The $^{40}$Ar/$^{39}$Ar Thermochronometry for Slowly Cooled Samples Having a Distribution of Diffusion Domain Sizes

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Many $^{40}$Ar/$^{39}$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 $^{40}$Ar/$^{39}$Ar age spectra and Arrhenius plots for $^{39}$Ar loss during step heating. For samples with a distribution of diffusion domain sizes, the form of the $^{39}$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 $^{40}$Ar/$^{39}$Ar and $^{39}$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 $^{39}$Ar release during step heating in the laboratory is also the mechanism responsible for argon loss or retention in the natural setting.

1. INTRODUCTION

The potassium-argon dating method, which uses the radioactive decay of $^{40}$K to stable $^{40}$Ar as the measure of time, has been widely and successfully applied to many different rock types of diverse ages [see Dalrymple and Lanphere, 1969]. Many common minerals lose Ar at geologically moderate temperatures, and thus the date obtained is not the time of crystallization but the time when the mineral was sufficiently cold to become an effectively closed system. This apparent shortcoming of the K-Ar system can be turned to advantage if the mechanism for loss is thermally activated, in which case a temperature can be associated with the age of each sample, making the system a thermochronometer.

Two developments were particularly important in K-Ar thermochronometry. The first was the realization by Merrihue and Turner [1966] that one can use neutron interactions to convert $^{39}$K to $^{39}$Ar, which led to what is now called the $^{40}$Ar/$^{39}$Ar dating method [see McDougall and Harrison, 1988]. By monitoring the release of $^{39}$Ar and $^{40}$Ar during step heating of a neutron-irradiated sample one obtains information on the amount of potassium present (based on total $^{39}$Ar released), the loss of argon, assumed to be due to molecular diffusion, as a function of temperature (from the amount of $^{39}$Ar released during each temperature step), and an age associated with each fraction of argon released. The measure of how the sample loses argon as a function of temperature is critical for estimating the closure temperature to which the age refers. The second development is theoretical, involving the formalism for defining and determining this closure temperature [Dodson, 1973].

Dodson assumed that the loss of argon is a thermally activated diffusion process which follows a simple Arrhenius equation of the form

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

(1)

where $D$ is the diffusion coefficient with value $D_0$ as the absolute temperature $T$ becomes very large, $R$ is the gas constant, and $E$ is the activation energy. The "frequency factor" $D_0$ and $E$ are determined from the release of $^{39}$Ar as a function of temperature in the step heating experiment. If the geological cooling of the sample near its closure temperature can be represented by a linear change with time of $1/T$, Dodson [1973] showed that the closure temperature $T_c$ of a uniform grain is given by

$$T_c = \frac{E}{R \ln \left( \frac{A_\tau D_0}{p^2} \right)}$$

(2)
where $\tau$ is the time required to diminish $D$ by a factor of $e$, $\rho$ is the characteristic size of the diffusion domains, which are often much smaller than the observed grain size, and $A$ is a numerical constant related to the geometry of the diffusion domains (see Dodson [1973] for values of $A$ for slabs, cylinders, and spheres). The time constant $\tau$ may also be expressed as

$$\tau = \frac{RT^2}{E(dT/dt)}$$

which requires some knowledge of the cooling rate $dT/dt$ as well as the activation parameters. For geologically reasonable cooling rates and typical $D_0$ and $E$ of common minerals, $T_c$ depends only weakly on $\tau$, and thus even a crude a priori estimate of $dT/dt$ is sufficient to determine $T_c$.

The Dodson theory for closure temperature, which we review in more detail in section 2, defines and gives the means for determining the temperature $T_c$ that the analyzed sample had at a time in the past corresponding to the age given by its total $^{40}\text{Ar}/^{39}\text{Ar}$, provided that the assumptions made in deriving the theory are met. Further analysis of the data generated by the $^{40}\text{Ar}/^{39}\text{Ar}$ method enables us to test these key assumptions. How a test might be devised is best illustrated by reviewing a recent effort to determine the cooling history of some plutonic rocks using this method.

Figure 1 shows the age spectra for three alkali feldspars from the Chain of Ponds pluton, northwestern Maine, measured in T. M. Harrison’s laboratory by Heizler et al. [1988]. The corresponding Arrhenius plots for these samples are shown in Figure 2. Note that in all three cases shown in Figure 2 there is a departure from linear behavior at temperatures above about 600°C. Heizler et al. invoked the suggestion by Harrison et al. [1986] that this high-temperature behavior reflected a structural breakdown of the sample during heating in the laboratory (i.e., an artifact of the laboratory experiment not relevant to the sample’s properties in nature), which had the effect of changing the diffusion properties. Therefore only data obtained at the lower temperatures were used to determine the diffusion parameters that in turn were used to calculate closure temperatures.

Closure temperatures were plotted against age based on the sample’s $^{40}\text{Ar}/^{39}\text{Ar}$, and we reproduce Heizler et al.’s [1988] Figure 12 as Figure 3. The three feldspar samples appear to define a smooth slow cooling history with changes of the order of 2°C–3°C per million years.

A test for the internal consistency of applying simple diffusion theory to such data is based on the realization that the shapes of the age spectra (Figure 1) contain information on the cooling rate experienced by each sample. If the system is behaving according to simple diffusion theory, then the rate of cooling that we deduce from the individual age spectra and that seen in Figure 3 should agree. In fact, these two estimates of the cooling rate do not agree.

The use of age spectra as estimators of the cooling rate is most easily illustrated by appropriately normalized theoretical age spectra such as we show in Figure 4. This particular representation of age difference ($\Delta$ age), normalized by $\tau$, as a function of cumulative $^{39}\text{Ar}$ loss is valid for all cooling rates and follows from the diffusive behavior of domains of uniform size. The key point is that the changes in age of an age spectrum are a measure of $\tau$, which in turn can be used to find $dT/dt$ (equation (3)).

The Arrhenius parameters $E$ and $D_0$ found from the low-temperature ($T < 600$°C) portions of Figure 2 together with the cooling rate implied by Figure 3 give a value for $\tau$ of about 7 Ma for all three samples. Calculated (assuming a single diffusion domain size) age spectra are compared with the observed age spectra normalized to this value of $\tau$ in...
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.

Figure 5. The changes in age in the observed spectra are significantly larger and affect much more of the sample's argon than those in the calculated spectra. Furthermore, the shape of the observed spectra have more structure (sometimes concave upward for the early released argon, a flat portion near 50% argon release, and a further increase in age between 60% and 100% argon release) than the smoothly increasing theoretical spectra. To quantify the discrepancy, we show in Figure 6 that the age spectra imply a much slower cooling rate \((dT/dt < 1°C/ Ma)\) corresponding to \(τ \sim 21 Ma\). Thus we see that if we assume a single diffusion domain size for the Chain of Ponds samples, we will arrive at two very different estimates of the cooling rate, one of order 3°C/Ma based on their closure temperatures versus time (Figure 3) and a slower cooling rate of < 1°C/Ma based on the shape of their age spectra (Figure 5). The conclusion is that for these three samples, and for numerous others that we have inspected but not explicitly modelled, the process of Ar loss is more complicated than that given by Dodson closure theory for diffusion domains of a single size.

The purpose of this paper is to identify the cause of the discrepancies noted above and to suggest new ways for treating the \(^{40}\text{Ar}/^{39}\text{Ar}\) data to arrive at results that are more nearly self-consistent. Because much of our analysis is based on an extension of Dodson's model for closure temperature, we begin in section 2 with a review of his model. In section 3 we consider if Dodson's assumption that \(1/T_{oct}\) is critical and if the observed discrepancy between the cooling rates derived from a set of closure temperatures and that determined by fitting curves to the age spectra might not arise from the fact that the samples had a cooling history with a different temperature dependence. We calculate \(^{40}\text{Ar}\) accumulation for cooling histories in which \(T, T^{-1/2},\) or \(T^{-1}\) varies linearly in time and interpret the results using Dodson's theory. We find that the temperature history is recovered almost perfectly even when the actual cooling was not that assumed in deriving the formula for closure temperature. In sections 4 and 5 we introduce the possibility that the samples analyzed consisted not of a single diffusion domain size but of a distribution of sizes, which Turner [1968] and Gillespie et al. [1982] already recognized as having an impact on the age spectra. In a more recent paper, Zeitler [1988] shows how a distribution of diffusion domain sizes will affect the Arrhenius curves as well. Not only are the observed age spectra better fit by the theoretical curves for appropriate choices of the distribution of domain sizes but so are the Arrhenius plots shown in Figure 2. The departure from linearity is due to the different domain sizes affecting different parts of the plot. The realization that the three samples from the Chain of Ponds pluton contain a distribution of diffusion domain sizes forces a reinterpretation of their cooling history with the expectation of increasing temperature by about 50°C above that originally estimated.

