DIFFARG: A PROGRAM FOR SIMULATING ARGON DIFFUSION PROFILES IN MINERALS

J. WHEELER

Department of Earth Sciences, Liverpool University, Liverpool L69 3BX, U.K.
(e-mail: johnwh@liv.ac.uk)

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Abstract—An understanding of argon transport is essential for the interpretation of K/Ar, $^{40}$Ar/$^{39}$Ar stepped heating and laser probe apparent ages of metamorphic rocks. The DIFFARG program, written in the Matlab 4.1 interpreted language, uses a finite-difference algorithm to simulate argon diffusion profiles and bulk ages of individual mineral grains for any thermal history and grain boundary argon history. Volume diffusion through the mineral lattice is assumed to be the dominant process, so the Ar diffusion coefficient is spatially homogeneous (though temperature dependent). The $^{40}$Ar concentration at the edge of the grain can be varied with time to model the diffusion of "excess" Ar from the surroundings. Plane sheet, cylindrical, or spherical grain shapes may be selected. The temperature history may be a linear decrease with time, to simulate slow cooling; a temperature pulse, to simulate a reheating event; or any temperature history composed of linear $T$-$t$ segments. The grain boundary $^{40}$Ar history is defined indirectly via the apparent age at the grain edge, itself dependent on time. Nonlinear temperature and grain boundary argon histories can be defined by the user if required. Numerical models are compared to analytical predictions which concern simple scenarios and real data. The program is useful particularly for interpreting $^{40}$Ar profiles obtained by laser microprobe $^{40}$Ar/$^{39}$Ar dating.

Key Words: Argon, Diffusion, Geochronology.

INTRODUCTION

The radioactive decay of $^{40}$K to $^{40}$Ar provides the potential for constraining ages and cooling histories of rocks (e.g. Mussett, 1969; Dodson, 1973; McDougall and Harrison, 1988). In rapidly cooled igneous rocks, all radiogenic $^{40}$Ar will be retained and the K/Ar ratio of K-bearing minerals such as micas and K-feldspar gives the crystallization age. However if the rock cools slowly, several processes affect $^{40}$Ar. Ar can escape by volume diffusion through the mineral lattice, diffusion through intracrystalline defects and along grain boundaries (Mussett, 1969). Advection of Ar in metamorphic fluids may transport it over larger distances (e.g. Roddick, Cliff, and Rex, 1980). Diffusion of $^{40}$Ar into the grain from an Ar-rich pore fluid can give high concentrations of "unsupported" or "excess" Ar within grains (e.g. Brewer, 1969; Harrison and McDougall, 1980), and excess Ar can also be "inherited" when the mineral crystallizes (Poland, 1979; McConville, Kelley, and Turner, 1988). These processes must be considered when interpreting the $^{40}$Ar distributions in rocks and minerals.

To explore such processes, begin by assuming that Ar diffuses in minerals according to Fick's second law,

$$\frac{\partial c}{\partial t} = D \nabla^2 c$$

(1)

where $c$ is the Ar concentration and $D$ is the diffusion coefficient. For a thermally activated process, the diffusion coefficient is defined by

$$D = D_0 e^{-E/RT}$$

(2)

where $D_0$ is the pre-exponential factor, $E$ is the activation energy, $R$ is the gas constant, and $T$ the absolute temperature. The diffusion coefficient is assumed to be spatially homogeneous, that is lattice diffusion is the dominant process. This is a reasonable first approximation for most minerals (e.g. McDougall and Harrison, 1988), although there is evidence for nonvolume pathways in K-feldspar (Parsons and others, 1988; Burgess and others, 1992) and hornblende (Lee, 1995).

Simple algebraic solutions to Equation (1) can be obtained for constant $D$. To take into account the strong temperature dependence of $D$ (Eq. 2), Dodson (1973, 1986) introduced the concept of closure temperature ($T_c$) which he defined as "the temperature of a mineral at the time corresponding to its apparent age". This is sometimes, erroneously, thought of as the temperature at which diffusion of Ar becomes negligible in the grain. It is a function of the parameters defining the thermal dependence of the diffusion coefficient (the pre-exponential fac-
and combining Equations (2) and (3), such cooling histories in which the diffusion coefficient for a given mineral diminished exponentially with time, so that

\[ D(t) = D(0)\exp(-t/\tau) \]  

and, combining Equations (2) and (3), such cooling histories are of the form

\[ E/RT = E/RT(0) + t/\tau. \]  

Then, the closure temperature is given by

\[ E/RT_c = \ln(AeD_0/a^2). \]  

