2. Open-system complex behavior

Ar can move around in samples prior to analysis.

If this happens via thermally-activated volume diffusion, we can make sense of it.

Figure 4-13 The first age spectrum diagram. After Turner et al. (1966). Data from two separate irradiations of the Bruderheim chondrite are shown together with model age spectra for spheres of uniform radius and spheres with a lognormal distribution of radii that have undergone 90% radiogenic argon loss 0.5 Ga ago.

Figure 4-14 Theoretical age spectra for both aggregates of uniform spheres (solid lines) and a lognormal distribution of sphere radii (dashed lines). After Turner (1968), with permission of author and publisher. In this example, a 4.5-Ga-old sample has experienced varying degrees of radiogenic argon loss during an event 0.5 Ga ago.
Fig. 3. Typical K-feldspar age and Arrhenius properties. (a) Age spectrum (right axis) and \( \log (r/r_0) \) spectrum (left axis) for N-13 K-feldspar (Harrison et al. 2000). Note correlated behaviour, particular over the interval of gas release between the disappearance of low-temperature Cl-correlated \( ^{40}\text{Ar}_\text{e} \) and the onset of melting above 1100 °C. \( C_{1g} \) refers to correlation coefficient calculated by Lovera et al. (2002). (b) Arrhenius plot showing measured diffusivities, reference Arrhenius law \( (r_o) \) defined by initial gas release (see text), and sample calculation of \( \log (r/r_o) \) value at 1000 °C (see text). (c) Distribution of best-fitted cooling histories. 90% confidence intervals of both the overall distribution (light blue) and its median (blue).
Tibetan tectonics from $^{40}\text{Ar}/^{39}\text{Ar}$ analysis of a single K-feldspar sample

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ABSTRACT

$^{40}\text{Ar}/^{39}\text{Ar}$ data on an alkali feldspar sample from the Quxu pluton, Gangdese batholith, southern Tibet, allow a detailed assessment of unroofing and uplift history between 35 and 18 Ma. The $^{39}\text{Ar}$ Arrhenius plot for this sample shows departures from a linear relationship between the effective diffusion parameter, $\log(D/r^2)$, and reciprocal temperature, which we interpret to be the result of a distribution of distinct diffusion-domain sizes. We use an alternative way of plotting the Arrhenius data that exhibits domain size versus cumulative $%^{39}\text{Ar}$ released during step heating. The $^{40}\text{Ar}/^{39}\text{Ar}$ age spectrum of the sample has features, such as local age plateaux, that are most easily explained in terms of the distinctive closure age of particular domains. The fact that the same distribution of diffusion-domain sizes explains both the Arrhenius data and the age spectrum is an indication that the diffusion properties operating in the laboratory are those of the sample while it was in its natural environment. Modelling of the age spectrum with a distribution of domain sizes results in the recovery of a continuous cooling-history segment rather than a single time-temperature datum. We demonstrate the robustness of the cooling-curve determination by showing the large misfits to the age spectrum that arise from relatively small changes in the cooling history. The best-fit cooling curve for the Quxu sample shows a decreasing rate of cooling in the time interval 35–18 Ma, followed by a very rapid cooling beginning at about 18 Ma. We have used a thermal model for the conductive cooling of an unroofing pluton to estimate the rate of unroofing required to explain the Quxu cooling curve, and find that in the 35–20 Ma time interval, the primary control of the thermal evolution is the conductive loss of magmatic heat with little or no unroofing (unroofing rates of approximately 0.05 mm/yr) followed by a brief period (< 5 Ma) of very rapid unroofing with rates of order 2 mm/yr.
Fig. 2. Arrhenius plot of log(D/τ^2) versus reciprocal absolute temperature for the sample PC-88-32. See Harrison and McDougall [31] for a description of how diffusion coefficients are calculated from \(^{39}\)Ar released during step heating. The diffusion domain geometry assumed is slabs, but this is not a key assumption in that experience with this and other samples has shown that as long as we use the same geometry for both data analysis and modelling, the cooling curve determined will be the same regardless of what specific geometry (slab, cylinder, or sphere) is used. The inset shows the temperature steps used to extract \(^{39}\)Ar. All but the last two steps are well below the melting temperature of the sample, which is important for resolving the diffusion properties of the largest domains in the sample. The dashed line corresponds to an activation energy \(E\) of 45.2 kcal/mol and an effective frequency factor, \(D_0/\tau^2\), of 30,300 s\(^{-1}\).

