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Argon release mechanisms of biotite in vacuo and the role of short-circuit diffusion and recoil

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Abstract

Understanding argon release mechanisms in K-bearing minerals is essential in interpreting the 40 Ar/ 39 Ar data and their application to geological studies. The release mechanisms of argon in vacuo have been examined in a series of 40 Ar / 39 Ar isothermal heating experiments on two biotite specimens with Fe/(Fe + Mg) (Fe[#]) = 0.50 and 0.87 respectively. The crystal structure of the biotite was also monitored during in vacuo heating by an in-situ high temperature X-ray diffractometer (HTXRD), and also examined by scanning electron microscopy (SEM). At temperatures greater than 600°C, argon release is mainly controlled by the structural decomposition of the biotite crystal arising from oxidation and dehydroxylation, whereas at temperatures less than 600°C, argon release appears to be controlled by a multipath-diffusion mechanism, with effective D/a^2 values about 2-4 orders of magnitude higher than those extrapolated from hydrothermal data. Both the argon diffusivity and Ar release patterns are strongly related to biotite composition, in which the Fe-rich biotite has a higher argon diffusivity and degasses at lower temperatures than the Mg-rich biotite. Unless contaminated by other phases, biotites will tend to yield flat age spectra for temperature steps higher than 600°C, regardless of the initial distribution of argon isotopes in the crystal structure, since the argon released at $T > 600^{\circ}$ C is strongly correlated with the decomposition process. At temperature steps lower than 600°C, however, biotite age spectra can exhibit discordant dates since the gas release is controlled mainly by defect-enhanced (short-circuit) diffusion mechanisms. Consequently, models using such low-T steps with the intent of extracting information on the spatial distribution of Ar will not lead to accurate interpretations of geologic histories, unless the potential effects of short-circuit diffusion are well-constrained. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Geochronology; Argon; Diffusion; Biotite

1. Introduction

One of the most important advantages of 40 Ar/ 39 Ar dating over conventional K–Ar dating is the ability

to infer the spatial distribution of ⁴⁰Ar* within the analyzed mineral using the step-heating technique. This inference is based upon the application of solid-state (or volume) diffusion theory to describe argon transfer in minerals during natural thermal events and laboratory experiments (McDougall and Harrison, 1988, and references therein).

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In natural events, the variation of biotite ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ total-gas or K-Ar dates observed near thermal contact aureoles and in some regional metamorphic terranes is consistent with volume-diffusion theory (Hart, 1964; Westcott, 1966; Hanson and Gast. 1967: Harrison and McDougall, 1980; Onstott et al., 1989). A number of other studies (as reviewed by Mc-Dougall and Harrison, 1988) have also obtained disturbed biotite age spectra which were interpreted to reflect thermal resetting as predicted by volumediffusion theory. Moreover, the good correlation between the grain size, corresponding ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ age, and cooling history for biotites suggests that Ar transfer mechanisms in biotite in natural settings are dominated by a volume-diffusion process (Wright et al., 1991). The diffusion-controlled distribution of argon in biotites has also been demonstrated recently by the ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ laser microprobe (Pickles et al., 1997).

There are several other ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ studies, however, in which the distribution of argon in biotite cannot be readily explained by volume diffusion, e.g., the laser microprobe studies of Phillips and Onstott (1988), Onstott et al. (1991), and Phillips (1991). Moreover, other studies have suggested that volume-diffusion theory may not be appropriate for interpreting the age spectra of biotite because the temperatures used in in vacuo 40 Ar / 39 Ar step-heating experiments extend beyond the stability field of biotite (Gaber et al., 1988; Lo and Onstott, 1989). Using XRD (X-ray diffraction) and SEM (scanning electron microscopy) techniques. Gaber et al. (1988) discovered that biotite experiences a complicated phase change in the temperature range of 600-800°C, resulting in the reduction of cell parameters, structural delamination and weight loss. In addition, the fraction of argon released from biotite at these temperatures in vacuo (600-800°C) greatly exceeded that predicted from volume diffusion. Consequently, they concluded that the rate of argon release from biotite during 40 Ar/ 39 Ar step-heating experiments is controlled by processes other than the volume diffusion, and that homogenization of the 40 Ar/ 39 Ar distribution should occur during such experiments (Gaber et al., 1988).