\( A \) is a scalar factor which depends on the grain shape: it is 55 for a sphere, 27 for a cylinder and 8.7 for a plane sheet; \( a \) is the grain radius (or half the width for a plane sheet). For other forms of cooling history,Dodson suggested that the value of \( \tau \) to be used was that defined at the closure temperature by

\[ \tau = -RT_c/(EdT/dt), \]  

so from Equations (5) and (6), the closure temperature \( T_c \) is given by

\[ E/RT_c = \ln\left(\frac{ART_c^2D_0}{a^2EdT/dt}\right). \]  

which can be solved iteratively for linear cooling histories (Dodson, 1973). In metamorphic terrains which have cooled over millions of years, there does appear to be a broad relation between the apparent ages registered by K-bearing minerals and the isograd temperatures (e.g. Purdy and Jäger, 1976). This supports the closure temperature concept, and indicates ranges of closure temperatures for different minerals (350–400°C for muscovite, 300–350°C for biotite, 500–550°C for hornblende and ca. 250°C for K-feldspar; Cliff, 1985). However, there are many exceptions to these patterns. Sometimes minerals appear to have closed in the wrong “order” (e.g. biotite is apparently older than muscovite, Brewer, 1969), or there are wide variations in apparent ages in small areas (Chopin and Maluski, 1980; Arnaud and Kelley, 1995). The argon laser probe technique (e.g. Kelley and Turner, 1991; Onstott, Phillips, and Pringle-Goodell, 1991) allows Ar distribution within individual grains to be characterised: these can be compared with concentration profiles predicted to develop within grains during slow cooling (Dodson, 1986). Many metamorphic mineral grains show complex patterns: for example the profile across a white mica grain shown in Reddy, Kelley, and Wheeler (1996) shows more ⁴⁰Ar at the edge of the grain than in the center, which must be excess argon.

There are several possible explanations for such behavior. Firstly, the thermal history of the rock is complex, and may involve reheating events. Dodson’s model only strictly applies to slow cooling where diffusion is initially rapid (i.e. \( t \gg a^2/D \) at \( t = 0 \)) and \( 1/T \) is a linear function of time. Secondly, the concentration of argon in the grain boundary network is significant, and may fluctuate through time. It is implicit in Dodson’s derivation of the closure-temperature value for a mineral that the Ar concentration in the grain boundary is zero: in other words, Ar is quickly lost to a notional “infinite reservoir” once it has reached the grain boundary by lattice diffusion. This is reasonable geologically if Ar transport is fast in the grain boundary network in comparison to within the lattice, and if the pathways along which radiogenic Ar escapes to the atmosphere (for instance, fluid-filled cracks) never sustain high concentrations of ⁴⁰Ar. However, if grains crystallize from a ⁴⁰Ar-rich fluid, they will incorporate ⁴⁰Ar during growth; if ⁴⁰Ar cannot be lost easily from the grain boundary network, then this will retard ⁴⁰Ar loss from the grain interiors (e.g. in mantle phlogopites, Phillips and Onstott, 1988); and if ⁴⁰Ar-rich fluids pass through a rock, it may move into grain interiors by diffusion (Brewer, 1969; Harrison and McDougall, 1981; Villa, 1990).

The DIFFARG program allows apparent age profiles within grains to be modeled as a function of any thermal history and boundary conditions. The possibility that rocks are in communication with ⁴⁰Ar-rich reservoirs, or cannot lose ⁴⁰Ar from the grain boundary network, from time to time in their histories, is included in the model. An important factor not encompassed by the DIFFARG program is the possible heterogeneity of diffusion pathways in grains (e.g. Mussett, 1969; Lee and Aldama, 1992), such as in highly altered K-feldspars (e.g. Parsons and others, 1988; Burgess and others, 1992), and due to inclusions (Kelley and Turner, 1991) and exsolution lamellae (Lee, Onstott, and Hanes, 1990) in hornblende. In these circumstances, the diffusion coefficient will be spatially heterogeneous and will constrain the applicability of this model: a multipath diffusion model recently has been presented by Lee and Aldama (1992) and Lee (1995). DIFFARG allows the quantitative prediction of diffusion profiles for specific XTt histories which can then be compared to Ar profiles measured using laser probe techniques. Equally importantly, it allows the user to investigate the general features of Ar profiles as a function of X and T histories, and thus acts as a learning tool.