Fig. 3. (a) \(^{40}\)Ar/\(^{39}\)Ar age spectrum for K-feldspar sample PC-88-32. (b) log(\(r/\tau_0\)) versus cumulative \(^{39}\)Ar calculated for the distribution of domains (shown in 3c) compared to the actual data from the Quxu sample. The last two fractions of \(^{39}\)Ar are ignored because they were extracted at such high temperature that the sample is beginning to melt and therefore the diffusion properties determined from these steps are not representative of the sample when in its natural environment. (c) size (\(r\)) and volume fraction (\(\phi\)) of domains used in modelling. The relative size (and volume fraction) of each domain, from largest to smallest are: 1.00 (10%), 0.320 (15%), 0.056 (30%), and 0.01 (45%), respectively.

Fig. 6. The top panel shows the geometry and boundary conditions for the thermal model of the cooling and uplift of the Quxu pluton. The stippled area represents the intrusion of the Quxu pluton at 41 Ma, which reaches to within 10 km of the surface. The large black dot shows the initial position of the model Quxu sample at 11 km depth. The intrusion temperature is taken to be 950°C (850°C + an additional 100°C to represent heat of crystallization) at those depths where this temperature is greater than that of the regional geotherm \(T(z)\), shown in the lower panel. This geotherm is a steady state solution to the heat conduction equation with heat sources \(Q(z)\) when the vertical velocity relative to the surface \(\dot{W}(t)\) is zero. The boundary conditions and our choices for \(Q(z)\) and \(\dot{W}(t)\) are discussed in the text.
An Assessment of $^{40}$Ar-$^{39}$Ar Dating of Incompletely Degassed Xenoliths

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The possibility of measuring the age of eruption of Pleistocene lavas by $^{40}$Ar-$^{39}$Ar analysis of entrapped ancient potassic xenoliths is demonstrated by a study of model systems. Upon inclusion in the hot magma such xenoliths are commonly only partially degassed of radiogenic $^{40}$Ar which has accumulated in them since their original crystallization. The residual $^{40}$Ar will increase the apparent K/Ar age of the xenolith. However, if a xenolith is of Cretaceous age or younger, then a plateau in its $^{40}$Ar-$^{39}$Ar age spectrum giving the age of eruption is expected to extend over 25–50% of the total $^{39}$Ar released if degassing of the xenolith in the magma exceeded 90% and if the phases in the xenolith are characterized by sufficiently different diffusion dimensions or activation energies. If diffusion was from a bimodal population of spheres, then the radii must differ by a factor of 10 or more (or the diffusion coefficients by a factor of 100 or more); or if the spheres were equal in size (and in diffusion coefficients), then the activation energies must differ by a factor of at least 1.5. That such requirements may be realized in real xenoliths containing K-feldspars is expected from published activation energies for microcline and from data determined on a granitic xenolith which was degassed in an early Pleistocene basalt flow. The experimental results appear to establish that old xenoliths may contain Ar in distinctive phases which degas at sufficiently different temperatures as to permit determination of the age of degassing or eruption.
Fig. 1. Schematic history of temperature and $^{40}$Ar accumulation in a model xenolith. From $t = -t_0$, the time of original crystallization, to $t = 0$, $^{40}$Ar accumulates without loss. The $^{40}$Ar is lost from the model xenolith during heating in the magma from $t = 0$ to $t = t_c$; and after cooling, $^{40}$Ar once again accumulates until $t_x$ and is added to the residue which was not degassed from $t = 0$ to $t = t_x$. All $^{40}$Ar is extracted during analysis from $t_x$ to $t_y$. For simplicity, $t_x$ and $t_x - t_y$ are considered to be much shorter time intervals than $t_0$ or $t_x - t_c$, and $^{40}$Ar accumulated during these short intervals is ignored.

