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Accepted Manuscript

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PII: S0016-7037(08)00171-3
DOI: 10.1016/j.gca.2008.03.018
Reference: GCA 5602

To appear in: Geochimica et Cosmochimica Acta

Received Date: 22 May 2007
Accepted Date: 25 March 2008


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REVISED MANUSCRIPT (W5010) SUBMITTED: 11th March 2008

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

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ABSTRACT

We have analysed two distinct generations of authigenic K-feldspar in Fucoid 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 Fucoid 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

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

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

1.2 Authigenic K-feldspar

Although step heating experiments originally designed to determine the age of authigenic K-feldspar overgrowths (Hearn & Sutter, 1985; Hearn et al., 1987; Girard et al., 1988; Spotl et al., 1996; Warnock & van der Kamp, 1999; Liu et al., 2003) have not directly enabled the distinction between detrital and authigenic generations, the data suggest that authigenic K-feldspar may record isotopic information relating to
diagenetic events. The introduction of laserprobe isotope extraction techniques has offered higher-spatial resolution than conventional methods, permitting Ar-extraction from individual grains and potentially eliminating problems of contamination from detrital feldspar. Initial laserprobe studies used Ar-ion and infrared laser systems for analysis of authigenic K-feldspar (Walgenwitz et al., 1990). Laser absorption by feldspar at such wavelengths is poor, however, and extensive heating occurred outside the site of laser-mineral interaction, resulting not only in the extraction of Ar from the overgrowth, but also from the detrital grain and surrounding minerals. The ultraviolet (UV, 266 nm) laserprobe (Kelley et al., 1994) has a greater spatial resolution than the Ar-ion and infrared laser systems (UV laser can achieve a spot resolution of 12 μm) and the wavelengths are absorbed strongly by the feldspar. As a consequence the UV laser does not heat the sample beyond the point of laser-sample interaction and therefore only extracts Ar from the desired locations. Investigations dating K-feldspar overgrowths using the UV laserprobe have yielded meaningful Ar-Ar growth ages (Hagen et al., 2001; Mark et al., 2005, 2008; Sherlock et al., 2005).

Authigenic K-feldspar overgrowths within sedimentary rocks from the Permo-Triassic of Elgin (Worden & Rushton, 1992), the Jurassic Humber Group of the North Sea (Lee & Parsons, 2003) and the Cretaceous Atlantic Margin Victory Formation (Mark et al., 2005), all show mineralogical and microtextural similarities. These overgrowths comprise mosaics of slightly misaligned submicron- to micron-sized subgrains, intercalated micropores, and nanometre growth bands orientated parallel to dislocation-rich subgrain boundaries. Overgrowths from Elgin and the Victory Formation have a regular subgrain size and well-developed crystal faces dominated by the {110} adularia habit. Subgrain boundaries of overgrowths from the Humber
Group are slightly curved with the {110} adularia habit. Subgrain size also increases with distance from the detrital grain-overgrowth interface. The presence of illite along subgrain boundaries at interfaces was noted in two studies (Worden & Rushton, 1992; Lee & Parsons, 2003).

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

Sherlock et al. (2005) modelled the thermal response of authigenic K-feldspar to an episode of tectonically induced heating. Because TEM was not used to characterise microtextures, the model was generic and covered a wide range of subgrain sizes but demonstrated that authigenic K-feldspar can potentially retain Ar. The first fully quantitative study of authigenic K-feldspar incorporating Ar diffusion modelling, Ar-Ar geochronology and TEM (Mark et al., 2005), modelled subgrain response in terms 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 Skiag Bridge, NW Highlands, two sites that are geographically 30 km apart (Fig. 2).
A documented enrichment of K-feldspar, up to 12 wt. % K₂O (Bowie et al., 1966) has been reported in the lower part of the Lower Cambrian An-t-Sron Formation (Fucoid Beds) thus providing an ideal geological context for assessing the retentiveness of authigenic K-feldspar with respect to Ar. This manuscript should be considered as a companion to Mark et al. (2007).