**MODEL DESCRIPTION**

To take into account production of ⁴⁰Ar within the grain, a source term \( S \) must be added to the diffusion Equation (1):

\[ \partial c/\partial t = D\nabla^2 c + S \]  

where \( S = \lambda^{(40}K)\lambda^{-1} \). Here, \( \lambda \) is the decay constant.
for $^{40}$K and [$(^{40}$K)], is the concentration of $^{40}$K at time $t = 0$. In this model, the rate of production $S$ is assumed to be constant since the half-life of $^{40}$K (1.25 Ga; Faure, 1986) is much longer than representative cooling times for metamorphic terrains (10–100 Ma), except in very slowly cooled terrains (e.g. Hodges, Hames, and Bowring, 1994). It is convenient to represent the concentration of $^{40}$Ar within the mineral as an "apparent age" at each point, rather than in, for example, ppb, because it is the apparent ages which provide the most direct link to theory. The K concentration of the mineral is assumed to be homogeneous and constant through time: then apparent age obeys Equation (8), with $S = 1$. The boundary condition is specified in terms of the apparent age at the edge of the grain, which may be a function of time. This in turn is determined by the amount of $^{40}$Ar in the grain boundary (either in a discrete fluid phase, or absorbed in the grain boundary).

Ar movement is controlled also by the concentration of Ar in the grain boundary network. This provides a boundary condition: the physics of this should be made clear. First, the apparent age is a function of the concentration of K in the mineral, which is assumed constant for all times and homogeneous. Second, there must be a partition coefficient between Ar in the grain boundary and Ar in the grain interior. If the partition coefficient were known, then the $^{40}$Ar concentration at the edge, but just inside the grain, could be predicted, assuming local equilibrium between grain edge and fluid. This concentration then could be converted into an apparent age, knowing the amount of K in the mineral. Despite there being data related to the solubility of noble gases in water (Benson and Krause, 1976) and silicate melts (Lux, 1987), data on the partitioning of Ar between fluids and minerals are sparse. Onstott, Phillips, and Pringle-Goodell (1991) estimate the partition coefficient between biotite and aqueous fluid as 0.02–0.002 cm$^3$ STP g$^{-1}$ atm$^{-1}$, which in molar terms implies that Ar partitions strongly into the fluid in preference to the mineral, as is predicted generally (e.g. McDougall and Harrison, 1988, p. 107). Because of the paucity of data, the boundary condition for DIFFARG modeling is expressed in terms of apparent age at the grain edge—which is permitted to vary with time, following possible variations in grain boundary argon concentration.

**PROGRAM DESIGN**

The program was developed using the Matlab 4.1 (MATLAB, 1993) interpreted language which is especially suited to concise development of numerical algorithms. It allows fast program development, easy debugging, and visual display of results. The

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The DIFFARG program 921

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**Figure 1.** Typical output from DIFFARG, showing evolution of apparent age profile (top left graph) in cylindrical muscovite grain, radius 0.1 mm, during slow cooling. Linear cooling history is from 415°C decreasing at 10°C/Ma (bottom right graph) in absence of excess argon (top right graph). Apparent age initially increases slowly, since grain is hot enough to lose substantial radiogenic argon, but later apparent and real ages increase together (bottom left graph). Stars marked on three time-dependent graphs indicate times at which profiles have been drawn. Here, profiles have been drawn every 1 Ma for 9 Ma.
same code has been tested on UNIX (Solaris 2.1, running on a Sun workstation) and on Windows 3.1 under DOS (running on a 486 4DX33 machine). Although the interpreted language runs slower than compiled code, the core algorithm is still fast. For instance, to generate Figure 1 using a vector of parameters (see section on “Advanced Operation” for details) took $104\,s$ on the PC and $80\,s$ on the Sun. The Matlab code is publicly available by anonymous FTP from the server at IAMG.ORG.

The core algorithm of the program is a routine to solve the diffusion equation in one dimension by finite difference within the mineral grain. The user specifies a time interval over which the model is allowed to evolve before the next display of apparent age profile in the grain. An arbitrary number of such “runs” is permitted. The diffusion equation is solved with a source term $S$ representing the argon produced by radioactive decay—since the $^{40}\text{Ar}$ concentration $c$ is recast as an apparent age, $S$ is numerically equal to 1, and Equation (8) becomes:

$$\frac{\partial c}{\partial t} = D\nabla^2 c + 1$$

(9)

For each grain shape, the diffusion equation is recast into a one-dimensional form reflecting the symmetry of that shape, i.e.

$$\nabla^2 c = \frac{\partial^2 c}{\partial r^2} + \frac{B}{r} \frac{\partial c}{\partial r}$$

