Pathways for $^{39}$Ar loss during step-heating of alkali feldspar megacrysts from the Shap granite (UK): Combined evidence from diffusion experiments and characterisation of heating-induced texture modifications

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Pathways for $^{39}$Ar loss during step-heating of alkali feldspar megacrysts from the Shap granite (UK): Combined evidence from diffusion experiments and characterisation of heating-induced texture modifications

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A R T I C L E  I N F O

Editor: Balz Kamber

A B S T R A C T

This study aims to identify the dominant fast pathways for $^{39}$Ar loss during step-heating $^{40}$Ar/$^{39}$Ar analysis of alkali feldspar from the Shap granite (UK). In our analysis we combined step-heating $^{40}$Ar/$^{39}$Ar data acquired from variably sized feldspar fragments (0.4 to 2.2 mm in the shortest dimension) and optical and electron microscopy observations of microtextural modifications caused by heating in a muffle furnace in air. Our optical and electron microscopy results suggest that laboratory heating of the Shap feldspar causes it to fracture. The resulting cracks form an interconnected network, which may link with some of previously documented nanoscale defects such as nanotunnels, slots, pull aparts and bubbles. Our step-heating $^{40}$Ar/$^{39}$Ar analyses yielded non-linear Arrhenius trajectories of $^{39}$Ar release. The non-linearity is best explained by heating-induced reduction of the effective diffusion length due to fracturing, likely with some contribution from nanotunnels, pull-aparts, slots and bubbles. Incoherent grain boundaries apparently played a minor role in providing fast pathways for $^{39}$Ar loss, if any. Importantly, unambiguous evidence for a reduction of the diffusion length during step-heating was only observed in experiments with large fragments ($\geq 1$ mm in the shortest dimension). The Arrhenius trajectory obtained from the smaller fragments ($\leq 0.5$ mm in the shortest dimension) appears to be consistent with the presence of variably-sized non-interacting intra-grain diffusion domains that existed prior to mineral separation. Heating-induced fracturing must be taken into account when interpreting $^{40}$Ar/$^{39}$Ar dates of alkali feldspar, with particular focus on the following two points. First, this process is clearly inconsistent with the underlying assumptions of commonly utilised multi-diffusion domain (MDD) theory, although it can result in $^{39}$Ar release patterns that appear consistent with them. Therefore, it is important to identify on a case by case basis the dominant fast pathways for $^{39}$Ar loss from alkali feldspar during step-heating before applying MDD theory. Second, if heating-induced fracturing is ubiquitous in alkali feldspar and affects even gem-quality samples, then presently available diffusion parameters of Ar in alkali feldspar structure may be inaccurate to some degree, since all of them were obtained without considering the presence of cracks.

1. Introduction

Alkali feldspar has been widely used for K–Ar and $^{40}$Ar/$^{39}$Ar dating due to its ubiquity and high K content. However, it was recognised as early as the 1960’s that K–Ar and $^{40}$Ar/$^{39}$Ar dates of alkali feldspar are frequently younger than dates obtained using other geochronometers, revealing the partial loss of $^{40}$Ar (e.g. Armstrong, 1966; Fechtig and Kalbitzer, 1966; Mussett, 1969). It was also shown that laboratory degassing of alkali feldspar by step-heating is frequently inconsistent with the presence of a single grain-scale diffusion domain whose intrinsic diffusion parameters are independent of temperature and time. The inconsistencies include (i) non-linear topology of Arrhenius trajectories of $^{40}$Ar release (e.g. Fechtig and Kalbitzer, 1966; Mussett, 1969; Zeitler, 1987; Lovera et al., 1989), (ii) poor or no correlation between the rates of $^{40}$Ar release and the physical sizes of the analysed fragments (for certain ranges of size-fractions; e.g. Evernden et al., 1960; Mussett, 1969; Lovera et al., 1989), and (iii) staircase topology of $^{40}$Ar/$^{39}$Ar age spectra (assuming that diffusion is the only mechanism of Ar loss over geological timescales; Zeitler, 1987; Lovera et al., 1989).

The multi-diffusion domain (MDD) theory Lovera et al. (1989) aimed to provide a unified explanation for the above-listed observations. One of the key assumptions behind this theory is that each alkali feldspar fragment contains a population of intra-grain diffusion domains that remain stable over the course of laboratory step-heating. The
stability of these domains was investigated in two previous studies utilising step-heating $^{40}$Ar/$^{39}$Ar analysis. Lovera et al. (1993) conducted a double-irradiation experiment, where the same alkali feldspar fragments were step-heated to 850 °C, before and following a second irradiation. Sanders (2008) compared step-heating $^{40}$Ar/$^{39}$Ar data derived from several aliquots of three alkali feldspar fractions, where some aliquots were partially outgassed at different temperatures prior to irradiation. Both studies found only a minor effect of laboratory heating on the properties and the size distribution of the hypothetical intra-grain diffusion domains over timescales relevant to conventional step-heating analysis. However, it remains unclear as to which features separate these domains from each other and provide fast diffusion pathways for the effective removal of Ar from their surfaces.

This study aims to identify and describe potential diffusion domains that degas during laboratory heating of alkali feldspar from the Shap granite (North West England, UK) and assess their stability throughout the analysis by comparing step-heating $^{40}$Ar/$^{39}$Ar data from variably-sized neutron-irradiated fragments (0.4 to 2.2 mm) with optical and electron microscopy observations of how unirradiated and neutron-irradiated fragments change after heating in a muffle furnace in air. We chose the Shap feldspar for our experiments because it is one of the most studied examples of commonly-occurring alkali feldspar, and its microtextural evolution during laboratory heating has been previously characterised in exceptional detail. Lee et al. (1995), Lee and Parsons (1997), Parsons et al. (1999), Fitzgerald et al. (2006) and Parsons et al. (2010) have shown that cm-scale megacrysts of the Shap feldspar have a complex microtexture. Most importantly, Parsons et al. (2010) have shown that the complex microtexture of the Shap feldspar is considerably modified during laboratory heating. The documented continuous microtextural evolution of the Shap feldspar during laboratory heating conflicts with the assumption that it hosts stable intra-grain diffusion domains, which is one of the key assumptions behind MDD theory. Similar processes can occur in any alkali feldspar (e.g. Parsons et al., 1999; Parsons et al., 2010), and therefore it is important to understand how the microtextural evolution of alkali feldspar affects step-heating $^{40}$Ar/$^{39}$Ar data before using MDD theory. The only published $^{40}$Ar/$^{39}$Ar study of alkali feldspar from the Shap granite (Short et al., 2011) provided a brief description of the data acquired from 250 to 500 μm fragments and did not report any inconsistency between Arhenius trajectories and predictions from MDD theory. Here we show that such a result may be related to the analysis of relatively small-size fractions, and that the microtextural evolution of this alkali feldspar profoundly affects its Ar release kinetics.

2. Material and methods

The Shap granite is 2 by 3 km intrusion, which was emplaced in the Early Devonian and yields a Rb–Sr isochron date of 400.3 ± 3.0 Ma (Wadge et al., 1978; recalculated using the decay constant from Villa et al., 2015). The intrusion was exhumed and partially eroded in the Early Carboniferous, and granitic clasts derived from it occur in the overlying conglomerates (Lee and Parsons, 1998). This event was followed by reburial, and the final exhaustion of the Shap granite occurred in the Late Mesozoic to Cenozoic, which is constrained by apatite fission track dates of 83.9 ± 7.0 and 73.4 ± 5.8 Ma (Green, 1986).

