Systematic analysis of K-feldspar $^{40}$Ar/$^{39}$Ar step heating results: I. Significance of activation energy determinations

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Abstract—To better understand the argon retention properties of basement K-feldspars, $^{40}$Ar/$^{39}$Ar step-heating results for 115 specimens representing a wide range of temperature-time evolution from a diverse array of geologic environments have been systematically evaluated. In carrying out the measurements, we instituted nonconventional analysis routines including: (1) duplicate isothermal steps; (2) multiple isothermal steps at 1100°C to extract as much gas as possible prior to melting; and (3) temperature cycling. To maintain a self-consistent approach, we systematically applied a weighted least square regression to determine the activation energies ($E$) and log($D_0/r_0^3$) values. Activation energies were found to define a normal distribution ($46 \pm 6$ kcal/mol) spanning over 30 kcal/mol. Corresponding log($D_0/r_0^3$) values ($5 \pm 3$ s$^{-1}$) were highly correlated with $E$, yielding a slope that reproduces the previously documented feldspar compensation relationship. Numerical analysis of this correlation permits us to rule out large systematic laboratory errors in our data. In applying the multiple diffusion domain (MDD) model, we observed general tendencies in the domain distribution of basement K-feldspars. For the majority of samples, most $^{39}$Ar resides in the larger domains. The smallest domains generally constitute <5% volume fraction of the sample and tend to plot ~2 orders of magnitude above log ($D_0/r_0^3$). Alternatively, the largest domains constrained by $^{39}$Ar released below melting have log($D/r^2$) values that are typically ~3 orders of magnitude smaller than log($D_0/r_0^3$).

Systematic analysis of the database demonstrates that the diffusion behavior predicted by the MDD model prevails for virtually all samples. However, two kinds of anomalous degassing behavior were observed. The first appears to be due to our inability to isolate effects resulting from distributions characterized by very small domains while the second may result from inhomogeneous K-distributions. Although these phenomena are capable of producing a wide range of calculated diffusion parameters, close inspection reveals that important systematics of the K-feldspar results cannot be accounted for these factors and remain best explained by real intrasample differences in diffusion properties. Finally, while uncertainties in $E$ determined from $^{40}$Ar/$^{39}$Ar step-heating experiments can produce significant dispersion in calculated temperatures ($\sim 10^6$C/kcal/mol), the overall form of the cooling history, usually the most important result for tectonic applications, is preserved. Copyright © 1997 Elsevier Science Ltd

1. INTRODUCTION

Argon diffusion studies (Sardarov, 1957; Foland, 1974; Harrison and McDougall, 1982; Zeitler, 1987) have long indicated that low-temperature alkali feldspars are characterized by variable argon retention properties. In order to utilize $^{40}$Ar/$^{39}$Ar step-heating measurements to recover the thermal history information recorded in these materials, we require an internally consistent and geologically meaningful interpretive framework. Several models have been proposed to explain the relationship between the laboratory degassing kinetics and the natural loss mechanisms of argon (Foland, 1974; Zeitler, 1987; Parsons et al., 1988; Lovera et al., 1989; Lee and Aldama, 1992; Foland, 1994). In attributing the variability in K-feldspar argon retentivity to the presence of a discrete distribution of noninteracting domains, the multiple diffusion domain (MDD) model (Lovera et al., 1989) reconciles the two distinct sources of information available from K-feldspar $^{40}$Ar/$^{39}$Ar step-heating experiments: the age spectrum reflecting radiogenic $^{40}$Ar ($^{40}$Ar$^*$) loss over geologic timescales, and the Arrhenius plot determined from the degassing systematics of reactor-produced argon (principally potassium-derived $^{39}$Ar or $^{39}$Ar$_K$) during laboratory heating. In the MDD model, domains are represented by activation energy ($E$), frequency factor ($D_0$), domain size ($\rho$), and volume fraction ($\phi$). Because, K-feldspar thermochronologic studies require extrapolation of laboratory determined $^{40}$Ar diffusion properties to crustal conditions, the magnitude of the diffusion parameters ($E$, $D_0$) are of particular significance in determining the temperature dependence of argon release. Accordingly, determining whether or not intrasample variation of these macroscopic parameters exists in basement K-feldspars is of fundamental importance. A related issue is whether it is possible to accurately determine their values in a $^{40}$Ar/$^{39}$Ar step-heating experiment (e.g., York and Hall, 1990). In systems described by a single diffusion length scale, determination of $E$ is obtained in a straightforward manner from the slope of the linear array of log($D/r^2$) values produced in an Arrhenius plot. In materials characterized by multiple diffusion domains however, nonlinear Arrhenius arrays result from differences in diffusive length scale ($\rho$) and argon concentrations ($\phi$) within the individual domains. Application of the MDD model to such materials, therefore, raises the following issues: can step-heating experiments provide the basis to distinguish between
the influence of E and the domain distribution parameters upon log(D/r²) values? Moreover, how do other factors such as the effect of nonuniform K distributions within dom-
ains affect the determination of E and D₀?

In an attempt to address these issues, we have analyzed the results of 115 individual ⁴⁰Ar/³⁹Ar step-heating experiments performed using low-temperature K-feldspars at UCLA over the last several years (Table 1; the complete contents of the database including individual data tables and derivative plots are available from the following WWW site: http://oro.ess.
ucla.edu/argon.html). The samples (see Table 1) represent a wide range of feldspar textural varieties collected from numerous distinct geologic environments. To maintain a self-consistent approach, we determine E and log(D₀/r²) values by systematically applying a weighted least square regression to the initial heating steps of each sample. Be-
cause this focus is geared towards addressing sample-to-
sample variation in diffusion parameters, the issue of whether individual samples can possess multiple activation energies (e.g., Harrison et al., 1991) is deferred to the discus-

sion. Our systematic analysis of these data permits examina-
tion of key aspects of the MDD model, clearly defines nor-
mal and aberrant kinetic behaviors of K-feldspars, permits comparison of results with alternative models (e.g., Lee and Aldama, 1992), and provides a basis for improvements to the application of MDD theory to recover geological thermal histories.

2. EXPERIMENTAL

The 115 K-feldspar samples used in this investigation are listed in Table 1 along with relevant information. In performing the step-
heating experiments on these samples, we have employed different types of heating schedules in an attempt to determine and assess the quality of ⁴⁰Ar diffusion parameters. In nearly half of these samples, we adopted the practice of performing isothermal duplicates (ob-
taining two or more successive measurements at the same tempera-
ture before proceeding to the next higher temperature step) during the initial stages of gas release (~450–750°C). Such a heating schedule allows both an indication of reliability of the estimate of activa-
tion energy (Lovera et al., 1993) and provides the basis for correcting ages for CI-correlated, excess ⁴⁰Ar (Harrison et al., 1994).

Another approach to step-heating involved cycling back to lower temperatures. The principal advantage of this method is to permit evaluation of the activation energy at later stages of the degassing (Lovera et al., 1991). An important consideration in all heating schedules is that the volume fraction of ⁴⁰Ar released prior to melting (above ~1150°C) be maximized. We achieve this by performing progressively longer heating steps at 1100°C. Finally, although the rates of ⁴⁰Ar release measured as the K-feldspar melts possess no geologic significance, all ¹⁹Ar that remains within the sample above 1100°C must be measured in order to estimate accurate fractional loss at each step from which to calculate diffusion coefficients.

Our ability to accurately monitor temperature and heating duration and ⁴⁰Ar release represent fundamental concerns in comparing results between K-feldspar ⁴⁰Ar kinetic experiments. Considerations of sec-

ondary importance in the calculation of diffusion parameters includ-
ing line blanks, irradiation parameters, and mass spectrometer cali-

bration procedures that may vary between samples. In most cases, appropriate experimental details for individual samples are provided in references listed in Table 1.

2.1. Temperature-Time Monitoring

The step-heating experiments were all performed at UCLA using double vacuum, resistance furnaces (Harrison and Fitz Gerald, 1986; McDougall and Harrison, 1988). Temperature control in all experi-
ments was achieved with a feedback loop between a W-Re thermocouple inserted upwards into a 2 mm diameter well bored into the 1 cm thick base plug of a vertical Ta crucible (~1–2 mm beneath the sample) and a thyristor unit that regulates power supplied to a split-ring Ta heating element. The duration of heating steps in our experiments varied from 10 min to over 24 h depending on the heating schedule and the desired fractional loss of ⁴⁰Ar. A run was considered to have begun when the temperature recorded by the thermocouple positioned at the base of the crucible matched the set temperature (normally ~2 min after the furnace is powered). The run was considered to be over upon power shutoff to the heating element. Although time can be measured with high precision, uncer-
tainty results from the thermal lag prior to achieving steady-state.