There are at least two very important practical implications if there exists a distribution of diffusion domain sizes. The first is that there will no longer be a single closure temperature; instead the analyzed properties of each sample will depend on a segment of the cooling curve that extends from the higher temperatures, where the largest grains begin to close, down to the colder temperatures at which the smallest grain size fraction finally closes. The second is that Arrhenius plots derived from step heating experiments on multidomain samples will reflect not only the relative sizes and volume fractions of the different domains but will also depend on the temperature and duration of the heating steps used. In other words, different heating schedules for the same sample will result in different Arrhenius plots. This
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.

being true, the effect of the heating schedule on the Arrhenius plot may well be the most direct demonstration of the existence of different diffusion domain sizes, and furthermore, variations of the heating schedule (i.e., cycling the temperature rather than having it monotonically increase) can be used to produce sufficiently diagnostic data for determining the size and diffusion properties of the various components of the distribution.

2. Dodson Theory and Extension

The Dodson theory for closure temperature makes use of the fact that solid diffusion processes are thermally activated and often obey a simple Arrhenius equation (1). The strong dependence on temperature of the diffusion coefficient makes the accumulation of $^{40}$Ar in a sample cooling from sufficiently high temperature pass through two distinct regimes. At high temperatures, $D$ is sufficiently large that virtually all $^{40}$Ar escapes as fast as it is produced and so does not accumulate, whereas at low temperatures the rate of escape becomes negligible and then $^{40}$Ar accumulates as for a closed system. There is a continuous transition from one regime to the other, and for the purpose of simplifying the analysis, the cooling history of the system during this transition is approximated by a linear increase in $1/T$ with
time. Then $D$ decreases as $D = D(0) \exp(-t/\tau)$, where $D(0) = D_0 \exp(-E/RT_0)$ with $T_0$ the temperature at $t = 0$, and $\tau$ is the time for $D$ to diminish by a factor $e$. The origin for time should be taken such that $T_0$ is sufficiently large for no argon to accumulate, and the expression for $\tau$ is given by equation (3).

The typical approach for finding the $^{40}$Ar/$^{39}$Ar cooling history of a set of samples is to first determine their Arrhenius parameters from the release of $^{39}$Ar during step heating and then to use (2) to assign a temperature $T_c$ to the age determined from each sample's total $^{40}$Ar/$^{39}$Ar. Calculating $T_c$ requires an estimate of $dT/dt$ through its dependence on $\tau$, and the process can be iterated to improve the estimate of $dT/dt$. The set ($T_c$, age) specifies the cooling history.

The dimensionless general accumulation equation with diffusion for a radiogenic daughter product can be written as

$$\frac{d(C/C_0)}{d\theta} = \tau D(0) \rho^{-2} e^{-\theta/\varphi} (C/C_0) + \lambda \tau e^{-\lambda \theta}$$

where $\varphi = t/\tau$, $C$ is the concentration of the daughter product and $C_0$ is the initial concentration of the parent, $\rho$ is a
characteristic linear dimension for the grains, and $\lambda$ is production rate of $^{40}$Ar by decay of $^{40}$K.

Let $^{40}\text{C}(r, \theta)$ be the solution to this equation with initial and boundary condition $^{40}\text{C} = 0$. It represents the present-day ($t = 0$) distribution of $^{40}$Ar in the sample before heating in the laboratory.

Dodson integrated $^{40}\text{C}(r, \theta)$ for samples of different geometry (spheres, cylinders, and slabs) subject to slow cooling to derive the relationship between the diffusion parameters and the closure temperature $T_c$ given in equation (2).

The $^{40}$Ar and $^{39}$Ar released during each step of heating in the laboratory can be calculated by again solving the above diffusion equation neglecting accumulation, with $C = 0$ as the boundary condition, and $C = ^{40}\text{C}(r, \theta)$ and $C = 1$ as initial conditions for $^{40}$Ar and $^{39}$Ar, respectively. In Appendix A we show how expressions given by Carslaw and Jaeger [1959] can be used to find the ratio of $^{40}$Ar/$^{39}$Ar for the $m$th heating step (from laboratory time $t_{m-1}$ to $t_m$). The resulting expression is

$$\frac{^{40}\text{Ar}/^{39}\text{Ar}}{m} = \sum_{n=1}^{\infty} \alpha_n^{-2} e^{-\alpha_n^2 \xi_m} \left[ e^{\alpha_n^2 \Delta \xi_m} - 1 \right] \left[ e^{-\lambda \tau \theta} \right]$$

where $J$ relates $^{39}$Ar to $^{40}$K, $\alpha_n$ depends on the geometry of the grain, being for spheres, plane slabs, and cylinders equal to $n \pi v r$, $(n - 1)(v r/2)$, and the positive roots of the Bessel function $J_n(x)$, respectively. $\Delta \xi_m$ is $\xi_m - \xi_{m-1}$, where $\xi_m$ is found by integrating the expression

$$\xi(t) = \int_0^t D(t')/\rho^2 \, dt'$$

from $t = 0$ to $t_m$.

All information about the cooling history is contained in the parameters $\xi_m$ which involve an integral expression (see Appendix A). Dodson determined $\xi_m$ for spheres, plane slabs, and cylinders assuming that $D(0)$ is large and that the system later became effectively closed. He obtained

$$\xi_n = \Gamma(1 + \lambda \tau)(\alpha_n^2 \tau D(0) \rho^2)^{-1}$$

where $\Gamma(x)$ is the gamma function. The dependence of $^{(40}\text{Ar}/^{39}\text{Ar})_m$ on cumulative fraction of $^{39}$Ar released ($^{39}f_m$) is obtained through their common dependence on $\xi_m$. The $^{39}f_m$ is related to $\xi_m$ by the expression

$$^{39}f_m = 1 - b \sum_{n=1}^{\infty} \alpha_n^{-2} e^{-\alpha_n^2 \xi_m}$$

where $b$ is a constant which depend on the geometry assumed ($b = 6, 2$, and $4$ for spheres, plane slabs, and cylinders, respectively). The age of Ar released during the $m$th step can be computed from equation (5),

$$\text{age}_m = \lambda^{-1} \ln \left[ 1 + J(^{40}\text{Ar}/^{39}\text{Ar})_m \right]$$

Another useful point is that in the limit $\lambda \tau << 1$ of expression (5), $(^{40}\text{Ar}/^{39}\text{Ar})_m$ depends on $\tau$ in such a way that we can obtain a universal curve by normalizing the age spectrum with $\tau$, as was first done by M. H. Dodson [see McDougall and Harrison, 1988]. The normalized age spectrum, for increments $\Delta \xi_m << \xi_m$, is then given by

$$\Delta \text{age}_m/\tau = \frac{2 \sum_{n=1}^{\infty} \ln(\alpha_n/\alpha_1) \exp(-\alpha_n^2 \xi_m)}{\sum_{n=1}^{\infty} \exp(-\alpha_n^2 \xi_m)}$$

where $\Delta \text{age}_m/\tau$ measures age differences along the age spectrum in units of $\tau$ relative to the age of the last argon extracted. Equations (9) and (7) can be used to calculate normalized age spectra for slowly cooled minerals of spherical, cylindrical, or plane slab geometry. Normalized spectra for spheres and plane slabs were shown in Figure 4, and we note that both curves have a flat portion for the last $^{39}$Ar released. From now on, we will use the word plateau to identify this flat portion of the age spectrum.