According to the existing mineralogical studies (Lee et al., 1995; Lee and Parsons, 1997; Fitzgerald et al., 2006; Parsons et al., 2010), ~70 vol% of the Shap feldspar megacrysts are optical pristine, while the remaining ~30 vol% appear turbid. The pristine regions are represented by magmatic feldspar that exolved by Na–K inter-diffusion to form coherent to semicoherent Na-rich lamellae in a K-rich matrix. Exsolution lamellae with thickness of ≥ 1 μm have a network of misfit dislocations at their boundaries, along which post-magmatic fluids sometimes dissolved feldspar and left behind nanotunnels. These lamellae are cross-cut by small cracks along the (001) and (010) cleavage planes, which are termed pull-aparts. The turbid regions are represented by feldspar that formed via fluid-induced dissolution-reprecipitation and include veins of replacement perthite (incoherent Na-rich and K-rich subgrains) and microcline (incoherent K-rich subgrains). Parsons et al. (2010) showed that exsolution lamellae begin to homogenise on the timescales of step-heating experiments at ≥ 500 °C. Complete homogenisation can be achieved at ≥ 700 °C, and the process is complete in < 4 h at 900 °C and in < 1 h at 1000 °C. At ≥ 500 °C pull-aparts within exsolution lamellae and nanotunnels at the edges of exsolution lamellae disappear or become less obvious, and arrays of slots (planar nanopores) propagate from these into the surrounding orthoclase at distances of up to several microns. Heating to ≥ 700 °C leads to the formation of abundant bubbles (subsuperhedral nanopores), which mainly occur around replacement perthite veins but also around exsolution lamellae, where they partly form at the expense of slots. Bubbles and remaining slots are destroyed by melting, which starts at 1100 °C. No significant Si–Al disordering occurs over the timescales of step-heating experiments, and coherent twin boundaries along with the twisted texture of orthoclase remain stable until melting. Incoherent boundaries of albite and microcline subgrains along with micropores between them also survive until melting.

A large sample of the Shap granite was provided by Joshua Davies, who collected it from a small tailings pile in the quarry in the southeastern part of the intrusion (N 54°28′05.5″, W 2°40′49.6″). This sample was cut into ~7 × 7 × 7 cm blocks, which were then disintegrated to cm-scale fragments using either a SelFrag (University of Bern) or a hydraulic press (University of Geneva). From these we selected cm-scale fragments of alkali feldspar megacrysts and trimmed off the remnants of the rock groundmass from their surfaces using a diamond blade saw. The remaining material was subsequently disintegrated using either a SelFrag or a jaw crusher (University of Geneva), and smaller 2–5 mm fragments of megacrysts were handpicked from it. Some of the cm-scale fragments provided material for step-heating $^{40}$Ar/$^{39}$Ar analysis, while other cm-scale and 2–5 mm fragments were used for heating experiments in air that were designed to track any textural modifications in response to heating and cooling.

The cm-scale fragments of megacrysts that provided material for $^{40}$Ar/$^{39}$Ar analysis were mounted in epoxy resin, characterised by optical microscopy, scanning electron microscopy (SEM) using a JEOL JSM7001F, phase and major-element semi-quantitative mapping using a QEMSCAN QUANTA 650F, and optical cathodoluminescence imaging using an ERI-MRTech stage (all equipment is housed at the University of Geneva; images and maps are presented in the Step-heated Megacrysts section in the Supplementary Figures). Following Flude et al. (2013) we minimised the exposure of these fragments to the electron beam and repolished them after the analyses. Subsequently, these fragments were cut out of the epoxy resin using a diamond blade saw, packed in Cu foil and irradiated along with Fish Canyon Tuff sanidine monitor for 22 h without Cd shielding (ICIT) in the B1 position of the TRIGA reactor at the Oregon State University. Smaller 0.4–2.2 mm fragments were broken off the cm-scale irradiated pieces using a scalpel and a small hammer (minimising the number of hits). These were prepared for $^{40}$Ar/$^{39}$Ar analysis by encapsulation in Cu foil, labelled using Indian ink and loaded into a glass sample holder mounted above a double vacuum resistance furnace. Monitors were analysed using CO₂ infrared laser heating. The furnace and the laser viewports were attached to a gas purification line with a cold trap (−130 °C) and SAES AP10 and GP50 (ST101) getters and a GV Instruments Argus V mass spectrometer fitted with four 10⁻¹² Ω Faraday collectors for $^{36}$Ar, $^{37}$Ar, $^{38}$Ar, and one 10⁻¹¹ Ω Faraday collector for $^{40}$Ar (University of Geneva). Prior to the analysis, the extraction and purification lines were degassed overnight at 180 °C, and the furnace was subsequently degassed at 1450 °C.

Furnace blank and sample analyses followed the same procedure. The furnace was rapidly heated and held at a target temperature to within ± 5 °C for the duration of any particular heating step (a type C
thermocouple was used to control the temperature). The liberated gas was allowed to passively diffuse into the purification line during ramping and heating. Furnace heating was switched off after a chosen heating time, and the furnace was sealed off from the purification line. When necessary, the gas trapped within the purification line was diluted to avoid saturation of the Faraday collectors in the mass spectrometer. Dilution occurred by isolation and evacuation of specific components of the purification line for 10 min followed by re-expansion of the remaining gas into them (dilution factors were estimated by analysing air aliquots following same procedures). The target gas was purified for additional 5 min and subsequently analysed on the mass spectrometer. Blank analyses were run before and after step-heating of each sample. Monitors were preheated (30 s at 0.2 W laser power) and then fused (30 s at 7.2 W laser power) via infrared laser heating. The gas released during preheating was evacuated, while the gas released during fusion was purified for additional 6 min and then expanded into the mass spectrometer. Intensity data were acquired over 12 cycles with 1 min integrations, and baseline intensities were measured before the first cycle for 30 s at +0.5 and −0.5 m/z and included in the peak intensity calculations. Peak intensity data were reduced using ArArCALC V2.4 software (Koppers, 2002). $^{40}$K decay constants of $\lambda_{e.c.} = 0.581 \times 10^{-10}$ yr$^{-1}$ and $\lambda_{q} = 4.962 \times 10^{-10}$ yr$^{-1}$ were used (Steiger and Jäger, 1977). Fish Canyon Tuff sanidine was used as a neutron flux monitor with an age of 28.201 ± 0.046 Ma (Kuiper et al., 2008). Mass discrimination factors were determined by analysing air with $^{40}$Ar/$^{36}$Ar = 295.5 (Steiger and Jäger, 1977).

The cm-scale and 2–5 mm fragments of megacrysts that were selected to investigate heating-induced textural modifications were loaded into ceramic crucibles and heated in air in a Borel FP1200-10 muffle furnace with a built-in temperature controller (University of Geneva). After heating, the large fragments were mounted by vacuum impregnation in epoxy resin dyed with a blue colorant and characterised using optical microscopy and the SEM. Some of them were also mounted in epoxy resin dyed with a blue colorant and characterised using optical microscopy. The SEM was operated in LV mode to allow back-scattered electron (BSE) imaging of very thin cracks in unpolished and uncoated fragments. These features were not visible in secondary electron (SE) images of fragments that had a ≤ 5 nm-thick gold coating, presumably because they had been filled by the coating.

3. Results

3.1. Heating experiments in a muffle furnace in air

We have conducted two types of experiments to identify how heating affects the texture of the Shap feldspar. The aim of the first type of experiments was to identify any textural modifications that occur in response to heating for a long time, with low heating and cooling rates compared to those used in conventional step-heating $^{40}$Ar/$^{39}$Ar analysis. Three batches of cm-scale fragments of alkali feldspar were placed into a muffle furnace and heated to 840 °C in regular increments of ~30 °C, which took 4 h. The first and second batches were quenched by removing them from the furnace after 1 and 5 days, respectively. The third batch was slowly cooled to room temperature inside the furnace.
after 10 days, which was done by switching off the furnace heating
element and took > 4 h. The second type of experiments was used to
characterise the rates of texture modification. Fragments of alkali
feldspar were repeatedly heated and cooled by placing them into a
preheated furnace for 10 min and then quickly taking them out to cool
to room temperature, emulating conventional step-heating experiments
that are used to collect 40Ar/39Ar data.