Laboratory studies of Ar diffusion in biotite have yielded equivocal results. Giletti (1974), Norwood (1974), Harrison et al. (1985) and Grove and Harrison (1996) reported that the amount of ${}^{40}\text{Ar}^*$ lost from hydrothermally-treated biotite held at temperatures and pressures within its stability field was similar to that expected from volume diffusion, although interestingly the shape of the corresponding age spectra from these biotites could not be explained by this same theory (Harrison et al., 1985; Hess et al., 1987). In another hydrothermal study, the argon distribution pattern in biotite as determined by laser microprobe also could not be explained by a simple volume-diffusion model (Onstott et al., 1991). These studies strongly suggest that the release mechanisms of argon from biotite during ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ in vacuo heating are different from those occurring in either natural or hydrothermal environments, and that a more detailed understanding of the Ar release mechanisms from biotite in vacuo is required.

2. Experimental procedures

In order to elucidate the argon release mechanisms for biotite in vacuo, a series of ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ isothermal heating experiments, incremental stepheating runs, in–situ high-temperature X-ray diffraction (HTXRD) heating experiments, and SEM studies were conducted on two pure biotite samples with distinct chemical compositions.

2.1. Starting materials

Two biotite samples were selected for this study: one (KM) is an Fe-rich biotite extracted from a Cretaceous granite (90-109 Ma) occurring on Chinmen island located off the coast of SE China; the other (CPC), is a relatively Mg-rich biotite extracted from a Tertiary tonalite (50-60 Ma) in the Coast Plutonic Complex Sill in SE Alaska. Previous ⁴⁰Ar/³⁹Ar studies showed that both plutonic bodies have experienced a simple and rapid cooling history without any notable reheating events (Wood et al., 1991; Lo et al., 1993). From these studies, both biotite separates yielded flat age spectra over more than 97% of ${}^{39}Ar_{\rm K}$ released with plateau dates of 97.2 ± 0.9 Ma for KM biotite and 56.4 ± 0.4 Ma for CPC biotite (Fig. 1). In thin section, KM biotite is greenish-brown to dark brown and coexists with K-feldspar, plagioclase, quartz and some accessory



Fig. 1. 40 Ar/ 39 Ar age spectra for KM and CPC biotite in the normal step-heating runs. Vertical length of the bars indicates two standard deviations for apparent age, and horizontal length shows the relative fraction of 39 Ar loss.

oxides; CPC biotite is greenish-brown to pale brown, associated with plagioclase, quartz, hornblende, titanite, epidote and oxides. Alteration phases are not evident in these biotites. Electron microprobe analyses show that the chemical composition of both samples is generally homogeneous over the mineral grains, and no significant chemical variation was detected on the thin-section scale. The major difference between the two biotites is that KM biotite exhibits higher Fe/(Fe + Mg) ($Fe^{\#} = 0.87$) and volatile contents ($\sim 4.68\%$) than CPC biotite (Fe[#] = 0.50 and 3.82%, respectively) (Table 1). Recasting the mineral formulae on the basis of 11 oxygens (assuming total Fe as Fe^{+2}), both biotites show a deficiency of cations in both the octahedral and interlayer sites; comparison of the cation occupancy between the biotites indicates that KM biotite has a lower number of octahedral vacancies and higher number of interlayer vacancies than CPC biotite (Table 1).

Samples were prepared by crushing a whole-rock sample in a stainless steel mortar. Material was repeatedly sieved in order to obtain as uniform a size of mineral grains as possible. A size fraction of 80-120 mesh was used for the isothermal experiments. Biotite separates were obtained using standard heavy liquid and magnetic separation techniques, and hand picking was performed to achieve maximum purity. Most of the biotite flakes have elliptical or rectangular outlines, with a mean short radius of 75 (+22) µm and a mean long radius of 118 (+34) µm for KM biotite, and 84 (+19) and 133 (+38) µm, respectively, for CPC biotite. The samples were then split into several aliquots for 40 Ar/ 39 Ar. X-ray diffraction and SEM experiments at various temperatures.