Using this system, the precision of the temperature measurement is nominally limited by the stability of the thyristor (better than 0.01 mV or ±1°C). Such precision applies only when heat-flow within the crucible has achieved steady-state. Because this condition must be established each time the furnace is powered, the uncertainty in the temperature measurement is considerably greater for short dura-
tion runs. In general, the measurement method appears to result in an overestimate of temperature. For example, tests performed with an independently-calibrated, chromel-alumel thermocouple inserted against the base of the crucible in the same position that the sample occupies indicate that more than 20 min may be required to achieve steady-state when the crucible is heated from room temperature. The dual thermocouple experiments indicate that reported temperatures are accurate to within ±10°C at the position of the sample between 500–1100°C provided that the furnace has been previously equil-
ibated at ~300–350°C for ~30 min prior to beginning heating steps. These conclusions are supported by melting experiments performed with pure tin, aluminum, and copper foils.

In general, we have attempted to begin all heating steps from a preheated condition (~150–200°C below the target temperature). Despite this, between 1 and 5 min elapse between the time the external thermocouple indicates the set temperature has been reached and the time the internal thermocouple attains steady-state. During this interval, temperature is typically indicated to be within 10°C of the set point. The decline in crucible temperature after cutting power to the furnace is typically between 50 and 100°C/min, depending upon initial temperature. This effect partially offsets the thermal lag during power up. In light of these uncertainties in temperature and the thermal lag time we estimate that relative uncertainties of ±5°C and ±1.5 min are representative for the great majority of our experi-
ments. Although the absolute uncertainty in temperatures character-
izing different experiments could be greater, we have routinely repro-
duced diffusion parameters in replicate analyses of the same material. For example, the spread in values of E obtained from six separate diffusion experiments performed with untreated MH-10 K-feldspar (~46–49 kcal/mol; (Lovera et al., 1991, 1993) essentially agree with an experimental uncertainty of ±1.5 kcal/mol calculated for the individual step-heating experiments. For comparison, a systematic temperature offset of 50°C between different experiments performed with the same material would result in a difference in activation energy of 6 kcal/mol.

2.2 Argon Analysis

Three separate mass spectrometers were employed in the step-
heating experiments reported in Table 1. Calibration of argon sensi-
tivity and mass discrimination in all three instruments was performed with air pipette systems containing splits of a common air argon ampoule. Most analyses were performed with either a VG 3600 or VG1200S mass spectrometer. Sample sizes were generally ~30 mg, and gas was transferred by expansion. The VG 3600 utilizes a Nier-Bright source yielding an Ar sensitivity of 2400 A/attorr at a resolving power (MRP) of 450. The VG1200S uses a Baur-Signer GS-98 ion source (Baur, 1980) which is characterized by a high argon sensitivity (~3 × 10⁻⁴ A/attorr) and very low pressure dependence. Typical operating MRP is 90. The reproducibility of manometric argon measurements in either instrument is typically better than 2%. For example, reproducibility of ³⁹Ar intensities for the VG 3600 determined from eighteen blocks of three to five replica-
ticte atmospheric argon aliquots measured over three months ranged
Table 1. K-Feldspar database.

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**Type of analysis**

- EG = Eldjura Granite, Greater Caucasus, Russia
- PRB = Peninsular Ranges Batholith, southern & Baja California
- RRSZ = Red River Shear Zone, Yunnan and Vietnam
- SH = Shandong Province, PRC
- GT = Gandense Thrust, southeastern Tibet
- PR = Puerto Rico
- VT = Vincent Thrust, southern California, USA
- HIM = High Himalaya
- RZT = Renbu Zedong Thrust
- SWT = Southwest Tibet
- SET = Southeast Tibet
- SEA = Southeast Australia

**References**

1. Leloup et al. (1993)
2. Harrison et al. (1992)
3. Ryerson et al. (1995)
4. Chen et al. (1992)
5. Grove and Lovera (1996)
6. Harrison et al. (1996)
7. Yin et al. (1994)
9. Dransfield et al. (1997)
14. Quelleur et al. (1997)
from 0.4 to 1.7% (mean of 1.1%). Similar analysis over an equivalent time period performed with the VG 1200S yielded a range of 0.1–2.9% (mean of 1.7%). Procedures implemented to regulate the amount of gas delivered to the mass spectrometer limited the dynamic range of pressures applicable to this study to a factor of about 20. Tests performed using atmospheric argon aliquots do not detect pressure nonlinearity effects at the percent level when the reproducibility of individual ion intensities are taken into account. About 10% of the samples were analyzed with a Nuclide 4.5-60-RSS mass spectrometer operated in the Faraday mode with an $^{40}$Ar sensitivity of $1.5 \times 10^{-13}$ mol/mV. Sample sizes were generally $\approx 200$ mg, and gas was transferred quantitatively by trapping it on activated charcoal maintained at liquid nitrogen temperatures. Because the total quantity of gas admitted to the mass spectrometer was governed using a leak valve, orifice corrections were required. Reproducibility of manometric argon measurements for this instrument were typically 1–2%.

3. RESULTS

3.1. Arrhenius Parameters

Low-temperature Arrhenius data for the K-feldspars contained within the database (Table 1) has been examined using a uniform set of criteria. Our ability to determine values of log($D/r^2$) is determined largely by the analytical uncertainties discussed in the previous section. Propagation of these uncertainties into the calculation of log($D/r^2$) is summarized in Appendix A. Based upon these calculations we estimate that errors in our log($D/r^2$) values are typically $\pm 0.05$ log units (in s$^{-1}$). A composite Arrhenius plot displaying representative experimental results from fifty-seven of our samples is shown in Fig. 1. The samples selected were chosen because all were processed using duplicate isothermal steps from 450 to 750°C. Note that despite the variety of materials examined (Table 2), log($D/r^2$) values from all samples define a spread of less than 2 orders of magnitude at any given temperature. This variability is significantly less than that obtained when step-heating results are normalized according to an estimated diffusion radius (Mussett, 1969). This observation is maintained when samples degassed with somewhat different heating schedules are also considered. In order to facilitate comparison of our results with those from other laboratories, we have also performed step-heating experiments with a sanidine glass synthesized at 1300°C (Fig. 1). The sanidine glass results are calculated in terms

![Graph](image)

Fig. 1. K-feldspar $^{39}$Ar kinetic results from UCLA (1993–1995): Arrhenius results obtained from step-heating of a single 40 mg fragment of sanidine glass (filled squares). Note that log($D/r^2$) values have been calculated assuming plane slab diffusion geometry and normalized to $r = 0.04$ cm to facilitate comparison with the K-feldspar results. Arrhenius results for fifty-seven K-feldspar samples analyzed following similar heating schedules (isothermal duplicates performed from 450 to 750°C). Shown for comparison are log($D/r^2$) results from two gem quality specimens, Benson Mines orthoclase and Madagascar orthoclase. The bulk loss (bold line) and step-heating results (open squares) for 127 μm diameter Benson Mines orthoclase grains were recalculated from Foland (1974) and Foland (1994), respectively, using plane slab geometry. Madagascar orthoclase results (filled circles) are from UCLA.
of $\log(D/r^2)$ using planar geometry and a length scale ($r = 0.04$ cm) to facilitate comparison with the K-feldspar data. Arrenhius results for two gem-quality orthoclasches (Benson Mines orthoclasche and Madagascar orthoclasche) are provided for additional reference. To ensure direct comparison with the database samples, the Arrenhius plots for Benson Mines were calculated from the Foland (1974, 1994) results using plane slab geometry. The measured K-feldspar diffusion coefficients plot intermediate between the $\log(D/r^2)$ values of the two reference materials. The data systematically converge with increasing temperature (to a spread of less than 1 order of magnitude) and become closer to the values obtained from Madagascar orthoclasche. According to the MDD model, a linear Arrenhius array of $\log(D/r^2)$ values with a slope proportional to the activation energy of the sample is expected as long as the K-derived $^{39}$Ar from the smallest diffusion domains present within the K-feldspar are degassed with the appropriate resolution. For

<table>
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<th>Sample name</th>
<th>$E$ (kcal/mol)</th>
<th>log($D/r^2$) ($s^{-1}$)</th>
<th>Goodness of fit</th>
<th>$N$</th>
<th>$f$</th>
<th>Sample name</th>
<th>$E$ (kcal/mol)</th>
<th>log($D/r^2$) ($s^{-1}$)</th>
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a plane slab diffusion geometry, this linearity is maintained as long as the fractional loss of $^{39}$Ar release from the smallest domain does not exceed about 60% (see Appendix C of Lovera et al. (1989), Eqns. C1–8). The likelihood of maintaining this linearity is generally improved by minimizing the fraction of $^{39}$Ar released during the initial steps. This is generally accomplished by beginning the step-heating experiment at temperatures below 500°C for heating durations of ~10 min. As $^{39}$Ar is exhausted in the smaller domains during progressive heating, log($D/r^2$) values of successive steps decline causing convex up curvature in the Arrhenius plot (Fig. 1).