2. GEOLOGICAL SETTING

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

3. METHODS (SMALL TEXT IN MANUSCRIPT)

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

3.2 High-resolution petrography

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

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

3.4 Ar-diffusion modelling

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

4. RESULTS

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

4.2 Authigenic K-feldspar microtextures

Foils for TEM study were cut (in samples from both An-t-Sron and Skiag Bridge) using the FIB from the detrital grain-$P_{1c}$ interface, $P_{1c}$ cement, and $P_{2c}$ cement (Fig. 3B; the fourth foil removed from trench 1 in Fig. 3B was destroyed during extraction). $P_{1c}$ and $P_{2c}$ are microtexturally distinct, in line with the contrasting properties of their fluid inclusion populations (Mark et al., 2007). The microtexture of $P_{1c}$ feldspar changes with distance from its interface with the detrital grain (Fig. 4). Proximal to the interface (trench 2), the feldspar is free of subgrains and micropores and has a low defect density (Fig. 4A). Further from the interface in trench 3 the $P_{1c}$ feldspar contains 2 to 3 μm sized subgrains whose boundaries are delineated by long and narrow micropores (Fig. 4B). Aggregates of a very fine (< 0.2 μm) and poorly crystalline mineral occur within the micropores along subgrain boundaries, but could not be identified unambiguously; their habit is suggestive of illite (Fig. 4c). By contrast, the $P_{2c}$ feldspar (trench 4) comprises a mosaic of 0.5-1 μm sized subhedral 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 \(\sim 30\) 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 \((y^*,\) or
‘triclinicity’, which is sensitive to Si, Al order-disorder) is \(90.7^\circ\) and value of \(d_{010}/d_{100}
\) (which is sensitive to composition) is 1.72. These values are similar to those of
P1\(_c\) and P2\(_c\) from both An-t-Sron and Skig Bridge display comparable
microtextures.

4.3 Ar-Ar geochronology

All Ar-Ar data are reported as 2\(\sigma\) 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 \(\pm\) 19.7 to 926 \(\pm\) 51.7 Ma \((n = 9)\). This variability is potentially a result of a
combination of factors including loss of radiogenic Ar \(^{40}\text{Ar}\ast\), deuteritic 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 \(\mu\)m 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<sub>C</sub> cement (entire P1<sub>C</sub> 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<sub>C</sub> and P2<sub>C</sub> cements was also optically identifiable. A 10 μm boundary was left on both sides of the P1<sub>C</sub> and P2<sub>C</sub> boundary to ensure there was no contamination during laser ablation. Ar-Ar ages from the P2<sub>C</sub> cements (entire zones of P2<sub>C</sub> cement, on average ~50 μm<sup>2</sup>, 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<br />et al., 2005), then some Ar-Ar age variation for P1<sub>C</sub> and P2<sub>C</sub> is expected. The two ages for P1<sub>C</sub> and P2<sub>C</sub> authigenesis broadly correspond with the Grampian (475 to 467 Ma; Dewey, 2005) and Scandian (435 to 420 Ma; Johnson<br />et al., 1985) episodes of the Caledonian Orogeny (Mark<br />et al., 2007).

5. DISCUSSION
5.1 Resolution of different generations of cement

Bimodal distributions for minimum fluid entrapment temperatures and salinities corresponding to both P1C and P2C at both An-t-Sron and Skig Bridge, supported by mineral compositional differences (Ba in P2C; Mark et al., 2007), show that the Ar-Ar ages from P2C represent a second episode of authigenesis. If only a single fluid inclusion population were present within both cement generations and there was no change in parent fluid composition (Mark et al., 2007), then we would have to consider Ar-loss from P1C and contamination of zone P1C with excess Ar as potential mechanisms of producing the observed Ar-Ar age differences between P1C and P2C. Due to differing parent fluid data and compositions for both generations we can discount these mechanisms.

5.2 Clay content

Aggregates of 20 by 100 nm sized crystals are present along subgrain boundaries within P1C (Fig. 4). These crystals are inferred to be illite from their habit and the findings of illite in two previous TEM studies of K-feldspar overgrowths from the UK (Worden & Rushton, 1992; Lee & Parsons, 2003). The replacement of K-feldspar by illite, or passive precipitation of illite within pores (processes which occur post-precipitation of the authigenic K-feldspar; Lee & Parsons, 2003) may potentially affect Ar-Ar ages because illite also contains \(^{40}\text{K}\) that will radiogenically decay to \(^{40}\text{Ar}^*\). However, considering the amount of illite present along subgrain boundaries, the K-ratio between illite and K-feldspar and placing both of these factors in context with the amount of material ablated in order to obtain a single P1C Ar-Ar age (whole
overgrowths), the input of $^{40}$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).