Table 1 Chemical composition of the studied biotites

	KM biotite	CRC biotite
SiO ₂	33.76	36.46
TiO ₂	1.63	3.06
Al_2O_3	16.24	15.57
FeO	31.13	19.79
MgO	2.60	11.17
MnO	1.20	0.35
CaO	0.06	0.27
Na ₂ O	0.08	0.10
K ₂ O	8.54	9.35
Cl	0.07	0.06
Anhydrous total	95.31	96.18
Fe/(Fe+Mg)	0.871	0.498
Ca/K	0.006	0.024
Cl/K	0.011	0.009
11(O)		
Si	2.747	2.768
Ti	0.100	0.175
Al ^{IV}	1.153	1.057
Σ	4.000	4.000
Al ^{VI}	0.405	0.236
Fe	2.118	1.256
Mg	0.315	1.264
Mn	0.083	0.023
Σ	2.926	2.902
Ca	0.005	0.022
Na	0.013	0.015
K	0.886	0.906
Σ	0.904	0.943
Cl	0.010	0.008

2.2. ⁴⁰Ar / ³⁹Ar experiments

The samples were wrapped in aluminum foil packets, stacked in an aluminum canister with the irradiation standard P-207 muscovite (82.6 + 1.0 Ma, Dalrymple et al., 1981), and irradiated in the 5C position of the McMaster University research reactor. One of the aliquots of KM biotite (KM-N) used for normal step-heating was irradiated with the irradiation standard Mmhb-1 (520.4 + 1.4 Ma. Sampson)and Alexander, 1987) in another canister, KM-N was irradiated for 20 h. whereas the remainder of the samples were irradiated for 10 h. The neutron flux gradient across the top and bottom of the irradiation canisters was less than 0.9%, as indicated by the variation of J values from the flux monitors. After irradiation, the samples were weighed, loaded into fused-silica boats, and heated with a Lindberg resistance furnace. The released gas was purified with a Ti sponge and Zr-Al getters, and analyzed with a Varian-MAT GD150 mass spectrometer. All isotope analyses were corrected for system blanks, the radioactive decay of the ³⁷Ar and ³⁹Ar isotopes, and minor interference reactions from Ca, Cl and K. The full ⁴⁰Ar/³⁹Ar analytical procedure and data reduction methods are outlined in Onstott and Peacock (1987). For the normal step-heating runs, the samples were stepwise-degassed according to a fixed schedule of 30 min/step from 550°C to 1150°C. In addition, a series of in vacuo heating experiments were conducted which combined isothermal and stepwise-heating methods. In these runs, the samples were heated to the desired isothermal temperature and analyzed over period of about 44 h; after completion of the isothermal portion of the run, the samples were then degassed following the schedule used in the normal step-heating run until sample fusion (usually around 1150-1190°C). The hightemperature isothermal runs (800°C) included two low-temperature steps (650°C and 750°C) lasting a total of an hour to permit gradual thermal equilibration before the furnace temperature was raised to 800°C. During the isothermal heating, the gas was collected in intervals ranging from 5 min to 10 h depending on the amount of gas release, and the heating time was recorded as the total time elapsed from the time that the temperature reading on thermocouple reached the desired isothermal temperature. The detailed time-temperature schedules and analytical data are given in Appendix A. The name of each 40 Ar/ 39 Ar run was chosen according to the temperature of the isothermal steps, e.g., KM-400 indicates a 400°C isothermal run for KM biotite. After complete degassing at ~ 1150°C, the samples were unloaded from the extraction line and reweighed to obtain the total weight loss.

2.3. High-temperature X-ray diffraction and SEM

In-situ high temperature X-ray diffraction (HTXRD) data were obtained from an automated Scintag PAD V diffractometer using CuK_a radiation and a scintillation detector, equipped with an in vacuo heating stage (a modified Anton Paar unit). Vacuum was held at about 10^{-3} Torr during the runs. Temperature was maintained using a PAAR HTK heat controller and measured using a Pt/ 13%Rh-Pt thermocouple, with an uncertainty of $+10^{\circ}$ C. The position of heating stage was previously calibrated using the thermal expansion of Pt, and a Pt sample holder served as an internal standard (Brown and Navrotsky, 1989). A crushed powder sample was first heated to 90°C to remove unbonded H₂O and scanned continuously from 5° to 70° 2 θ . Subsequently, the samples were incrementally heated from 400°C to 1000°C, in steps of 100°C for KM biotite and 50°C for CPC biotite. The duration for each step was 2 h for KM biotite and 70 min for CPC biotite. XRD peaks were step-scanned in $0.01^{\circ} 2\theta$ increments at a rate of 0.5°/min and multi-scan mode was used to reduce the duration for each temperature step, except for the 1000°C run which was continuously scanned from 5° to 70°. An additional isothermal HTXRD run at 700°C for 12 h was performed on KM biotite to examine any kinetic effects on the biotite phase change. Unit cell parameters and estimated errors were obtained by the refinement of 10 reflections [including (001), (002), (003), (004), $(113), (005), (1,3,\overline{5}), (204), (060), (\overline{3}31)$ over the range $5^{\circ} < 2\theta < 70^{\circ}$ using the least squares procedure of Appleman and Evans (1973). SEM analyses were performed on CPC biotite grains after being heated at high temperatures under vacuum conditions, using a JEOL scanning electron microscope at Department of Biology, Princeton University.