Fig. 6. Apparent age as a function of $^{39}$Ar released from samples crystallized 100 m.y. ago and partially degassed of $^{40}$Ar 1 m.y. ago. Letters on curves refer to the same models as in Figure 5. The age spectra here differ from the $dN_{op}/dn_p$ $^{39}$Ar spectra of Figure 5 due to the uniform accumulation of new $^{40}$Ar from $t = t_x$ to $t = t_x$. In the case of identical spheres, essentially all $^{40}$Ar must be degassed in the magma to achieve low-temperature plateaus of any size. However, extensive low-temperature plateaus corresponding to the age of eruption can be achieved for xenoliths with a gross difference in grain sizes or a small difference in activation energies.
ARGON DIFFUSION IN PARTIALLY OUTGASSED ALKALI FELDSPARS: INSIGHTS FROM $^{40}\text{Ar}/^{39}\text{Ar}$ ANALYSIS

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Abstract


Two microclines showing saddle-shaped $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra, a rapidly cooled orthoclase, and a sanidine from the Fish Canyon Tuff (Colorado, U.S.A.) were subjected to laboratory degassing in an attempt to better understand Ar diffusion systematics in alkali feldspars. The microclines and orthoclase show age spectra that confirm that these samples, and probably most alkali feldspars, comprise diffusion domains of widely varying grain size (greater than a factor of 10). The sanidine shows an age spectrum consistent with the range of grain sizes found in the dated mineral separate. Activation energies derived from the $^{39}\text{Ar}$ release are correlated with intensity of outgassing as well as initial structural state. Despite evidence that much of the excess $^{40}\text{Ar}$ contained in the microclines is situated near grain boundaries, dry degassing, even at 800 °C, has little effect on this component. However, hydrothermal treatment at 400 °C facilitates significant loss of this excess $^{40}\text{Ar}$, providing evidence that it is sited in anion vacancies. The fact that most alkali feldspars are likely to comprise a range of effective grain sizes for diffusion has important implications for the interpretation of age spectra, and will complicate the derivation of diffusion parameters from $^{39}\text{Ar}$ released during step-heating.
The $^{40}\text{Ar}/^{39}\text{Ar}$ Thermochronometry for Slowly Cooled Samples Having a Distribution of Diffusion Domain Sizes

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Many $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra for alkali feldspars are significantly different from the model age spectra calculated for slowly cooled samples composed of diffusion domains of a single size, and the Arrhenius plots for these samples show departures from linearity that are inconsistent with diffusion from domains of equal size. The most plausible explanation for these discrepancies is the existence of a distribution of diffusion domain sizes. We have extended the single-diffusion-domain closure model of Dodson so that it applies to minerals with a distribution of domain sizes and have used it to explain many commonly observed features of $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra and Arrhenius plots for $^{39}\text{Ar}$ loss during step heating. For samples with a distribution of diffusion domain sizes, the form of the $^{39}\text{Ar}$ Arrhenius curve is a function of the heating schedule (i.e., the temperature and duration of the steps used), and thus different heating schedules will result in different curves for the same sample. This effect can be used to confirm the existence of a distribution of diffusion domain sizes and to optimize the information contained in the Arrhenius plot. The multiple diffusion domain size model is used to reinterpret the age spectra, Arrhenius plots, and cooling history of three feldspars from the Chain of Ponds pluton, northwestern Maine, earlier interpreted assuming a single domain size. Interpreting the $^{40}\text{Ar}/^{39}\text{Ar}$ and $^{39}\text{Ar}$ released during step heating in terms of a single domain size gives rise to a large discrepancy between the cooling rate determined from the age and closure temperature of the three samples compared to the cooling rate required to explain the shape of the individual age spectra. The single domain size model fails also to account for the observed departures from linearity of the Arrhenius plots. We show that a particular domain size distribution in each sample can explain in detail both the shape of the age spectra and the Arrhenius plots, and results in the three samples defining a common cooling history. There is thus good evidence for the three alkali feldspar samples studied here that the thermally activated diffusion measured by $^{39}\text{Ar}$ release during step heating in the laboratory is also the mechanism responsible for argon loss or retention in the natural setting.
Fig. 1. Age spectra for Chain of Ponds pluton alkali feldspars [from Heizler et al., 1988, Figure 8]. The one standard deviation error bars for age are of order ±1 Ma and therefore not shown.

Fig. 2. Arrhenius plot for alkali feldspars from the Chain of Ponds pluton. $D/\rho^2$ for orthoclases calculated using a spherical geometry model and a planar geometry for the microcline sample [from Heizler et al., 1988, Figure 9]. One standard deviation error bars are shown when they are larger than the size of the symbol.