Our approach to estimating K-feldspar values of $E$ and log ($D_o/r_0^2$) for $^{39}$Ar diffusion in step-heating experiments is illustrated in Fig. 2 and described in detail in Appendix B. In calculating the best-fit solution, we increase the number of points used in the regression until the goodness of fit weighted by the number of data points achieves a maximum. Because the first data point is likely to misrepresent the diffusion properties of the sample due to surface anisotropy, recoil and/or small scale compositional variations, we considered it as an outlier if it lies more than 2 standard deviations from the resulting line. We emphasize that only the first datum is dealt with in this manner and that less than 10% of our samples were affected.

Values of $E$ and log($D/r^2$) calculated for our K-feldspars are displayed in Fig. 3a and 3b, respectively. One sigma uncertainties in $E$ reported in Table 1 are typically 1–2 kcal/mol. A modified Kolmogorov-Smirnov goodness-of-fit test using the Kuiper statistic (Press et al., 1988) indicates that the distribution of $E$ and log($D/r^2$) values both define crudely normal distributions (Fig. 3a,b). The overall dispersion in $E$ shown in Fig. 3a is about 30 kcal/mol. A plot of $E$ vs. fraction of $^{39}$Ar used in the regression (Fig. 3c) shows a sharp drop in intrasample variation of activation energy as the regressed gas fraction increases. At the same time it is important to point out the permissible fraction of $^{39}$Ar regressed by the method outlined in Appendix B is an intrinsic property of each sample. In other words, increasing the number of steps (and hence the $^{39}$Ar fraction) used in calculating activation energies for low-gas fraction samples in Fig. 3c would shift all the $E$ values to lower values maintaining the observed high dispersion but reducing the overall quality of fit. A final observation is that calculated $E$ and log($D_o/r_0^2$) values exhibit a high degree of correlation (correlation coefficient = 0.97; Fig. 3d).

Analysis of the mathematical formulation of the MDD model (Lovera et al., 1989, Eqns. C1–8) shows that negligible difference in log($D/r^2$) between successive isothermal steps ($\Delta$log($D/r^2$)) are expected when the smallest domains retains at least 40% of their initial $^{39}$Ar concentration. Values of $\Delta$log($D/r^2$) within experimental uncertainty, therefore, are expected to represent a sufficient condition to obtain an accurate value of $E$. Accordingly, we have examined $\Delta$log($D/r^2$) values to evaluate both the capability of the isothermal duplicates method to identify this condition (smallest domain releasing less than 60% of its $^{39}$Ar) and the ability of the approach summarized in Fig. 2 to yield the activation energy of the sample.

Plots of $\Delta$log($D/r^2$) vs. $E$ for the first three pairs of isothermal duplicates (450, 500, and 550°C) are shown in Fig. 4a-c. Note that while $\Delta$log($D/r^2$) values for the first duplicates (450°C) exhibit more dispersion than those obtained for the 500°C duplicates, a mean value of 0.04 was obtained in each case. The larger dispersion of the first set of duplicates (Fig. 4a) may be due to the second order effects mentioned above that primarily affect the first step. The distribution of $\Delta$log($D/r^2$) values for the third duplicate pair (550°C; Fig. 4c) show a marked shift toward positive values (mean value of 0.11). This shift towards positive values characterizes all subsequent duplicate pairs measured at higher temperatures than 500°C and appears to reflect the progressive depletion of the smallest domains in most of our samples. A plot of weighted mean $\Delta$log($D/r^2$) values vs. $E$ calculated from results measured at 450 and 500°C is shown in Fig. 4d. The sign of the weighted mean corresponds to that obtained from the sum of both $\Delta$log($D/r^2$) values.

A histogram of the weighted mean of the 450 and 500°C $\Delta$log($D/r^2$) values reveal a Gaussian distribution with a mean of 0.01 and a standard deviation of 0.13 (Fig. 5a). Samples lying more than one standard deviation from the mean tend to exhibit the systematic behavior shown in either Fig. 5b or Fig. 5c. Most of the deviant samples yield positive $\Delta$log($D/r^2$) values (see 37/90 K-feldspar in Fig. 5b). A more unusual phenomenon involves systematic increase in the log($D/r^2$) value for the second of two isothermal steps (see YN-27 K-feldspar in Fig. 5c). Numerical analysis described in Section 4.2. indicate that the strongly positive $\Delta$log($D/r^2$) values obtained from samples similar to 37/90 K-feldspar (Fig. 5b) could lead to underestimation of their activation energies. Alternatively, similar calculations suggest that samples resembling YN-27 K-feldspar (Fig. 5c) would lead to overestimation of activation energies when our calculation scheme is applied. In spite of these expectations, we note that no correlation exists between mean $\Delta$log($D/r^2$) values and calculated activation energies.

3.2. Domain Distribution Parameters

The form of the Arrhenius plot (log($D/r^2$) vs. 1/T) or its associated log($r/r_0$) plot (Richter et al., 1991) is a function of the parameters that characterize the individual diffusion domains (activation energy ($E$), frequency factor ($D_0$), domain sizes ($\rho$), and volume fractions ($\phi$); see Fig. 6a). We have recently incorporated routines (Quidelleur et al., 1997) that employ Levenberg-Marquardt methods (a generalization of least square routines to nonlinear cases; see Press et al., 1988) to find the maximum likelihood estimate of the domain distribution parameters ($\rho$, $\phi$) by minimizing the chi-square quantity

$$x^2 = \sum_{i=1}^{N} \left( \frac{y_i - \phi(x_i, a_1, \ldots, a_M)}{\sigma_i} \right)^2$$

where $\sigma_i$ = standard deviation, $y_i$, $x_i$ = data points, $a_i$ = model parameters, $N$ is the number of laboratory steps available, and $M$ is the number of independent parameters of the model. For example, when the Arrhenius results are modeled using $S$ diffusion domains, $M = 2 \cdot S - 2$, due to the following normalizations: $\rho_S = 1$ and $\Sigma \sigma = 1$. For each
$E = 41.6 \pm 1.1$ kcal/mol
$\log(D_o/r_o^2) = 3.7 \pm 0.3$ s$^{-1}$

- Measured below melting
- Measured above melting
- Values used for least square fit

10000/T(K)

Fig. 2. Method employed to calculate Arrhenius parameters ($E$ and log($D_o/r_o^2$)) from K-feldspar samples. (a) Arrhenius plot for 93-NG-17 K-feldspar. Uncertainties ($\pm 1\sigma$) shown for individual diffusion coefficients were calculated following the procedure outlined in Appendix A. Diffusion coefficients used to calculate the indicated values for $E$ and log($D_o/r_o^2$) are indicated by filled symbols. The solid line represents a weighted, least squares fit to these data (see Appendix B for details); (b) Variation in $E$ resulting from least squares fitting of successive data points ($N$) starting from the initial measured value; (c) Variation of the goodness of fit ($q$) as a function of $N$. As discussed in Appendix B, the set of the first $N$ diffusion coefficients corresponding to the maximum value of $q \times N$ was regressed to obtain the diffusion parameters. The filled symbols in (b) and (c) represent this condition.

Sample there is both a minimum number of domains required to adequately fit the experimental results and an upper limit to the number of domains beyond which the overall fit is not appreciably improved (Lovera et al., 1991). To facilitate intersample comparison of domain distribution parameters we have used eight domains for all samples which results in acceptable distributions. For most K-feldspars, this number of domains lies between the above-mentioned limits.
Fig. 3. Arrhenius parameters calculated for K-feldspars contained in the database: (a) Histogram of activation energies for all 115 samples. A modified Kolmogorov-Smirnov goodness-of-fit test using the Kuiper statistic (Press et al., 1988) indicates that the data satisfy criteria for a normal distribution; (b) Histogram of \( \log(D_0/\rho^2) \) values for all samples. Again the data define a normal distribution; (c) \( E \) vs. Cumulative fraction of \(^{39}\)Ar released for the steps used to calculate the diffusion parameters for each of the samples. Variability in calculated \( E \) decreases sharply as the gas fraction defining the reference line (\( \log(D_0/\rho^2) \)) increases; (d) \( E \) vs. \( \log(D_0/\rho^2) \) for all 115 K-feldspars. The plot exhibits a high degree of correlation.

In order to illustrate the approach, the model domain distribution parameters determined for 93-NG-17 K-feldspar are shown in Fig. 6a. The diffusion properties of each of the eight domains are represented by the dotted lines. Note that the \( \log(D_0/\rho^2) \) values of the smallest domain plot \( \sim 2 \) orders of magnitude above the reference line (\( \log(D_0/\rho^2) \)) while those of the largest domains occur \( \sim 3 \) orders of magnitude beneath \( \log(D_0/\rho^2) \). The associated \( \log(r/r_0) \) plot (Richter et al., 1991) for this sample is shown in Fig. 6b. Note that only 68\% of the total \(^{39}\)Ar released was degassed at temperatures below melting. Since the domain distribution can only be constrained by \(^{39}\)Ar release below melting, there is a large uncertainty in the size and concentration of the largest domain (\( \phi = 33\% \), Fig. 7a). Provided that only \(^{40}\)Ar/\(^{39}\)Ar ages calculated from gas extracted below melting are used to constrain the possible \( T - t \) paths experienced by the sample, this ambiguity does not have an effect on the determination of the thermal history.

