Diffusion vs. fluid alteration in alkali feldspar $^{40}\text{Ar}/^{39}\text{Ar}$ thermochronology: does cross-correlation of log($r/r_0$) and age spectra validate thermal histories?

POPOV, Daniil, SPIKINGS, Richard Alan

Abstract

For six decades geoscientists have been trying to quantitatively understand the nature of radiogenic Ar loss from alkali feldspar. Some researchers suggest that volume diffusion is the dominant mechanism, and they use conventional step-heating $^{40}\text{Ar}/^{39}\text{Ar}$ data from alkali feldspar to recover the thermal histories of rocks. They argue that a high degree of correlation between log($r/r_0$) and $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra, which is observed in a number of natural examples, justifies this hypothesis. In contrast, other investigators suggest that fluid-mediated recrystallisation and alteration control the radiogenic Ar redistribution, hence rendering alkali feldspar useless as a thermochronometer. By means of numerical modelling, we found that the latter mechanism as well is able to produce samples with highly correlated log($r/r_0$) and $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra. In addition, we show that apparent thermal histories recovered for altered alkali feldspar crystals by interpreting step-heating $^{40}\text{Ar}/^{39}\text{Ar}$ data may be grossly inaccurate, and yet seemingly fit the prevailing understanding of regional geology. Such [...]
Diffusion vs. fluid alteration in alkali feldspar $^{40}$Ar/$^{39}$Ar thermochronology: Does cross-correlation of log($r/r_0$) and age spectra validate thermal histories?

Daniil V. Popov⁎, Richard A. Spikings

Department of Earth Sciences, University of Geneva, 13 Rue des Maraichers, Geneva 1205, Switzerland

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A B S T R A C T

For six decades geoscientists have been trying to quantitatively understand the nature of radiogenic Ar loss from alkali feldspar. Some researchers suggest that volume diffusion is the dominant mechanism, and they use conventional step-heating $^{40}$Ar/$^{39}$Ar data from alkali feldspar to recover the thermal histories of rocks. They argue that a high degree of correlation between log($r/r_0$) and $^{40}$Ar/$^{39}$Ar age spectra, which is observed in a number of natural examples, justifies this hypothesis. In contrast, other investigators suggest that fluid-mediated recrystallisation and alteration control the radiogenic Ar redistribution, hence rendering alkali feldspar useless as a thermochronometer. By means of numerical modelling, we found that the latter mechanism as well is able to produce samples with highly correlated log($r/r_0$) and $^{40}$Ar/$^{39}$Ar age spectra. In addition, we show that apparent thermal histories recovered for altered alkali feldspar crystals by interpreting step-heating $^{40}$Ar/$^{39}$Ar data may be grossly inaccurate, and yet seemingly fit the prevailing understanding of regional geology. Such inaccurate apparent thermal histories can be obtained even from alkali feldspar crystals that underwent volumetrically low degrees of alteration. Therefore, we conclude that conventional step-heating $^{40}$Ar/$^{39}$Ar data are insufficient to support the assumption that radiogenic Ar loss from alkali feldspar occurred solely by volume diffusion and validate the constrained thermal histories, even if upheld by a priori knowledge of regional tectonics. We further suggest that all thermochronological constraints obtained using such data should be supported by detailed petrological characterisation of alkali feldspar.

1. Introduction

A very wide range of natural phenomena result in temperature changes in rocks, and thus thermochronological methods are used to investigate them. A great majority of thermochronological studies have used the fission track and (U-Th)/He methods to generate continuous time(T)-Temperature(T) paths at ~40–180 °C (e.g. Reiners et al., 2005). At higher temperatures, continuous T-T paths are constrained, for example, by interpreting U-Pb dates of apatite (~350–550 °C; Cochrane et al., 2014; Chew and Spikings, 2015; Paul et al., 2018). The temperature gap between these techniques (~180–350 °C) may be accommodated by interpreting $^{40}$Ar/$^{39}$Ar data acquired from alkali feldspars by step-heating using the multi-diusion domain (MDD) theory of Lovera et al. (1989). However, many petrological observations question the validity of using this approach to constrain thermal histories of rocks (e.g. Parsons et al., 1999; Villa, 2006; Chafe et al., 2014). The primary aim of this work is to test the hypothesis that volumetrically low degrees of monomineralic alteration of alkali feldspar have little effect on the accuracy of continuous T-T solutions obtained by interpreting step-heating $^{40}$Ar/$^{39}$Ar data derived from it, and that the same $^{40}$Ar/$^{39}$Ar data can be used to validate the accuracy of these T-T solutions.

Similar to most thermochronological methods, MDD theory is founded on the assumption that the daughter isotope ($^{40}$Ar) is redistributed and lost from crystals by volume diffusion. One of the additional assumptions behind MDD theory is that the experimental technique used to acquire the $^{40}$Ar/$^{39}$Ar data for a given sample emulates the mechanisms that drove Ar loss during its geologic past (Lovera et al., 1989, 1997, 2002). While multiple studies suggest that step-heating $^{40}$Ar/$^{39}$Ar data can be used to obtain sensible Ar diffusion parameters and thermal histories for alkali feldspar crystals (e.g. Lovera et al., 1989, 1997, 2002; Dunlap and Fossen, 1998; Foster and John, 1999; Spikings et al., 2002; Reiners et al., 2004; McLaren et al., 2007; Sanders, 2008; Metcalf et al., 2009; Wong et al., 2010), some

⁎ Corresponding author.