**TABLE 2. Diffusion Parameters**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E$, kcal/mol</th>
<th>$D_0/\rho^2$, s$^{-1}$</th>
<th>$\tau$, s</th>
<th>$T_c$, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>MH-8</td>
<td>40.15 ± 2.56</td>
<td>73.5 ± 21.9</td>
<td>2.13 × 10$^{14}$</td>
<td>242.0 ± 15.0</td>
</tr>
<tr>
<td>MH-10</td>
<td>49.93 ± 0.73</td>
<td>2634.0 ± 119.0</td>
<td>1.99 × 10$^{14}$</td>
<td>317.0 ± 5.0</td>
</tr>
<tr>
<td>MH-42</td>
<td>37.70 ± 1.25</td>
<td>1603.0 ± 137.0</td>
<td>2.27 × 10$^{14}$</td>
<td>185.0 ± 6.0</td>
</tr>
</tbody>
</table>

From Heizler et al. [1988].
If this is "true," we should be able to take the t-T history and predict the evolution of $^{40}\text{Ar}^*$ concentration within the single domain that is the K-spar, then use that to predict what the $^{40}\text{Ar}/^{39}\text{Ar}$ step heating spectrum should look like...

Fig. 3. Heizler's cooling curve for the Chain of Ponds pluton as defined by mineral ages and assigned closure temperatures [from Heizler et al., 1988, Figure 12]. The error bars are one standard deviation.
New Ar Arrhenius plot for MH-10.

Fig. 3. Arrhenius plot for sample MH-10.bm obtained from another split of MH-10 using the extraction temperatures shown in the inset. The heating schedule was similar to that used in Figure 2, but now the temperature was held below the melting point until 99% of the sample’s argon was released. Only two steps (solid squares) were at higher temperatures, releasing less than 1% of the total argon. Again the activation energies of the different domains appear quite similar, keeping in mind that the scatter in the data points for the largest domain are due to very small amounts of gas being released per temperature step.
Normalized age spectrum example.

\[ D = D_0 \exp \left( - \frac{E}{RT} \right) \]

\[ T_c = \frac{E}{R \ln \left( \frac{A \tau D_0}{\rho^2} \right)} \]

\[ \tau = -\frac{RT_c^2}{E(dT/dt)} \]

\( \tau = \) time required to diminish D by a factor of e.

\( \rho = \) characteristic size of diffusion domains

\( A = \) geometry factor

Fig. 4. Normalized age spectra for slowly cooled minerals of spherical and planar geometry as calculated by M. H. Dodson [see McDougall and Harrison, 1988]. The vertical \( \Delta \) age/\( \tau \) axis measures differences in age along the spectra in units of the time constant \( \tau \) (see equation (3) for definition of \( \tau \)). The curve for cylindrical geometry falls between these two curves and was not plotted.
Fig. 5. Age spectrum normalized by $\tau - 7$ Ma for the three samples from the Chain of Ponds pluton compared to the appropriate theoretical curves from Figure 4. This value of $\tau$ was calculated from equation (3) using the diffusion parameters given in Table 1 and the cooling history (Figure 3) from Heizler et al. [1988]. MH-8 and MH-10 were compared to the theoretical curve corresponding to spheres while a planar geometry was used for MH-42. The rates of cooling shown in Figure 3 and those implied by the individual age spectra are inconsistent.
Fig. 6. Age spectra for the same samples of Figure 5 now normalized using larger $\tau$ chosen to cause the theoretical age spectra conform more closely to the measured spectra. These are a result of the cooling history shown in Figure 3 and the diffusion parameters given in Table 1. Note that even though this figure shows a significant improvement in the fitting of the age spectra, the shapes of the real age spectra have more structure than the smoothly increasing theoretical spectra.
Fig. 1A–C Drawings illustrating the contrast between real micro-textures and those required for the MDD model. A What the microscopist sees. Microtextures in a typical ~100 μm cleavage fragment of alkali feldspar from the Shap granite. The larger features are approximately to scale, but the size of the smaller features has been exaggerated to make them visible. The crystal is a complex assemblage of touching and interacting domains, with a variety of blind and open ‘fast pathways’ between them, some of which may be sealed reservoirs for Ar. The microtexture has a protracted evolution, the first potential fast pathways appearing below 500 °C with continuous modification to near-surface temperatures. B What MDD theory demands. There are three domain sizes in this example, all of which must be present, and remain unmodified, during the entire cooling history. The spheres do not touch and are suspended in a vacuum. C A more sophisticated MDD model, again with three domain sizes. The lamellae have infinite extent in two dimensions.
typical assumptions are that domains have identical $E_a$, $D_0$, and no interaction (e.g., are not nested)