Prior to heating the cm-scale Shap feldspar fragments were rigid,
transparent in some regions and turbid in others, and had a light ter-
racotta colour. BSE imaging of their texture showed that the transparent
zones correspond to pristine regions of exsolved alkali feldspar (Na-rich
exsolution lamellae in K-rich feldspar), while the turbid zones corre-
spond to veins of replacement perthite (Na- and K-rich feldspars) and
microcline (only K-rich feldspar) with abundant micropores (Fig. 1A;
more images are provided in Supplementary Figures, section Step-he-
tated Megacrysts). After heating to 840 °C for 1, 5 and 10 days (the first
type of experiments) these fragments became very fragile and could be
easily disintegrated by hand. They became non-transparent, and their
colour changed to very pale beige. The textural modif-
ications that were
observed in BSE images include homogenisation of exsolution lamellae and
partial re-equilibration of K-rich and Na-rich feldspars in veins of
replacement perthite and microcline and plagioclase inclusions
(Fig. 1B; more images are provided in Supplementary Figures, section
Long Heating Experiments In Air). The former locations of exsolution
lamellae are sometimes darker than the surrounding areas in high-
contrast BSE images, which is probably related to the presence of pores
and defects rather than a higher concentration of Na (such darker
shades had similar abundances after 1, 5 and even 10 days at 840 °C).
The range of textures observed in the unheated alkali feldspar
fragments and above-mentioned textural modifications that occurred in
response to heating are in good agreement with previous more detailed
and higher-resolution work of Lee et al. (1995), Lee and Parsons (1997),
Fitz Gerald et al. (2006) and Parsons et al. (2010). However, we ad-
ditionally observed numerous open cracks in the heated fragments,
which were not explicitly reported in previous studies. The cracks are
consistently parallel to each other and cross-cut exsolution lamellae in
the BSE images (Fig. 1B). They are present in both the replacive and
pristine regions and extend over much longer distances (fre-
quently ≫ 10 μm) than the previously documented pull-aparts and
slots. Some cracks have a near-micron thickness, while others are very
narrow and barely visible. The abundance of cracks is similar in the
quenched and slowly cooled fragments. The heated fragments were
mounted using epoxy resin dyed with a blue colorant, which partially
infiltrated the feldspar fragments and revealed that the cracks form an
interconnected network (Fig. 1D; compare this to an analogous image
of unheated fragment in Fig. 1C). The occurrence of the cracks does not
always correlate with the occurrence of other textures: although gen-
erally they are most abundant around replacive veins, some regions
around replacive veins are poor in cracks (e.g. note the white replacive
veins in Fig. 1D that were not infiltrated by the epoxy resin).

Fig. 2. LV BSE images of uncoated (010) cleavage surfaces of a neutron-irradiated alkali feldspar fragment (top and middle rows) and an alkali feldspar fragment that has not been irradiated (bottom row). The images were taken in the same regions before step-heating (left column), after one 10-minute heating step at 550 °C (middle column) and after additional eight 10-minute heating steps at 600–825 °C (right column). Blue arrows show exsolution lamellae. Green arrows highlight replacement perthite veins (darker areas are rich in Na while brighter areas are rich in K, black dots in these veins are micropores). Yellow arrows show cracks. Arrows with a black outline indicate cracks that did not disappear with progressive heating. Arrows with an orange outline indicate cracks that appeared after 1 heating step and became invisible after 9 heating steps. For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.
Further evidence for cracking is provided by step-heating of 2–5 mm fragments of alkali feldspar in air (the second type of experiments). We have conducted two sets of such experiments. In the first set of experiments six batches of 50 fragments were step-heated to different temperatures (up to 1000 °C) and then compared with unheated fragments. Comparisons were made by optical imaging of polished and unpolished fragments and by LV BSE imaging of the surfaces of unpolished fragments. Generally, more cracks were observed in fragments that were heated to higher temperatures (see section Step-heating Experiments In Air in Supplementary Figures). In the second set of experiments we monitored how cracking progressed with step-heating in one neutron-irradiated unpolished fragment and one unirradiated unpolished fragment. Two perpendicular cleavage surfaces of these fragments were characterised by LV BSE imaging at different stages of the step-heating experiments, which were (i) prior to step-heating, (ii) after 1 heating step that lasted for 10 min and (iii) after 9 heating steps, each of which lasted for 10 min. This experiment confirmed that cracking progresses with step-heating and showed that it predominantly occurs along the (001) cleavage plane, which lies at an angle of ~74° to the exsolution lamellae (Figs. 2 and 3). Interestingly, some cracks that were visible after 1 heating step could not be observed after 9 heating steps (bottom row of Fig. 2), suggesting that they either became too thin to be resolved by BSE imaging, or they were fully annealed. We observed no systematic differences between cracking of the neutron-irradiated and unirradiated fragments.

3.2. Repetitive step-heating 40Ar/39Ar analyses

We have conducted three repetitive step-heating experiments to characterise the kinetics of 39Ar release from the Shap feldspar. 40Ar/39Ar data were acquired from one batch of four fragments with the shortest dimension length of ~0.4 mm (experiment 7cSF) and two single fragments with the shortest dimension lengths of ~1 mm (experiment 7c4) and ~2.2 mm (experiment 4a). All of these fragments had a similar microtexture, and replacement perthite and microcline veins in them accounted for ~30 vol% (see section Step-heated Megacrysts in Supplementary Figures). The heating schedules for all three experiments included three heating cycles, in each of which a series of 10-minute steps at successively increasing temperatures was followed by a series of 90 to 360-minute steps repeated at the same or similar temperatures (Fig. 4C, F and I). The first cycle included heating steps at 550–825 °C, the second at 850–1000 °C and the third at

![Fig. 3. LV BSE image of the (001) cleavage surface of a neutron-irradiated alkali feldspar fragment after nine 10-minute heating steps at 550–825 °C. Blue arrows show exsolution lamellae. Green arrow highlights replacement perthite veins (darker areas are rich in Na while brighter areas are rich in K, black dots in these veins are micropores). Note the absence of cracks along (010). For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.](image)

![Fig. 4. A comparison of step-heating 40Ar/39Ar data obtained for alkali feldspar fragments of different size. A, D and G: Arrhenius trajectories obtained from the fragments, stereo microscope images of which are shown in the top right parts of the diagrams (their shortest dimension is perpendicular to the viewing direction). B, E and H: age spectra from the same crystals. C, F and I: heating schedules of the experiments that were used to obtain the data (alkali feldspar fragments were rapidly cooled to < 200 °C following each heating step). Different colours indicate different heating cycles. Within each heating cycle, smaller light-coloured markers correspond to the initial 10-minute heating steps, while larger and darker markers correspond to the repeated 90 to 360-minute steps.](image)
1000–1150 °C. The analysed fragments were subsequently degassed at 1200–1450 °C. Following each heating step these fragments were rapidly cooled to <200 °C. The obtained 40Ar/39Ar data are provided in Supplementary Tables.