(10)

where $r$ is the grain radius (or half-width of a slab) and $B$ is a geometric factor (0 for the plane sheet, 1 for a cylinder, and 2 for a sphere). Two finite-difference algorithms are provided for solving this equation numerically: a fully explicit algorithm, and a Crank–Nicholson algorithm (Crank, 1975, p. 141, 144; Press and others, 1989, p. 838, 840). Both of these algorithms involve defining a grid of points between and including $r = 0$ and $r = a$, at each of which the quantities on the RHS of Equation (9) are approximated. For a defined timestep the new values for $c$ are then calculated for each grid point. In DIFARG, the user specifies the number of grid points and hence the grid spacing ($\delta r$). More grid points give greater precision, but increase the computation time. In the fully explicit scheme, the numerical approximations are given by Crank (1975) equations 8.12, 8.33, and 8.38 for the plane sheet, cylinder, and sphere respectively. Though the user specifies the (arbitrary) time interval for each “run” (discussed previously), this will be divided by DIFARG into smaller time steps which are not arbitrary. In the fully explicit scheme numerical instabilities develop if the time step ($\delta t$) is too large. For the case of a plane sheet ($B = 0$), the stability criterion is $\delta t < (\delta r)^2/2D$ (e.g. Press and others, 1989, p. 838). Thus, the time step is smaller if the grid spacing is smaller, giving a further overhead on computing time. For the other geometries, Jenkin and others (1994), developing stable isotope diffusion models, found that the stability criterion for spheres and cylinders is $\delta t < 0.35(\delta r)^2/D$; those authors chose $\delta t = 0.3(\delta r)^2/D$, and this value is used in DIFARG, with $\delta t = 0.49(\delta r)^2/D$ for plane sheet geometries. As $D$ varies with time (becoming smaller on a typical cooling path), DIFARG calculates the required timestep at the start of each “run”. In contrast the Crank–Nicholson scheme is stable for all sizes of timestep: choosing a large timestep allows this algorithm to run faster in principle; however, as matrix inversion is involved, the gain is not always great. In both schemes, the apparent age at the outer edge of the grain (the last grid point) is set to the user-defined value. Physically this will be determined by the $^{40}\text{Ar}$ concentration in the grain boundary. It is implicit in the program that this is not affected directly by how much argon is exchanged with the grain—in other words the grain boundary is linked to a notional “infinite” reservoir of argon. The program reflects this by asking the user to define an “apparent age at edge of grain versus time” relationship: this relationship reflects the possible time-dependence of $^{40}\text{Ar}$ in the grain boundary network.

The rest of the program is concerned with presenting the results of the simulation. As well as the apparent age profiles in the grain through time, the bulk age of the grain is shown as a function of time. This is the volume-averaged apparent age of each point, and represents the age that would be obtained by bulk analysis of K and $^{40}\text{Ar}$ in the grain. Numerically it is approximated from the age profile using Simpson’s Rule; the grain geometry (plane sheet, cylinder, or sphere) means a radius-dependent weighting factor is involved also.

**STANDARD OPERATION OF THE PROGRAM**

The program can be used in a completely menu-driven fashion. After initiating Matlab, the user types “diffarg” at the Matlab prompt (> > ). Use of the program can be subdivided into two activities: defining model parameters, and letting the model run for geological time periods. When DIFARG is first invoked, the parameters must be defined: in subsequent invocations, they will be carried over. Model parameters fall into four groups: those defining the temperature history, the grain edge age history, the mineral description, and calculation and display options. In the first invocation, the user is forced to define all these. Subsequently, the main menu allows the user to select which parameters to modify.

**New temperature history**

(1) Linear temperature history: This is defined in terms of the initial temperature, and the cooling rate, for which the user is prompted. Zero
or negative cooling rates are allowed, but the program halts cooling at 0°C. An example of this scenario is the slow cooling of a large metamorphic terrain being exhumed.

(2) Flat-top pulse of temperature: A temperature pulse is defined by the background temperature (that before and after the pulse) and a pulse temperature. The duration of the pulse is defined by the start time and the end time (in Ma after the start of the model). Normally, the pulse temperature will be hotter than the background, and this history can be regarded as an approximation to a reheating event, such as the effect of a nearby igneous intrusion.

(3) Piecewise linear: This provides a general way of defining a temperature history, as a set of time–temperature points: it is assumed that the temperature changes linearly with time between successive points. Complex cooling and reheating histories could be defined if required. The two previous options are special cases of this general method.

(4) User defined history: An arbitrary temperature history, involving, for instance, non-linear changes of temperature with time, may be defined by the user if they are familiar with Matlab, via a function userthst.m (see section on “Advanced use of the program”, below).

New grain edge age history

(1) Linear edge age history:
(2) Flat-top pulse of edge age:
(3) Piecewise linear: The grain boundary $^{40}$Ar history is defined in a way precisely analogous to that for temperature: numerically, it is expressed in terms of the apparent age of the edge of the grain, which may depend on time. Physically this depends on two grain boundary properties: the $^{40}$Ar concentration in the grain boundary, and the partition coefficient. So, for instance, a sudden influx of argon into a grain boundary network from which argon could previously escape easily, such as that outgassing from the thermal aureole of an intrusion, could be described by a pulse on a zero background level. If the partition coefficient changes with temperature, as suggested by Lee, Onstott, and Hanes (1990), then the apparent age at the grain edge can change, even if the $^{40}$Ar concentration in the grain boundary is constant. These different effects are not distinguished in the way the DIFFARG parameters are defined, due to paucity of partitioning data as discussed above.