E-mail addresses: d.v.popov@gmail.com, Daniil.Popov@unige.ch (D.V. Popov).

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researchers argue that these assumptions are rarely met. For example, Parsons et al., 1999; Villa (2006) and Chafe et al. (2014) suggest that alkali feldspar commonly undergoes fluid-mediated recrystallisation and alteration, which may significantly impact $^{36}$Ar displacement over geologic timescales and overprint variations in $^{40}$Ar concentration that formed by volume diffusion. Moreover, it has been suggested that Ar migration during conventional in vacuo step-heating experiments may be severely affected by structural transitions and textural modifications caused by sample preparation and laboratory heating (Poland, 1994; Arnaud and Kelley, 1997; Wartho et al., 1999; Parsons et al., 1999; Parsons et al., 2010; Villa, 2006; Cassata and Renne, 2013; Chafe et al., 2014).

Here we use numerical modelling to investigate the effect of fluid-induced dissolution-replication of alkali feldspar on the ability of MDD theory to accurately constrain the thermal histories of rocks, and on the usefulness of criteria used by $^{40}$Ar/$^{39}$Ar thermochronologists to compare the migration mechanisms of $^{40}$Ar in alkali feldspar that operate over laboratory and geologic timescales. We focus on testing the ability of the cross-correlation coefficient (see below; Lovera et al., 2002) to identify whether volume diffusion or fluid-mediated recrystallisation and alteration dominated $^{40}$Ar loss from alkali feldspar during its geologic past, and on evaluating the potential effect of volumetrically low degrees of alteration on the accuracy of MDD best-fit thermal histories. For the purpose of this work, we consider that the assumptions behind MDD theory that are not related to the mechanisms of $^{40}$Ar removal from alkali feldspar during its geologic past are valid. In other words, our modelling assumes that Ar isotopes are only displaced by volume diffusion through a structurally and texturally homogenous and stable medium during laboratory degassing, thus reducing potential complications arising from conventional in vacuo heating techniques.

2. Previous work

MDD theory has been used in many studies to reconstruct the thermal histories of intrusive and high-grade metamorphic rocks by inversion modelling of step-heating $^{40}$Ar/$^{39}$Ar data obtained from alkali feldspar from these rocks (e.g. Dunlap and Fossen, 1998; Foster and John, 1999; Spikings et al., 2002; Reiners et al., 2004; McLaren et al., 2007; Sanders, 2008; Metcalf et al., 2009; Wong et al., 2010). Such interpretations rely on the assumption that frequently observed non-linear Arrhenius trajectories of $^{39}$Ar release from alkali feldspar reflect the presence of multiple non-interacting diffusion domains within the analysed grains (Lovera et al., 1989, 2002). The nature of these intra-grain domains is poorly understood, but it is nonetheless generally assumed that they are represented by incoherent subgrains (Fitz Gerald and Harrison, 1993; Parsons et al., 1999; Cassata and Renne, 2013; see also Parsons et al., 1988; Burgess et al., 1992). Further, it is assumed that the intra-grain domains form at temperatures significantly exceeding their closure temperatures (~150–350 °C), remain intact throughout their geologic history and laboratory step-heating experiment, and lose $^{40}$Ar solely by volume diffusion (Lovera et al., 1989, 2002). However, a number of petrological studies suggest that incoherent subgrains in alkali feldspar are formed in many cases by fluid-induced dissolution-replication, which can occur at near-surface temperatures leading to non-diffusive loss of $^{40}$Ar (e.g. Lee et al., 1995; Parsons et al., 1999; Parsons et al., 2015).