5.3 Excess Ar and fluid inclusions

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.

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 $^{38}\text{Ar}_{C}/^{39}\text{Ar}_{K}$ 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 ~ 0.1 µm (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 µm$^2$), any potential effect of $^{39}$Ar movement by ~0.1 µm 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 isplot/Ex program (Ludwig, 2003). $P_{1C}$ at An-t-Sron has a weighted mean of $472.3 \pm 5.1$ Ma (mean square weighted deviation [MSWD] 3.9) and at Skiag Bridge a weighted mean of $467.0 \pm 6.0$ Ma (MSWD 2.6). $P_{2C}$ at An-t-Sron has a weighted mean of $435.9 \pm 7.3$ Ma (MSWD 1.8) and at Skiag Bridge a weighted mean of $430.2 \pm 5.1$ 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
The Ar-diffusion model uses forward projection to test the Ar-Ar ages by establishing a thermal history (Wheeler, 1996) against which assumed Ar-Ar ‘growth ages’ can be evaluated in terms of Ar-loss. In the model, 0 Ma corresponds to ages of authigenesis for both generations of authigenic K-feldspar (~470 and 432 Ma for P1C and P2C, respectively), and 470 and 432 Ma in the model correspond to the present day for P1C and P2C, respectively. Prior to thrust sheet emplacement at 430 Ma, the model assumes that the temperature in the Fucoid Beds is represented by the fluid entrapment temperatures that were determined previously (90 and 128 °C for P1C and P2C, respectively; Mark et al., 2007). Note that P2C is younger and contains smaller subgrains than P1C. Therefore, although small P2C subgrains appear have lost less Ar than larger P1C subgrains in some instances, P1C was subjected to an extra 30-40 Ma of heating pre-thrusting.

5.5.1.1 8 Ma, 200 °C thermal event. During thrust sheet emplacement (thrusting inferred to start at 430 Ma; Johnson et al., 1985; Kinny et al., 1999), a stepped gradient developed within the footwall and the temperature at the thrust sheet-footwall interface was 0.5T (200 °C), where T is the temperature at the thrust sheet base prior to emplacement (~ 400 °C). Rapid thermal re-equilibration of the footwall occurred as heat was conducted away from the thrust front (Johnson et al., 1985) through the over-thrustsed successions. The footwall cooled from palaeo-maximum temperatures (~ 200 °C) in response to syn- and post-uplift erosion. Assuming a standard erosion rate of 1 km/Myr for a continent-continent collision (current Himalaya erosion rates of 2.1 to 2.9 mm/yr; Galy & France-Lanord, 2001) and a geothermal gradient of 30 °C/km, the Fucoid Beds cooled to 150 °C by 422 Ma. We infer a simple linear cooling trend from 422 Ma to present day, and an approximated temperature of 10 °C to
represent the current Fucoid Bed surface temperature. It is important to note that much of the recent Fucoid Bed temperature-time path has had insignificant effects on the diffusion of Ar in the K-feldspar subgrains (Fig. 6).

Diffusion domain sizes determined from TEM work were used to represent the effective diffusion dimensions (Dodson, 1973; subgrains equated to spheres and corresponding radii determined from Fig. 4). P1C is relatively featureless and has large subgrains (~15 μm in diameter) adjacent to the detrital grain-overgrowth boundary and smaller subgrains (~3 μm diameter) further from the boundary (Fig. 4A-B). From TEM observations and cooling rates calculated using the tectono-thrust model outline above (Fig. 6; 430-422 Ma = 6.25 °C/Ma; and 422-present day = 0.33 °C/Ma), it is possible to calculate the theoretical closure temperatures of the K-feldspar subgrains within the Fucoid Bed samples (Dodson, 1973). 15 and 3 μm subgrains respectively have theoretical closure temperatures of 200 and 212 °C, and 155 and 170 °C for cooling rates of 0.33 and 6.25 °C/Ma. Subgrains are smaller (~1 μm) and more abundant, but irregularly distributed within the P2C cements (Fig. 4D-F). 1 μm subgrains have a Tc of 143 and 154 °C for cooling rates of 0.33 and 6.25 °C/Ma. Ar-diffusion models were run to quantitatively determine the amount of Ar-loss from both cement generations.