Dodson [1973] suggested that a "closure" temperature could also be associated with $^{40}\text{C}(0, \theta_0)$, the "age" of the argon at the central point of a mineral grain. The problem is that laboratory extractions of argon do not directly determine $^{40}\text{C}(0, \theta_0)$ and the "age" of argon at the central point is not the same as the age of the last argon extracted in a step heating experiment. What we need is the closure temperature corresponding to the age of the last gas released. We give below relations for what we will call a plateau temperature ($T_p$) corresponding to the plateau age ($\text{age}_m$ in the limit $\xi_m \gg 1$). One reason for stressing the age and closure temperature of the last gas released by a grain (plateau age and plateau temperature) is that in the case of multidomain samples these are more easily interpreted than the total argon age of the sample.

Let $\tau \theta_0$ be the plateau age, then taking the limit $\xi_m \gg 1$ (so that only the first term of the series in equation (5) is important), equation (8) reduces to

$$\lambda \tau \theta_0 = \ln(I e^{\lambda \tau \theta_0})$$

Substitution of $I$ from equation (6) gives

$$\theta_0 - \theta_p = -\frac{\ln(\Gamma(\lambda \tau + 1)) \rho^2 \tau D(0)}{\lambda \tau} + \ln(\alpha_1^2 \tau D(0)^{-2}) - E$$

By definition [see Dodson, 1973] we have

$$\theta_0 - \theta_p = \frac{E}{RT_p} - \frac{E}{RT_0}$$

so the plateau temperature ($T_p$), in the limit of $\lambda \tau << 1$ (appropriate to geological systems) is given by

$$T_p = \frac{E}{R \ln(\gamma s^2 \tau D(0)^{-2})}$$

where $s$ is Euler's constant. $T_p$ is the correct temperature to associate with the age of the last argon released.

3. EFFECT OF DIFFERENT COOLING HISTORIES

Many published $^{40}$Ar/$^{39}$Ar age spectra (i.e., Figure 1) show important discrepancies when compared to theoretical
age spectra calculated on the assumption of a single grain size (Figure 4). Examples of such discrepancies in both magnitude and shape are given in Figures 5 and 6.

In an effort to find the cause of these discrepancies we studied the effect of Dodson's assumption that over a limited range of temperatures, near $T_c$, the cooling history of a geochronological system can be approximated by a linear increase in $1/T$ with time. The question is whether a formalism based on this particular thermal history can be used, without systematic error, to analyze samples that underwent a different cooling history. We first calculated the accumulation of $^{40}$Ar in spherical or planar samples having different activation energies and subjected to various cooling histories ($T, T^{-1},$ and $T^{-1}$ changing linearly with time). By so doing, we have created a set of theoretical samples with known cooling histories. These theoretical samples are then subjected to step heating, much as one would do in the laboratory, and the release of $^{40}$Ar and $^{39}$Ar is calculated. Given the Arrhenius parameters and these synthetic data, we can use Dodson's theory to calculate the closure temperature and age for each sample. We can then compare the set ($T_c$, age) from samples having the same cooling history with their actual cooling history. For the set of samples with temperature history $T^{-1}$ linear in time (Dodson's assumed cooling history) the agreement should be perfect, and indeed it is as shown in Figure 7. The samples plotted in this figure differ slightly from each other in activation energy, which accounts for the spread in ages and closure temperatures. Somewhat surprisingly, equally good agreement is found even when the cooling history is quite different from $T^{-1}$ (Figures 8 and 9). We take this as evidence that the assumption made by Dodson regarding the form of the cooling curve when deriving the relation for closure temperature is not at all critical.

In terms of our present purpose it seems clear that the source of the discrepancy between the rate of cooling derived from a set of closure temperatures and that deter-
4. Generalization of Dodson Theory for a Mixture of Grains

In developing the theory of closure temperatures, Dodson [1973] generated expressions for the deficiency in $^{40}\text{Ar}/^{39}\text{Ar}$ in crystals of different geometry, subject to slow cooling, relative to what would be present had no diffusive losses occurred. In Appendix B we generalized these relationships for mixtures of grains of different sizes. The term grain is used here loosely in that what is relevant for argon loss is the distance argon diffuses before it finds a more rapid path of escape. Thus a distribution of grain sizes in our model could just as well (and in fact most probably does) refer to a distribution of effective sub-grain size diffusion distances. The "grains" are assumed to have identical diffusion parameters ($E, D_0$), and no interactions among themselves.

For a mixture of grains the normalized age spectrum ($\text{A} \Delta \text{age} / \tau$) will depend on the grain sizes $p_j$ and their volume fractions $\phi_j$, as shown by the relationships obtained in Appendix B for $\text{A} \Delta \text{age} / \tau$.

\[
\Delta \text{age}_m / \tau = 2 \sum_{j=1}^{S} \phi_j p_j^{-2} \sum_{n=1}^{\infty} \ln \left( \frac{\alpha_n \rho_j / \alpha_{1,0}}{\alpha_{n,0}} \right) \exp \left( -\alpha_{n,0}^2 \rho_j^2 / \rho_j^2 \right) \cdot \left( \sum_{j=1}^{S} \phi_j p_j^{-2} \sum_{n=1}^{\infty} \exp \left( -\alpha_{n,0}^2 \zeta_m / \rho_j^2 \right) \right)^{-1} \tag{14}
\]

and for the cumulative fraction argon released ($39f_m$),

\[
39f_m = \sum_{j=1}^{S} \phi_j \left( 1 - b \sum_{n=1}^{\infty} \alpha_n^{-2} \exp \left( -\alpha_{n,0}^2 \zeta_m / \rho_j^2 \right) \right) \tag{15}
\]

Without loss of generality we can normalized the volume fractions, setting $\Sigma \phi_j = 1$. Note that equations (14) and (15) reduce to Dodson's result (equations (6) and (7) for $s = 1$, for a single grain). Equations (14) and (15) can be used to construct normalized age spectra for a variety of different mixtures of grain sizes. Figure 10 shows age spectra for mixtures of the same three spherical grains ($\rho_1 = 0.02, \rho_2 = 0.2, \rho_3 = 1.$), but in different volume fractions ($\phi_j$). Next, we can keep the volume fraction of different grains constant and vary the radius of the grains to produce the curves of Figure 11. The general result is that the different size components, if sufficiently distinct, can produce local plateaus in the age spectra with the age of the local plateau depending on the size of the grains ($\rho_j$) and its position with respect to cumulative $39\text{Ar}$ released depending on the volume fractions of the different diffusion domains ($\phi_j$).

Our next step was to investigate the Arrhenius plots of samples containing a mixture of diffusion domains of different sizes. The relevant expressions are given in Appendix C, and we find that there exist only two limits (when the
cumulative fraction $39f$ is negligible or when the sample is almost exhausted, where the spectrum remains a linear function of $1/T$. Following the traditional method used for uniform grains, we obtain from the increment of $39f$ released per temperature step, the increment in a parameter we call $\Delta \xi_m^m$, and produce a plot of $\log(\Delta \xi_m^m/\Delta t_m)$ versus $1/T$. In both limits $\Delta \xi_m^m$ can be written as

$$\Delta \xi_m^m = (D_0/\hbar^2) \exp(-E/RT_m) \Delta t_m \tag{16}$$

This expression is identical to that for one uniform grain with $\hbar$ representing an effective grain size. In the case of a mixture the effective size $\hbar$ is a function of $\phi_j$ and $\rho_j$. In the limit of very little gas lost, $\hbar$ has a heavy bias toward the smallest grain size as can be seen from relation (C8):

$$\hbar(\phi_j, \rho_j) = \left\{ \sum_{j=1}^{\infty} \frac{\phi_j}{\rho_j} \right\}^{-1} \tag{17}$$

while in the second limit, when almost all the argon has been released, $\hbar$ coincides with the radius of the largest grain. In the intermediate range of Ar release, $\log(\Delta \xi_m^m/\Delta t_m)$ is no longer a linear function of $1/T$, as shown in Figure 14 for the different mixtures listed in Table 1.

The similarity between some of the multigrain model curves (age spectra from Figures 10–13 and the Arrhenius curves in Figure 14) and those obtained from real samples (Figures 1 and 2) suggests that we should look for specific mixtures of grain sizes that can approximate both the age spectrum and Arrhenius plots of the real samples. This we do in the next section along with a reinterpretation of the cooling history of the Chain of Ponds pluton.