Evidence for fluid-induced dissolution-replication is ubiquitous in alkali feldspar from intrusive and high-grade metamorphic rocks (e.g. Waldron et al., 1993; Brown and Parsons, 1993; Fitz Gerald and Harrison, 1993; Lee et al., 1995; Walker et al., 1995; Parsons et al., 2013; Chafe et al., 2014; Parsons et al., 2015; examples of alkali feldspar crystals affected by interaction with fluid are shown in Fig. 1). This process is largely driven by the release of the elastic strain energy (Brown and Parsons, 1993; Lee et al., 1995; Parsons et al., 2013; Parsons et al., 2015), which accumulates in alkali felspar as it cools due to Si-Al ordering and the development of a nm-scale tweed texture and due to diffusive exsolution into a nm- to μm-scale intergrowth of Na-rich and K-rich feldspars (Eggleton and Buseck, 1980; Brown and Parsons, 1993). The framework of Al and Si tetrahedra remains uninterrupted during both Si-Al ordering and exsolution, and the crystal lattice of alkali feldspar is distorted proximal to the boundaries between the ordered and antidered domains because of the differences in their crystallographic orientation (Eggleton and Buseck, 1980; Brown and Parsons, 1993) and between the regions of different composition because of the misfit of their crystal structures (Brown and Parsons, 1993). In the event of a fluid ingress this complex intergrowth undergoes partial dissolution with subsequent reprecipitation of Na-rich and/or K-rich feldspars with undistorted crystal lattices, which releases the stored strain energy (Brown and Parsons, 1993; Lee et al., 1995; Parsons et al., 2013; Parsons et al., 2015). Such fluid-mediated recrystallisation mostly leads to the formation of incoherent subgrains that range in size from fractions to several hundred μm (Fitz Gerald and Harrison, 1993; Lee et al., 1995; Parsons et al., 2013; Parsons et al., 2015). Semicoherent overgrowth of the residual pre-existing alkali feldspar has also been documented (Waldron et al., 1993; Lee et al., 1995; Parsons et al., 2015; see also Worden and Rushton, 1992). At volumetrically low to moderate degrees of recrystallisation, the newly formed subgrains are generally smaller than the coherent to semicoherent remnants of the pre-existing alkali feldspar (Fitz Gerald and Harrison, 1993; Lee et al., 1995; Parsons et al., 2015). Recrystallisation is estimated to occur at temperatures below ~500 °C (Lee et al., 1995; Parsons et al., 1999; Parsons et al., 2013; Parsons et al., 2015). The lower temperature limit for this process is defined by the ability to crystallise alkali feldspar, which theoretically can happen even at 0 °C (at these temperatures nearly pure Na-rich and K-rich feldspars form; Helgeson et al., 1969; Kastner and Siever, 1979). Other phases such as clay minerals can also be formed by fluid-induced dissolution-replication of alkali feldspar, particularly at low temperatures during weathering (Helgeson et al., 1969; Kastner and Siever, 1979; Wilson, 2004). However, in many recrystallised alkali feldspar crystals these phases occur in subordinate quantities, if at all (Waldron et al., 1993; Fitz Gerald and Harrison, 1993; Lee et al., 1995; Walker et al., 1995; Parsons et al., 2013; Parsons et al., 2015). Recrystallisation can postdate the formation of the pre-existing alkali feldspar by hundreds of millions of years (Sanders, 2008; Harrison et al., 2010).

To rule out potential complications arising from fluid-mediated recrystallisation and validate the accuracy of thermal histories reconstructed using MDD theory, Lovera et al. (2002) used numerical modelling to explore how this process affects the $^{40}$Ar/$^{39}$Ar systematics of alkali feldspar. They modelled geologic histories and step-heating experiments for several hypothetical alkali feldspar crystals and then compared the resulting synthetic $^{40}$Ar/$^{39}$Ar data with each other. Some of their simulations followed all the assumptions behind MDD theory: crystals with multiple intra-grain diffusion domains that remained intact throughout both their geologic history and laboratory heating have lost $^{40}$Ar solely by volume diffusion. For these crystals they were able to recover the original t-T paths using MDD theory. Further, they found that such crystals yield highly correlated log($t$/$t_0$) and $^{40}$Ar/$^{39}$Ar age spectra (normalized cross-correlation coefficient $C_{fg} > 0.95$). In other simulations one of the assumptions behind MDD theory was violated, which was claimed to mimic fluid-mediated recrystallisation of alkali feldspar. In these simulations crystals with multiple intra-grain diffusion domains were fragmented at various temperatures during their geologic history, although they again lost $^{40}$Ar solely by volume diffusion. Lovera et al. (2002) could not recover the original t-T paths using MDD theory for model crystals undergoing volumetrically significant alteration of the distribution of intra-grain diffusion domains (>6 vol

1 As defined in Section 3.5 in Lovera et al. (2002); see Appendix for discussion.
%)) at low temperatures (≤350 °C). Some of these model crystals yielded poorly correlated log(r/r0) and 40Ar/39Ar age spectra (C0 ≤ 0.95), making them distinctly different from the model crystals that complied with all the assumptions behind MDD theory. This led Lovera et al. (2002) to conclude that the frequent observation of high degrees of correlation between log(r/r0) and 40Ar/39Ar age spectra in natural samples indicates that in general laboratory degassing of alkali feldspar adequately emulates the process that occurred during its geologic past, implying that volume diffusion is the dominant mechanism of 40Ar loss and thus validating t-T paths constrained using MDD theory. However, other model crystals that underwent alteration of the distribution of intra-grain diffusion domains yielded highly correlated log(r/r0) and 40Ar/39Ar age spectra, making them indistinguishable from the model crystals that complied with all the assumptions behind MDD theory. Lovera et al. (2002) acknowledged that erroneous thermal histories obtained for such crystals using MDD theory can be mistakenly perceived as accurate. However, they argued that only volumetrically significant alteration (≥ 6 vol%) can substantially reduce the accuracy of these thermal histories, and that such alteration is rare and only occurs proximal to faults, unconformities, zones of hydrothermal alteration, or at relatively high temperature (> 350 °C). Additionally, it has been suggested that t-T paths constrained using MDD theory are generally accurate (Lovera et al., 2002; Harrison and Lovera, 2014), because in some cases they agree with the constraints from other thermochronological methods and correlate with independent knowledge of regional tectonic histories (e.g. Dunlap and Fossen, 1998; Spikings et al., 2002; Reiners et al., 2004; Metcalf et al., 2009; Wong et al., 2010).