3. Volume diffusion equations and computational method of diffusion parameters

Argon diffusion in biotite has been best described as volume diffusion via cylindrical geometry (Giletti, 1974; Grove and Harrison, 1996). The fraction of gas lost from an infinite cylinder is given as (Crank, 1975):

$$F = 1 - 4\sum_{n=1}^{\infty} \frac{1}{\alpha_n^2} \exp\left(-\frac{\alpha_n^2 Dt}{a^2}\right)$$
(1)

where *a* is the diffusion radius, α_n are the roots of $J_0(a\alpha_n) = 0$ (where $J_0(x)$ is the Bessel function of the first kind of order zero), *D* is the diffusion coefficient, and *t* is the heating time. The change of *D* with temperature (*T*) is described by the Arrhenius relation $D = D_0 \exp(-E/RT)$, where D_0 is the pre-exponential coefficient, *E* is the activation energy, and *R* is the gas constant. Since Eq. (1) does not converge rapidly for small *F*, two useful approximations have been utilized (Jost, 1960; Crank, 1975):

(1) for
$$0 < F < 0.6$$
: $F = \frac{4}{\pi^{1/2}} \left[\frac{Dt}{a^2} \right]^{1/2} - \frac{Dt}{a^2}$
 $-\frac{3}{\pi^2} \left(\frac{\pi^2 Dt}{a^2} \right)^{3/2}$ (2)
(2) for $0.6 < F < 1$: $F = 1 - \frac{4}{\alpha_1^2} \exp\left[-\frac{\alpha_1^2 Dt}{a^2} \right]$
(3)

where α_1 is the first root of the Bessel function $J_0(a\alpha_n) = 0$.

From Eqs. (2) and (3), an integrated D/a^2 value can be computed for the argon release from biotite, given the total fraction lost (F) and the total heating time (t) for each isothermal run. However, since the present experiments were designed to see if any changes in the argon release mechanism occurred during the isothermal runs, D/a^2 values for each step were calculated by considering the diffusivity of argon during the interval of time between each step by using the following equations:

(1) for
$$0 < F < 0.6$$
: $(D/a^2)_{i+1}$

$$= \frac{8}{\pi t} \left[\sqrt{1 - \frac{\pi}{4} F_i} - \sqrt{1 - \frac{\pi}{4} F_{i+1}} + \frac{\pi}{8} (F_i - F_{i+1}) \right] \text{ for } i = 0, n-1 \quad (4)$$
(2) for $0.6 < F < 1$: $(D/a^2)_{i+1}$

$$= \frac{1}{\alpha_1^2 t} \ln \left[\frac{(1 - F_i)}{(1 - F_{i+1})} \right] \quad (5)$$

where *n* is the total number of steps in the isothermal run; $F_0 = 0$, and F_i and F_{i+1} are the cumulative fractions lost in the *i*th and (i + 1)th isothermal steps; and $t = t_{i+1} - t_i$. Eq. (4) is derived from Eq. (2) using the first two terms and Eq. (5) is derived from Eq. (3). A detailed examination and discussion of the errors caused by these approximation equations in computing D/a^2 are given in Appendix B.

4. HTXRD and SEM results

The HTXRD-derived cell parameters of both biotite samples heated in vacuo are plotted against temperature (Fig. 2). All cell parameters lengthen from 90°C to 500°C, suddenly decrease at around 600°C, reaching minimum values in the temperature range of 600-850°C, and then gradually increase again to 1000°C. All of the reflection peaks persist to 1000°C with a slight decrease of reflection intensities after 950°C. In a separate isothermal HTXRD run of KM biotite at 700°C (Fig. 3), the unit cell parameter, b, decreased with time during the first 5 h and then remained relatively constant during the latter stages of isothermal heating; the *a* and *c* cell parameters also decreased slightly, although the magnitude of the changes were much smaller than b. This is consistent with the findings of Gaber et al. (1988), who also noted a decrease in cell parameter dimensions over the temperature range of 600-800°C, accompanied by a weight loss of 0.72-0.83%.