The release of 39Ar from the batch of four alkali feldspar fragments with the shortest dimension length of ~0.4 mm followed a non-linear Arrhenius trajectory, in which ln(D/r²) values yielded by the 10-minute steps of the first heating cycle are higher than those yielded by the 90-minute steps repeated at the same temperatures (Fig. 4A; D – diffusion coefficient, r – radius; see Supplementary Text for details on the calculation of D/r² values and their uncertainties). Similar ln(D/r²) values were obtained for the 10-minute and the same temperature 90-minute steps of the second heating cycle. During the third heating cycle this Arrhenius trajectory followed a looped path, such that ln(D/r²) values increased over the series of 10-minute steps at 1050–1150 °C, then decreased over the consecutive 90-, 180- and 360-minute steps at 1000 °C, and then increased over the series of 90-minute steps at 1050–1150 °C. All of the 10-minute steps at 1050–1150 °C yielded higher ln(D/r²) values than the 90-minute steps at the same temperature.

Both single fragments of alkali feldspar with the shortest dimension lengths of ~1 mm and ~2.2 mm degassed following non-linear Arrhenius trajectories, in which ln(D/r²) values obtained for the initial 10-minute steps of the first and second heating cycles are lower than those obtained for the 90-minute steps repeated at the same temperature (Fig. 4D, G). However, the later 10-minute steps of the first heating cycle yielded higher ln(D/r²) values than the same temperature 90-minute steps, while the later 10-minute steps of the second heating cycle yielded ln(D/r²) values that are similar to those obtained for the same temperature 90-minute steps. Similar to the ~0.4 mm fragments, the Arrhenius trajectories of both ~1 mm and ~2.2 mm fragments looped during the third cycle, although the variations of ln(D/r²) values are not as significant.

The 90-minute steps at 850–1000 °C in all of these degassing experiments define a linear array in Arrhenius space, which corresponds to an E_a of ~220 kJ/mol (Fig. 5; E_a – activation energy). Furthermore, there is a correlation between these ln(D/r²) values and the physical size of the analysed fragments of alkali feldspar, such that larger fragments yielded lower ln(D/r²) values for any given temperature. However, the difference in ln(D/r²) values obtained for the batch of four fragments with the shortest dimension length of ~0.4 mm and for the single fragment with a shortest dimension length of ~2.2 mm does not exceed 1 ln unit.

Similar to the previous work of Short et al. (2011), all of our degassing experiments yielded flat 40Ar/39Ar age spectra with age plateaus that account for > 90% of 39Ar released (Fig. 4B, E, H). The plateau dates range from 395 to 400 Ma. The individual step dates that are significantly younger or significantly older than the plateau dates were only obtained from ~1 mm and ~2.2 mm alkali feldspar fragments during the initial heating steps.

4. Discussion

4.1. Fracturing of alkali feldspar in response to heating and cooling

The most prominent textural modification of the Shap feldspar caused by our heating experiments in air was the formation of abundant cracks along the (001) cleavage plane. These cracks frequently extend for far > 10 μm and sometimes span the entire fragment. The cracks form an interconnected network and are usually more abundant around the replacive veins. Previous experimental studies of the Shap feldspar (Fitz Gerald et al., 2006; Parsons et al., 2010) did not report the presence of such cracks, and the review of Ian Parsons suggests that only a few were observed (e.g. Fig. 4a in Parsons et al., 2010). The exact cause of the discrepancy between previous work and our results is unclear, although some methodological differences may be of importance. A significant portion of previous observations was made using transmission electron microscopy, and it is likely that only those samples without abundant cracks could be successfully prepared for examination via this technique. Many previous observations were made by SE imaging of coated HF-etched fragments. This approach is expected to reveal cracks widened by HF-etching, which are unlikely to be filled with coating like cracks in our samples. However, most of the SE images presented in previous studies were acquired from (001) cleavage surfaces, where the observation of cracks parallel to (001) is difficult, if at all possible. Finally, previous experiments were conducted on smaller fragments than in the current study, while our experience suggests that cracks are most apparent in large cm-scale fragments.

The interconnected cracks observed here together with previously reported nanotunnels, pull-aparts, slots and bubbles (Fitz Gerald et al., 2006; Parsons et al., 2010) represent noticeable breaks in the continuity of the alkali feldspar crystal structure, which separate previously adjacent atoms at ≈ nm scale distances. The width of the resulting gaps significantly exceeds the van der Waals diameter of Ar (0.388 nm, e.g. Vogt and Alvarez, 2014). Therefore, it seems reasonable to assume that if cracks, nanotunnels, pull-aparts, slots and bubbles connect with each other and the surface of the fragments, then they can serve as fast pathways for Ar loss during laboratory degassing. Considering that cracks are much wider and extend over significantly greater distances than nanotunnels, pull-aparts, slots and bubbles, they probably play a key role in Ar loss. Isolated cracks, nanotunnels, pull-aparts, slots and bubbles probably can serve as traps, which accumulate and retain Ar until they connect to the surface of alkali feldspar fragments or disappear during melting (see our Argument 2 in Section 4.2 for further support of these suggestions). Furthermore, evidence for continuous cracking (this work) and the modification of nanotunnels, pull-aparts, slots and bubbles (Parsons et al., 2010) with progressive heating suggests that the inventory of fast pathways and traps changes throughout the step-heating analysis. The apparent disappearance of some cracks with progressive heating indicates that the full inventory of fast pathways and traps that affected any particular fragment may not be easily observable after cooling to room temperature.

The abundance of cracks is similar in the experiments with fast and slow heating and cooling rates, suggesting that they are not caused by thermal shock. Fracturing apparently occurs due to the change in
temperature itself, and not due to the high rate of this change. A high abundance of cracks around replacive veins suggests that some of them may have formed by the thermal expansion of fluids in micropores. However, many cracks were found far from the replacive veins and micropores. Therefore, we suggest that observed fracturing is largely related to some other phenomenon, which may be the thermal expansion of feldspar. The Shap feldspar is a composite of coherent domains and incoherent subgrains of K-rich and Na-rich feldspars with different states of order (see above; Lee et al., 1995; Lee and Parsons, 1997; Fitz Gerald et al., 2006; Parsons et al., 2010). These feldspars have different unit cell parameters that change differently with heating or cooling (Fig. 6; Henderson, 1979; Kroll et al., 1980; Hovis and Graeme-Barber, 1997). For example, at room temperature Na-rich feldspars have smaller unit cells with considerably higher interaxial $\alpha$ angles compared to K-rich feldspars. The difference in the unit cell sizes and $\alpha$ angles decreases with increasing temperature. In exsolving alkali feldspar in a slowly cooled rock, local stresses caused by increasing differences in the unit cell parameters are partly accommodated by the formation of crystal defects and albite/pericline polysynthetic twins within exsolution lamellae (Lee et al., 1995; Parsons et al., 2010). These stresses are further mitigated by low-temperature fluid-mediated recrystallisation, which is driven by the release of strain energy that accumulated in exsolved alkali feldspar via its replacement with K-rich and Na-rich feldspars with unstrained crystal structures (Lee et al., 1995; Lee and Parsons, 1997). None of these processes occur during laboratory heating as they require the presence of fluid and Si–Al inter-diffusion, which is negligible on any relevant laboratory timescales (Fitz Gerald et al., 2006; Parsons et al., 2010). Therefore, the described structural and textural changes that partly accommodated local stresses in exsolved alkali feldspar during its geologic past are not reversed during laboratory heating. However, the unit cell parameters of any particular region within its structure are instantaneously reversed during laboratory heating to an extent permitted by the temperature of heating and by the current state of order and composition. This creates local stresses around compositionally different domains within coherent regions and misaligned subgrains within recrystallised areas, which are released through the formation of cracks. The cracks predominantly form along the weakest (Deer et al., 1971) cleavage plane (001). Notably, the most significant change in unit cell parameters of Na-rich feldspars is that of the $\alpha$ interaxial angle, which defines the angle between the $b$ and $c$ crystallographic axes and thus the angle between the (010) and (001) cleavage planes.