The fluid-mediated recrystallisation of alkali feldspar modelled in Lovera et al. (2002) was simulated by only causing fragmentation of intra-grain diffusion domains, leaving volume diffusion as the sole mechanism of 40Ar displacement. However, an essential consequence of fluid-induced dissolution-reprecipitation of alkali feldspar is that it can remove 40Ar from the affected zones and reset their age to the time of interaction (e.g. Lee et al., 1995; Parsons et al., 1999; Villa, 2006; Chafe et al., 2014; consider also Ar partitioning behaviour between minerals and fluids, e.g. Kelley, 2002). How would such non-diffusive loss of 40Ar affect correlations between the log(r/r0) and 40Ar/39Ar age spectra? Can we ignore volumetrically low degrees of fluid-mediated recrystallisation and alteration of alkali feldspar (≤6 vol%; see Lovera et al., 2002) when constraining thermal histories of rocks using MDD theory? Can we find a geologically reasonable scenario of fluid-mediated recrystallisation that would result in an MDD best-fit t-T path that seems reasonable when correlated with independent knowledge of the regional tectonic history?

3. Method

To test the relevance of the C0 coefficient and evaluate the potential effects of fluid-mediated recrystallisation, we have simulated geologic histories and step-heating experiments for six hypothetical alkali feldspar crystals (#1, #2, #3, #4, #5 and #6). Modelled geologic histories followed three ‘end-member’ scenarios that invoked different mechanisms of 40Ar loss from alkali feldspar (Fig. 2). The first end-member scenario follows the assumptions behind MDD theory: the loss of 40Ar was governed solely by volume diffusion, and the size and distribution of intra-grain diffusion domains did not change through time (crystals #1 and #2). The second and the third end-member scenarios contradict the assumptions behind MDD theory: 40Ar loss was dominated by fluid-mediated dissolution and reprecipitation of alkali feldspar. Due to the choice of sufficiently low residence temperatures of the modelled alkali feldspar crystals, diffusive loss of 40Ar in these scenarios was negligible. In the second scenario (crystals #3 and #4) alkali feldspar was dissolved from the surfaces of intra-grain diffusion domains and then epitaxially reprecipitated on them, so that the size and distribution of the intra-grain diffusion domains effectively did not change with time. In the third scenario (crystals #5 and #6) interaction with fluid led to partial dissolution and fragmentation of large intra-grain diffusion domains, and the reprecipitation of new overall smaller intra-grain diffusion domains. In all of the modelled scenarios during laboratory degassing Ar was assumed to be lost solely by volume diffusion in the absence of feldspar structure and texture modifications. Apart from the exceptions listed above, all the assumptions that we make in our modelling are intrinsic to MDD theory (Lovera et al., 1989).

The second and the third scenarios are clearly a simplification of the natural process of fluid-induced dissolution-reprecipitation of alkali...
feldspar, which can form both coherent rims around the remnants of pre-existing alkali feldspar and new incoherent subgrains within a single grain (e.g. Lee et al., 1995). However, if these two ‘end-member’ scenarios can yield identical step-heating $^{40}\text{Ar}/^{39}\text{Ar}$ data, then the same step-heating $^{40}\text{Ar}/^{39}\text{Ar}$ data can also be obtained by a combination of both, which would probably mimic the natural process more closely. Furthermore, while the third scenario simulates the reprecipitation of alkali feldspar, it is also representative of the reprecipitation of other minerals, such as clay minerals formed during weathering (Wilson, 2004), provided that during step-heating these reprecipitated minerals degas before the residual pre-existing alkali feldspar and appear as the smallest diffusion domain during MDD modelling.

Ar radiogenic ingrowth and diffusion were modelled in MATLAB using the Crank-Nicolson finite difference method adopted for a spherical geometry and zero boundary conditions (Crank, 1975). Ar diffusion parameters for alkali feldspar were taken from Foland (1974). Fluid-induced dissolution and reprecipitation of alkali feldspar was assumed to reset the concentration of $^{40}\text{Ar}$ in the affected zones to zero at the time of interaction, following the partition coefficients of Kelley (2002). Each domain was forward modelled separately with respect to the chosen geologic history (Fig. 3A, D, G) and step-heating experiment (Fig. 4). The final $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra (Fig. 3B, E, C; Supplementary Tables (modelled step-heating data)) and Arrhenius trajectories (Fig. 5A, C, E) are obtained by step-by-step summation of the quantities of $^{40}\text{Ar}$ and $^{39}\text{Ar}$ released during the experiment from each domain, and are weighted in accordance with their relative frequency (given below and in Supplementary Tables (distribution of domains)); summation was done in Microsoft Excel.