A very important property of samples with a distribution of domain sizes is that different sequences of step heating will produce different Arrhenius plots. Zeitler [1988] recognized this and illustrated it by showing the effect on the Arrhenius plot of changing the duration of monotonically increasing temperature steps. Our goal is not only to demonstrate the existence of diffusion domains of different size but also to optimize the determination of kinetic parameters for argon loss from each component of the size distribution. For this purpose it may well prove more effective to cycle the temperature rather than to increase it monotonically. As an example, we show in Figure 15 the calculated Arrhenius curve for a thermally cycled experiment with the same distribution of grain sizes and Arrhenius parameters used earlier for curve 6 in Figure 14a. The heating schedule is such that we start with the sample at a high temperature but avoid coming too close to melting. The temperature is then rapidly reduced and later cycled, as shown in the inset. The Arrhenius curve shows that at first we obtain information on the properties of the smallest grains alone but that as the extraction of argon continues, the properties of the larger grains begin to be mapped out. The advantage of temperature cycling is that by repeatedly reducing the temperature one can obtain much more complete data with which to constrain the activation energy of the different size fractions present.

The effect illustrated in Figure 15 can also be seen in

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Curve & $\rho_1$ & $\phi_1$ & $\rho_2$ & $\phi_2$ & $\rho_3$ & $\phi_3$ \\
\hline
1 & 0.02 & 0.0 & 0.2 & 0.0 & 1.0 & 1.0 \\
2 & 0.02 & 0.0 & 0.2 & 0.32 & 1.0 & 0.68 \\
3 & 0.02 & 0.0 & 0.2 & 0.55 & 1.0 & 0.45 \\
4 & 0.02 & 0.083 & 0.2 & 0.50 & 1.0 & 0.417 \\
5 & 0.02 & 0.154 & 0.2 & 0.46 & 1.0 & 0.386 \\
6 & 0.02 & 0.267 & 0.2 & 0.40 & 1.0 & 0.333 \\
7 & 0.001 & 0.267 & 0.2 & 0.40 & 1.0 & 0.333 \\
8 & 0.0001 & 0.267 & 0.02 & 0.40 & 1.0 & 0.333 \\
\hline
\end{tabular}
\caption{Diffusion Domain Distribution}
\end{table}
Fig. 14. Theoretical Arrhenius plots calculated for the mixtures used in Figures 10-13. Figure 14a shows the Arrhenius plots for mixtures of spheres and Figure 14b for mixtures of plane slabs. The plots are for increasing temperature steps of 30°C held for 15 min. In both figures, departures from linearity are due to a distribution of domain sizes.

5. REINTERPRETING THE COOLING HISTORY OF THE CHAIN OF PONDS

We can now reinterpret the results obtained by Heizler et al. [1988] for the three samples from Chain of Ponds pluton. The departure from linear behavior at high temperatures in their Arrhenius plots (Figure 2) was attributed by them to a change in the diffusion parameters due to a structural break-

experiments with natural samples degassed by nonmonotonic heating schedules. Figure 16 shows the original Arrhenius plot points for sample MH-8 along with new data for a split from the same sample obtained by varying the temperature as shown in the inset. The new data are clearly superior. To begin with, the earliest gas released no longer indicates anomalously low diffusivities. Why the original data showed this departure from linearity for the first few temperature steps we do not know. The new and old data are in good agreement in terms of what we now interpret to be the Arrhenius parameters of the smallest grain size fraction.

Note, however, that because shorter time steps were used, the new data extend along a linear trend to significantly higher temperatures than the old data, which we take as evidence that the eventual departure of the data from a single linear trend is not due to structural decomposition once the sample exceeds some critical temperature but instead reflects the exhaustion of gas coming from the smallest domain size. Both the old and new data show the existence of more retentive domains, which we interpret as resulting from a larger diffusion domain size, but only the new data characterize these domains over a sufficiently large range of temperature to provide a useful constraint on their activation energy. It appears that the activation energy of the different sized domains of this sample (MH-8) are quite similar.

Fig. 15. Arrhenius plot for the same sample used for curve 6 (Figure 14a and Table 1) but now thermally cycled. The heating schedule is such that we start with the sample at a high temperature but avoid coming too close to melting, then the temperature is rapidly reduced (open squares), and later cycled (first triangles and later solid squares) as shown in the inset. When an open square and a triangle coincide, the square appears to be solid. The Arrhenius plot (using the same symbols) shows that at first we obtain information on the properties of the smallest grains alone but that as the extraction of argon continues, the contributions from the larger grains begin to be mapped out. This figure suggests that thermal cycling can be used to demonstrate the existence of different diffusion domain sizes within a single sample and, if the cycles are judiciously chosen, to map out the Arrhenius parameters of the different size fractions.
lowered again (solid diamond) and finally raised (solid triangles) in linear trend with lower diffusivity. The temperature was then in their center) and later raised (open squares) to bring out a second trend. The temperature was then lowered (open squares with a dot) first raised (solid squares) until the data began to depart from a linear extraction temperatures shown in the inset. The temperature was

and further show that the activation energies of these domains are a much clearer indication of at least two distinct diffusion domains while in its natural environment. The result shown in Figure 16 supports this claim rather dramatically in the case of sample MH-8 by showing that reruning the sample with shorter time steps shifts the departure from linearity to much higher temperature.

We do not yet have a formalism for directly finding the optimum distribution of domain sizes and therefore have proceeded by trial and error. As a starting point we will insist that the smallest grain size fraction be such as to reproduce the linear low-temperature portion of the Arrhenius curve. From the slope of this linear range we determine the activation energy $E$, which we assume is representative for all the size fractions. That all domains have the same activation energy is the simplest assumption and is supported by a number of Arrhenius plots from recent experiments using thermal cycling (O. M. Lovera et al., manuscript in preparation, 1989). The volume fraction of the smallest grain size is given by the point at which the data in the Arrhenius plot depart from linearity. We then turn to the age spectra for estimates of the volume fractions and relative sizes of the larger domains. Recall that the model spectra given earlier showed that the difference in age between local age plateaus is a measure of relative size, while the extent of the plateaus will give an estimate of the volume fractions. In most cases, inspection of the Arrhenius plot and the age spectrum is sufficient to fix the distribution function for relative size and volume fraction. The only remaining degree of freedom is then the shape of the cooling curve for the interval over which the various domains close, which may be as long as 100 m.y. We adjust the cooling history for each sample until we obtain a satisfactory fit to the entire age spectrum. In general, we find the age spectra to be quite sensitive to the detailed structure of the cooling curve. For example, in the case of the three samples studied here the shape of the spectra for the first 30% $^{39}$Ar released requires a significant slowing down of the rate of cooling compared to that during the closure of the larger grain size fractions.

![Graph](image)

**Fig. 16.** Remeasured Arrhenius plot for sample MH-8 using the extraction temperatures shown in the inset. The temperature was first raised (open squares) until the data began to depart from a linear trend. The temperature was then lowered (open squares with a dot in their center) and later raised (open squares) to bring out a second linear trend with lower diffusivity. The temperature was then lowered again (solid diamond) and finally raised (solid triangles) in steps to fusion. The crosses show the original data for MH-8 (from Figure 2) obtained by Heizler et al. [1988] using monotonically increasing temperature steps each lasting 15 min. The new data give a much clearer indication of at least two distinct diffusion domains and further show that the activation energies of these domains are similar.

<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 $\times 10^{14}$</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 $\times 10^{14}$</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 $\times 10^{14}$</td>
<td>185.0 ± 6.0</td>
</tr>
</tbody>
</table>

From Heizler et al. [1988].