An additional cause of stresses that lead to fracturing during laboratory heating may be Na–K inter-diffusion, which also leads to significant changes in unit cell parameters (Kroll et al., 1980; Hovis and Graeme-Barber, 1997). Experimental evidence for fracturing due to this process was provided by Scheidl et al. (2014) and Petrishcheva et al. (2019). They report periodic cracks close to (100) in K-rich sanidine that formed due to contraction of the $\alpha$ dimension of a unit cell, which was caused by cation exchange with Na-rich salt melt and K–Na inter-diffusion. We did not observe cracks close to (100) in the heated fragments of alkali feldspar from the Shap granite, which suggests that compositional changes associated with lamellae homogenisation and re-equilibration of subgrains in replacement perthite and microcline veins were not sufficient for their formation. However, these compositional changes could amplify the stresses related to the differences in thermal expansion of K-rich and Na-rich feldspar, thus facilitating fracturing along the weakest (001) cleavage plane. For example, similar to the effect of increasing temperature, the diffusion of K into Na-rich feldspars should decrease the $\alpha$ interaxial angles (Kroll et al., 1980; Hovis and Graeme-Barber, 1997).

Fracturing caused by laboratory heating was previously reported in three studies related to the interpretation of step-heating $^{39}$Ar/$^{39}$Ar data derived from alkali feldspar. Fitz Gerald and Harrison (1993) conducted in vacuo isothermal heating experiments at 750–1150 °C with 180–250 μm fragments of alkali feldspar from the Chain of Ponds pluton (using the same sample that was used to establish MDD theory; Lovera et al., 1989). They observed minor fracturing along cleavage planes that was concentrated around recrystallised zones and suggested that it may largely be a consequence of sample preparation subsequent

| K/(K+Na) | Disordered | Ordered |
|---------|------------|---------|
| ~0      | - (Kroll et al., 1980) | - (Hovis and Graeme-Barber, 1997) |
| ~1      | - (Henderson, 1979) | - (Hovis and Graeme-Barber, 1997) |

Fig. 6. The temperature dependence of unit cell parameters in ordered and disordered Na-rich and K-rich feldspars (Henderson, 1979; Kroll et al., 1980; Hovis and Graeme-Barber, 1997).
to their experiments. Sanders (2008) conducted in vacuo isothermal heating experiments at 650–1100 °C with 180–500 μm fragments of alkali feldspar from the Klokken intrusion and observed cracks in both exsolved and recrystallised areas. This study suggested that cracks were formed during heating. Finally, Poland (1994) reported fragmentation of gem-quality alkali feldspar extracted from Benson Mines pegmatite after in vacuo heating. Fitz Gerald and Harrison (1993) and Sanders (2008) concluded that fracturing plays no important role in laboratory degassing of alkali feldspar, while Poland (1994) argued that fracturing significantly affects the kinetics of 39Ar release and the topology of 40Ar/39Ar age spectra. These points are discussed in the following sections.

4.2. Non-linear Arrhenius trajectories of 39Ar release from alkali feldspar

All of our step-heating 40Ar/39Ar analyses of the Shap feldspar yielded non-linear Arrhenius trajectories of 39Ar release. As discussed in Section 1, non-linear Arrhenius trajectories are common for alkali feldspar and are inconsistent with the presence of a single grain-scale diffusion domain whose intrinsic diffusion properties are independent of temperature and time. Some researchers explain the non-linearity by suggesting that the effective diffusion length is shorter than the physical size of the analysed fragment. This may be related to the presence of multiple non-interacting intra-grain diffusion domains with different sizes (Zeitler, 1987; Lovera et al., 1989), or to the presence of fast pathways for Ar loss, Ar traps and their modifications with progressive heating (Poland, 1994; Arnaud and Kelley, 1997; Parsons et al., 1999; Fitz Gerald et al., 2006; Parsons et al., 2010). Other researchers suggested that non-linear Arrhenius trajectories may at least in part result from modifications of the intrinsic diffusion properties due to heating-induced structural transitions (Evernden et al., 1960; Wartho et al., 1999; Cassata and Renne, 2013; Villa, 2013; Chafer et al., 2014), annealing of structural damage produced by neutron irradiation (Poland, 1994), homogenisation of compositionally different domains within crystals (Evernden et al., 1960) or switching between different vacancy-specific mechanisms of diffusion (Wartho et al., 1999; Villa, 2006).

The topology of the Arrhenius trajectories obtained for alkali feldspar from the Shap granite depends on the shortest dimension length of the analysed fragments (Fig. 4A, D, G), suggesting that it is not dominantly controlled by changes to intrinsic diffusion properties. This is because any modifications of the structure, texture or composition that change the intrinsic diffusion properties are expected to occur at the same temperature in fragments with different sizes, resulting in Arrhenius trajectories with similar topologies. Therefore, we conclude that the topology of the obtained Arrhenius trajectories reflects the presence of some features that reduce the effective diffusion length relative to the physical size of the analysed fragments. This conclusion is further supported by the correlation of ln(D/r2) values with the size of the analysed fragments. While there is some correlation between these parameters (Fig. 5), the observed differences cannot be explained by assuming that the half-width of the analysed fragments approximates the effective diffusion length. For example, there is < 1 ln unit difference between ln(D/r2) values obtained for the fragments with half-widths of ~0.2 mm and ~1.1 mm during the same temperature 90-minute steps at 850–1000 °C. If the effective diffusion length of these fragments was approximated by their half-width, this difference should have reached ~3.4 ln units.

The Arrhenius trajectory that we obtained for the batch of four alkali feldspar fragments with the shortest dimension length of ~0.4 mm (experiment 7cSF; referred to below as small fragments) suggests that during the first two heating cycles the effective diffusion length increased with progressive heating (Fig. 4A). This pattern of 39Ar release is typical of alkali feldspar and is frequently interpreted to reflect the presence of variably-sized non-interacting intra-grain diffusion domains that existed before mineral separation and remained intact during laboratory heating (e.g. Lovera et al., 1989, 1991, 1993, 1997, 2002). Following this interpretation, the increase of the effective diffusion length is explained by earlier outgassing of smaller diffusion domains. The only preceding 40Ar/39Ar study of the Shap feldspar used 250–500 μm fragments for step-heating analysis and did not report any inconsistency between the obtained Arrhenius trajectories and predictions from MDD theory (Short et al., 2011).

The single fragments of alkali feldspar that had shortest dimension lengths of ~1 mm and ~2.2 mm (experiments 7c4 and 4a, respectively; referred to below as large fragments) had very different degassing behaviour. Their Arrhenius trajectories suggest that during each of the first two heating cycles the effective diffusion length decreased over a series of 10-minute heating steps and then increased over a series of 90-minute heating steps repeated at the same temperatures (Fig. 4D, G). This result cannot be explained by degassing of variably-sized non-interacting intra-grain diffusion domains that existed prior to mineral separation and remained intact during step-heating. At least some of the features that reduced the effective diffusion length gradually developed during step-heating. Considering the results of our heating experiments in air (see Sections 3.1 and 4.1), it seems likely that these features were inter-connected cracks with some contribution from nanotunnels, pull-aparts, slots and bubbles. Fracturing and modification of nanoscale defects within the crystal structure also occur gradually with progressive heating. It should be noted that cracks are wider and extend over longer distances than nanotunnels, pull-aparts, slots and bubbles, so they probably played a key role in providing fast pathways for Ar loss from the deep interiors of the alkali feldspar fragments. Most of the listed nanoscale defects are probably isolated from the surface of these fragments in the absence of cracks and thus act as Ar traps (see below our Argument 2 for further support of these suggestions). Therefore, we will now focus on the role of fracturing, although some contribution from nanoscale defects is always implied (e.g. those directly connected to the surface of the analysed fragments). We will outline below our two arguments that fracturing is the dominant cause of the reduction of the effective diffusion length in the Shap feldspar, and it is likely that these apply to other samples of alkali feldspar.