(4) User defined history: An arbitrary grain edge age history may be defined by the user if they are familiar with Matlab, via a function userxhst.m (see next section).

New mineral and/or grain geometry

The user is prompted for the type of mineral required. The program includes the diffusion parameters for “H muscovite” (Hamilton, Kelley, and Fallick, 1989), “R muscovite” (data from Robbins, 1972 for the same mineral), biotite (Harrison, Duncan, and McDougall, 1985), and hornblende (Harrison, 1981). Possible grain shapes are a plate, a cylinder, or a sphere, and any grain radius is allowed. The required “mesh length” is requested also. Unlike the other parameters, this is not of physical significance—instead it defines the resolution of the grid for the finite difference calculations. The bigger this number, the finer the grid point spacing, and the higher the precision of the calculation. However, finer grid spacings also cause the program to run more slowly, for the simulation of a fixed duration of geological time. Large mesh lengths always are preferable, but users may experiment to find mesh lengths which allow models to run tolerably fast without losing too much precision: a mesh length of 20 is a reasonable beginning.

Options

Finite-difference scheme

(1) Fully explicit
(2) Crank–Nicholson

The user has the choice of numerical algorithm. For the fully explicit method, the timestep is defined as described above. For the Crank–Nicholson method, the timestep is increased by a user defined factor.

Enter scaling factor for Crank–Nicholson timestep

If the user enters 10, for instance, then the timestep used will be ten times more than that in the fully explicit method. The other set of options relate to the display.

Display style

(1) No display
(2) Summary figure with four graphs
(3) Summary and individual figures

The display can be omitted, or the four relevant graphs (see later) displayed in a single figure (c.f. 1), or displayed separately as well as combined.

Start model running

After initialization or alteration of these parameters is complete, the user selects a menu option to start the model running. The prompt is

Enter time to next display in Ma (or 0 to quit, –1 to print).

If the user wishes the model to run for another 3 Ma, then 3 is entered. The output is shown in a Matlab figure window with four subplots (i.e. four graphs) arranged within it (e.g. Fig. 1). The first
(upper left) graph is the apparent age profile as a function of position in the grain, displayed together with the age profiles for all the previous stages of the model. The other three graphs are: the bulk age of the grain, the temperature, and the apparent age at the grain edge, each plotted against time. When a run is initiated, the user is informed how many time iterations will be involved. If this number is large, the run may take a long time to complete, and the user may choose to alter the mesh length and re-run the model.

To print a simulation, the user inputs -1: the simulation may then be continued. To exit, the user inputs 0. Matlab allows the user to input a vector of values, separated by spaces and enclosed in square brackets. These will then be run in sequence by the program. For instance, if the user inputs

\[ [1 \ 2 \ 5] \]

in response to the prompt, then the program will run the model for 1 Ma, display the results, then run the model for another 2 Ma and 5 Ma (taking it up to 8 Ma in total), updating the display at each stage.

After exiting from a simulation, the following main menu is displayed to allow alteration of model parameters as described above:

1. New temperature history
2. New grain edge age history
3. New mineral and/or grain geometry
4. Options
5. Start model running
6. Quit program

Any subsequent simulation will begin from time zero, and wipe the display from the preceding simulation.

**Example 1: profiles developed during slow cooling**

A grain of H muscovite, cylindrical, with a radius 0.1 mm, crystallizes without any initial \(^{40}\text{Ar}\). It cools at 1.5°C/Ma from 415°C with no \(^{40}\text{Ar}\) in the grain boundary network. What is the apparent age profile every 1 Ma for the subsequent 9 Ma? The calculation uses a fully explicit scheme with 31 nodes.

**Temperature history** Enter 1, 415, 15
**Grain edge age history** Enter 1, 0, 0
**New mineral and/or grain geometry** Enter 1, 2, 0.1, 30
**Options** Enter 1, 2
**Start model running** Enter 1, nine times, or enter [1 1 1 1 1 1 1 1 1 1]

**Example 2: approach steady state profile**

Consider a grain held at constant temperature indefinitely. If there is grain boundary \(^{40}\text{Ar}\), then the apparent age profile begins at zero throughout the grain, but builds up to a *steady-state* profile over time. If temperature is high, this profile can develop on geologically reasonable timescales: the grain will have an apparent age, however hot it is, though it will appear younger, the hotter it is. The concept of closure temperature is not useful in this scenario—the cooling rate is zero, so Equation (2) is not relevant. In the Appendix are derived analytical solutions in this case, for any of the three grain geometries. For large times, the shape of the profile approaches parabolic.