**TABLE 3. Size Distribution**

<table>
<thead>
<tr>
<th></th>
<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>
<td>$\rho_j$</td>
</tr>
<tr>
<td>1</td>
<td>0.018</td>
<td>0.15</td>
<td>0.008</td>
</tr>
<tr>
<td>2</td>
<td>0.182</td>
<td>0.30</td>
<td>0.333</td>
</tr>
<tr>
<td>3</td>
<td>0.545</td>
<td>0.40</td>
<td>1.0</td>
</tr>
<tr>
<td>4</td>
<td>1.0</td>
<td>0.15</td>
<td>1.0</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th></th>
<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>
<td>38.0 ± 1.0</td>
</tr>
<tr>
<td>$D_0/\rho^2$, s$^{-1}$</td>
<td>3.1 ± 0.2</td>
<td>78.0 ± 2.0</td>
<td>3.6 ± 0.2</td>
</tr>
<tr>
<td>$T_p(\rho_1)$, °C</td>
<td>315.0 ± 15.</td>
<td>357.0 ± 15.</td>
<td>235.0 ± 15.</td>
</tr>
<tr>
<td>$T_p(\rho_2)$, °C</td>
<td>354.5 ± 5.0</td>
<td>369.0 ± 5.0</td>
<td>312.0 ± 5.0</td>
</tr>
<tr>
<td>$T_p(\rho_3)$, °C</td>
<td>296.0 ± 15.</td>
<td>314.0 ± 15.</td>
<td>217.0 ± 15.</td>
</tr>
<tr>
<td>$T_p(\rho_4)$, °C</td>
<td>348.0 ± 5.0</td>
<td>353.0 ± 5.0</td>
<td>297.0 ± 5.0</td>
</tr>
<tr>
<td>$T_p(\rho_5)$, °C</td>
<td>265.0 ± 15.</td>
<td>254.0 ± 15.</td>
<td>200.0 ± 15.</td>
</tr>
<tr>
<td>$T_p(\rho_6)$, °C</td>
<td>335.0 ± 5.0</td>
<td>293.0 ± 15.</td>
<td>282.0 ± 5.0</td>
</tr>
<tr>
<td>$T_p(\rho_7)$, °C</td>
<td>204.0 ± 15.</td>
<td>156.0 ± 15.</td>
<td>234.0 ± 15.</td>
</tr>
</tbody>
</table>
Fig. 17. Measured age spectra for the three alkali feldspars from the Chain 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.

The reinterpreted results for the three samples from the Chain of Ponds pluton are summarized in Tables 3 and 4 and Figures 17–19. Table 3 gives the size distribution and Table 4 gives the activation energy \( E \) and frequency factor \( D_0 \) (with \( \rho_s \) normalized to 1) for all three samples. Figure 17 shows the degree of fit to the age spectra obtained with these parameters using the cooling curves shown for each sample in Figure 19. Figure 18 shows the degree to which the parameters given in Tables 3 and 4 are able to reproduce the observed Arrhenius data. The improvement over the fit that can be obtained by assuming a single diffusion domain size is dramatic.

A new estimate for the cooling history of the Chain of Ponds pluton can be made using the individual segments of
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.

This history seen by each of the samples. These segments are shown in Figure 19 along with points corresponding to the closure temperature of each grain size fraction to give an indication of which size fraction determines the various parts of the segment. In Table 4 we list the closure temperatures (from equation (2)) along with the age along the appropriate segment when this temperature is achieved. The most obvious effect of our reinterpretation is to shift the cooling curve to higher
temperature relative to Heizler et al.'s [1988] interpretation. The main reason for this is that Heizler et al. used the Arrhenius parameters for the smallest domain size to calculate a closure temperature that they then associated with an age corresponding to the largest domains in the distribution. Consequently, their closure temperature was too low.

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 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 trend defined by eight other grain fractions is not clear. The reason for this is that Heizler et al. used the Arrhenius parameters for the smallest domain size to calculate a closure temperature that they then associated with an age corresponding to the largest domains in the distribution. Consequently, their closure temperature was too low.

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% 39Ar 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.

6. SUMMARY AND DISCUSSION

The present study began as an effort to test a basic assumption of the 40Ar/39Ar method, which is that Ar loss from geological samples is the result of thermally activated diffusion and that geologically relevant diffusion parameters can be obtained by laboratory step heating experiments. The test involves comparing the rate of cooling, determined by joining a set of closure temperature-age estimates (using Dodson's formalism for the closure temperature of minerals composed of a single dominant grain size), to the rate of temperature change needed to account for the shape of the individual 40Ar/39Ar age spectra. Had we found good agreement between these two estimators of the cooling rate, the case for simple diffusive behavior would have been compelling. In fact, we did not find good agreement; the discrepancy in the estimated rate of cooling was greater than a factor of 3. The cause of this discrepancy does not appear to be differences in the actual cooling history from the linear increase in 1/T with time assumed by Dodson, and thus something more profound appears to be wrong with the commonly used formalism for interpreting 40Ar/39Ar data when applied to the samples considered here.

An important clue as to cause of the discrepant estimates of cooling rate already exists in the Arrhenius plots, which show departures from the linearity one would expect for thermally activated diffusion from domains of equal size and activation energy. These departures from linearity can be explained if there is a distribution of different grain sizes within each sample. To explore this possibility, we developed a formalism for calculating age spectra and Arrhenius plots for such multidomain samples and then calculated synthetic spectra and Arrhenius plots for a variety of different grain size distributions as a guide to reinterpreting the data from Chain of Ponds pluton.

We showed that the Arrhenius plots for samples with a distribution of diffusion domain sizes depend not only on the activation energy, frequency factor, and size distribution but also on the specific heating schedule (the temperature and duration of each step) used. This suggested that subjecting a given sample to different heating schedules would provide a way of demonstrating the existence of diffusion domains of different sizes. Furthermore, careful design of heating schedules will produce Arrhenius plots that more clearly expose the properties of the various size fractions separately. We showed this by a remeasurement of sample MH-8.

We reinterpreted three Chain of Ponds pluton samples using a model containing a distribution of grain sizes. We found for each sample a distribution of domain sizes such that we were able to fit both the observed age spectrum and the Arrhenius plot and also to constrain a segment of the cooling history, which should be consistent with the cooling history segments found from the other samples. The degree to which we have succeeded is shown in Figures 17-19. Differences among the various cooling history segments provide a measure of the uncertainty one should attach to the overall cooling history of the pluton.

The revised cooling history of the Chain of Ponds pluton shown in Figure 19 lies above the Heizler et al. [1988] curve.
defined by the closure temperatures estimated using a single domain size model, primarily because in the single grain size model the diffusion parameters of the smallest grain size fraction were used to determine \( T_c \) but the age assigned was that of the largest grains. If Arrhenius parameters appropriate to the large grain fraction had been used instead, the closure temperatures would fall much closer to our reinterpreted curve. An interesting question is whether a revision of the cooling history of the magnitude we show is important. Depending on one’s point of view, a few tens of degrees more or less might seem insignificant. However, an important application of the \( ^{40}\text{Ar}/^{39}\text{Ar} \) method is to situations where samples such as those studied here are reheated (in a sedimentary basin for example), and one hopes to use the associated loss of argon to say something about magnitude and duration of this reheating event (e.g., will it lead to hydrocarbon maturation?). In this type of application, errors of the order of tens of degrees for tens of millions of years are unacceptably large. Even in the case of slow cooling there is good reason to strive for the greatest accuracy possible. The slow cooling recorded by the alkali feldspars from areas such as the Chain of Ponds pluton is in all likelihood due to uplift and erosion, and thus an accurate cooling curve is critical for the determination of reliable estimates of the timing and rate of uplift.

Perhaps the single most important conclusion of this study is that thermally activated diffusion is indeed the mechanism controlling Ar loss from feldspar minerals and that the formalism due originally to Dodson, when modified to allow for the possibility multiple diffusion domain sizes, can be used to recover a reliable thermochronometric information. This view is not shared by Parsons et al. [1988], who argue that argon loss from alkali feldspars in nature occurs by a different process than in the laboratory and thus age spectra for such minerals are not reliable. This contrast in views may result in part from the altered nature of the samples used by Parsons et al. [1988]. Their Arrhenius plots apparently show a great deal of scatter even at low temperatures, a condition that we have rarely observed and certainly does not occur for the samples used in the present study. The strength of our conclusion rests on the fact that both the Arrhenius data, derived in the laboratory over the course of a few hours, and the details of the age spectra, which were produced in nature over millions of years, are quite consistent once one allows for a distribution of diffusion domain sizes.