The Ar-diffusion model (Fig. 7) indicates that the 3 μm subgrains will have lost 33 % of their initial 40Ar* (Table 1), and so will yield Ar-Ar ages 140 Ma younger than the growth age. The 15 μm subgrains will have lost 28 % of their 40Ar* and will have yielded Ar-Ar ages 120 Ma younger than the growth age (Table 1). However, because entire P1C overgrowths were ablated in order to obtain the maximum amount of Ar for
each mass spectrometer measurement, each P1C 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 P1C 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 P1C authigenesis to be ~600 Ma. The same Ar-diffusion thermal model used
for P1C (Fig. 6) indicates that 1 μm P2C subgrains (which are younger than the P1C
subgrains) have lost 32 % 40Ar*, resetting the P2C Ar-Ar age by 127 Ma and thus
indicating a ‘model’ Ar-Ar age for P2C authigenesis of 559 Ma (Fig. 7).

Comparison of the modelled Ar-Ar ages for ‘modelled crystallization’ of P1C (600
Ma) and P2C (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
summarised in Fig. 7. The lowest maximum palaeotemperature of 140 °C causes little
(4 %) $^{40}$Ar*-loss from 15 μm subgrains and reduces Ar-Ar ages by only ~ 16 Ma.
$^{40}$Ar*-loss from 3 μm (7 % $^{40}$Ar*-loss) and 1 μm (9 % $^{40}$Ar*-loss) subgrains, thereby
producing widely scattered Ar-Ar ages that are reduced by 27 and 33 Ma, respectively
(Table 1).

Despite a geographical separation of 30 km between the two sampling sites, the two
generations of cement in both samples have similar Ar-Ar age distributions, implying
that P1c and P2c Ar-Ar ages at both sites have lost exactly the same amounts of $^{40}$Ar*
(i.e. experienced identical thermal histories resulting in equal resetting of both
samples). In order for authigenic K-feldspar at both sites to have been reset
identically, the thrust induced increase in thermal gradient must have been
synchronous and uniform over the 30 km distance between the sites as any variation
in temperature or timing, would have resulted in different thermal histories and hence,
different Ar-Ar ages. Thermal synchronicity between the two sites is not consistent
with field and laboratory data.

Dewey (2005) showed that the impingement of the colliding landmasses during the
Scandinian episode of the Caledonian Orogeny occurred first in the south and resulted
in the northern sector of the colliding landmass swivelling into the Laurentian margin.
Thrusting was not synchronous across the entire 180 km Moine Thrust Zone. Fluid
inclusion data (Baron et al., 2003; Mark et al., 2007) also show that thrust induced
heat flow within the Caledonian Foreland was neither synchronous nor uniform.
During thrust emplacement, sites in the south (close to Skiag Bridge) were 30 to 40
°C cooler than those in the north (close to An-t-Sron). Data show that equal resetting
of both $P_{1C}$ and $P_{2C}$ in both samples is highly unlikely. Furthermore, we know that temperatures reached a minimum of 200 °C in the Fucoid 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 $P_{1C}$ and $P_{2C}$ (Fig. 8). The model shows that $P_{1C}$ 15 μm subgrains would lose 4% $^{40}$Ar* and 3 μm subgrains would lose 6% $^{40}$Ar*, whilst $P_{2C}$ 1 μm subgrains would lose 4% $^{40}$Ar* (Fig. 9). Assuming a 1:1 subgrain ablation ratio for $P_{1C}$ subgrains (15 and 3 μm), Ar-Ar ages
would have been reset by ~ 20 Ma, and P2C 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 $^{40}$Ar* 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
In order to answer fundamental questions regarding the magnitude and mechanisms of Ar-loss from authigenic K-feldspar, what this paper sets out to address, it is pertinent to consider the properties of superficially similar patch perthite microtextures within deuterically altered alkali feldspars from plutonic igneous rocks (Fig. 1). Direct comparisons have been made between the Ar retention properties of these microtextures and authigenic K-feldspar (Lee & Parsons, 2003). Patch perthites form by deuteric/hydrothermal alteration of strain-controlled exsolution microtextures (unzipping reactions; Parsons & Lee, 2005) and are composed of aggregates of sub-\(\mu\)m to \(\mu\)m-sized subgrains. Microporous patch perthites form veins of networks that develop as fluids have penetrated the grain interior (Fig. 1). As a consequence, deuterically altered alkali feldspars are highly permeable in zones where recrystallization has occurred (Worden et al., 1990). Burgess et al. (1992) showed that these volumes of recrystallized alkali feldspar lose significant volumes of Ar over time.