In our modelling we used two MATLAB files (provided in Supplementary Materials; see also notes in the code). Diffusion_KArDiffSphereCN.m was used to simulate a thermal history and/or generate a set of variables that are needed to simulate a step-heating experiment (such as diffusion domain size, diffusion properties, $^{40}\text{K}$ and $^{40}\text{Ar}$ concentration profiles, etc.). HeatingExperimentArAr.m was used to simulate a step-heating experiment and calculate the amounts of $^{39}\text{Ar}$ and $^{40}\text{Ar}$ released from each domain during each heating step. Microsoft Excel was then used to sum up the amounts of $^{39}\text{Ar}$ and $^{40}\text{Ar}$ released from the different domains during each heating step. MATLAB was used to simulate a step-heating experiment for a chosen diffusion domain radius (crystals #5 and #6 – radius of a domain that appears after interaction with fluid); (ii) manually adjusted the core-rim $^{40}\text{Ar}$ concentration profile in a variable called Ar in accordance with the chosen geologic history (in crystals #3 and #4 to step-function profiles, in crystals #5 and #6 to uniform concentration, as shown in the rightmost plots in Fig. 2); (iii) executed HeatingExperimentArAr.m file. This crude approach could be used due to the choice of sufficiently low residence temperatures of crystals #3, #4, #5 and #6, at which diffusive transport of $^{40}\text{Ar}$ over geologic time was negligible.

4. Results

Geologic histories and step-heating experiments were modelled for six alkali feldspar crystals (#1, #2, #3, #4, #5 and #6). During geologic histories crystals #1 and #2 only lost $^{40}\text{Ar}$ by volume diffusion, while crystals #3, #4, #5 and #6 only lost $^{40}\text{Ar}$ by fluid-induced dissolution-reprecipitation. The choice of distributions of intra-grain domains was arbitrary, as was the choice of thermal histories for crystals #1 and #2. The thermal and fluid-interaction histories of crystals #3, #4, #5 and #6 were designed by trial and error to ensure that (i) the timing of the inflection points in the thermal histories is the same as, for crystals #1 and #2, (ii) no significant diffusive loss of $^{40}\text{Ar}$ occurs, and (iii) the $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra of crystals #3 and #5 resemble that of crystal #1, while the $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra of crystals #4 and #6 resemble that of crystal #2. Below we provide geological explanations for the modelled histories and then compare the synthetic $^{40}\text{Ar}/^{39}\text{Ar}$ data.

Crystals #1 and #2 had spherical diffusion domains with radii of 150, 50 and 16 μm which occurred in a proportion of 1:5:150. Both crystals grew from magma at 170 Ma and rapidly cooled to a lower temperature (Fig. 3A). Crystal #1 cooled to 230 °C and crystal #2 cooled to 190 °C. Both crystals began to exhume at 130 Ma, causing them to cool to 100 °C at 100 Ma, and to 0 °C in the near past.

Crystals #3 and #4 also had spherical diffusion domains with radii of 150, 50 and 16 μm occurring with a relative frequency of 1:5:150. Both crystals grew from magma at 170 Ma and rapidly cooled to an ambient temperature of 150 °C (Fig. 3D). These crystals began to exhume at 130 Ma, which caused them to cool to 50 °C at 100 Ma, and to 0 °C in the near past. Crystals #3 and #4 spent most of their existence at temperatures too low to lose a significant amount of $^{40}\text{Ar}$ by volume.
Fig. 3. Simulated geologic histories, resulting 40Ar/39Ar age spectra and MDD best-fit thermal histories for six modelled crystals. Each row starts with a schematic sketch depicting the scenario of 40Ar loss. A, D and G: the simulated thermal histories with an indication of the timing of interaction with fluid. B, E and H: the resulting synthetic 40Ar/39Ar age spectra. C, F and I: the MDD best-fit thermal histories obtained for the synthetic 40Ar/39Ar age spectra in comparison with the originally modelled t-T paths from A, D and G. See text for details.

Fig. 4. The step-heating schedule used to obtain the synthetic 40Ar/39Ar age spectra shown in Fig. 3 and the synthetic Arrhenius trajectories shown in Fig. 5. Colour and shape of the markers correspond to those in the Arrhenius plots in Fig. 5. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

diffusion. However, exhumation was accompanied by an ingress of aqueous fluid, which led to the dissolution of the same thickness of material from each of the intra-grain diffusion domains followed by the epitaxial overgrowth that restored these domains to the initial size. Fluid interaction occurred at 130 Ma, 120 Ma and 110 Ma, reprecipitating respectively the outer 8 μm, 1.5 μm and 0.5 μm in crystal #3, and the outer 1.3 μm, 0.3 μm and 0.03 μm in crystal #4. The affected zones account for ~28 vol% of crystal #3, and for ~6 vol% of crystal #4.