Our use of a diffusion domain size distribution to explain the \( ^{39}\text{Ar} \) Arrhenius plots and \( ^{40}\text{Ar}/^{39}\text{Ar} \) age spectra of alkali feldspars warrants speculation as to the nature of the domain boundaries. It has long been suggested [e.g., Foland, 1974] that exsolution lamellae, which form in alkali feldspars during slow cooling, define a continuum in which argon transport proceeds by a volume diffusion process and their boundaries act as pathways for rapid argon transport. This view was recently criticized by Parsons et al. [1988], who argue that their observations that perthite lamellae are often coherent rules these features out as fast diffusion boundaries. Nonetheless, a strong relationship between argon loss and manifestly coherent exsolution lamellae has previously been documented for Huttenlocher exsolution in calcic plagioclase [Harrison and McDougall, 1981] and for hornblende-cummingtonite exsolution in amphibole [Harrison and Fitz Gerald, 1986]. These studies suggest that coherency is not a strict measure of argon permeability, although the precise nature of argon transport along these zones is not understood. Other suggested features such as dislocations, stepped twins and orthoclase enclaves in microcline [Zeitler and Fitz Gerald, 1986] are plausible, although the absence of a domain size continuum is suggestive of a more regulated mechanism. We view as unlikely the notion that adsorption of argon on the walls of micron-sized tubes [Parsons et al., 1988] is responsible for the low retentivity release.

Assuming that the frequency factor obtained by Foland [1974] for homogeneous orthoclase is intrinsic to all alkali feldspars, we can use our estimates of \( D_0/\rho^2 \) for the various domain sizes (Tables 3 and 4) to determine the actual sizes involved. For a slab geometry, the smallest domain size for the three ranges from 3 to 9 \( \mu \text{m} \), roughly the dimension separating the twin boundary steps and dislocation sub-boundaries in the study by Zeitler and Fitz Gerald [1986] and the spacing of perthite lamellae in MH-42. The largest domain size in all cases is approximately 250 \( \mu \text{m} \), somewhat less than the particle size analyzed by Heizler et al. [1988]. Important added information comes from a study presently under way involving \( ^{40}\text{Ar}/^{39}\text{Ar} \) measurements of a single grain from the original MH-8 separate. The preliminary result is that even a single physical grain contains a distribution of diffusion subdomains not unlike that found when analyzing several grains together. The subdomains appear to be an intrinsic property of the alkali feldspars, not separable by careful selection of the grains to be analyzed, and thus requiring the methods developed here for their use as thermochronometers.

**Appendix A: \( ^{40}\text{Ar}/^{39}\text{Ar} \) Released by Step Heating: Single Grain Theory**

In order to calculate the \( ^{40}\text{Ar} \) released during each heating step in the laboratory we first must determine \( 40C(r, t_0) \), the distribution of \( ^{40}\text{Ar} \) contained in the sample at \( t = t_0 \) (i.e., immediately before laboratory degassing). \( 40C(r, t_0) \) is the solution of equation (4) with zero as both boundary and initial condition. To determine the release of \( ^{40}\text{Ar} \) in the laboratory, we must solve the diffusion equation but now using \( 40C(r, t_0) \) as the initial condition. Following Dodson [1973], equation (4) can be reduced to the diffusion equation with a time dependent boundary condition by applying a change of variable of the form

\[
V = 1 - e^{-\lambda t\theta} - C \\
\xi(\theta) = \tau \int_0^\theta D(t')/\rho^2 dt'
\]

the governing equation becomes

\[
dV/d\xi = \nabla^2 V
\]

with

\[
V(r, 0) = 0
\]

and

\[
V(r, \xi) = 1 - e^{-\lambda \tau \theta(\xi)}/2
\]

at the boundary.

A solution is found applying Duhamel’s theorem [Carslaw and Jaeger, 1959], and it can be written as
where \( V = \sum_{n=1}^{\infty} (-1)^{n+1} \alpha_n U(a_n r) \int_0^\xi [1 - e^{-\lambda r \theta(x)}] e^{-a_n^2 (\xi - x)} \, d\chi \) (A3)

where \( U(a_n r) \) are the eigenfunctions of the Laplace's operator satisfying the boundary condition and \( \alpha_n \) are its eigenvalues.

Integrating the term independent of \( \theta(x) \), we have

\[
V = \sum_{n=1}^{\infty} (-1)^{n+1} \alpha_n^{-1} U(a_n r) [1 - I_n] \quad (A4)
\]

where

\[
I_n = e^{-a_n^2 \xi} + \alpha_n^2 \int_0^\xi e^{-\lambda r \theta(x)} e^{-a_n^2 (\xi - x)} \, d\chi \quad (A5)
\]

The eigenfunctions \( U(a_n r) \) form a complete set; therefore they satisfy orthogonality and completeness relationships of the form

\[
\frac{1}{\Omega} \int_{\Omega} U(a_n r) U(a_m r) \, d\Omega = \delta_{mn} \quad (A6)
\]

\[
\frac{1}{\Omega} \sum_{n=1}^{\infty} U(a_n r) U(a_n r') = \delta(r - r') \quad (A7)
\]

where \( \Omega \) is the volume of the sample, \( \delta_{mn} \) is the Kronecker delta, \( \delta(r - r') \) is the Dirac delta, and \( b \) is a constant which depends on the particular geometry involved. In the cases of spherical, planar, or cylindrical geometry the eigenfunctions and eigenvalues are given by

**Spherical**

\[
U(a_n r) = \frac{2 \sin (\alpha_n \pi)}{r} \quad (A8a)
\]

\[ 1 \geq r \geq 0 \quad b = 6 \quad \alpha_n = n \pi \]

**Planar**

\[
U(a_n r) = 2 \cos (\alpha_n r) \quad (A8b)
\]

\[ 1 \geq r \geq -1 \quad b = 2 \quad \alpha_n = \frac{(2n-1)\pi}{2} \]

**Cylindrical**

\[
U(a_n r) = \frac{2(-1)^{n+1} J_0(a_n r)}{J_1(a_n)} \quad (A8c)
\]

\[ 1 \geq r \geq 0 \quad b = 4 \quad \alpha_n = \text{positive roots of } J_0 \]

\( J_0(r) \) and \( J_1(r) \) are the Bessel functions of the first kind. Substitution of these eigenfunctions in equation (A4) led to the same expressions obtained by Carslaw and Jaeger [1959]. Thus the distribution of \( ^{40}\text{Ar} \) in the sample at the present day is

\[
^{40}\text{C}(r, \theta_0) = 1 - e^{-\lambda r \theta_0} - \sum_{n=1}^{\infty} (-1)^{n+1} \alpha_n^{-1} U(a_n r) [1 - I_n] \quad (A9)
\]

where \( \theta_0 \) represents a nondimensional time in the past when the \( ^{40}\text{Ar} \) in the sample was effectively zero. Dodson [1973] determined \( I_n \) for slow cooling samples (equation (6)) by integrating equation (A5).

Now, let \( C(r, \zeta_m) \) be the concentration in the sample after \( m \) laboratory heating steps \( (t = t_m) \), where \( \zeta_m \) is defined as

\[ \zeta_m(t_m) = \int_0^{t_m} D(t')/\rho^2 \, dt' \]

Then \( C(r, \zeta_m) \) is the solution of

\[ dC/d\zeta = \nabla^2 C \quad (A10) \]

with

\[ C(r, 0) = ^{40}\text{C}_0(r, \theta_0) \]

and

\[ C(r, \zeta) = 0 \]

at the boundary.