KM biotite was also observed to lose about 5.43-5.54% in weight after being heated to 1200° C, whereas CPC biotite lost 3.19-3.65%. These weight



Fig. 2. Change in the cell parameters of (a) KM biotite and (b) CPC biotite with temperature.

losses are very close to the volatile contents of samples, as inferred from the total anhydrous content obtained by microprobe analyses (Table 1).

SEM analyses show that CPC biotite grains did not change their structure below 640°C, although they started to decompose along the surfaces of the cleavage planes at this temperature (Fig. 4). At temperatures above 700°C, the biotite grains show sub-



Fig. 3. Change in b cell parameter of KM biotite with time for a 700°C HTXRD isothermal run.



Fig. 4. SEM images of a flake of CPC biotite (a) before heating; (b) after heating at 640°C for 30 min in vacuo, some decomposition has taken place along the cleavage planes and on the grain surface; (c) after heating at 700°C for 30 min, partings with spacing of few μ m are well-developed.

stantial morphological changes, in which partings with spaces of a few microns gradually developed along the original cleavage planes as a result of reaction-induced delamination (Fig. 4c).

5. 40 Ar $-^{39}$ Ar results

5.1. Age spectra

The ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ analytical data are presented in Appendix A and plotted as age spectra in Fig. 5. All of the age spectra exhibit plateaus over more than 97% of the 39 Ar_K released and the plateau dates are indistinguishable among all of the isothermal runs for each sample. In the first few steps of the lowtemperature isothermal runs (400°C and 500°C). anomalous low dates, comprising the first $\sim 1\%$ of $^{39}\text{Ar}_{\kappa}$ release for CPC biotite and ~3% for KM biotite, gradually climb to the plateau dates. This staircase feature is also evident in the first two steps of the KM-600 isothermal run, but does not occur in the 800°C isothermal runs (Fig. 5). The plateau dates obtained in this study are in agreement with those originally reported by Wood et al. (1991) and Lo et al. (1993).

The estimated K₂O, CaO and Cl contents, as derived from the concentrations of ³⁹Ar_K, ³⁷Ar_{Ca} and ³⁸Ar_{Cl} for each sample are in the ranges of 8.00–8.84%, 0.09–0.16% and ~0.6% for KM biotite, and 10.01–10.24%, 0.06–0.12% and 0.11–0.12% for CPC biotite. These values are generally in agreement with those obtained by microprobe analyses (Table 1), and the Ca/K spectra yield flat profiles (Fig. 5), indicating that the above age discordances in the initial stages of the low-temperature isothermal runs are not due to the outgassing of impurities in the samples.

5.2. Argon loss during isothermal heating

The isothermal 40 Ar/ 39 Ar heating data are plotted as *F* vs. (time)^{1/2} in Fig. 6 (all runs) and Fig. 7 (low-temperature runs). Volume-diffusion argon loss curves for various D/a^2 values using a cylindrical geometry (Eq. (1)) are also shown for comparison.

The argon release curves during the low-temperature isothermal runs (400°C and 500°C) are very close to those predicted by volume diffusion for both biotite samples. The release curves of the high-temperature isothermal-heating runs (600° C and 800° C), however, are significantly different from those predicted by volume diffusion (Fig. 6). The rate of argon release at these temperatures (> 600° C) is very similar to that observed by Gaber et al. (1988) for the Std. 8 biotite, where argon loss was very rapid in the early stages of heating and gradually diminished with time. From Fig. 6, it is evident that the rate of argon loss at temperatures greater than 600° C from KM biotite and CPC biotite is not consistent with a volume-diffusion mechanism.

If argon release is controlled by a single diffusion mechanism, then the calculated D/a^2 values should be constant over the entire isothermal portion of the experiment. Consequently, calculated D/a^2 values are plotted against $(time)^{1/2}$ in Fig. 7 for the isothermal runs. From Fig. 7, the variation among the D/a^2 values in the low-temperature isothermal runs is within about factor of five, which is much less than that in the high-temperature isothermal runs. With the exception of the CPC-400 run, the D/a^2 increases from minimum values to a maximum in 30-60 min, and then flattens out over the remainder of the run; the CPC-400 run yields constant D/a^2 values after about an hour of isothermal heating. The variations in D/a^2 in these low-temperature isothermal runs cannot be readily explained by the effects of a range of diffusion radii and/or the use of approximation equations (Eqs. (4) and (5)) in calculating D/a^2 , since the total fraction lost for each sample over the entire period of isothermal heating is much less than 0.4 and the variation of D/a^2 is much greater than that which can be attributed to either the effects of a distribution of diffusion radii or the use of the approximation equations (as discussed in Appendix B).