Crystals #5 and #6 initially had spherical domains with radii of ~166.5 μm, which were subsequently fragmented and partially dissolved to form new domains (see below and in Supplementary Tables (distribution of domains)). These crystals grew from magma at 170 Ma and rapidly cooled to an ambient temperature of 150 °C (Fig. 3G).

began to exhumate at 130 Ma, causing them to cool to 50 °C at 100 Ma, and to 0 °C in the near past. Crystals #5 and #6 resided at temperatures too low to lose a significant amount of 40Ar by volume diffusion during most of their existence. Furthermore, exhumation did not result in fluid-induced dissolution-reprecipitation of these crystals. However, dissolution-reprecipitation occurred later, at 60 Ma, when a magmatic body intruded nearby and triggered the circulation of aqueous fluid around the crystals (with no significant temperature perturbation). In crystal #5 each of the intra-grain diffusion domains was partially dissolved and fragmented to 1, 2 and 100 new domains, with radii of 150 μm, 50 μm and 16 μm, respectively. These fragments of the pre-existing domains preserved all of the 40Ar that accumulated in them by the time of interaction with fluid. The dissolved material was reprecipitated to form each of the pre-existing domains 1, 10, 40, 200, 550 and 5173 new domains, with radii of 50 μm, 25 μm, 16 μm, 8 μm, 3 μm and 1.5 μm, respectively. These domains contained no 40Ar at the time of reprecipitation. Likewise, in crystal #6 partial dissolution, fragmentation and reprecipitation led to the replacement of each of the intra-grain domains by (i) 1, 5 and 116 new domains with radii of 150 μm, 50 μm and 16 μm, respectively, which preserved all of the 40Ar that accumulated in them by the time of interaction with fluid, and (ii) 2, 6, 25, 100, 720 and 11,466 new domains, with radii of 25 μm, 16 μm, 8 μm, 5 μm, 3 μm and 1.5 μm, respectively, which contained no 40Ar at time of interaction with fluid. The newly formed domains account for ~13 vol% of crystal #5 and for ~3 vol% of crystal #6.

All six crystals were subjected to a virtual repetitive step-heating experiment (Fig. 4). They yield non-linear Arrhenius trajectories and non-plateau log(r/r0) spectra, reflecting the variation of the domain sizes (crystals #1, #2, #3 and #4 ~ Fig. 5A; B; crystal #5 ~ Fig. 5C, D; crystal #6, Fig. 5E, F). The 40Ar/39Ar age spectra of all six crystals begin with a date of 108–118 Ma, which then gradually increases and eventually forms a flat segment at 169–170 Ma (Fig. 3B, E, H). The flat segment accounts for the last 30–40% of 39Ar released in the age spectra obtained from crystals #1, #3 and #5, and for the last 70–90% in the

2 Due to negligible diffusive loss of 40Ar from crystals #5 and #6 over geological time, this is equivalent to fragmentation and partial replacement of a single grain-scale diffusion domain whose volume is a multiple of $4/3 \times \pi \times 166.5^3 \mu m^3$. 

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5. Discussion

Our results indicate that a high degree of correlation between the log(r/t<sub>0</sub>) and 40Ar/39Ar age spectra does not imply that the displacement of 40Ar over geologic timescales was controlled by volume diffusion, as it can be achieved when the loss of 40Ar was associated with fluid-induced dissolution and reprecipitation. High C<sub>fg</sub> values only suggest that on average the apparent ages of the diffusion domains observed during laboratory degassing increase with increasing size, which is the key prediction of MDD theory (Lovera et al., 1989). However, as we show here, fluid-mediated recrystallisation and alteration can also account for such a relationship (consider also the discussion in Section 2), although in case of these processes there is no strict requirement that the apparent ages of the diffusion domains are positively correlated with their sizes, and thus that the C<sub>fg</sub> values are high. The fact that high C<sub>fg</sub> values can in principle be accounted for by models involving fluid-assisted removal of 40Ar suggest that these values alone cannot be used to validate thermal histories obtained using MDD theory. This contests the conclusions of Lovera et al. (2002), who argued that highly correlated log(r/t<sub>0</sub>) and 40Ar/39Ar age spectra indicate that Ar loss from alkali feldspar over geologic and laboratory timescales occurred in the same manner, implying that Ar loss was driven solely by volume diffusion and thus validating the accuracy of thermal histories reconstructed using MDD theory. In our theoretical analysis, crystals #3, #5, #6 and, arguably, #4 yield high C<sub>fg</sub> values, even though they only lost 40Ar by fluid-mediated dissolution-reprecipitation during their geologic past, and thus the best-fit thermal histories obtained for them using MDD theory are inaccurate.

The assumption that 40Ar is lost from alkali feldspar only by volume diffusion over geologic timescales and the accuracy of thermal histories obtained using the MDD approach have also been validated by correlating the topology of the best-fit t-T paths, such as the timing of inflection points, with known tectonic events (e.g. Dunlap and Fossen, 1998; Spikings et al., 2002; Metcalf et al., 2009; Wong et al., 2010; see also Lovera et al., 2002; Harrison and Lovera, 2014). The best-fit t-T paths for crystals #3, #4, #5 and #6 (Fig. 3F, I) in our study illustrate a potential danger of such an approach because the inflections in them temporally coincide with those in the true thermal history. An a priori expectation of rapid cooling caused by exhumation between 130 and 100 Ma could lead to the conclusion that the best-fit t-T solutions are accurate, while in fact they are grossly inaccurate.