Figure 7a displays the \( \log(D_0/\rho^2) \) values vs. their corresponding \(^{39}\)Ar concentrations (\( \phi \)) for the diffusion domain.
Fig. 4. Difference in log(D/r²) values between successive isothermal steps (Δlog(D/r²)) vs. calculated activation energy for fifty-seven samples for which appropriate data are available. Errors for Δlog(D/r²) represent ±1σ, and were calculated assuming no correlation. Results from isothermal duplicates performed at 450, 500, and 550°C are shown in (a), (b), and (c), respectively. The proportion of Δlog(D/r²) values that are zero within uncertainty are 60% and 80% for 450°C and 500°C, respectively. As indicated in (c), Δlog(D/r²) values for isothermal duplicates at 550°C, and higher temperatures tend not to be zero within uncertainty. (d) Weighted mean between 450 and 500°C results used to discuss results presented later in the text.
Fig. 5. Examples of different types of systematic Arrhenius behavior exhibited by K-feldspar in low-temperature step-heating experiments. (a) Weighted Mean of $\Delta \log(D/r^2)$ values calculated from 450\(^\circ\)C and 500\(^\circ\)C isothermal duplicates. Nearly 80% of the samples yield values within uncertainty of zero (Type I behavior; see 93-NG-17 in Fig. 2a); (b) Type II behavior refers to samples in which $\log(D/r^2)$ drop by an amount greater than experimental uncertainty in successive isothermal duplicate pairs; (c) Type III behavior refers to the opposite tendency (see text for details).

distribution used to model \(^{39}\)Ar data of 93-NG-17 K-feldspar as shown in Fig. 6a. The ambiguity in the determination of the largest domain and the uncertainties in measured \(^{39}\)Ar values leads to a multitude of solutions that fit the experimental data in an equivalent manner. For example, one hundred equivalent domain distributions calculated from the \(^{39}\)Ar results of 93-NG-17 were used to construct the weighted histogram in Fig. 7b. In producing this plot, mean \(^{39}\)Ar concentrations for each $\log(D/r^2)$ bin were obtained by summing the individual $\log(D/r^2)$ values weighted by their corresponding volume fractions. We then normalized these values by the total number of solutions. The individual distributions of both the largest and smallest domains constrained by \(^{39}\)Ar release prior to melting are indicated by different shades of gray. Note that a substantial portion of the larger domains in the distribution were not constrained by our data since their \(^{39}\)Ar content were released above melting (striped pattern). The dispersion observed in the larger domains results from the lack of constraints in our data. Note also that the concentration of the smallest domains is quite small with their relative size well constrained.

A weighted histogram of the $\log(D/r^2)$ values calculated from the domain distributions obtained for selected samples from the database are presented in Fig. 7c. Because values of $\log(D/r^2)$ are strongly correlated with activation energy (Fig. 3d), we have restricted our analysis to the seventy-six samples whose activation energies lie within $\pm 1\sigma$ of the mean (Fig. 3a). The data define a broad peak centered on $\log(D/r^2) = 2.5$ s\(^{-1}\) with an asymmetric tail extending to higher values (i.e., less retentive domains). Note that the spread in the largest domain sizes of Fig. 7c is almost twice the spread obtained for 93-NG-17 (Fig. 7b). A larger contrast appears at the other extreme of the spectrum, where the spread of the distribution of smallest domains is now several orders of magnitude. The composite domain size distribution of Fig. 7c reflects the typical domain properties of low-temperature potassium feldspars: (1) the majority of \(^{39}\)Ar resides in the largest domains; (2) the smallest domains typically constitute <5% volume fraction of the samples (black columns) and tend to plot $\sim 2$ orders of magnitude above $\log(D/r^2)$ (Fig. 3c); and (3) the largest domains constrained by the samples ($\sim 20\%$ by volume; gray columns) have $\log(D/r^2)$ values that are typically $\sim 3$ orders of magnitude below $\log(D/r^2)$ (Fig. 7c). The $\log(D/r^2)$
Fig. 7. (a) $^{39}$Ar concentration vs. the corresponding size ($\log(D_i/r^2)$) for the domain distribution shown for 93-NG-17 in Fig. 6. We have distinguished domains determined by $^{39}$Ar released below melting from those corresponding to gas released at higher temperatures; (b) Weighted histogram from 100 equivalent domain distributions (all using eight domains). Distributions were calculated as in (a) above and both $E$ (≈41.6 kcal/mol) and $\log(D_i/r^2)$ (≈ 3.7 s$^{-1}$) were held constant. These best-fit solutions yield similar $\chi^2$ values between 0.06–0.09. Values of $\log(D_i/r^2)$ for each domain were weighted by their corresponding $^{39}$Ar fractions ($\phi$) and then summed into bins of 0.2 to calculate the histogram. Note that while larger domains are not uniquely constrained, smaller domains are sharply resolved; (c) Weighted histogram for database samples with $E$ between 40–52 kcal/mol calculated as in (b) above. The asymmetric distribution reflects the typical domain distribution properties of low-temperature potassium feldspars. Specifically the smallest domains constitute <5% volume fraction of the samples (black columns) and tend to plot ~2 orders of magnitude above $\log(D_i/r^2)$. Alternatively, the largest domains constrained by $^{39}$Ar released below melting (~20% by volume; gray columns) have $\log(D_i/r^2)$ values that are typically ~3 orders of magnitude smaller than $\log(D_i/r^2)$. The $\log(D_i/r^2)$ value for Benson Mines orthoclase determined by reducing the Foland (1974) bulk loss experiments data using infinite slab diffusion geometry is shown for reference.

4. DISCUSSION

Understanding the intersample variation in activation energies determined in $^{40}$Ar/$^{39}$Ar K-feldspar step-heating experiments (Fig. 3a) is crucial to evaluating the accuracy of thermal histories calculated from the laboratory results. Whether or not the observed distribution represents real variation in the diffusion behavior of the materials examined or is an artifact that results from limitations in the model systematics used to characterize sample properties or from hidden systematic errors in laboratory measurements is important for accurate determination of thermal histories. Below we explore possible causes that could produce large errors in estimating the diffusion parameters. We first examine the possible significance of the correlated relationship between $E$ and $\log(D_i/r^2)$. In particular, we analyze the possible effects of hidden systematic laboratory errors in producing the observed correlation. We next test for the effects of random domain distributions and nonuniform $^{39}$Ar distribution upon $E$. Having investigated possible explanations for errors in the diffusion parameters, we explore the effects of these uncertainties upon thermal histories calcu-
lated with the MDD model. Finally we discuss other models proposed to explain Ar release from K-feldspar. We emphasize that while these alternative models might explain some of our experimental results, they fail to predict other important features. In any case, their generality precludes extrapolation of laboratory results to Ar loss in nature which in turn severely limits their applicability to determining thermal histories.

4.1. Correlated Relationship Between $E$ and $\log(D_0/r_0^2)$

The high degree of correlation between $E$ and $\log(D_0/r_0^2)$ shown in Fig. 3d is potentially a manifestation of the Meyer-Neldel rule, (i.e., compensation between kinetic parameters in Arrhenius-type functions; Meyer and Neldel, 1937). Alternatively, the relationship could also result from underestimation of uncertainties that are highly correlated. In spite of these possibilities, we point out that the restricted range of experimental conditions encountered in our data (i.e., in $1/T$ vs. $\log(D/r_0^2)$ space) could reduce or eliminate the apparent statistical significance of this correlation which limits our ability to confirm the existence of a Meyer-Neldel relationship. To test whether the observed relationship occurs as a result of a limited range of experimental conditions, we have performed the following numerical experiment. Using Monte Carlo simulations, we generated 100 values of $E$ and $\log(D/r_0^2)$ at 450°C which define the Gaussian distributions shown in Fig. 8a and 8b. The median value of the Gaussian distributions were selected to resemble our K-feldspar distribution (Fig. 3, 46 ± 6 kcal/mol and 8.7 ± 1 s⁻¹ at 450°C). Each activation energy was then randomly paired with a $\log(D_{95}/r_0^2)$ value. From each pair of values, the corresponding $\log(D/r_0^2)$ value at $1/T = 0$ was calculated (i.e., $\log(D_0/r_0^2)$). Because the resulting plot of $E$ vs. $\log(D_0/r_0^2)$ (Fig. 8c) reproduces the same strong correlation as observed for our empirical results (Fig. 3d), it is possible that the empirical relationship simply reflects the narrow range of $T-1$ conditions employed in our experiments. Thus while a compensation relationship cannot be ruled out, the statistical significance of the observed correlation is substantially muted.