The analytical solutions are compared with numerical simulations of the approach to steady state in Figure 2, where muscovite grains of different shapes are held at 370°C for 16 Ma. Note that if such profiles had developed through time and were then preserved by rapid cooling, the age differences between center and edge might erroneously be attributed to slow cooling, since profiles developed during slow cooling (Dodson, 1986) have a superficially similar form to that of Figure 2.

**Example 3: “excess argon”**

The closure temperature is defined as “the temperature of the system at the time represented by its apparent age” (Dodson, 1973). It is sometimes thought of, erroneously, as the temperature at which diffusion of \(^{40}\text{Ar}\) becomes negligible in a grain. This is not the situation, as is clear from Dodson (1986) in the example of slow cooling without excess argon, and as is highlighted in this example. Reddy, Kelley, and Wheeler (1996) document an apparent age profile in a phengite grain of radius 1.73 mm from an Alpine eclogite facies schist (Figs 3 and 4). Older ages at the edge compared to those in the grain center must imply that \(^{40}\text{Ar}\) has diffused in from the grain edge. The profile shape cannot be used to determine a unique temperature and \(^{40}\text{Ar}\) history, but one scenario discussed by Reddy, Kelley, and Wheeler (1996) is that the grain crystallized in a \(^{40}\text{Ar}\)-bearing fluid, giving it an initial apparent age of roughly 20 Ma. It then cooled slowly, for instance at 10°C/Ma, and then a fluid much richer in \(^{40}\text{Ar}\) was introduced, causing diffusion of \(^{40}\text{Ar}\) into the grain interior. Figure 3 presents a slight modification of this model (DIFFARG takes into account production of radiogenic \(^{40}\text{Ar}\) during profile development, which was not built in to the analysis of Reddy, Kelley, and Wheeler, 1996). In the absence of \(^{40}\text{Ar}\) diffusion parameters for phengite, those for muscovite are used. The closure temperature for a grain of this size cooling at 10°C/Ma is then 467°C, from Equation (7). The model begins with phengite crystallization at 507°C at 64 Ma in a fluid with a \(^{40}\text{Ar}\) content which, when initially in equilibrium with the phengite, gives it an age of 17 Ma. The grain then cools at 10°C/Ma, so that it passes through its closure temperature at 60 Ma. At 59.3 Ma (460°C) a \(^{40}\text{Ar}\) rich fluid is introduced into the grain boundaries; the edge of the phengite equilibrates with this fluid to acquire a new
Figure 2. Numerical simulations of radiogenic $^{40}$Ar buildup at constant temperature, and comparison with algebraic solutions. Top row: apparent age profiles for 0.1 mm radius grain of muscovite held at 370°C in absence of excess argon, calculated using DIFFARG. Profiles are shown for plane sheet, cylindrical and spherical geometries, and are displayed at 2 Ma intervals up to 16 Ma (16 Ma profile being uppermost in each instance). Fully explicit numerical scheme was used, with 30 nodes. Each set of profiles converges on steady state: approach to steady state is fastest for sphere, as indicated by closeness of 14 Ma and 16 Ma profiles. Bottom row: difference (in Ma) between algebraic series solution (see Eqs. A5–A8, with series truncated after 6 terms) and DIFFARG output shown in top row.

Figure 3. Apparent age profiles for cylindrical muscovite grain radius 1.735 mm affected by sudden influx of excess argon whilst cooling: model for one of observed age profiles of Reddy, Kelley, and Wheeler (1996) (see text for details of temperature and edge age history). Model is initiated at 64 Ma before present, and situation is shown here after 10 Ma, at 54 Ma before present, with profiles drawn every 1 Ma. See Figure 4 for present-day predicted profile.
apparent age of 100 Ma. This diffuses into the grain during the rest of the cooling history. Thus, the entire “excess” argon diffusion profile develops below the closure temperature.

**ADVANCED OPERATION OF THE PROGRAM**

Advanced features of DIFFARG can be accessed with a modest understanding of Matlab. A nonlinear temperature or grain boundary argon history can be defined by creating files called `userthst.m` and `userxhst.m` respectively, within which function of the same name are declared in standard Matlab fashion. The function `userthst(t)` must return the temperature in °C as a function of time `t` in Ma. Nonlinear grain edge age histories are defined in a similar fashion. The function `userxhst(t)` must return the apparent age of the grain edge (in Ma) as a function of time `t`.