**Argument 1.** Our step-heating experiments with large alkali feldspar fragments show that fracturing leads to a significant decrease of the effective diffusion length with progressive heating (Fig. 4D, G). Thus, at a fixed temperature the increase in ln(D/r2) values between the initial 10-minute and repeated 90-minute heating steps reached ~4.7 ln units in experiment 7c4 (at 700 °C; Fig. 4D) and ~3.8 ln units in experiment 4a (at 625 °C; Fig. 4G). Assuming that D did not change, these differences suggest shortening of the effective diffusion lengths by factors of ~10.3 and ~6.5, respectively. Even greater shortening is implied by the log(r/t0) spectra (Fig. 7), which were calculated for all of our experiments assuming that Ea is 220 kJ/mol (see Section 3.2) and that t0 is the effective diffusion length observed during the first heating step in experiment 7cSF and the second heating step in experiments 7c4 and 4a (no 39Ar was detected during the first heating step in these experiments). The log(r/t0) spectra of the large fragments indicate that the effective diffusion length approached its maximum value during the initial 6 heating steps (only 4 are visible in Fig. 7) and then decreased to its minimum value during the following 5 to 9 heating steps. The dispersion of log(r/t0) values in these spectra reaches 1.7 log units, suggesting that the effective diffusion length was reduced by a factor of ~14.8. This is comparable in magnitude with a ~25-fold variation of the effective diffusion length that is suggested by the log(r/t0) spectra of the small fragments from our study and many other samples of alkali feldspar (Fig. 7; assuming that sample 93-NG-17 in Lovera et al., 1997, is representative of other samples from their database). Therefore, fracturing can account for these variations.

**Argument 2.** There is evidence suggesting that no features other than cracks can provide fast pathways for instantaneous removal of Ar from the interiors of step-heated alkali feldspar fragments. While the nature of fast pathways for Ar loss in alkali feldspar has not been firmly...
established, most authors suggest that incoherent boundaries between subgrains act as such (e.g. Parsons et al., 1988; Burgess et al., 1992; Fitz Gerald and Harrison, 1993; Parsons et al., 1999; Cassata and Renne, 2013). However, previous studies of alkali feldspar from the Klokken intrusion (Burgess et al., 1992; Sanders, 2008) provide evidence to question this suggestion. Burgess et al. (1992) compared the spacing between incoherent grain boundaries in microtexturally different fractions of the Klokken feldspar and concluded that pristine fractions that are almost devoid of such boundaries should have ~10⁻⁷ times greater effective diffusion lengths than intensively recrystallised fractions that have abundant incoherent subgrains with sub-μm sizes. However, as discussed in Sanders (2008), these microtexturally different fractions yield overlapping Arrhenius trajectories, suggesting that they have similar effective diffusion lengths (e.g. Fig. 3.28 in Sanders, 2008; see also Fig. 2b in McLaren et al., 2007). This suggests that some features other than incoherent grain boundaries provide fast pathways for Ar loss during laboratory heating, unless the effective diffusion lengths are significantly shorter than the half-width of the smallest subgrains. These other features could be cracks, which were observed by Sanders (2008) in heated alkali feldspar fragments. Our experiments with the Shap feldspar likewise suggest that incoherent grain boundaries do not act as efficient fast pathways for Ar loss during laboratory heating. Furthermore, these experiments indicate that fast pathways for Ar loss provided by nanotunnels, pull-aparts, slots and bubbles play subordinate role over timescales relevant to conventional step-heating analysis. All of the fragments that we analysed had similar microtexture, and thus the spacing between intra-grain incoherent grain boundaries and the concentration of nanoscale defects should have also been similar. Hence, if any of these features dominated among fast pathways for Ar loss, we should have obtained similar Arrhenius trajectories from fragments with different sizes. However, significantly different Arrhenius trajectories were obtained from fragments with different sizes (Fig. 4A, G, D), and there is a correlation between their coordinates in Arrhenius space and the size of the analysed fragments (Fig. 5). Therefore, we conclude that incoherent grain boundaries, nanotunnels, pull-aparts, slots and bubbles are not the dominant fast pathways for Ar loss during step-heating analysis of the Shap feldspar, leaving cracks as the main candidates for this role.

If fracturing is the dominant cause of the effective diffusion length reduction during step-heating analysis, then why is there no evidence for gradual fracturing in the Arrhenius trajectory that we obtained for the small fragments of alkali feldspar from the Shap granite? We suggest that this is because of the dynamics of crack propagation. Clearly, in smaller fragments there is a greater chance that cracks forming during the first heating step will intersect the surface. In contrast, many consecutive heating steps may be required in larger fragments before the cracks interconnect to form pathways to the surface, which is consistent with the topology of their Arrhenius trajectories. The fast development of cracks that intersect the surface during the first heating step would account for the results of Lovera et al. (1993) and Sanders (2008), who analysed small (~500 μm) alkali feldspar fragments and concluded that step-heating analysis does not significantly alter the network of fast pathways for Ar loss that define intra-grain diffusion domains.

Considering the points made above, we conclude that the features responsible for the reduction of the effective diffusion length in the Shap feldspar are largely formed during step-heating and are represented by interconnected cracks with some contribution from nanotunnels, pull-aparts, slots and bubbles. Furthermore, it seems probable that cracks represent dominant fast pathways for Ar loss in many other alkali feldspars, while the role of incoherent boundaries between subgrains may be overestimated. Two previous studies that acquired step-heating ⁴⁰Ar/³⁹Ar data from alkali feldspar also suggested that the reduction of the effective diffusion length results from fracturing, either during step-heating (Poland, 1994) or during sample preparation (Arnaud and Kelley, 1997). Notably, one of these studies additionally used in situ ³⁹Ar analysis to document enhanced diffusion parallel to the (001) cleavage plane (Arnaud and Kelley, 1997), which is the dominant direction of fracturing observed in our experiments. Furthermore, some recent in situ experimental studies on ⁴⁰Ar diffusion in alkali feldspar interpret rim to core variations in ⁴⁰Ar concentration assuming the presence of fast pathways (Baxter, 2010 and therein). Our conclusion corroborates all of these suggestions.

All of the Arrhenius trajectories that we obtained in this study looped during the third heating cycle that included heating steps at 1000–1150 °C (most evident in Fig. 4A), which is probably related to partial melting of the analysed fragments. According to the experiments of Parsons et al. (2010), partial melting commences in the Shap feldspar at 1100 °C. Therefore, some amount of melt should form within the analysed fragments during heating to 1150 °C and subsequently crystallise during the consecutive 90-, 180- and 360-minute steps at 1000 °C. Both melting and crystallisation have the potential to release Ar. Molten alkali feldspar is characterised by higher diffusivity (cf. Baxter, 2010; Behrens, 2010), while crystallisation may expel Ar from the melt, considering its partitioning behaviour during this process (Kelley, 2002). The proposed explanation is thus consistent with the observations.