typical nomenclature for domains:
size = $\rho_j$
volume fraction = $\phi_j$

Fig. 1. Symbolic representation of the degassing of a two-phase multi-diffusion domain sample. Cross-sections through the initially filled spheres are uniformly black and progressively tend towards light grey as the diffusing gas is lost from the solid at the sphere boundaries. The two domains differ in radius by a factor of 10 and are assumed to contain equal volumes. (a) Initial uniform distribution of diffusant (i.e. $^{39}$Ar) in both size domains. (b) Gas loss is limited to the periphery of the single large domain while the smaller domain size has been substantially degassed. (c) The smaller domains are now completely degassed and no longer contribute to a mixture. (d) Both large and small domains are completely degassed. (e) Schematic of the Arrhenius plot produced by a two domain sample subject to step heating.
Figure 6-5 Theoretical age spectra for mixtures of three spherical grains with relative sizes of 0.02, 0.2, and 1 but with varying volume fractions shown in inset. After Lovera et al. (1989).

Figure 6-6 Theoretical age spectra for three domains of volume fractions $\phi_1 = 0.27$, $\phi_2 = 0.40$, and $\phi_3 = 0.33$ but varying the relative domain sizes as shown in the inset. Curve 6 is identical to that shown in fig. 6-5, but with differing relative domain sizes. After Lovera et al. (1989).

Figure 6-7 Arrhenius plots for the domain distributions shown in insets of figs. 6-5 and 6-6. After Lovera et al. (1989).
Fig. 5.8. Simulated Arrhenius plots for step-heating release experiments involving all prograde steps (a) and cycled prograde and retrograde steps (b) all of 3600 s durations for samples with $E_a$ of 165 kJ/mol, $D_0$ of 0.01 cm$^2$/s, and comprising mixtures of four discrete domain sizes of varying size (labeled diagonal lines). Gray fill represents a mixture with equal proportions of the domains, and the white and black filled symbols represent higher proportions of smaller and larger domains, respectively.
Fig. 3. Arrhenius plot for sample MH-10.bm obtained from another split of MH-10 using the extraction temperatures shown in the inset. The heating schedule was similar to that used in Figure 2, but now the temperature was held below the melting point until 99% of the sample’s argon was released. Only two steps (solid squares) were at higher temperatures, releasing less than 1% of the total argon. Again the activation energies of the different domains appear quite similar, keeping in mind that the scatter in the data points for the largest domain are due to very small amounts of gas being released per temperature step.

Fig. 4. Theoretical log (r/r_0) plots for the synthetic sample of Figure 1, calculated for both the monotonic (heavy line) and cycled (solid line with symbols) heating schedules shown in the inset of Figure 1. Note that even though the Arrhenius data for the two heating schedules in Figure 1 (heavy line and discrete points) are different, the log (r/r_0) plots show only a very small difference due to the finite temperature steps used to generate the data. Thus the log (r/r_0) plot is seen to be relatively independent of the heating schedule.
Fig. 5.9. The $\ln(a/a_0)$ (also called $\log(r/r_0)$ plot in many applications). This index is one half the difference in the vertical displacement (apparent difference in $\ln(D/a^2)$) of successive steps in the step-heating experiments shown in Fig. 5.8. This is used to constrain the distribution and proportions of domain sizes in step-heating results measured on multidomain samples. These $\ln(a/a_0)$ trends are not sensitive to heating schedule, and are the same for both examples shown in Fig. 5.8. Dashed horizontal lines represent tenfold differences in domain sizes.
Fig. 7. Log \((r/r_0)\) plot from sample MH-10.bm (solid curve) compared to the theoretical plot (dotted curve) obtained using the distribution parameters shown in the inset.

Fig. 6. Log \((r/r_0)\) plot and age spectrum from the remeasured MH-10 sample (MH-10.bm). Since all but the last two extraction temperatures were below the melting point, no anomalously low log \((r/r_0)\) values are observed in the first 99% of the \(^{39}\)Ar released.
### TABLE 2. Diffusion Parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E$, kcal/mol</th>
<th>$D_0/\rho_s^2$, s$^{-1}$</th>
<th>$\tau$, s</th>
<th>$T_c$, °C</th>
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</thead>
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</tr>
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<td>MH-42</td>
<td>37.70 ± 1.25</td>
<td>1603.0 ± 137.0</td>
<td>2.27 × 10$^{14}$</td>
<td>185.0 ± 6.0</td>
</tr>
</tbody>
</table>

From Heizler et al. [1988].