The DIFFARG parameters can be set up noninteractively. DIFFARG can be called with a parameter by entering `diffarg(pvec)` in response to the matlab prompt. The parameter `pvec` is a vector used as noninteractive input. DIFFARG reads each number from the vector as if it were keyboard input, until the end of the vector is reached, at which stage input becomes interactive again. For example to run Example 1 (discussed above) and generate Figure 1 the following vector is input.

(Note that the continuation marks ... are inserted for clarity—each line then corresponds to an option from the main menu. The continuation marks can be omitted, and the numbers typed on a single line).

```
diffarg([1 1 415 15...
  2 1 0 0...
  3 1 2 0.1 30...
  4 1 2...
  5 1 1 1 1 1 1 1 1 1 1 1 -1 0...
  6])
```

This sets up a cooling history of 15°C/Ma from 415°C at time zero, with no grain boundary ⁴⁰Ar (so that the grain edge age is always zero), for a cylindrical muscovite grain of radius 0.1 mm and a mesh length of 30. Fully explicit finite difference is chosen as the calculation method, with a single summary figure. The model then runs for 9 Ma, displaying the situation at intervals of 1 Ma, prints the final situation, and then exits. Such vectors can be given Matlab names for brevity (e.g. `modell`), and can also be altered in systematic ways. For instance, a loop could be written in which the grain size is changed from one invocation of DIFFARG to the next, whilst keeping the XTt history the same. This could be used to compare the response of grains with a range of sizes to the same XTt history. When initiated interactively, DIFFARG stores user input
in a global vector called \textit{paramvec} which can be accessed after a given invocation of DIFFARG is terminated. Such vectors can be stored and used in subsequent calls to DIFFARG. Note that other global quantities also can be accessed outside DIFFARG.

**DISCUSSION**

This program allows the simulation of apparent K/Ar age profile development within mineral grains as a function of time for a variety of temperature and excess argon histories. It serves as a tool to investigate general aspects of \(^{40}\)Ar behavior in minerals, and their implications for geochronology, and also to model particular datasets in detail. Conventional K/Ar ages may be modeled, if available from a variety of grain sizes, but \(^{40}\)Ar/\(^{39}\)Ar laserprobe data from profiles across, or maps of, individual grains are the most useful for this task (e.g. Lee, Onstott, and Hanes, 1990; Hodges, Hames, and Bowring, 1994; Kelley, Arnaud, and Turner, 1994; Reddy, Kelley, and Wheeler, 1996). Such data are subject to analytical uncertainty in the apparent age, and also to spatial uncertainty due to finite fusion spot size (see error bars on Fig. 4). Infrared laser light from sources such as Nd-YAG fuses spots at least 50–100 \(\mu\)m in diameter (e.g. Lee, Onstott, and Hanes, 1990; Reddy, Kelley, and Wheeler, 1996), and so Ar variations on shorter length scales cannot be investigated. Ultra-violet laser light (e.g. from a quadrupled Nd-YAG source; Kelley, Arnaud, and Turner, 1994) is absorbed efficiently by K-bearing silicates including K-feldspar and plagioclase and also by quartz (the latter three minerals are not good absorbers of IR light). Therefore, spatial and depth resolutions of 10 \(\mu\)m or less are possible.

A key assumption in the program is that diffusion is spatially homogeneous and dependent only on temperature. The validity of this assumption should be assessed prior to and during modeling using DIFFARG. For instance, apparent age patterns produced by homogeneous diffusion should always be concentric. Kelley and Turner (1991) give age profiles from hornblends which show complex forms related partly to fast diffusion pathways created by biotite incursions; nevertheless, some profile segments can be modeled in terms of homogeneous volume diffusion. Lee, Onstott, and Hanes (1990) show maps of apparent age obtained from hornblende grains: these are crudely concentric, but not precisely, perhaps due to the presence of submicroscopic exsolution lamellae which would create nonvolume, fast, diffusion pathways. As a final example, the grain from which the profile in Figure 4 was taken (Reddy, Kelley, and Wheeler, 1996) shows older ages in its center, apparently related to kinking and associated fast diffusion of Ar along the kinked region. Again, a portion of the profile can be modeled in terms of homogeneous diffusion, as discussed previously. Other minerals also may exhibit "non-Fickian" diffusion behavior, such as K-feldspar (e.g. Parsons and others, 1988; Villa, 1994). Modeling of such "multipath" diffusion requires data on the rates of exchange of Ar between slow and fast diffusion pathways: Lee and Aldama (1992) give details in the absence of a radiogenic source term, and Lee (1995) includes the source term, though the effects of possible grain boundary \(^{40}\)Ar are not included.