4.3. Implications for the interpretation of ⁴⁰Ar/³⁹Ar dates of alkali feldspar

⁴⁰Ar/³⁹Ar dating of alkali feldspar is frequently used to constrain temporal variations of rock temperatures between ~150-350 °C. Time-temperature paths are usually obtained by inversion modelling of step-heating ⁴⁰Ar/³⁹Ar data using MDD theory of Lovera et al. (1989), which assumes that the topology of Arrhenius trajectories of ³⁹Ar release

Fig. 7. A comparison of the log(r/t₀) spectra that we obtained for our experiments with alkali feldspar from the Shap granite and that reported for sample 93-NG-17 in Lovera et al. (1997). The log(r/t₀) spectra of the Shap feldspar were calculated assuming that Eₐ is 220 kJ/mol (see Section 3.2) and that t₀ is the effective diffusion length observed during the first heating step in experiment 7cSF and the second heating step in experiments 7c and 4a (no ²⁶⁰Ar was detected during the first heating step in these experiments). N is a constant that was used to move the log(r/t₀) spectra relative to each other in the diagram space. We used a logarithmic scale on the x axis to allow observation of how log (r/t₀) values change during the initial heating steps.
reflects the presence of variably-sized non-interacting intra-grain diffusion domains that existed in the analysed fragments prior to mineral separation. However, as we show above, Arrhenius trajectories that seem consistent with such an interpretation may also result from a reduction of the effective diffusion length due to fracturing during laboratory heating, which is inconsistent with this interpretation. Furthermore, our data indicate that obtaining such Arrhenius trajectories that erroneously appear consistent with MDD theory may be restricted to the analysis of alkali feldspar fragments that are smaller than 500 μm in the shortest dimension. Step-heating 40Ar/39Ar data acquired from sufficiently large fragments of alkali feldspar from the same rock (≥ 1 mm in case of the Shap granite) may be in clear conflict with the underlying assumptions of MDD theory. However, fragments larger than 500 μm in the shortest dimension are not usually analysed. These results indicate that a better understanding of alkali feldspar behaviour during step-heating analysis is required before interpreting 40Ar/39Ar data using MDD theory.

Two previous studies reported cracks in alkali feldspar that was subjected to laboratory heating and suggested the formation of these cracks does not significantly affect the kinetics of 39Ar release and the topology of 40Ar/39Ar age spectra. Fitz Gerald and Harrison (1993) argued that fracturing is minor and could largely occur during sample preparation subsequent to their experiments. The results of our experiments in air demonstrate that at least in some samples of alkali feldspars significant fracturing occurs during step-heating, while our step-heating 40Ar/39Ar data show that the effect of this process on 39Ar release kinetics is substantial. Sanders (2008) argued that if the effect of fracturing was significant, it would not be possible to explain why MDD modelling of step-heating 40Ar/39Ar data derived from alkali feldspar frequently yields thermal history solutions that appear to be accurate. However, as we discuss in the next paragraph, obtaining apparently accurate time-temperature solutions by MDD modelling of step-heating 40Ar/39Ar data may be fortuitous and thus does not prove that the effect of fracturing is insignificant. Before we get to this discussion, we would like to recall that many researchers suggest that volume diffusion may not be the main mechanism of 40Ar loss over geological timescales, so we will proceed by taking into account that other mechanisms such as fluid-mediated dissolution-reprecipitation may be at play (Parsons et al., 1999; Villa, 2006; Villa, 2013; Villa and Hanchar, 2013; Chafe et al., 2014; Popov and Spikings, 2020).

Fracturing was documented in all three samples of commonly-occurring alkali feldspar where the microtextural evolution during laboratory heating was investigated using electron microscopy (this study; Fitz Gerald and Harrison, 1993; Sanders, 2008). In all cases fracturing was more intense around replacive veins that are formed by fluid-induced dissolution-reprecipitation. Such veins are ubiquitous in all alkali feldspar and can form long after its primary crystallisation (e.g. Lee et al., 1995; Lee and Parsons, 1997; Parsons et al., 1999; Villa, 2006; Chafe et al., 2014; Parsons et al., 2015 and therein). For example, (some) replacive veins in alkali feldspar from the Klokken intrusion post-date its emplacement by hundreds of millions of years, while pristine regions yield dates that are close to the crystallisation age (Sanders, 2008; Harrison et al., 2010). Therefore, step-heating analysis creates more cracks in younger regions that were affected by dissolution-reprecipitation than in older regions that did not interact with fluids. This can create an overall positive correlation between the 40Ar/39Ar date and the distance from cracks, and thus result in a monotonously increasing 40Ar/39Ar age spectrum. Popov and Spikings (2020) show that step-heating 40Ar/39Ar data obtained in such cases may appear compatible with the assumptions behind MDD theory, and MDD modelling of these data may yield a time-temperature path that mimics the timing of known tectonic events. This temporal match may be coincidental or occur if recrystallisation was related to these tectonic events. If recrystallisation occurred at temperatures close to the closure temperatures inferred using MDD theory, the constrained thermal history may also mimic the real time-temperature path. Considering this, it seems possible that in some cases MDD modelling of step-heating 40Ar/39Ar data derived from alkali feldspar that was fractured during the analysis would yield apparently accurate thermal history solutions. For example, MDD modelling of the 40Ar/39Ar data that we acquired from the batch of four Shap feldspar fragments with the shortest dimension lengths of ~0.4 mm yields a time-temperature path (Fig. 8) that is reconcilable with the known geologic history of the Shap granite (see Section 2). The best-fit thermal history obtained using MDD theory suggests that the Shap granite cooled to ≤100 °C in less than a million years following its emplacement, and a minimal reheating event sufficient to account for the apatite fission track data of Green (1986) does not affect the topology of the 40Ar/39Ar age spectrum (i.e. there is no inconsistency between alkali feldspar 40Ar/39Ar and apatite fission track data). Furthermore, there might be a bias towards only publishing apparently successful results, given that negative results are frequently not published (Fanelli, 2012; Mlinarić et al., 2017). Therefore, the apparent success with the reconstruction of time-temperature paths using MDD theory does not prove that fracturing has an insignificant effect on laboratory degassing of alkali feldspar.

4.4. Implications for the interpretation of Ar diffusion experiments with alkali feldspar

An important consequence of heating-induced fracturing of alkali feldspar is that the retentivity of any given sample with respect to diffusive loss of 40Ar over geological timescales cannot be estimated using sample-specific E₀ and (D₀/r²) values obtained by step-heating analysis. Its retentivity should rather be estimated using the diffusion parameters of Ar in the crystal structure of alkali feldspar (i.e. E₀ and D₀ values). Obtaining these parameters on a case-by-case basis may be extremely challenging, as it requires a careful consideration of every crack within the analysed sample. Therefore, it would probably be more
practical to use $^4$He diffusion parameters that were obtained from ideal samples, which could be gem-quality alkali feldspars. However, as we discuss below, gem-quality alkali feldspars may also be affected by heating-induced fracturing.

Diffusion experiments with gem-quality alkali feldspars sometimes yield non-linear Arrhenius arrays (Foland, 1974; Foland, 1994; Arnaud and Kelley, 1997; Wartho et al., 1999; Cassata and Renne, 2013). Such arrays were obtained using both step-heating analysis and in situ depth profiling in partly outgassed fragments, and their interpretation is controversial. For example, non-linear Arrhenius trajectories of $^{39}$Ar release during step-heating were obtained from gem-quality alkali feldspars from both Benson Mines pegmatite (Foland, 1994) and Itrongay pegmatite (Arnaud and Kelley, 1997; Cassata and Renne, 2013). In the case of Benson Mines pegmatite, non-linearity was associated with fracturing (Foland, 1994), although it was suggested that there was no reduction of the effective diffusion length due to fracturing in the bulk loss experiments (Foland, 1974; Foland and Xu, 1990; Foland, 1994). This conclusion was disputed by Lovera et al. (1997), who showed that the bulk loss experiments are compatible with a reduction of the effective diffusion length due to the presence of multiple intra-grain diffusion domains that existed prior to mineral separation. In the case of Itrongay pegmatite, non-linearity was related to either the presence of fast pathways for $^4$He loss (Arnaud and Kelley, 1997) or some intrinsic change of the $^4$He diffusion parameters (Cassata and Renne, 2013). Notably, the latter conclusion was disputed in Lovera et al. (2015), who showed that the underlying results are compatible with the presence of multiple intra-grain diffusion domains. However, Cassata and Renne (2015) argued that in this case the proportion of small-size domains should depend on the size of the analysed fragment, which they deemed illogical. The results of in situ depth profiling in alkali feldspar from Itrongay pegmatite are also controversial. Wartho et al. (1999) obtained a non-linear Arrhenius array for alkali feldspar fragments that were heated to different temperatures prior to the analysis. They related the non-linearity to an intrinsic change in diffusion parameters due to heating and rejected the hypothesis that some fast pathways for $^4$He loss are present. However, an earlier study of Arnaud and Kelley (1997) suggested that $^{39}$Ar diffusion in experimentally outgassed fragments is sometimes enhanced parallel to the (001) cleavage plane due to the presence of fast pathways for $^4$He loss, possibly cracks. Later interpretations of in situ data obtained from this alkali feldspar also concluded that fast pathways were utilised during $^4$He degassing (Baxter, 2010 and therein).