We can again write the solution using the Laplacian eigenfunction expansion; thus

\[
C(r, \zeta_m) = \sum_{n=1}^{\infty} \frac{1}{b\Omega} \int_{\Omega} U(a_n r) e^{-a_n^2 \zeta_n} \int_0^{t_m} D(t')/\rho^2 \, dt' \, U(a_n r') \, 40\text{C}(r', \theta_0) \, d\Omega \quad (A11)
\]

Expressions given by Carslaw and Jaeger [1959] are recovered by substituting the particular eigenfunctions given in (A8) into (A11). For the three geometries considered, the eigenfunctions satisfy the integral relation

\[
\frac{1}{\Omega} \int_{\Omega} U(a_n r) \, d\Omega = \frac{b(-1)^{n+1}}{\alpha_n} \quad (A12)
\]

which is used when integrating twice the completeness relation (A7) to obtain

\[
b \sum_{n=1}^{\infty} \alpha_n^{-2} = 1 \quad (A13)
\]

The cumulative \( ^{40}\text{Ar} \) released per unit volume \( (^{40}f_m) \) after the \( m \)th heating step is simply

\[
^{40}f_m = \frac{1}{\Omega} \int_{\Omega} \left[ ^{40}\text{C}(r, \theta_0) - C(r, \zeta_m) \right] \, d\Omega \quad (A14)
\]

Substitution of expressions (A9) and (A11) in equation (A14), then using the orthogonality relationship (A6) and equations (A12) and (A13) gives

\[
^{40}f_m = b \sum_{n=1}^{\infty} \alpha_n^{-2} [1 - e^{-a_n^2 \zeta_m}] I_n - e^{-\lambda r \theta_0} \quad (A15)
\]

Similarly, the cumulative fraction of \( ^{39}\text{Ar} \) released after the \( m \)th step, \( ^{39}f_m \) given by equation (7), is obtained by solving the diffusion equation (A11) with the same boundary condition as above but with \( C = 1 \) as the initial condition.
Equation (5) for the ratio \((^{40}\text{Ar}/^{39}\text{Ar})_m\) is determined by calculating the \(^{40}\text{Ar}_m\) and \(^{39}\text{Ar}_m\) released at the \(m\)th heating step, subtracting from the cumulative argon the argon released in the previous steps, \((^{40}\text{Ar}_m = {^{40}\text{Ar}}_{f_{m-1}} - {^{40}\text{Ar}}_{f_m})\), \(^{39}\text{Ar}_m = J e^{-\lambda t_0} (^{39}\text{Ar}_{f_{m-1}} - {^{39}\text{Ar}}_{f_m})\). The factor \(J e^{-\lambda t_0}\) is the total \(^{39}\text{Ar}\) extracted in the laboratory per unit concentration of \(^{40}\text{K}\).

**APPENDIX B: GENERALIZATION OF DODSON THEORY FOR A MIXTURE OF GRAINS**

Here we will generalize relationships for a single grain to the equivalent expressions for a mixture of grains of different sizes. The different grain size fractions are assumed to be identical in their diffusion parameters \((E, D_0)\) and potassium concentration. It is further assumed that there is no interaction among the different grain size fractions.

Let \(\phi_j\) be the volume fraction of diffusion domains with characteristic dimension \(p_j\). A measure of the argon loss during heating is given by

\[
\Delta t_m = t_m - t_{m-1}
\]

\[
= D_0 \exp \left(\frac{-E}{RT_m}\right) \Delta t_m \quad \text{(B1)}
\]

where \(T_m\) and \(\Delta t_m\) are the temperature and duration of the \(m\)th heating step and \(t_0 = 0\).

The generalization to multiple diffusion domains is now quite simple since the total amount of \(^{40}\text{Ar}\) and \(^{39}\text{Ar}\) loss in the \(m\)th heating step is obtained by adding up the release from each separate size fraction:

\[
^{40}\text{Ar}_m = \phi_j \sum_{j=1}^{s} \alpha_n^{-2} \exp \left(-\alpha_n^2 \Delta \xi_m / p_j^2\right) \sum_{n=1}^{\infty} \exp \left(-\alpha_n^2 \xi_m / p_j^2\right) - 1 \quad \text{(B2)}
\]

\[
^{39}\text{Ar}_m = J e^{-\lambda t_0} \phi_j \sum_{j=1}^{s} \alpha_n^{-2} \exp \left(-\alpha_n^2 \Delta \xi_m / p_j^2\right) \sum_{n=1}^{\infty} \exp \left(-\alpha_n^2 \xi_m / p_j^2\right) - 1 \quad \text{(B3)}
\]

where \(s\) is the number of different diffusion domain sizes in the distribution and \(\phi_j\) is the present time relative to and arbitrary origin \(t = 0\) when the sample is still sufficiently hot so that it does not retain any \(^{40}\text{Ar}\).

When the cooling history is of the form \(1/T \propto t\), then

\[
I_n = \Gamma(1 + \lambda \tau) (\alpha_n^2 D(0) p_j^2)^{-1} - \lambda \tau \quad \text{(B4)}
\]

For all other cooling histories one can choose \(\tau\) equal to that corresponding to the largest domain size and find \(I_n\) by numerically integrating (A5), defining for each domain size

\[
\xi(\theta) = \xi_f(\theta) = \tau \int_0^\theta D(t') / p_j^2 dt' 
\]

Finally, the age at the \(m\)th step is again given by

\[
\text{age}_m = (1/\lambda) \ln \left(1 + \left(^{40}\text{Ar}_m / ^{39}\text{Ar}_m\right) / J\right) \quad \text{(B5)}
\]

In the limit of \(\lambda \tau \ll 1\) (i.e., cooling duration short compared to the half-life) we can combine (B2)–(B5) to obtain the age spectrum normalized by \(\tau\):

\[
\Delta \text{age}_m / \tau = -2 \sum_{j=1}^{s} \phi_j \sum_{n=1}^{\infty} \alpha_n^{-2} \ln \left(\alpha_n^2 p_j / \alpha_1 p_j\right) - \exp \left(-\alpha_n^2 \Delta \xi_m / p_j^2\right) \sum_{n=1}^{\infty} \exp \left(-\alpha_n^2 \xi_m / p_j^2\right) \left(\sum_{n=1}^{\infty} \exp \left(-\alpha_n^2 \xi_m / p_j^2\right) - 1\right) \quad \text{(B6)}
\]

which without loss of generality has been normalized to give \(\Delta \text{age}_m / \tau = 0\) for \(\xi_m \gg 1\).

In the limit \(\Delta \xi_m \ll \xi_m\), we can obtain a simpler equation, which is very useful for carrying out the actual calculations, namely,

\[
\Delta \text{age}_m / \tau = -2 \sum_{j=1}^{s} \phi_j \sum_{n=1}^{\infty} \ln \left(\alpha_n^2 p_j / \alpha_1 p_j\right) - \exp \left(-\alpha_n^2 \Delta \xi_m / p_j^2\right) \sum_{n=1}^{\infty} \exp \left(-\alpha_n^2 \xi_m / p_j^2\right) \left(\sum_{n=1}^{\infty} \exp \left(-\alpha_n^2 \xi_m / p_j^2\right) - 1\right) \quad \text{(B7)}
\]

The normalized age spectrum is a plot of \(\Delta \text{age}_m / \tau\) (age change along the spectrum relative to the age of the last argon released measured in units of \(\tau\)) as a function of cumulative percent \(^{39}\text{Ar}\) released during step heating. The generalized expression for \(^{39}\text{Ar}_{f_m}\) was given in equation (15).

**APPENDIX C: ARRHENIUS PLOTS FROM A DISTRIBUTION OF GRAINS**

In his formalism for argon release from a single uniform grain size, Dodson [1973] assumed that solid diffusion processes follow the simple Arrhenius equation (1). We will here treat a distribution of grain sizes, retaining the assumption that each size fraction obeys the Arrhenius equation and that aside from size, all fractions have the same activation energy \(E\) and frequency factor \(D_0\).

The cumulative argon loss at the \(m\)th step of heating in the laboratory from a sample containing different domain sizes will be given by

\[
^{39}\text{Ar}_m = \phi_j \sum_{j=1}^{s} \alpha_n^{-2} \exp \left(-\alpha_n^2 \Delta \xi_m / p_j^2\right) \sum_{n=1}^{\infty} \exp \left(-\alpha_n^2 \xi_m / p_j^2\right) \left(\sum_{n=1}^{\infty} \exp \left(-\alpha_n^2 \xi_m / p_j^2\right) - 1\right) \quad \text{(C1)}
\]

where \(g_j(\xi_m)\) represents the cumulative argon released by the \(j\)th diffusion domain size.