Our simulations additionally show that even volumetrically low degrees of recrystallisation and alteration (~6 vol% in crystal #4 and ~3 vol% in crystal #6) can significantly reduce the accuracy of t-T paths that were reconstructed using MDD theory. This also contests the conclusions of Lovera et al. (2002), who suggested that recrystallisation and alteration need to be volumetrically significant (>6 vol%) to have a considerable negative impact on the t-T solutions. Many of previous studies inferring the mechanisms of 40Ar loss from alkali feldspar disregarded the presence of small volumes of replacive Na-rich and/or K-rich feldspars as well as other alteration phases within the analysed grains. For example, Fitz Gerald and Harrison (1993) have documented as much as 5 vol% of turbid microcline formed by fluid-induced dissolution-reprecipitation in MH-10 sample of alkali feldspar from the Chain of Ponds pluton, which was used to establish MDD theory (Lovera et al., 1989). A subsequent study of alkali feldspar from the same location suggested that the proportion of this replacive K-rich feldspar exceeds 14 vol% and proposed that the loss of 40Ar occurred due to interaction with fluid (Chafe et al., 2014). Another example is provided by alkali feldspar samples 140182, 149175 and 140115 from the Klokken intrusion, which were considered to have lost 40Ar solely by...

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3 All cross-correlation coefficients were calculated for the first 65% of 39Ar release, as only these data are used for inversion modelling in MDD programs; see Appendix for discussion.
volume diffusion and thus to be suitable for the accurate reconstruction of thermal histories using MDD theory (McLaren et al., 2007; Sanders, 2008). While these alkali feldspar samples are generally described as “pristine” with “almost nonexistent” turbidity (Parsons et al., 1988), they still show some evidence for interaction with fluid, such as trails of fluid inclusions (Parsons et al., 1988; Burgess et al., 1992) and minor patchy alteration in occasional grains (Sanders, 2008), which collectively account for a few vol% (e.g. note the light grey veins in Fig. 1 in McLaren et al., 2007). Furthermore, as shown by 40Ar/39Ar and K-Ca dating of “turbid” alkali feldspar samples from the Klokken intrusion, there was an ingress of fluid that occurred several hundreds of millions of years after magmatic emplacement (Sanders, 2008; Harrison et al., 2010).

Notably, alkali feldspar from the Chain of Ponds pluton yields 40Ar/39Ar age spectra with individual step dates that gradually increase over the first ~60% of 39Ar released and then remain nearly constant over the last ~40% of 39Ar released (Lovera et al., 1989; Chafe et al., 2014), which is similar to our crystals #3 and #5 with ~28 and ~13 vol% of replacement, respectively. “Pristine” alkali feldspar from the Klokken intrusion yields 40Ar/39Ar age spectra in which individual step dates that are significantly younger than the crystallisation age are found in the initial 20% or less of 39Ar released (e.g. Sanders, 2008; McLaren et al., 2007), which is similar to our crystals #4 and #6 with only 6 and 3 vol% of replacement, respectively. These similarities suggest that in both cases the younger dates of the initial heating steps can in principle be linked to the fluid-alteration phases that are present in the samples. They also show that this possibility needs to be tested on a case-by-case basis, for example by inferring how the observed fluid-alteration phases can affect the topology of 40Ar/39Ar age spectra, and then comparing these inferences with the observed 40Ar/39Ar age spectra.

Thus, we conclude that conventional step-heating 40Ar/39Ar data are insufficient to identify the transport mechanisms of 40Ar that operate within alkali feldspar over geologic timescales and to validate the thermal histories that were obtained using these data. We further suggest that careful consideration of fluid-mediated recrystallisation and alteration is required in each study. The effect of these processes on the accuracy of the reconstructed thermal histories can be significant in some cases, and not as much in others. For the simulated scenarios of fluid alteration, the maximum temperature discrepancy between the actual thermal history and that predicted using MDD theory ranges from ~50 °C for crystals #4 and #6 to ~80–100 °C for crystals #3 and #5. The mismatch could be even greater, given that the loss of 40Ar in these scenarios was only related to interaction with fluid, and the modelled crystals could have resided at much lower temperatures and still yield the same 40Ar/39Ar age spectra. The maximum temperature offset depends on the lowest temperature at which replaceable feldspar or other alteration phases that will mimic feldspar behaviour during laboratory degassing can crystallise. Theoretically this can happen even at 0 °C (Helgeson et al., 1969; Kastner and Siever, 1979), suggesting a maximum discrepancy between the best-fit and true t-T paths of ~200 °C for crystals #4 and #6, and ~230–250 °C for crystals #3 and #5. On the other hand, fluid alteration and volume diffusion can act simultaneously, which can diminish the gap between the actual and predicted thermal histories.