Fracturing may account for the controversy surrounding the diffusion experiments with gem-quality alkali feldspars. Although these feldspars are in general microtexturally simple (Cassata and Renne, 2013 and therein) and are not expected to be intensively fractured, some fracturing may still occur (e.g. Foland, 1994). If the newly formed cracks are small and do not connect with each other, then only those cracks that are located in the outer regions of the alkali feldspar fragments and connect to their surface would serve as fast pathways for $^4$He loss. Such cracks may emulate multi-path diffusion that was suggested based on the in situ data (Baxter, 2010 and therein; note also that many in situ profiles in Wartho et al., 1999, have a similar topology to that shown in Baxter, 2010). As discussed in Arnaud and Kelley (1997), the presence of fast pathways for $^4$He loss in the outer regions of alkali feldspar fragments can account for the results of their step-heating experiments. Furthermore, if fast pathways are confined to the outer regions of the analysed fragments that have similar widths, then their influence on the non-linearity of the Arrhenius trajectories is expected to depend on the surface area to volume ratio. This would address the concerns of Cassata and Renne (2015) because for fragments of similar geometry the surface area to volume ratio depends on the size, and thus the inferred proportion of small-size domains would also depend on the size (Fig. 9). Therefore, we conclude that the possibility of fracturing should also be considered when interpreting the results of $^4$He diffusion experiments with gem-quality alkali feldspar crystals. Importantly, all of the above-mentioned previous interpretations of such experiments are not fully compatible with the presence of cracks solely in the outer region of the analysed fragments, suggesting that the inferred parameters of $^4$He diffusion in alkali feldspar may be inaccurate to some degree (for example, see Lovera et al., 1997, who discussed the implications of not considering the effective diffusion length reduction when interpreting bulk-loss and step-heating data).

5. Conclusions

(i) Laboratory heating of alkali feldspar from the Shap granite causes it to fracture, predominantly along the (001) cleavage plane. Fracturing is generally more intense around recrystallised areas, although some recrystallised areas are poor in cracks. Fracturing probably occurs due to different and anisotropic thermal expansion of compositionally and structurally different feldspars, which is expected to create stresses around coherent Na-rich lamellae and misaligned Na-rich and K-rich subgrains in recrystallised areas. These stresses may be further amplified by Na–K inter-diffusion. The resulting cracks form an interconnected network, which may link with some of previously documented nanoscale defects such as nano-tunnels, slots, pull-aparts and bubbles.

(ii) Step-heating $^{40}$Ar/$^{39}$Ar analysis of the Shap feldspar yields non-linear Arrhenius trajectories of $^{39}$Ar release. The non-linearity is best explained by heating-induced reduction of the effective diffusion length due to the formation of cracks. Some contribution from nano-tunnels, pull-aparts, slots and bubbles is also expected. In contrast, incoherent boundaries between subgrains may not serve as fast pathways for $^4$He loss during laboratory heating. Importantly, the effect of fracturing on the topology of Arrhenius trajectories depends on the size of the analysed fragments. Unambiguous evidence for a reduction of the diffusion length during step-heating was only observed in experiments with large fragments ($\geq 1$ mm across). The Arrhenius trajectory obtained from the smaller fragments ($\leq 0.5$ mm across) appears to be consistent with the presence of variably-sized non-interacting intra-grain diffusion domains that existed prior to mineral separation. This suggests that such Arrhenius trajectories may be an artefact of the small size of step-heated fragments, and they do not

![Fig. 9. The dependence of the inferred proportion of the small-size domains on the half-width of the analysed fragments that was observed in Cassata and Renne (2015). Orange squares show the proportions expressed as a percent of that inferred for the fragment with the half-width of 100 μm. The grey line shows the dependence of the surface area to volume ratios on the half-width of 1.5 mm by 1.5 mm slabs. The blue line shows the dependence of the ratios between the volume of the outer 1 μm rim and the volume of the entire slab on the half-width of 1.5 mm by 1.5 mm slabs. For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.](image)
unequivocally validate the application of MDD theory.

(iii) Heating-induced reduction of the effective diffusion length due to fracturing must be taken into account when interpreting $^{40}$Ar/$^{39}$Ar dates of alkali feldspars. Two aspects need to be considered. First, this process is clearly inconsistent with the underlying assumptions of MDD theory of Lovera et al. (1989), although it can result in $^{39}$Ar release patterns that appear consistent with the presence of multiple non-interacting intra-grain diffusion domains of different size. It is therefore important to identify on a case by case basis how $^{40}$Ar is released from alkali feldspar before applying MDD theory. Second, if heating-induced fracturing is ubiquitous in alkali feldspar, then its retenitivity with respect to diffusive loss of $^{40}$Ar over geological timescales should be estimated using the diffusion parameters of $^{40}$Ar in the crystal structure rather than $E_D$ and $D_p/r^2$ values obtained from step-heating experiments. These could be obtained from diffusion experiments with gem-quality alkali feldspars. However, if gem-quality alkali feldspars are also affected by heating-induced fracturing, then presently available diffusion parameters of $^{40}$Ar in alkali feldspars may be inaccurate to some degree (all of them were obtained without considering the presence of cracks).

Declaration of competing interests

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

Acknowledgments

We are grateful to our colleagues at the Department of Earth Sciences, University of Geneva for several useful discussions. Joshua Davies is thanked for providing a sample of the Shap granite. Jean-Marie Bocard and François Gischig are thanked for their advice on electron microscopy. Danijela Miletic Doric is thanked for her assistance. Ian Parsons and François Gischig are thanked for their advice on using a SelFrag. We are grateful to Balz Kamber for handling and editing our manuscript. Patrick Davies is thanked for providing a sample of the Shap granite. Jean-Marie Bocard and François Gischig are thanked for their advice on electron microscopy. Danijela Miletic Doric is thanked for her assistance. Ian Parsons and François Gischig are thanked for their advice on using a SelFrag. We are grateful to Balz Kamber for handling and editing our manuscript. Patrick Davies is thanked for providing a sample of the Shap granite. Ian Parsons and François Gischig are thanked for their advice on using a SelFrag. We are grateful to Balz Kamber for handling and editing our manuscript. Patrick Davies is thanked for providing a sample of the Shap granite. Jean-Marie Bocard and François Gischig are thanked for their advice on electron microscopy. Danijela Miletic Doric is thanked for her assistance. Ian Parsons and François Gischig are thanked for their advice on using a SelFrag. We are grateful to Balz Kamber for handling and editing our manuscript. Patrick Davies is thanked for providing a sample of the Shap granite.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemgeo.2020.119677.

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