Patch perthite subgrains are typically incoherent and so their boundaries are dislocation-rich (Worden et al., 1990). As a consequence, it has been suggested that short-circuit diffusion, which takes place at a rate 4-5 orders of magnitude greater than lattice volume diffusion (Wartho et al., 1999), must be the principle mechanism of Ar-loss from patch perthites and not volume diffusion (Lee, 1995). Whereas most alkali feldspars from slowly cooled igneous rocks have discrete patches or veins of the subgrain-rich microtexture (Parsons et al., 1999), entire authigenic K-feldspar overgrowths are composed of subgrains (Worden & Rushton, 1992; Lee & Parsons, 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
direct route for the Ar to escape authigenic K-feldspar on the scale of tens or hundreds
of microns as micropores are not connected and therefore diffusion cannot operate at
enhanced rates in authigenic K-feldspar as it does in microporous/microporous
patch perthite (Fig. 10). Once an approximate equilibrium is established between the
concentrations of Ar in the subgrains, the micropores and dislocation-rich boundaries,
diffusion from the subgrains into the porous regions of the mineral will be controlled
by re-equilibration over time (i.e. the Ar is trapped within dislocations, micropores
and subgrain boundaries and therefore violates the assumption that such features act
as infinite reservoirs with zero concentrations of Ar). Re-equilibration will occur as
further Ar within subgrains is produced by radioactive decay and Ar diffuses out of
the K-feldspar subgrains via volume diffusion into dislocations, micropores and
subgrain boundaries.

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

We can quantitatively test the theoretical model by re-running the Ar diffusion models
with different effective diffusion dimensions. P1c overgrowths have a maximum
thickness of ~ 40 μm and P2c overgrowths are up to ~ 100 μm thick (Fig. 3). Using a
heating event at 430 Ma with duration of 8 Ma and peak temperature of 200 °C (the
original Ar-diffusion model; Fig. 6) and effective diffusion dimensions of 40 and 100
μm, the Ar-diffusion model was re-run to test the theoretical model outlined in Fig.
10. Grains were approximated to spheres (geometry is not a massively significant
variable with respect to the effective diffusion dimension and temperature and
duration of heating) and no excess Ar was input into the model. Results are shown in
Fig. 11. 470 Ma 40 μm thick overgrowths have been reset by 13 Ma (lost 3 % ⁴⁰Ar*)
and 432 Ma 100 μm thick overgrowths have been reset by 3 Ma (lost < 1 % ⁴⁰Ar*).
The Ar-diffusion model produces data that are consistent (considering that the model
used the maximum effective diffusion dimension for P1C and P2C and there was a lot
of variability in overgrowth thickness) with the determined Ar-Ar ages, thereby
supporting a thermal model of transient heating (Fig. 11) that is also consistent with
the regional geology.

It could be argued that the consistency between the model incorporating transient
heating to 200 °C and overgrowth thickness as the effective diffusion dimension (Fig.
11) with the Ar-Ar age data is due to an overestimation of the true effective diffusion
dimensions (i.e. use of grain size rather than subgrain size determined from TEM
imaging), especially as previous studies successfully modelled Ar diffusion using
subgrain diameter as the effective diffusion dimension (Mark et al., 2005). Although
Mark et al. (2005) successfully modelled Ar diffusion using subgrain size rather than
overgrowth thickness, the rocks were only exposed to low post-growth temperatures
following authigenesis (125 °C). Hence, the variation in effective diffusion dimension
is not as significant as it is with respect to the Fucoid Bed case study, and had a
limited impact on the Ar-loss data.