### TABLE 3. Size Distribution

<table>
<thead>
<tr>
<th>MH-8 Orthoclase</th>
<th>MH-10 Orthoclase</th>
<th>MH-42 Microcline</th>
</tr>
</thead>
<tbody>
<tr>
<td>$j$</td>
<td>$\rho_j$</td>
<td>$\phi_j$</td>
</tr>
<tr>
<td>1</td>
<td>0.018</td>
<td>0.15</td>
</tr>
<tr>
<td>2</td>
<td>0.182</td>
<td>0.30</td>
</tr>
<tr>
<td>3</td>
<td>0.545</td>
<td>0.40</td>
</tr>
<tr>
<td>4</td>
<td>1.0</td>
<td>0.15</td>
</tr>
</tbody>
</table>

### TABLE 4. Activation Energy $E$ and Frequency Factor $D_0$

<table>
<thead>
<tr>
<th>MH-8 Orthoclase</th>
<th>MH-10 Orthoclase</th>
<th>MH-42 Microcline</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$, kcal/mol</td>
<td>43.00 ± 1.0</td>
<td>50.00 ± 1.0</td>
</tr>
<tr>
<td>$D_0/\rho_s^2$, s$^{-1}$</td>
<td>3.1 ± 0.2</td>
<td>78.0 ± 2.0</td>
</tr>
<tr>
<td>$T_p(\rho_1)$, °C</td>
<td>315.0 ± 15.0</td>
<td>357.0 ± 15.0</td>
</tr>
<tr>
<td>$Age_p(\rho_1)$, Ma</td>
<td>354.5 ± 5.0</td>
<td>369.0 ± 5.0</td>
</tr>
<tr>
<td>$T_p(\rho_2)$, °C</td>
<td>296.0 ± 15.0</td>
<td>314.0 ± 15.0</td>
</tr>
<tr>
<td>$Age_p(\rho_2)$, Ma</td>
<td>348.0 ± 5.0</td>
<td>353.0 ± 5.0</td>
</tr>
<tr>
<td>$T_p(\rho_3)$, °C</td>
<td>265.0 ± 15.0</td>
<td>254.0 ± 15.0</td>
</tr>
<tr>
<td>$Age_p(\rho_3)$, Ma</td>
<td>335.0 ± 5.0</td>
<td>293.0 ± 15.0</td>
</tr>
<tr>
<td>$T_p(\rho_4)$, °C</td>
<td>204.0 ± 15.0</td>
<td></td>
</tr>
<tr>
<td>$Age_p(\rho_4)$, Ma</td>
<td>266.0 ± 15.0</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 17. Measured age spectra for the three alkali feldspars from the Chair of Ponds pluton (squares) compared to calculated data (solid line) obtained using the domain size distribution and diffusion parameters (Tables 3 and 4) which fit the Arrhenius plots (Figure 18) and the cooling history segments for each sample shown in Figure 19. The new fit to the age spectra is a significant improvement over that given by spectra calculated for grains having a single diffusion domain size (upper solid curve) and a cooling rate corresponding to $\tau = 7$ Ma.
Fig. 18. Experimentally derived Arrhenius plots for the three samples from Chains of Ponds pluton (squares), compared to Arrhenius plots (solid curves) calculated using the size distribution given in Table 3 and the diffusion parameters of Table 4. The almost perfect fit now obtained for the three samples (ignoring the very highest temperature point where the sample is starting to melt) is a great improvement over any single straight-line segment one would get for a single grain size. The key point is that the departure of these plots from linearity is no longer attributed to a structural breakdown during heating in laboratory but is now believed to be a real feature of the diffusive behavior of these samples while they were in their natural environment.
An important attribute of having segments of the cooling history from each sample, as opposed to a single point, is that even with a small number of samples, one has an estimate of the reliability of the thermal history in the degree to which the various segments overlap. For the three samples studied here all but the smallest grain size fractions give a very consistent history. Why the temperatures given by the smallest grains in MH-10 and MH-8 fall above the general trend defined by eight other grain fractions is not clear. The data that cause them to fall where they do are the ages of the first 30% $^{39}$Ar in the age spectra. In order to fit this portion of the age spectra the rate of cooling has to be significantly less than that "seen" by the larger domains. One should keep in mind that the smallest domains are the most "fragile" in terms of any additional Ar loss, and thus the least reliable as estimators of the actual cooling history. Accordingly, we suggest that the best estimate of the cooling history of the Chain of Ponds pluton is given by combining the three cooling curve segments ignoring the smallest domain size of MH-10 and MH-8.