In the laboratory experiment one measures \(^{39}\text{Ar}_{f_m}\), which in the case of a single grain size can be inverted to recover \(^{39}\text{Ar}(\xi_m)\). A plot of \(\log (\Delta \xi_m / \Delta t_m)\) versus \(1/T\) will be linear and sufficient to determine \(D_0\) and \(E\). Unfortunately, when there exists more than one characteristic grain size, this inversion of \(^{39}\text{Ar}_{f_m}\) for \(\xi_m\) is no longer possible because of the
summation over the unknown grain size distribution in equation (C1). We can still proceed in the traditional way by assuming a relationship of the form

$$39f_m = 1 - b \sum_{n=1}^{\infty} \alpha_n^{-2} \exp\left(-\alpha_n^2 \xi_m^*\right)$$  \hspace{1cm} (C2)

which defines $\xi_m^*$, but this will only be useful if we can relate $\xi_m^*$ to $\xi_m$ since it is only $\xi_m$ that contains the relevant information on diffusion as a function of temperature. Given laboratory data on $39f_m$, we can invert (C2) for $\xi_m^*$ and plot $\log (\Delta \xi_m^* / \Delta t_m)$ versus $1/T$ as in the traditional Arrhenius plot. However, we will find that the function log ($\Delta \xi_m^* / \Delta t_m$) is no longer linear in $1/T$ for most $m$, since $\Delta \xi_m^*$ is not a linear function of $\xi_m$. Equations (C1) and (C2) can still be used to relate in particular limits $\Delta \xi_m^*$ (that which we can obtain from laboratory measurements) to $\Delta \xi_m$ (that which contains information on the Arrhenius parameters of the grains).

Approximate forms of equation (C2) are useful for interpreting $\xi_m^*$, and these are given by Crank [1975], Jain [1958], Jost [1960], and Reichenberg [1953]. We reproduce some of these below for different geometries:

### Spheres

$$39f_m = 1 - b \frac{\xi_m^*}{\alpha^2} \exp\left(-\alpha_m^2 \xi_m^*\right) \hspace{1cm} 39f_m > 0.85$$  \hspace{1cm} (C3a)

$$39f_m = b \left(\frac{\xi_m^*}{\pi}\right)^{1/2} - 3\xi_m^* \hspace{1cm} 0 < 39f_m < 0.85$$

### Plane slabs

$$39f_m = 1 - b \frac{\xi_m^*}{\alpha_m^2} \exp\left(-\alpha_m^2 \xi_m^*\right) \hspace{1cm} 39f_m > 0.60$$  \hspace{1cm} (C3b)

$$39f_m = b \left(\frac{\xi_m^*}{\pi}\right)^{1/2} \hspace{1cm} 0 < 39f_m < 0.60$$

### Cylinders

$$39f_m = 1 - b \frac{\xi_m^*}{\alpha_m^2} \exp\left(-\alpha_m^2 \xi_m^*\right) \hspace{1cm} 39f_m > 0.45$$  \hspace{1cm} (C3c)

$$39f_m = b \left(\frac{\xi_m^*}{\pi}\right)^{1/2} - \xi_m^* \hspace{1cm} 0 < 39f_m < 0.60$$

In much the same way we can approximate the functions $g_j(\xi_m)$ in equation (C1). Because of the nonlinearity of the relation $\xi_m^*(\xi_m)$, we will only consider here two important limiting cases for which $\xi_m^*$ becomes a linear function of $\xi_m$, and therefore log ($\Delta \xi_m^* / \Delta t_m$) is expected to be linear in $1/T$. These limiting cases will permit us to recover the diffusion parameters for at least some of the grain sizes making up the size distribution.

First, consider the limit when only small amounts of argon have been released ($\xi_m \ll 1$) and the functions $g_j(\xi_m)$ can be approximated by

$$g_j(\xi_m) = \frac{b}{\rho_j} \left(\frac{\xi_m}{\pi}\right)^{1/2} \hspace{1cm} \forall j$$  \hspace{1cm} (C4)

Substitution of equation (C4) in equation (C2) then gives

$$39f_m = b \left(\frac{\xi_m}{\pi}\right)^{1/2} \sum_{j=1}^{S} \left(\frac{\phi_j}{\rho_j}\right)$$  \hspace{1cm} (C5)

and since $39f_m$ is also small, equations (C3) become

$$39f_m = b \left(\frac{\xi_m}{\pi}\right)^{1/2}$$  \hspace{1cm} (C6)

Thus, when the amount of argon loss is small, we obtain

$$\Delta \xi_m = \Delta \xi_m^* \left\{ \sum_{j=1}^{S} \left(\frac{\phi_j}{\rho_j}\right) \right\}^{-2}$$

$$= \left(\frac{D_0}{\mathcal{R}(\phi_j, \rho_j)}\right) \exp\left(-\frac{E}{RT}\Delta t_m\right)$$  \hspace{1cm} (C7)

where $\mathcal{R}$ represents an effective diffusion dimension given by

$$\mathcal{R}(\phi_j, \rho_j) = \left\{ \sum_{j=1}^{S} \left(\frac{\phi_j}{\rho_j}\right) \right\}^{-1}$$  \hspace{1cm} (C8)

It follows from (C7) that a plot of log ($\Delta \xi_m^* / \Delta t_m$) versus $1/T$ will be linear giving the diffusion parameters $D_0$, $E$ with $\mathcal{R}$ as the apparent grain size. This apparent grain size is biased toward the smallest grains in the distribution (equation (C8)) as we would expect since we are in the limit of the very first argon released.

Another important limit corresponds to the situation when most of the $39\text{Ar}$ has been lost ($\xi_m \gg 1$), for which the functions $39f_m$ and $g_j(\xi_m)$ can be approximate by the first term in the summation over grain size in equation (C1). By combining equations (C1) and (C2) we write

$$1 - \frac{b}{\alpha_m^2} \exp\left(-\alpha_m^2 \xi_m^*\right) = 1 - \frac{b}{\alpha_m^2} \sum_{j=1}^{S} \phi_j \exp\left(-\alpha_m^2 \xi_j / \rho_j^2\right)$$

which leads to

$$-\alpha_m^2 \xi_m^* = \ln \left\{ \sum_{j=1}^{S} \phi_j \exp\left(-\alpha_m^2 \xi_j / \rho_j^2\right) \right\}$$  \hspace{1cm} (C10)

and finally, subtracting the value of the previous step ($\xi_m^* - 1$), we get

$$-\alpha_m^2 \Delta \xi_m^* = \ln \left[ \frac{\sum_{j=1}^{S} \phi_j \exp\left(-\alpha_m^2 \xi_j - \Delta \xi_m / \rho_j^2\right)}{\sum_{j=1}^{S} \phi_j \exp\left(-\alpha_m^2 \xi_j / \rho_j^2\right)} \right]$$  \hspace{1cm} (C11)

As a further simplification, we consider now the case where $\Delta \xi_m \ll \xi_m$ (which can be realized in a laboratory
experiment by limiting the duration of each temperature step for which $\alpha_i^2 \Delta \xi_m \ll 1$, and equation (C11) can be approximated by

$$-\alpha_i^2 \Delta \xi_m \approx \ln \left( \frac{\sum_{j=1}^{s} \phi_j \rho_j^{-2} \exp \left( -\alpha_i^2 \xi_m - i \rho_j^2 \right)}{1 - \alpha_i^2 \Delta \xi_m} \right) \sum_{j=1}^{s} \phi_j \exp \left( -\alpha_i^2 \xi_m - i \rho_j^2 \right)$$

(C12)

If we define a new effective grain size $\mathcal{R}$ to be

$$\mathcal{R}^2(\phi_j, \rho_j, \xi_m - i) = \sum_{j=1}^{s} \phi_j \rho_j^{-2} \exp \left( -\alpha_i^2 \xi_m - i \rho_j^2 \right)$$

(C13)

we recover equation (C7). Note that $\log (\Delta \xi_m / \Delta t_m)$ will still not be linear in $1/T$, since $\mathcal{R}^2$ depends on the previous step ($\xi_{m-1}$). However, for $\xi_{m-1}$ sufficiently large (the limit being considered), $\mathcal{R}^2$ becomes independent of the previous step and is given by

$$\mathcal{R}^2 = \rho_j^2$$

(C14)

$\rho_j$ being the largest grain in the sample. In this limit then the properties of the largest grains in the distribution exhibit their diffusion parameters. Physically, this corresponds to that part of the Arrhenius plot for which all the smaller grains are exhausted, and only the biggest one contributes to the gas released in the final steps.

In general, insistence on a relation of the form (C2) will lead to Arrhenius plots that depart from linearity except for the very first gas released (lowest temperature steps), which will reflect the smallest grains in the distribution, and for the last gas released (highest temperature steps) which will reflect the properties of the largest grain size.

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