In spite of this conclusion, the fact that we were able to reproduce the slope of Fig. 3d using a Monte Carlo simulation has important implications concerning the possible existence of hidden systematic errors in our laboratory measurements. Note that the slope obtained in Fig. 3c, (i.e., $E$ (kcal/mol) = 29.7 ± 3.3 log($D_0/r_0^2$)), is in agreement with the value obtained from the diffusion of a variety of species (e.g., Na, O, K, Rb, Ar) in feldspar (Gilleti, 1990) of $E$ (kcal/mol) = 50.7 ± 3.4 log($D_0$) (Harrison et al., 1991). We interpret the offset (i.e., 50.7–29.7 = 21.0) between the two lines to reflect the average effective diffusion domain size of our samples. That is, an effective size ($r_0$) of ~6 μm is required to reconcile (Hart, 1981) relationship with the line defined by our K-feldspar values in Fig. 4d. This is intermediate between our previous estimates of the size of the largest (~100 μm) and the smallest (~1 μm) domains of MH-10 K-feldspar (Fitz Gerald and Harrison, 1993; Lovera et al., 1993). For an activation energy of 43.8 kcal/mol (i.e., Benson Mines orthoclase), this estimate of $r_0$ yield a frequency factor of $D_0 = 0.0063 ± 0.005$ s⁻¹, somewhat lower but within uncertainty of the 0.00982 s⁻¹ value reported by (Folland, 1974). Note that the $D_0$ value calculated from the $E$ vs. $\log(D_0/r_0^2)$ relationship is only an effective frequency factor for these samples and may not reflect the intrinsic $D_0$ value of K-feldspar.

4.1.1. Hidden systematic experimental errors

Although we consider it unlikely that our results are significantly influenced by hidden systematic experimental errors, we investigated the possible implications of unanticipated problems in experimental methods. The variable with the highest potential for producing spurious errors is temperature. The well-behaved nature of the isothermal duplicate measurements and the reproducibility found in our experiments (Lovera et al., 1993) rule out errors in relative temperature control greater than ±5°C (Fig. 4). However, the accuracy of the absolute temperature calibration was not tested on a regular basis. If large systematic errors in temperature calibration (i.e., ± ± 50°C) that varied from sample to sample affected our experiments, then the resulting diffusion parameters would yield a distribution resembling that shown in Fig. 1. Specifically, runs performed with true temperatures systematically lower than that read from the thermocouple would yield anomalous low $\log(D/r_0^2)$ values while actual temperatures higher than those yielded by the thermocouple would produce the opposite effect. However, close inspection of our experimental results reveal important features that either cannot be explained by, or contradict, the hypothesis that large systematic errors in temperature varying from sample to sample occur in our laboratory. Specifically, systematic errors in temperature calibration (~50°C) would result in a $E$ vs. $\log(D_0/r_0^2)$ correlation characterized by a slope that is twice as large (~7 for $E = 46$ kcal/mol; $\log(D_0/r_0^2) = 5$ s⁻¹) as that indicated by our data (3.3; Fig. 3d). The agreement between the slope value obtained from the experimental data (3.33, Fig. 3d) and that yield by our Monte Carlo simulation (3.13, Fig. 8c) indicates that any systematic errors affecting our data must be small. In addition, if the spread in $E$ results solely from systematic errors in temperature, then a relatively narrow range of $\log(D_{95}/r_0^2)$ values (−8.8 ± 0.4 s⁻¹) should be associated with samples yielding similar activation energies (46 ± 1 kcal/mol). However, samples from the database characterized by $E = 46 ± 1$ kcal/mol yield the same spread of $\log(D/r_0^2)$ values at a given temperature as is obtained from all samples (i.e., ~2 log units, Fig. 1).

4.2. Intersample Variation in Activation Energy

Consideration of the results summarized in Table 1 indicates that our approach to determining activation energies for individual samples normally results in an uncertainty on the order of 1–2 kcal/mol. Errors of this magnitude are appreciably less than those required to explain the spread of values (~30 kcal/mol) for $E$ indicated in Fig. 3a. Although certain effects, such as variation in diffusion geometry, will alter the calculated value of $E$, the magnitude of this effect is unlikely to exceed the quoted uncertainty in activation
energy (Lovera et al., 1991). In this section, we investigate factors not taken into account in our calculations that can increase the uncertainties of the diffusion parameters.

4.2.1. Effect of nonuniform $^{39}$Ar concentrations

One of the underlying assumptions of the MDD model is that $K$ and, therefore, the initial $^{39}$Ar concentration inside each domain within the sample, is uniform (Lovera et al., 1989). However, the presence of perthite and other common microstructures in basement K-feldspars suggest that some departure from this ideal condition could be found in our samples. We analyzed the effect of nonuniform $^{39}$Ar distributions upon activation energies estimated following the method outlined in Appendix B and Fig. 2. In this approach (subsequently referred to as Model A) $^{39}$Ar concentrations within individual domains were described by $c(x) = \cos^3(\alpha + mx)$ where $x$ is distance from the boundary. Different $^{39}$Ar distributions were obtained by randomly varying $\alpha$ and $m$ using Monte Carlo methods (see inset in upper right corner of Fig. 9a). The activation energy was set to 46.5 kcal/mol in all the numerical simulations, and the same domain distribution was used for all runs. Log($D/r^2$) values were then calculated using a heating schedule which began at 450°C and involved isothermal duplicate steps up to 650°C. Figure 9a shows a representative sampling of thirty Arrhenius plots calculated from Model A. Note that the second diffusion coefficient of successive isothermal steps plot either above or below the first value. A histogram of 100 activation energy results from Model A appears in the lower left corner of Fig. 9a. The activation energy recovered from 37% of the runs agree to within ±2.5 kcal/mol with the activation energy used in the model. Note that in extreme instances, nonuniform $^{39}$Ar distribution will cause activation energies to be dramatically overestimated (>30 kcal/mol) when the approach of Appendix B is applied. In addition, significant underestimation of $E$ (on the order of 3–4 kcal/mol) can also be expected.

4.2.2. Effect of domain distribution parameters

A second effect that could possibly interfere with our estimates of $E$ involves our potential inability to separate the effects of domain distribution from those of the diffusion
parameters ($E$ and $D_0$). Note that domain distributions that include extremely small domains are unlikely to yield a linear Arrhenius array of $\log(D/r^2)$ values with slope proportional to the activation energy of the sample because the smallest diffusion domains will lose a substantial proportion of their K-derived Ar as the step-heating experiment progresses (see Appendix C of Lovera et al. (1989) Eqs. C1-8). Because of the low $^{39}$Ar retentivity of extremely small domains, even minor temperature increase or protracted isothermal heating will exhaust these domains of $^{39}$Ar causing convex up curvature in the Arrhenius plot and resulting in underestimation of activation energy. Moreover, use of erroneously low activation energies results in miscalculation of the domain distribution parameters. Specifically, the smallest domains are overlooked in the fitting process because of the compensating effect of low $E$.

In order to evaluate these effects, we have produced random domain distributions (herein referred to as Model B) and subjected them to the same heating schedule as used in Model A above. Ten domains were used in all representations to allow greater variation in our distributions. The domain distribution parameters ($\rho$, $\phi$) were calculated using Monte Carlo methods. Only two restrictions were applied. The parameters were subject to the normalization condition ($\sum \phi = 1$) and were permitted to differ by up to 20 orders of magnitude. Representative Arrhenius plots produced from Model B are shown in Fig. 9b. Note that in contrast to the behavior exhibited in Model A, $\log(D/r^2)$ values corresponding to the second step of isothermal duplicate pairs are always lower than the first. A histogram of the calculated activation energies appears as an inset in Fig. 9b. The activation energies calculated for over half the runs agree within $\pm 2.5$ kcal/mol with the input activation energy. Note that this model yields only calculated activation energies equal to, or lower than, the true value (i.e., 46.5 kcal/mol). In extreme instances, values of $E$ more than 20 kcal/mol below the true value result from application of the method of Appendix B.