6. Concluding remarks

Low temperature alteration of alkali feldspar, including fluid-induced dissolution-reprecipitation, represents a serious obstacle to constraining thermal histories of rocks by inversion modelling using multi-diffusion domain theory. Even volumetrically low degrees of alteration (3–6 vol%) can result in gross inaccuracies in predicted t-T paths. Furthermore, alkali feldspars which have experienced fluid assisted 40Ar loss can yield highly correlated log(r/r0) and 40Ar/39Ar age spectra, while certain features in the topology of the significantly inaccurate best-fit t-T solutions, such as the timing of inflections, can correlate with the timing of known tectonic events. Therefore, neither cross-correlation of log(r/r0) and 40Ar/39Ar age spectra, nor comparisons with the expected time of inflection points in t-T space provide sufficient evidence to support the assumption that 40Ar loss over geologic timescales was solely driven by volume diffusion and validate the accuracy of the constrained t-T paths. We recommend that detailed petrological characterisation accompanies all attempts to recover t-T information by interpreting step-heating 40Ar/39Ar data obtained from alkali feldspar by step-heating, and that the potential effects of the observed alterations are carefully considered.

Declaration of competing interest

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.

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Appendix A

The normalized cross-correlation coefficient Cfg is defined in Section 3.5 in Lovera et al. (2002) as “Normalized Cfg = Experimental Cfg/MDD model Cfg”, where experimental Cfg and MDD model Cfg are normalized cross-correlation coefficients (in common statistical parlance) for log(r/r0) and 40Ar/39Ar age spectra obtained from experimental analysis and MDD modelling, respectively (more strictly, for two different functions that are obtained from log(r/r0) and 40Ar/39Ar age spectra). While both experimental Cfg and MDD model Cfg must lie within the range [−1,1], for a given sample, the experimental Cfg can be slightly greater than the MDD model Cfg, and therefore the normalized Cfg can be > 1 (e.g. samples mca994kf, n13, n9, yans1 in Lovera et al. (2002); in their Table 2, the value in the column LAB Cfg needs to be divided by that in the column MDD Cfg). In fact, normalized Cfg can take any value in the range [−∞, +∞], and 1 is only the expected value if all the assumptions behind MDD theory are accurate (following Lovera et al., 2002, we term values around 1 as high in the present study). The normalization procedure was used by Lovera et al. (2002) because experimental Cfg and MDD model Cfg can be low for certain thermal histories even if diffusion was the only mechanism for 40Ar loss. This, for example, includes thermal histories leading to small fractional loss of 40Ar, such as that experienced by crystal #2 in our study, for which experimental Cfg = 0.59, MDD model Cfg = 0.56 and normalized Cfg = 1.04 (compare this to crystal #1, for which experimental Cfg = 0.96, MDD model Cfg = 0.94 and normalized Cfg = 1.01).

In our experience, high normalized Cfg values (i.e. around 1) are inevitably obtained if (i) both log(r/r0) and 40Ar/39Ar age spectra are monotonically increasing functions, (ii) there is a good match between the measured 40Ar/39Ar age spectrum and that predicted by MDD modelling, and (iii) long intervals of log(r/r0) and 40Ar/39Ar age spectra are being correlated (Figs. 6, 7). We only observed low normalized Cfg values when these conditions were significantly violated (Fig. 7).
Calculating normalized Cfg is not straightforward. The corrff.exe program in the MDD_programs package (created by Oscar Lovera) only calculates the experimental Cfg. MDD model Cfg can be calculated by extracting the best-fit model data from the outputs, creating new input files with these data (using the mddfiles_lst.exe program) and executing the corrff.exe program. Normalized Cfg can be subsequently calculated by dividing experimental Cfg by MDD model Cfg.

Fig. 6. (Appendix). Experimental Cfg, MDD model Cfg and normalized Cfg for crystals #1 (A) and #3 (B) from our study as a function of the percent of 39Ar released included in the calculation of these values (i.e. Cfg values were calculated from 0 to a given percent of 39Ar released).

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Fig. 7. 40Ar/39Ar age spectra of additional hypothetical alkali feldspar crystals #A1, #A2 and #A3 and the results of MDD modelling of these spectra. Crystals #A1, #A2 and #A3 are simple mixtures of spheres that have different dates and have no 40Ar concentration gradients, and their 40Ar/39Ar age spectra were obtained in the same way as those of crystals #5 and #6. The relative quantities of spheres and their dates are indicated in the bottom part of the figure, while the 40Ar/39Ar age spectra are provided in Supplementary Tables (data from Appendix). A–C: a comparison of 40Ar/39Ar age spectra of crystals #A1, #A2 and #A3 and 40Ar/39Ar age spectra obtained during MDD modelling. D–F: Experimental Cfg, MDD model Cfg and normalized Cfg for crystals #A1, #A2 and #A3 as a function of the percent of 39Ar released included in the calculation of these values (i.e. Cfg values were calculated from 0 to a given percent of 39Ar released). Note that only crystal #A3 yields low normalized Cfg.