6. CONCLUSION

The Ar-Ar ages two generations of Fucoid Bed authigenic K-feldspar (P1c and P2c)
record different stages of mineral growth and have undergone minimal Ar-loss and
Ar-Ar age resetting. Two separate models have been proposed, both of which are
consistent with the geological context of the samples (heating to a minimum of 200
°C) and can account for the apparent robustness of the authigenic K-feldspar with
respect to microtextural repetitiveness of Ar: short-term hot fluid flushing (assuming
subgrain sizes are appropriate estimations of the effective diffusion dimension) and
transient heating (assuming overgrowth thickness as an appropriate estimation of the
effective diffusion dimension).

We highlight that although K-feldspar microtextures appear to be microporous, it is
potentially micropermeability that is the critical factor with respect to Ar-loss and the
ability of a mineral phase to record meaningful Ar-Ar isotopic data. This project is not
intended to be the definitive study of Ar-diffusion within authigenic K-feldspar, but
provides a suitable starting point for discussions of factors governing the reliability of
Ar-Ar dating using authigenic K-feldspar and the importance of understanding Ar
trapping mechanisms within different feldspar microtextures. More experimental
work is required to develop and test (prove/disprove) the theoretical model outlined in
this paper. The collection of quantitative Ar-Ar data from authigenic K-feldspar that
has been exposed to a range of high-temperature settings is required before the
validity of the model proposed here can be confirmed.

ACKNOWLEDGEMENTS

This work is supported by the Natural Environment Research Council (NERC) Ocean
Margins Project, research grant number: 3220/GL021/GRA0782. We thank Professor
Alan Craven for access to the FIB-TEM facilities in Glasgow University and Billy
Smith, Colin How, John Still and James Schwanethal for technical assistance.
Associate Editor Y. Amelin is thanked for comments leading to improvement of this
manuscript. Three reviewers, J.A. Wartho, J.K.W. Lee and G.D. Vincenzo are also
thanked for detailed reviews, comments and constructive suggestions.

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$^{40}$Ar/$^{39}$Ar analysis of perthite microstructures and fluid inclusions in alkali feldspars


**FIGURE CAPTIONS**

Fig.1: Bright-field TEM image of alkali feldspar grain from the Lower Devonian Shap Granite. The image shows a vein of patch perthite cross-cutting otherwise pristine 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.

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

Fig. 3: Sample shown from An-t-Sron. (A) Backscattered electron SEM image
showing generation 1 (P1c) K-feldspar overgrowths on detrital alkali feldspar grains.
Generation 2 K-feldspar cement (P2c) envelopes P1c 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.

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 P1c 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
defect density and a fine-scale modulated microtexture. The indexed SAED pattern
(from the detrital grain) shows that the electron beam is parallel to [312]. Scale bar 1
μm. (B) Subgrains (2 to 3 μm in size) within P1c K-feldspar further from the interface
with the detrital grain. Their boundaries (arrowed) have been etched by fluids to form
long and narrow pores (arrowed). Scale bar 500 nm. (C) A subgrain boundary within
P1c cement along which have formed clumps of fibrous and poorly crystalline
minerals, probably illite. Scale bar 500 nm. (D) P2c cement that contains a number of
sub-μm to μm-sized subgrains, all of which have dislocation-rich boundaries. The
euhedral subgrains have a {110} adularia habit. Some small micropores have also
formed along one of the subgrain boundaries. Electron beam parallel to [001]. Scale
bar 1 μm. (E) One subgrain in the P2c cement. Areas of strain contrast highlight
dislocations along subgrain boundaries and sub-μm sized angular micropores also
occur at subgrain boundaries. Electron beam parallel to [001]. Scale bar 100 nm. (F)
Subgrains within P2c cement with more irregular but still dislocation-rich boundaries.
Bend countours in the foil help highlight a diffuse microtexture with modulations
approximately parallel to a* and b*. Electron beam parallel to [001]. Scale bar 500
nm. Note due to a technical failure of the double-tilt axis during TEM examination,
the reciprocal lattice directions are not shown in all images.