4.2.3. Implications for experimental results

Neither Model A nor Model B alone are capable of describing the observed range of activation energies calculated from the initial low-temperature steps in $^{39}$Ar/$^{38}$Ar step-heating experiments. Of the two, Model A comes closest. However, combination of features in Model A and Model B could produce $\pm 25$ kcal/mol apparent variation in $E$ which is comparable to the spread of our experimental results (Fig. 3a). To further evaluate similarities of Model A and Model B behavior to the experimental results, we have focused upon the relationship between activation energy and $\Delta \log(D/r^2)$ values calculated for duplicate isothermal steps. These relationships are illustrated in Fig. 10. Calculated values of $E$ vs. the weighted mean of the 450 and 500$^\circ$C $\Delta \log(D/r^2)$ values for Models A and B are shown in Fig. 10. Note the overall strong correlation between $E$ and $\Delta \log(D/r^2)$. Specifically, underestimation of $E$ corresponds with positive values of $\Delta \log(D/r^2)$ and vice versa. We emphasize that this correlation does not exist for the experimental data (Fig. 4d). For example, the total variation in $E$ for $\Delta \log(D/r^2)$ = 0 in Fig. 4b is over 30 kcal/mol whereas the spread in Fig. 10 is on the order of 5 kcal/mol. In addition, note that the span in activation energy observed in our experimental data for $|\Delta \log(D/r^2)|$ values in excess of 0.1 is also large (Fig. 4). Such dispersion around the mean value of $E$ (46.5 kcal/mol) at almost any given value of $\Delta \log(D/r^2)$ is not represented by the numerical simulations (Fig. 10). It is clear that in both models, over or underestimation of $E$ of more than 5 kcal/mol is directly correlated to the $\Delta \log(D/r^2)$ values of the first two duplicates steps and can, therefore, be linked to the method (i.e., Appendix B) used to calculate the activation energy. This does not appear to be the case in our K-feldspar samples where the same dispersion in $E$ was obtained for almost any value of $\Delta \log(D/r^2)$.

4.3. Step-Heating vs. Bulk Loss Experiments

Differences in the experimental approach between the step-heating experiments presented here with isothermal,
bulk loss experiments (i.e., Folland, 1974) need to be considered when comparing results from the two approaches. In a bulk loss experiment, a diffusion coefficient is calculated from the measured fractional loss and the duration of heating. A number of such measurements performed at different temperatures and heating durations are required to characterize the Arrhenius plot of a sample. Although it is often asserted that a linear Arrhenius array can only be produced from such an experiment if the sample contains a single diffusion length scale (Folland, 1974; Harrison et al., 1985; Folland, 1994), this is not necessarily the case. Because the argon is extracted in a single step, the result tends to emphasize the average diffusion properties of the sample and can yield apparently linear arrays for samples containing multiple diffusion domains. This is particularly true when the sample contains a dominant intermediate-sized domain (i.e., one that comprises >70% of the $^{39}$Ar). In such cases, the measured loss from the aggregate is insensitive to the two lower volume fraction components (i.e., the larger and smaller domains) which tend to self-compensate yielding an average result close to that of the middle domain value. For example, bulk loss experiments on Benson Mines orthoclase appears compatible with a sample containing only a single diffusion length-scale (Folland, 1974). This conclusion was based upon the following observations: (1) diffusion coefficients calculated between 400 and 800°C yield a linear Arrhenius array; (2) the measured fractional loss from a single grain size at 700°C for varying lengths of time plot close to the curve predicted for a single domain size; and (3) results from different grain sizes yield the similar diffusion coefficients at a given temperature when normalized for size. Although these arguments are consistent with the Benson Mines orthoclase containing a single length scale, they are not diagnostic. Specifically, step-heating experiments carried out on a 127 μm aliquot of Benson Mines orthoclase that had been previously heated at 700°C produced both an age spectrum and an Arrhenius plot that exhibit a diffusion behavior compatible with multiple diffusion domains (see Figs. 13 and 14 of Folland, 1994).

To illustrate why the above criteria are in fact not diagnostic of a single diffusion length scale, we have numerically simulated bulk loss and step-heating experiments (Fig. 11) for a sample with a domain distribution that produces bulk loss results similar to that found for Benson Mines orthoclase.
Because of the averaging process intrinsic to bulk loss experiments, the activation energy calculated for a sample possessing multiple diffusion domains following this approach will likely be lower than the value obtained from step-heating results. For example, the value of $E$ used in our synthetic K-feldspar was 47 kcal/mol while the Arrhenius data from the bulk loss simulation yielded only 44 kcal/mol, similar to the value obtained by Foland (1994). We point out that depending upon the heating schedule, step-heating results from the same synthetic sample could also result in an erroneously low activation energy.

Finally we note that an $^{40}$Ar diffusivity calculated directly from a measured depth profile of the homogeneous Madagascar orthoclase yields $D_{\text{SFPC}} = 2.4 \times 10^{-13}$ cm$^2$/s (Kelley et al., 1994) which is a factor of 6 lower than the value predicted by Foland (1974). Assuming similar argon diffusion behavior in the two gem quality samples, this suggests that the Foland (1974) use of the measured grain size resulted in an overestimation of the argon diffusivity because the effective domain size was significantly smaller than the measured value.

To summarize, the Benson Mines orthoclase bulk loss results (both the Arrhenius and $f$ vs. $t^{1/2}$ plots) and subsequent $^{40}$Ar/$^{39}$Ar age spectrum and Arrhenius data (Foland, 1974, 1994) all appear consistent with the sized aggregates containing a modest but significant distribution of diffusion domain sizes, similar to the one given in the caption of Fig. 11. It seems apparent that the Benson Mines orthoclase contains a mosaic of internal diffusion boundaries (e.g., cleavage) that endow this sample with minor multi-diffusion domain properties. We conclude that the multi-domain diffusion theory is better able to explain all the Benson Mines orthoclase data than the mechanisms invoked by Foland (1994) to reconcile the bulk loss and step-heating results (e.g., synheating grain fracturing, defect trapping of argon, annealing at high temperatures). In addition, these mechanisms appear inconsistent with cycling and double irradiation experiments designed to test for, but that did not reveal, these phenomena in MH-10 K-feldspar (Harrison et al., 1991; Lovera et al., 1991, 1993).

4.4. Effect of Uncertainties in Kinetic Parameters upon Calculation of Thermal Histories

Having described the range of variation of the diffusion parameters calculated from K-feldspar $^{40}$Ar/$^{39}$Ar step-heating experiments, it is now important to investigate the effect of uncertainties in these parameters upon our primary goal, the reconstruction of a thermal history. Until recently, a lack of reasonable estimates for the uncertainties of the kinetic parameters had prevented us from performing calculations of confidence intervals required to address the statistical significance of calculated K-feldspar thermal histories. Instead, we based the uncertainty estimates for our thermal history almost exclusively upon the measured uncertainty in fitting the age spectrum. With the insights into uncertainties of kinetic parameters we have drawn from the K-feldspar database and the development of automated routines to model the kinetic and age properties of K-feldspar $^{40}$Ar/$^{39}$Ar step-heating results (Lovera et al., 1993),
et al., 1995; Quidelleur et al., 1997), our ability to address the statistical significance of K-feldspar thermal history results has been significantly improved.

Below we describe this new approach using results from 93-NG-17 K-feldspar as an example (see Grove and Lovera (1996) for additional information regarding this sample). As previously described, regression of the initial low-temperature heating steps following the method described in Appendix B yielded and activation energy of 42 $\pm$ 1 kcal/mol and 3.7 $\pm$ 0.3 $s^{-1}$, respectively (Fig. 2). Using Monte Carlo simulations, we produced Gaussian distributions for $E$ and $\log(D_0/r_0)$ in agreement with their respective uncertainties. Values of $E$ and $\log(D_0/r_0)$ possessed the same correlation as seen in Fig. 3d ($R = 0.97$). Size distributions consisting of eight domains were then calculated for each pair of $E$ and $\log(D_0/r_0)$ values by fitting the $^{39}$Ar data in the usual manner. A weighted histogram of the $\log(D_0/r^2)$ values (calculated in the same manner as Fig. 7) is shown in Fig. 12a. Comparison of the two plots illustrates the effect of introducing uncertainty in the diffusion parameters upon the domain distribution. Variation in the diffusion parameters and uncertainty in the $^{39}$Ar data combined with the fact that about 30% of the $^{39}$Ar in the sample was released at temperatures beyond 1100°C (i.e., above incongruent melting) results in multiple equivalent solutions for the distribution parameters. Despite this, maxima corresponding to the smallest domains are clearly resolved.

Thermal histories were then calculated for each set of diffusion parameters ($E, D_0$) and their corresponding set of domain distribution parameters ($\rho, \phi$) using a modified Levenberg-Marquardt method described in Quidelleur et al. (1997). The form of the cooling history was assumed to be monotonically increasing. Five runs were performed for each set of parameters with different random input values used to initialize each run. The solution that yielded the lowest $\chi^2$ value was accepted as the best-fit result. This process was repeated for all 100 sets of parameters. Representative calculated age spectra and their corresponding thermal history solutions are shown in Fig. 13a. In addition, we have also calculated the 90% confidence intervals for the median and overall distribution of $T - t$ solutions as a function of age. These results are represented graphically in Fig. 14.

In order to demonstrate the effect of larger uncertainties in the diffusion parameters we calculated an additional set of thermal history solutions following the same process described above but employing uncertainties in $E$ and $\log(D_0/r_0)$ of $\pm 6$ kcal/mol and $\pm 3$ $s^{-1}$, respectively. The resulting domain distributions are shown in Fig. 12b. Our use of larger uncertainties in the diffusion parameters was motivated by the dispersion in these parameters exhibited by our database samples (Fig. 5). Propagation of the larger uncertainties in the diffusion parameters results in significantly greater dispersion in calculated $T - t$ histories Fig. 13c than that illustrated in Fig. 13b.