Fig. 19. Cooling curves for the Chain of Ponds samples required to explain the age spectra given the grain size distribution and Arrhenius parameters of each sample given in Tables 3 and 4. The squares along each of the cooling curve segments indicate the closure temperature $T_c$ of the different grain size fractions making up each sample, and they give an idea as to what size fraction determines the different parts of each segment. Our best estimate of the overall cooling curve for this pluton is a composite of the three segments ignoring the youngest part of each segment which is determined by the smallest and most fragile size fraction. The fact that the smallest size fractions see a cooling history that falls above the general trend may be the result of further gas loss due to a very mild reheating. For comparison, we show the earlier Heizler et al. [1988] cooling curve, which was based on a single dominant grain size. Note that we are in good agreement with the closure temperature and age of the biotite sample but fall well above the cooling history given by single grain closure of the three feldspars.
Fig. 3. Typical K-feldspar age and Arrhenius properties. (a) Age spectrum (right axis) and log($r/r_0$) spectrum (left axis) for N-13 K-feldspar (Harrison et al. 2000). Note correlated behaviour, particular over the interval of gas release between the disappearance of low-temperature Cl-correlated $^{40}$Ar$_{fg}$ and the onset of melting above 1100 °C. $C_{fg}$ refers to correlation coefficient calculated by Lovera et al. (2002). (b) Arrhenius plot showing measured diffusivities, reference Arrhenius law ($r_0$) defined by initial gas release (see text), and sample calculation of log ($r/r_0$) value at 1000 °C (see text). (c) Distribution of best-fitted cooling histories. 90% confidence intervals of both the overall distribution (light blue) and its median (blue).
The multi-diffusion domain model: past, present and future

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Abstract: It is axiomatic that application of closure theory – the foundation of isotope-based thermochronology – requires an empirical diffusion model. It is therefore surprising that the majority of thermochronological studies have not met this requirement. The advent of the multi-diffusion domain (MDD) model transcended this limitation yielding both diffusion and age information via routine $^{40}$Ar/$^{39}$Ar step-heating of K-feldspar. Observed correlations between age and Arrhenius spectra show that Ar diffusion occurs by the same mechanisms in nature as in the laboratory. Under certain conditions, these data permit the recovery of a unique, cooling history. The community reaction included some unproductive lines of argument but some stimulated refinements of the MDD model that benefited the development of thermochronology. The MDD model was recently applied to muscovite upon recognition that the same diffusion mechanism operates in vacuum step-heating as in nature. The advent of $^{40}$K–$^{40}$Ca closure profile dating opens up a new thermochronological approach. Initial results confirm that muscovite intragrain defects can restrict effective diffusion length scales in white micas from 10–100 s of microns. Our hope for the future of the MDD model is that it be subject to aggressive and sceptical testing by the community in which quantification is valued over assertion.
ARU08 Muscovite

![Graphs showing measured ages and MMD model fits](image)

**Fig. 4.** $^{40}$Ar/$^{39}$Ar results for Himalayan muscovite AR08: (a) age and log($r/r_0$) spectra, (b) Arrhenius plot and (c) thermal history derived from inversion of data in (a) and (b). The correlated inflections between the age and log($r/r_0$) spectra is evidence that the conservation of diffusion mechanism and boundary assumption is met despite the metastable nature of muscovite during vacuum heating.
Systematic analysis of K-feldspar $^{40}$Ar/$^{39}$Ar step heating results II: Relevance of laboratory argon diffusion properties to nature