Fig. 5: (A) Weighted average plot showing Ar-Ar data for P1c and P2c from An-t-
Sron and Skig Bridge (error: 2σ in relation to Fucoid Bed deposition, the Grampian
and Scandian episodes of the Caledonian Orogeny. (B) Relative probability
distribution plot for Ar-Ar data from An-t-Sron. (C) Relative probability distribution
plot for Ar-Ar data from Skig Bridge. Both data sets (B&C) show a bimodal
distribution suggesting K-feldspar growth from two distinct episodes of authigenesis.
Fig. 6: Diagrams showing reconstructed thermal history, with which K-feldspar subgrains are modelled. The software is a forward modelling program, hence, 0 Ma corresponds to ages of authigenesis, and 470 and 432 Ma correspond to present day. (A) \( P_{1C} \) authigenesis, 200 °C peak temperature. (B) \( P_{2C} \) authigenesis, 200 °C peak temperature. (C) \( P_{1C} \) authigenesis, 180 °C peak temperature. (D) \( P_{2C} \) authigenesis, 180 °C peak temperature. (E) \( P_{1C} \) authigenesis, 160 °C peak temperature. (F) \( P_{2C} \) authigenesis, 160 °C peak temperature. (G) \( P_{1C} \) authigenesis, 140 °C peak temperature. (H) \( P_{2C} \) authigenesis, 140 °C peak temperature.

Fig. 7: Typical DIFFARG output showing modelled response of different sized (15, 3 and 1 μm) subgrains (diffusion domains) to a 200, 180, 160 and 140 °C thermal episode (Fig. 6). The Ar –diffusion model determines the amount of Ar-loss and therefore the degree that each Ar-Ar age is reset, data are summarised in Table 1. (A) \( P_{1C} \) 15 μm subgrain (left: Ar evolution of spherical subgrains of known radius; right: bulk age showing apparent age post exposure). (B) \( P_{1C} \) 3 μm subgrain (left: Ar evolution of spherical subgrains of known radius; right: bulk age showing apparent age post exposure). (C) \( P_{2C} \) 1 μm subgrain (left: Ar evolution of spherical subgrains of known radius; right: bulk age showing apparent age post exposure).

Fig. 8: Diagrams showing short term heated fluid thermal history, against which K-feldspar subgrains are modelled. The software is a forward modelling program, hence, 0 Ma corresponds to ages of authigenesis, and 470 and 432 Ma correspond to present day. (A) \( P_{1C} \) model, 470 Ma to present day. (B) \( P_{2C} \) model, 432 Ma to present day.
Fig. 9: Typical DIFFARG output showing modelled response of different sized (15, 3 and 1 μm) subgrains (diffusion domains) to a short term fluid heating event, 10,000 years at 200 °C (Fig. 6). (A) P1_C 15 μm subgrain (left: Ar evolution of spherical subgrains of known radius; right: bulk age showing apparent age post exposure). (B) P1_C 3 μm subgrain (left: Ar evolution of spherical subgrains of known radius; right: bulk age showing apparent age post exposure). (C) P2_C 1 μm subgrain (left: Ar evolution of spherical subgrains of known radius; right: bulk age showing apparent age post exposure).

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

Fig. 11: Typical DIFFARG output showing modelled response of 100 and 40 μm subgrains to the thermal history shown in Fig. 5.10A&B. Left: Ar evolution of
spherical grains of known radius. Right: bulk age showing apparent age post exposure
to the thermal history. Note, DIFFARG is a forward modelling programme, hence for
the 100 μm subgrain 0 corresponds to 432 Ma and 432 corresponds to present day.
For the 40 μm subgrain 0 Ma corresponds to 470 Ma and 432 Ma corresponds to
present day. The model shows that 100 μm subgrains are reset from 432 to 429 Ma
and 40 μm subgrains are reset from 470 to 457 Ma.

TABLE CAPTIONS

Table 1: Amount of $^{40}\text{Ar}^*$-loss and Ar-Ar age resetting by thermally activated Ar
diffusion.
<table>
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<th>Cement generation</th>
<th>Subgrain size (µm)</th>
<th>Ar-Ar age (Ma)</th>
<th>Peak temperature during thrusting (°C)</th>
<th>Heating duration (Ma)</th>
<th>Ar-loss (%)</th>
<th>Ar-loss (Ma)</th>
<th>Model Ar-Ar age (Ma)</th>
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