Finally, we demonstrate an alternative approach that exploits the fact that by simply taking experimental uncertainty into account, a single set of diffusion and distribution parameters is capable of producing a whole family of equivalent solutions. We generated the solutions shown in Fig. 13d from the domain distribution parameters of Fig. 6 by considering all solutions for which $|\Delta \chi^2|/\chi^2_{\text{min}} < 0.3$ to be equivalent. The parameter $\chi^2_{\text{min}}$ is the minimum value of $\chi$ obtained for all runs (Fig. 13d). Note that the resulting confidence
Fig. 13. Thermal history results for 93-NG-17 K-feldspar. (a) Measured (filled gray boxes) and calculated (bold line) age spectra. (b) Thermal histories calculated for 93-NG-17 K-feldspar using domain distributions shown in Fig. 12a ($E = 41.6 \pm 1.3$ kcal/mol and $\log(D_0/r_0) = 3.7 \pm 0.3$ s$^{-1}$). (c) Calculated thermal histories using domain distributions shown in Fig. 12b ($E = 42 \pm 6$ kcal/mol and $\log(D_0/r_0) = 4 \pm 3$ s$^{-1}$). (d) Thermal histories calculated from a single domain distribution by allowing the degree of approximation to vary according to $|\Delta \chi^2|/\chi^2_{\text{min}} < 0.3$, where $\chi^2_{\text{min}}$ was the minimum value obtained for all the runs. Ninety-seven solutions out of 200 runs satisfied this criteria.

Intervals (Fig. 14c) are similar to those obtained propagating the laboratory determined uncertainties into the thermal histories (Fig. 14a). Calculation of a set of cooling history following the later approach (Fig. 14c) is appealing in that it involves significantly less computational time. Note that both methods (Fig. 14a,c) will yield equivalent results only when the uncertainties in $E$ are $\sim 1$ kcal/mol. In addition, appropriate $\chi^2_{\text{min}}$ values will need to be determined empirically for each sample.

In considering all results in Fig. 14, it is clear that under the assumption of monotonic cooling, the $^{39}$Ar/$^{40}$Ar results from 93-NG-17 K-feldspar tightly constrain the thermal history of the sample between 55 and 40 Ma but provide significantly less information at earlier or later times. In addi-
Lee (1995) demonstrated that inflections can be expected from Arrhenius plots calculated by the MP model using heating steps involving monotonic increase in temperatures. This behavior reflects transition from conditions under which diffusion in high-diffusivity pathways predominates due to a large Ar transfer towards SC-paths to conditions for which diffusion through the lattice is most important. Beginning at low temperature, Arrhenius plots exhibit either convex upwards or convex downward curvature depending upon whether exchange coefficients are held constant or are allowed to increase with temperature (see Fig. 6 of Lee, 1995). This behavior renders the MP model a potential candidate to explain some of the effects observed in our samples. Specifically, the observed dispersion in calculated activation energies (Fig. 3) could result from samples having the same activation energy for lattice diffusion if they were characterized by significantly different exchange coefficients. A crucial property of the MP model as defined by Lee and Aldama (1992) and Lee (1995) is that the value of \( \log(D/r^2) \) at a given temperature is a constant determined by the exchange coefficients. This implies that duplicate isothermal steps will not show separation since the exchange between the lattice and SC-paths will replace the argon loss from the SC-paths during the heating steps. Such behavior potentially accounts for the behavior shown in Fig. 5 where a spread in activation energy exists despite no separation in \( \log(D/r^2) \) values obtained from successive isothermal steps.

In spite of these properties, the MP model fails to describe the fundamental behavior observed for K-feldspars subjected to temperature cycling in step-heating experiments. The interaction requirement in the MP model causes depleted SC-paths to be replenished during backward cycling of temperature such that the resulting \( \log(D/r^2) \) values reproduce those previously measured as temperature was increased during the forward cycle. Although over a third of the K-feldspars in Table 1 were analyzed with heating schedules involving temperature cycling backwards from elevated temperature (~750°C or higher), the \( \log(D/r^2) \) values obtained during initial, low-temperature \(^{39}\)Ar release were never reproduced (Harrison et al., 1991; Lovera et al., 1993). Instead, \( \log(D/r^2) \) values measured during backward temperature cycling are 1–2 orders of magnitude lower than those previously determined at a given temperature. The actual difference observed is a function of the heating schedule and the properties of the sample.

Arnold and Kelley (1997) proposed that the failure of the Lee and Aldama (1992) MP model to reproduce the effects observed in the temperature cycling experiments can be explained if annealing of SC-paths prior to backward cycling of temperature occurs. The magnitude of the effect of annealing under these conditions appears to be relatively small for at least some samples, however. The effect of annealing in low temperature \(^{39}\)Ar release from MH-10 K-feldspar, for example, was addressed in a double-irradiation experiment described in Lovera et al. (1993). In this experiment, a split of MH-10 K-feldspar previously at temperatures reaching 850°C for several hours was re-irradiated to replenish out-gassed regions with \(^{39}\)Ar. Near duplication of the previously measured Arrhenius plot in the subsequent step-heating experiment clearly indicated a minimal role for an-

### 4.5. Role of Nondiffusive Argon Transport

The multi-path (MP) hypothesis features nondiffusive transport between lattice and regions of enhanced Ar diffusion (short-circuit pathways). The most highly developed form of the MP model is that presented by Aifantis (1979) and refined by Lee and Aldama (1992) and Lee (1995). From a mathematical point of view, their approach actually represents a generalization of the MDD model. The principle difference is that interaction is permitted between the lattice and short-circuit pathways in the MP model whereas domains are noninteracting in the MDD model. Eliminating interaction reduces the MP model to a mathematical formulation equivalent to the MDD model with two domains (Lee, 1995). The chief difficulty in applying the MP model is that while argon transport in both the lattice and within short-circuit pathways is characterized by volume diffusion parameters that differ in magnitude, the process that permits interaction (i.e., mass transfer between the regions) is not specified. This generality prevents the exchange coefficients from being constrained by laboratory experiments.
nealing during low-temperature $^{39}$Ar release for this sample (Lovera et al., 1993).

4.6. Final Considerations

The lack of viability of other potential descriptions of the transport of argon in K-feldspars such as multi-path behavior, force us to conclude that the observed intersample variation in diffusion parameters reflects real differences in the diffusion properties of these materials and that uncertainties calculated via the method of Appendix B are valid estimates. We recognize that a minority of our samples (represented by the examples of Fig. 5b and c) exhibit behavior that is quite consistent with the predictions of Models A and B. Although we cannot rule out minor tendencies toward Model A or Model B behavior for the majority of our samples (i.e., those for which mean square root $\Delta \log(D/r^2)$ for successive isothermal duplicate pairs is less than 0.1), we point out that the likely error in activation energy will be less than 5 kcal/mol (Fig. 10).

Because the observed dispersion in $E$ and $D_0$ (Fig. 3a) is well in excess of what could be explained by experimental error, and because the processes considered in Model A or Model B (Fig. 10) do not reproduce our empirical observations (Fig. 4), we conclude that there is a real variation in calculated activation energy of argon in K-feldspar of at least 10 kcal/mol. The observed spread in the values of $E$ and $D_0$ may reflect intrinsic differences in diffusion mechanism at the atomic scale (Harrison et al., 1991), but could also simply result from the macroscopic nature of the diffusion model aimed at describing the complex microscopic behavior. The macroscopic parameters only reflect the average properties of the sample, and it is thus conceivable that this averaging changes from sample to sample. Furthermore, the separation between the macroscopic parameter governing the exponential temperature dependence ($E$) and the parameter which should be related to the geometry and scaling of the sample ($D_0$) is probably not fully accomplished due to the limited range of our experimental conditions (i.e., in $1/T$ and $\log(D/r^2)$), as the clear compensation correlation observed in Fig. 3 demonstrates. For example, if $E$ and $D_0$ each have a weak temperature dependence, our inability to accurately partition these effects into the two macroscopic parameters would contribute to a measurable spread in observed activation energies. However, the impact of this broad range in calculated activation energies when extrapolating diffusivity to geological temperatures will be significantly diminished because of the correlated compensation relationship between $E$ and $D_0$. For example, a difference in $E$ of 1 kcal/mol corresponds to a temperature difference of only $\pm 10^\circ \text{C}$ rather than $>30^\circ \text{C}$ if $E$ were changed independent of $D_0$. Furthermore, the form of the calculated thermal history remains unaffected by the manner in which $E$ is varied.

