (A) Weighted average plot showing Ar-Ar data for P1_C and P2_C from An-t-
 953 Sron and Skiag Bridge (error: 2 σ in relation to Fucoid Bed deposition, the Grampian
 954 and Scandian episodes of the Caledonian Orogeny. (B) Relative probability
 955 distribution plot for Ar-Ar data from An-t-Sron. (C) Relative probability distribution
 956 plot for Ar-Ar data from Skiag Bridge. Both data sets (B&C) show a bimodal
 957 distribution suggesting K-feldspar growth from two distinct episodes of authigenesis.

958

959 Fig. 6: Diagrams showing reconstructed thermal history, with which K-feldspar
 960 subgrains are modelled. The software is a forward modelling program, hence, 0 Ma
 961 corresponds to ages of authigenesis, and 470 and 432 Ma correspond to present day.
 962 (A) P1_C authigenesis, 200 °C peak temperature. (B) P2_C authigenesis, 200 °C peak
 963 temperature. (C) P1_C authigenesis, 180 °C peak temperature. (D) P2_C authigenesis,
 964 180 °C peak temperature. (E) P1_C authigenesis, 160 °C peak temperature. (F) P2_C
 965 authigenesis, 160 °C peak temperature. (G) P1_C authigenesis, 140 °C peak
 966 temperature. (H) P2_C authigenesis, 140 °C peak temperature.

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968 Fig. 7: Typical DIFFARG output showing modelled response of different sized (15, 3
 969 and 1 µm) subgrains (diffusion domains) to a 200, 180, 160 and 140 °C thermal
 970 episode (Fig. 6). The Ar –diffusion model determines the amount of Ar-loss and
 971 therefore the degree that each Ar-Ar age is reset, data are summarised in Table 1. (A)
 972 P1_C 15 µm subgrain (left: Ar evolution of spherical subgrains of known radius; right:
 973 bulk age showing apparent age post exposure). (B) P1_C 3 µm subgrain (left: Ar
 974 evolution of spherical subgrains of known radius; right: bulk age showing apparent
 975 age post exposure). (C) P2_C 1 µm subgrain (left: Ar evolution of spherical subgrains
 976 of known radius; right: bulk age showing apparent age post exposure).

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978 Fig. 8: Diagrams showing short term heated fluid thermal history, against which K-
 979 feldspar subgrains are modelled. The software is a forward modelling program, hence,
 980 0 Ma corresponds to ages of authigenesis, and 470 and 432 Ma correspond to present
 981 day. (A) P1_C model, 470 Ma to present day. (B) P2_C model, 432 Ma to present day.

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983 Fig. 9: Typical DIFFARG output showing modelled response of different sized (15, 3
984 and 1 μm) subgrains (diffusion domains) to a short term fluid heating event, 10,000
985 years at 200 $^{\circ}\text{C}$ (Fig. 6). (A) P1_C 15 μm subgrain (left: Ar evolution of spherical
986 subgrains of known radius; right: bulk age showing apparent age post exposure). (B)
987 P1_C 3 μm subgrain (left: Ar evolution of spherical subgrains of known radius; right:
988 bulk age showing apparent age post exposure). (C) P2_C 1 μm subgrain (left: Ar
989 evolution of spherical subgrains of known radius; right: bulk age showing apparent
990 age post exposure).

991
992 Fig. 10: Simple schematic diagram (not drawn to scale and spheres used to represent
993 subgrains as used in DIFFARG model, true subgrains would have triple-junctions that
994 can not be represented by spheres) showing the fundamental differences between
995 patch perthite (left) and authigenic K-feldspar (right) microtexture. Within both
996 subgrained structures Ar diffusion from the subgrains into the micropores occurs via
997 volume diffusion. However, patch perthite micropores are interconnected and Ar can
998 diffuse out of the micropores via short-circuit diffusion and from the perthite
999 boundary via volume diffusion. Due to a lack of permeability with the authigenic K-
1000 feldspar microtexture, Ar can only diffuse through the grain boundary via volume
1001 diffusion. Short-circuit diffusion within authigenic K-feldspar is reduced. Hence,
1002 whereas currently subgrain size is used as the effective diffusion dimension (A), it
1003 may be more suitable to use the overgrowth thickness (B) to accurately model Ar-
1004 diffusion.

1005
1006 Fig. 11: Typical DIFFARG output showing modelled response of 100 and 40 μm
1007 subgrains to the thermal history shown in Fig. 5.10A&B. Left: Ar evolution of

1008 spherical grains of known radius. Right: bulk age showing apparent age post exposure
1009 to the thermal history. Note, DIFFARG is a forward modelling programme, hence for
1010 the 100 μm subgrain 0 corresponds to 432 Ma and 432 corresponds to present day.
1011 For the 40 μm subgrain 0 Ma corresponds to 470 Ma and 432 Ma corresponds to
1012 present day. The model shows that 100 μm subgrains are reset from 432 to 429 Ma
1013 and 40 μm subgrains are reset from 470 to 457 Ma.

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1015 **TABLE CAPTIONS**

1016

1017 Table 1: Amount of $^{40}\text{Ar}^*$ -loss and Ar-Ar age resetting by thermally activated Ar
1018 diffusion.

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Cement generation	Subgrain size (μm)	Ar-Ar age (Ma)	Peak temperature during thrusting ($^{\circ}\text{C}$)	Heating duration (Ma)	Ar-loss (%)	Ar-loss (Ma)	Model Ar-Ar age (Ma)
P1 _c	15	470	200	8	28.1	120.0	350.0
P1 _c	15	470	180	8	4.8	20.0	450.0
P1 _c	15	470	160	8	4.3	18.0	452.0
P1 _c	15	470	140	8	4.0	16.5	453.5
P1 _c	3	470	200	8	32.6	140.0	330.0
P1 _c	3	470	180	8	11.9	50.0	420.0
P1 _c	3	470	160	8	7.4	31.0	439.0
P1 _c	3	470	140	8	6.5	27.0	443.0
P2 _c	1	432	200	8	31.9	127.0	305.0
P2 _c	1	432	180	8	10.8	42.0	390.0
P2 _c	1	432	160	8	9.8	38.0	394.0
P2 _c	1	432	140	8	8.6	33.5	398.5

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