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Abstract—We examine a database containing the results of $^{40}$Ar/$^{39}$Ar step-heating experiments performed on 194 basement K-feldspars to recover thermal history information. Qualitative examination of $^{40}$Ar/$^{39}$Ar systematics reveals that about half of the K-feldspars examined are sufficiently well behaved to be suitable for thermal history analysis. Correlation algorithms are developed to quantitatively assess the degree to which age and $^{40}$Ar release spectra are compatible with the same volume diffusion process. Upon applying these methods, we find that 65% of all samples yield correlation coefficients in excess of 0.8, whereas roughly 40% give values above 0.9. We further compare the observed correlation behavior with that predicted from the multi-diffusion domain model and find good agreement for samples with correlation coefficients above 0.9. In contrast, hydrous phases unstable under in vacuo heating and K-feldspars with highly disturbed age spectra yield poorly correlated age and diffusion properties. The high degree of correlation exhibited by the majority of K-feldspars we have analyzed validates extrapolation of experimentally determined diffusion properties to conditions attending natural Ar loss within the crust. Despite this, a significant number of basement K-feldspars analyzed by the step-heating method yield $^{40}$Ar/$^{39}$Ar systematics that are clearly problematic for thermal history analysis. We numerically explore the effects of low-temperature alteration of K-feldspar on thermochronological analysis and identify a range of conditions under which information is progressively lost. Finally, we demonstrate the insensitivity of thermal history calculations to detailed knowledge of the diffusion mechanism by introducing the heterogeneous diffusion model. We find that the multi-diffusion domain approach can successfully recover imposed thermal histories from heterogeneous diffusion—type crystals and conclude that most details of the interpretive model employed are of secondary importance. The only requirement for recovering thermal histories from K-feldspar $^{40}$Ar/$^{39}$Ar step-heating results is that argon loss proceeds by volume diffusion and that laboratory argon release adequately mimics the natural diffusion boundaries and mechanisms—a requirement implicitly met by those samples exhibiting high degrees of correlation.

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Fig. 3. Examples of age and log(t/$\rho_{\text{in}}$) spectra we have examined with our correlation algorithm. The portion of the spectra for which we have performed calculations is indicated in black. Correlation values, $C_{\text{xy}}$, are indicated on the figures. Filled gray symbols represent the crossover points $x_0$ and $x_1$ (see text for explanation). (a) Examples of highly correlated K-feldspar age and log(t/$\rho_{\text{in}}$) spectra. Note that the values of $x_0$ and $x_1$ for both spectra N-12 and N-13 are coexisting K-feldspars from hanging wall of Ganglande Thrust, Tibet (Harrison et al., 2000). (c, d) Examples of moderately to poorly correlated K-feldspar age and log(t/$\rho_{\text{in}}$) spectra. Note that the value of $C_{xy}$ decreases as the values of $x_0$ and $x_1$ diverge. (e, f) Examples of correlation results from K-feldspars with intermediate age maxima. Correlation coefficients are diminished even when the values of $x_0$ and $x_1$ are nearly equal. (g, h) Examples of poorly correlated age and log(t/$\rho_{\text{in}}$) spectra from hydrous phases that decompose during in vacuo heating. Correlation results from 8-1-22 phengite (Grove and Belouso, 1995) and 78-618 hornblende (Wartho, 1995) illustrate progressive degradation of $C_{xy}$ as natural and experimental argon loss processes become more dominant (see text).
Figure 1. A: Generalized bedrock geology map showing sampling location (white star). BIF—banded iron formation; Mz—Mesozoic; Pz—Paleozoic. B: Mine sites and ages. C: Hand sample photographs of the dated hematite samples.
Figure 3. A: Inferred temperature (temp.) histories for each of the hematites. The Ne bulk age ± 1σ of each sample and a modern temperature of 20 ± 10 °C were the only imposed constraints. Bold colored line and shading indicate the expected thermal history and its 95% confidence interval (CI; note that no single path actually follows this bound) (Gallagher, 2012). For sample MI-45, the starting temperature was restricted to the 95% CI bounds of the MI-81 thermal history. Dashed green lines define the 95% CI without this constraint. B: Model fits (colored lines) to the observed age spectra (gray shaded boxes) and the observed and modeled bulk He ages. Colored lines indicate the modeled age spectrum and its 95% CI for the expected thermal history in panel A.
Remember that, typically, monotonic cooling is assumed...

Figure 7. Thermal history results from GR13 K-feldspar are representative of most of the samples we have examined. (a) The measured age spectrum and model fits produced by best-fit thermal histories; (b) measured and model diffusion values calculated from $^{39}$Ar diffusivities and the MDD model, respectively; (c) calculated thermal histories when reheating is permitted; and (d) calculated thermal histories assuming monotonic cooling. See text and Appendix C for details on how the curves were calculated and Plate 2 (solutions allowing reheating) and Plate 4d (monotonic cooling solutions only) for contours of the raw output data.