DIFFARG allows the user to define an arbitrary history of apparent age at the grain edge, which reflects the (possibly changing) \(^{40}\)Ar concentration in the grain boundary network. Physically, the implication is that Ar concentration in the grain boundary network is controlled from outside the rock (i.e. is externally buffered), for instance by fluid flow advecting Ar in solution. Alternatively radiogenic and nonradiogenic isotopes and elements may sometimes be internally buffered, with exchange between minerals but no larger-scale gain or loss. For nonradiogenic systems, isotopes and elements redistribute between minerals as temperature changes because partition coefficients change: the behavior of such systems is governed not only by the diffusivities in each phase, but also by their model abundances and their partition coefficients. Oxygen isotope exchange has been modeled in this fashion (Ehlers, Baumgartner, and Valley, 1992, Eiler, Valley, and Baumgartner, 1993; Jenkin and others, 1994), as has Fe/Mg exchange (Ehlers and Powell, 1994; Ehlers, Powell, and Stüwe, 1994). For radiogenic systems, the different production rates of radiogenic daughter isotope in different minerals are an additional cause of isotope redistribution (e.g. Jenkin and others, 1995 consider exchange of radiogenic \(^{87}\)Sr between two minerals). \(^{40}\)Ar may sometimes behave in this fashion (e.g. Foland, 1979), but detailed information is lacking. In both the externally and internally buffered cases, DIFFARG will model the response to the changing grain boundary concentration: in the internally buffered case this will, however, itself depend on the partitioning and diffusive exchange with other phases in the rock.

In summary, DIFFARG can be used for fitting theoretical apparent age profiles produced by any \(\mathrm{XTt}\) history to observed profiles, when the assumption of homogeneous volume diffusion of Ar is considered appropriate. If a predicted profile passes through observed data points within error, this does not necessarily prove that the \(\mathrm{XTt}\) history chosen is correct, but such a comparison will allow unlikely scenarios to be rejected. The program could be used to model the movement of radiogenic daughter isotopes in any decay scheme,
not just that of K to $^{40}$Ar, though the technology is not yet firmly established to measure other radiogenic isotope profiles within grains.

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REFERENCES


The DIFFARG program


APPENDIX

Derivation of analytic solutions for constant temperature and zero 40Ar at grain edge

The solution to Equation (9),

\[ \frac{\partial c}{\partial t} = D \nabla^2 c + 1 \]  
(A1)

can be derived when temperature (and hence D) is fixed, \( c = 0 \) at the grain edge \( (r = a) \), and \( c = 0 \) at \( t = 0 \). First define a new function \( p \) to be the steady state solution to Equation (9), that is \( \frac{\partial p}{\partial t} = 0, p = 0 \) at \( r = a \) so

\[ O = D \nabla^2 p + 1 = D (\frac{\partial^2 p}{\partial r^2} + \frac{\partial p}{\partial r}) + 1 \]  
(A2)

By inspection the solution is

\[ p = \frac{1}{2(B + 1)D} (a^2 - r^2) \]  
(A3)

so the steady-state distribution is parabolic. Now let \( c = p + q \) so that, from Equation (A1) to (A3) the time-dependent function \( q(x, t) \) satisfies

\[ \frac{\partial q}{\partial t} = D \nabla^2 q; \quad q(a, t) = 0; \quad q(r, 0) = -\frac{1}{2(B + 1)D} (a^2 - r^2) \]  
(A4)

Thus, \( q \) satisfies the diffusion equation without a source term, posed in a form appropriate for solution by equation (4.16) of Crank (1975) for the plane sheet geometry, equation (5.18) for the cylinder and the method of section 6.3.1 for the sphere (Crank, 1975). The resulting solutions are:

\[ q(r, t) = \frac{16a^2}{\pi^2 D} \sum_{n=1}^{\infty} \frac{(-1)^n}{(2n - 1)^3} \exp \left( \frac{(2n - 1)\pi r}{2a} \right) \cos \left( \frac{(2n - 1)\pi r}{2a} \right) \]  
(A5)

for a plane sheet;

\[ q(r, t) = -\frac{2a^3}{\pi^3 D} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^3} \exp(-Dn^2\pi^2 t/a^2) \sin \left( \frac{n\pi r}{a} \right) \]  
(A6)

for a cylinder, where \( p_n \) is the nth root of \( J_n(x) \); and

\[ q(r, t) = -\frac{2a^3}{\pi^3 D} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^3} \exp(-Dn^2\pi^2 t/a^2) \sin \left( \frac{n\pi r}{a} \right) \]  
(A7)

for a sphere. The apparent age versus time is then

\[ c(r, t) = \frac{1}{2(B + 1)D} (a^2 - r^2) + q(r, t) \]  
(A8)