Finally, it is important to ask whether the observed dispersion in the diffusion parameters (Fig. 3) is a consequence of the method used to calculate them (Appendix B). Although it is possible that more elastic criteria could produce better results with less dispersion, we point out that while we have tried other methods, they also produced essentially the same result. In fact, the appearance of Fig. 3 does not change materially if it is compiled from diffusion parameters obtained by nonuniform and subjective criteria used by different individual analysts.

5. CONCLUSIONS

Determining the diffusion parameters in K-feldspar $^{40}$Ar/$^{39}$Ar step-heating experiments is one of the most crucial, yet problematic tasks involved in recovering thermal history information. According to the MDD model, it should be possible to estimate the diffusion parameters from the initial stages of a step-heating experiment. Despite this, use of an inappropriate heating schedule or selection of an unsuitable number of heating steps to calculate the diffusion parameters can yield misleading results. In particular, a heating schedule that degasses the sample too quickly (starting at too high a temperature for example) will likely cause the smallest domains to be exhausted in the first or second heating steps and result in an erroneously low value for $E$. Regardless of the heating schedule employed, it appears that a minority of samples will challenge our ability to estimate the diffusion parameters if a single set of criteria to select values for $E$ and $\log(D_0/r^2)$ is applied.

Our principal conclusions are: (1) Calculated activation energies among basement K-feldspars vary by more than 10 kcal/mol. (2) Results from all $^{40}$Ar/$^{39}$Ar step-heating measurements of K-feldspar exhibit a high degree of correlation between $E$ and $\log(D_0/r^2)$ with a slope that reproduces the previously documented feldspar compensation relationship. The statistical significance of the correlation is not sufficient to confirm the existence of a Meyer-Neldel law for argon diffusion in basement K-feldspars. Because systematic errors in temperature produce a correlated relationship between $E$ and $\log(D_0/r^2)$ that is significantly different from what we observe, this type of laboratory error can be ruled out. (3) The MDD model is able to account for the majority of data we have obtained from basement K-feldspars. (4) We identify general tendencies in the domain distribution of basement K-feldspars. For the majority of samples, most $^{39}$Ar resides in the larger domains. The smallest domains generally constitute <5% volume fraction of the sample and tend to plot ~2 orders of magnitude above $\log(D_0/r^2)$. Alternatively, the largest domains constrained by $^{39}$Ar released below melting have $\log(D/r^2)$ values that are typically ~3 orders of magnitude smaller than $\log(D_0/r^2)$. (5) Two kinds of anomalous degassing behavior are observed. The first seems to reflect limitations in the intrinsic domain distribution while the second is potentially explained by inhomogeneous K-distributions. However, the observed variation in $E$ does not appear to be accounted for by these factors. (6) Although uncertainties in the diffusion parameters calculated from $^{40}$Ar/$^{39}$Ar step-heating experiments can produce significant dispersion in calculated temperatures (approximately $10^\circ \text{C/kcal/mol}$), the overall form of the cooling history is preserved. Because it is usually the relative variation in thermal history between samples that is most important in tectonic applications, the uncertainty in activation becomes less relevant.
References


APPENDIX A

Propagation of Errors in the Calculation of log \((D/\tau^2)\)

Measurements of the cumulative fraction of \(^{39}\text{Ar}\) released \((f)\) and time duration \((\tau)\) of each step heating are using to calculate the log \((D/\tau^2)\) values plotting on a tradition Arhenius plot vs. the inverse of the absolute temperatures \((1/T)\). Following Lovera et al. (1989), the log \((D/\tau^2)\) value for the \(m\)th step can be written as

\[
\log \left( \frac{D}{\tau^2} \right)_m = \frac{\Delta \xi_m}{\Delta \tau} = \xi_m - \xi_{m-1} \Delta \tau
\]  

(A1)

where \(\xi_m\) can be obtained from inversion of the approximate expressions for \(f(\xi_m)\) given by Eqs. C3 in Lovera et al. (1989). The \(f(\xi_m)\) value of the \(m\)th step is obtained summing the measured fractions of \(^{39}\text{Ar}\) released at each step \((A_i)\)

\[
f_m = \sum_{i=1}^{\infty} A_i
\]

(A2)

where \(A_r = \sum A_i\), \(N = \) total # of steps

Therefore, the error on \(\Delta \xi_m\), \((\sigma_{\Delta \xi_m})\), is given by

\[
\sigma_{\Delta \xi_m} = \sqrt{\sum_{i=1}^{N} \left( \frac{\partial \xi_m}{\partial A_i} \right)^2 \sigma_i^2}
\]  

(A3)

\(G_i\) is the error associated with \(A_i\). The calculation of this expression differs slightly depending on the specific geometry used to model the diffusion property of the sample. Here, we calculate as an example the error expressions corresponding to plane slab domains. Generalization to other geometries will involve simple algebraic calculations. An expression for \(\Delta \xi_m\) in terms of \(f_m\) can be found in Lovera et al. (1989) (Appendix C, Eqs. C3):

\[
\Delta \xi_m = \left\{ \begin{array}{ll}
\frac{\pi}{b^2} (f_{m-1}^2 - f_{m-1}) & \text{for } f_m = 0.6 \\
-\alpha \Delta \tau \ln \left[ \left(1 - f_m \right) / \left(1 - f_{m-1} \right) \right] & \text{for } f_m > 0.6
\end{array} \right.
\]  

(A4)

Now, calculation of the derivative of \(\Delta \xi_m\) respect to each fraction of gas released \((A_i)\) is obtained in a straightforward fashion using Eqs. A2 and A4

\[
\frac{\partial \Delta \xi_m}{\partial A_i} = \left\{ \begin{array}{ll}
\frac{2\pi \left( \theta_{i,m} - f_m \right) f_m - \left( \theta_{i,m-1} - f_{m-1} \right) f_{m-1}}{b^2 A_i} & \text{for } f_m = 0.6 \\
\frac{-1}{\alpha^2 \Delta \tau A_i \left(1 - f_m \right)} & \text{for } f_m > 0.6
\end{array} \right.
\]

where \(\theta_{i,m} = \left\{ \begin{array}{ll}
1 & \text{if } i = m \\
0 & \text{if } i > m
\end{array} \right.\)

(A5)

Substitution of Eqn. A5 into Eqn. A3, led after some algebra to

\[
\sigma_{\Delta \xi_m} = \left\{ \begin{array}{ll}
4 (\Delta \xi_m)^2 \left[ \left( \frac{\sigma_i^2}{A_i} \right)^2 + \frac{1 - 2 (f_m + f_{m-1})}{(f_m + f_{m-1})^2} \sum_{i=1}^{\infty} \sigma_i^2 \right] & \text{for } f_m = 0.6 \\
\frac{1}{\alpha^2 \Delta \tau} \left[ \left( \frac{f_m - f_{m-1}}{(1 - f_m)^2} \right)^2 \sum_{i=m}^{\infty} \sigma_i^2 \right] & \text{for } f_m > 0.6
\end{array} \right.
\]  

(A6)

\[
\sigma_{\log} = \left[ \frac{\sigma_{\xi_m}^2}{(D/\tau^2)} + \frac{\sigma_{\Delta \xi_m}^2}{(\Delta \xi_m)} \right] \log(e)
\]  

(A7)

APPENDIX B

Calculation of Kinetic Parameters

One of the most important issues regarding the calculation of the diffusion parameters from samples having a distribution of diffusion domains is how to establish criteria for selecting the points on the Arrhenius plot that define these parameters. Linear Arrhenius arrays with slope proportional to activation energy are expected if the smallest domains are not significantly outgassed of \(^{39}\text{Ar}\). Unfortunately, because, the domain distribution parameters are not known a priori, we are forced to use arbitrary criteria to select the Arrhenius data used in the regression performed to define the kinetic. Below we describe the consistent approach we have employed throughout this paper. For all samples we begin with the first four points and then decide whether to add subsequent points based upon the following set of statistical criteria.

For each set of data points we calculated a set of kinetic parameters by applying the explicit least-squares approach of Mahon (1996). Errors for log \((D/\tau^2)\) were obtained by the method discussed in Appendix A and temperature uncertainty was assumed to be \(\pm 5^\circ\text{C}\). Although the least-squares fitting routine is not formulated to accommodate the correlations between data points that are imparted by the nature of the step-heating approach, our method for propagating correlated errors (see Appendix A) ensures that this effect is reflected in the overall uncertainty of individual data points. The goodness of fit (GOF) and Mean Square Weighted Deviate (MSWD) were calculated for each set of points. Close inspection of results from our samples led us to select the diffusion parameters corresponding to the maximum value of the GOF multiply by the number of data points (Fig. 2). This criteria appears better than simply selecting the set of points with maximum GOF since increasing the number of points tends to reduce the GOF but permits a more robust determination of the kinetic parameters. In some of our samples, the data first point is significantly displaced from the linear trend defined by the subsequent points. For these cases in which the first data point caused the maximum GOF to drop below 0.05, we treated it as an outlier and recalculated the regressions without this point.