Upon close examination of the argon release curves for the low-temperature isothermal runs (Fig. 7a–d), the curves can be subdivided into three segments. The first segment reflects a period of relatively fast change in the argon release rate during the initial stages of heating (0–30 min at 500°C and 0–60 min at 400°C). The remaining two segments are approximated by linear trends with different D/a^2 values. The first linear array has a larger D/a^2 and extends from 1 to 10 h for KM-400,





Fig. 6. The argon release from (a) KM biotite and (b) CPC biotite during isothermal in vacuo heating at 400°C (circles), 500°C (squares), 600°C (crosses) and 800°C (triangles). For the low-temperature isothermal runs (400 and 500°C), 40 Ar* release is shown with solid circles and squares, whereas 39 Ar_k is shown by open circles and squares. For the high-temperature isothermal runs (600°C and 800°C), only 40 Ar* is displayed because there are negligible differences between the two argon isotopes. Theoretical volume diffusion curves obtained from Eq. (1) for a cylindrical crystal with various D/a^2 values are also presented on the same diagram for comparison. The data for the 800°C isothermal runs exclude the argon released in the first two steps (650°C and 750°C — 30 min/step).

0.5–4 h for KM-500 and 0.5–11 h for CPC-500; the data from the later stages of isothermal heating for all of the samples form the second array. In each array, the D/a^2 values calculated from the release of ${}^{39}\text{Ar}_{\text{K}}$ and ${}^{40}\text{Ar}^*$ are generally consistent with each other within 1σ . The mean D/a^2 for the first array is usually about 2–3 times higher than the second array. The CPC-400 run, however, only exhibits a single linear trend after 6 h.

The time at which the transition occurs from the high-diffusivity linear trend to the lower-diffusivity linear trend varies between the runs (Fig. 7a–d). This transition point appears to be inversely correlated with the isothermal temperature for each sample. although it occurs roughly at the same cumulative fraction lost F. For instance, in the case of KM biotite, the change in D/a^2 occurs at ~ 5% of the total ${}^{39}Ar_{V}$ lost, while for CPC biotite, the transition takes place at ~11% (Fig. 7a, b and d). This implies that a fixed amount of gas is lost faster than the gas released in the later stages of isothermal heating. If this is the case, then the CPC-400 run, which only shows a single linear trend on the F vs. $t^{1/2}$ diagram (Fig. 7c), records degassing of only the first argon component, since the total amount of argon lost during the isothermal portion of the experiments was only $\sim 2.7\%$ (Fig. 6b).

 D/a^2 values for all high-temperature isothermal runs exponentially decrease with time (Fig. 7e–g). The D/a^2 decreases by about one order of magnitude in the KM-600 run and about 2 orders of magnitude in the 800°C isothermal runs.

5.3. Argon release during step-heating

The argon release patterns from the normal stepheating runs (KM-N and CPC-N) exhibit two main pulses of Ar release (Fig. 8a–d). The peak of first pulse is centered at $\sim 650^{\circ}$ C for both biotite samples. The peak of the second pulse, however, appears

Fig. 5. 40 Ar/ 39 Ar release spectra for biotites isothermally heated for ~ 44 h compared with the original biotite spectra (from normal step-heating). The Ca/K ratio for each gas fraction is also shown in the same diagram. The original age spectra are outlined, whereas the age spectra from the corresponding isothermal run are plotted with two patterns: black — includes all steps obtained isothermally, shaded — includes the remaining steps obtained by incremental heating.



Fig. 7. Plots of log D/a^2 and cumulative fraction lost vs. (time)^{1/2} for the low-temperature (400°C and 500°C) isothermal runs (a–d) and plots of log D/a^2 vs. (time)^{1/2} for the high-temperature (600°C and 800°C) runs (e–g). Open circles represent ³⁹Ar_K, whereas solid circles represent ⁴⁰Ar^{*}. In the plots for the low-temperature isothermal runs (a–d), the solid line indicates the mean D/a^2 of all points in the second linear array, while the dashed line represents the mean D/a^2 of all points in the first array. Reference lines with different D/a^2 values are also shown in the log D/a^2 vs. (time)^{1/2} plots for the low temperature runs for comparison. For a more detailed discussion of these arrays, please see text.



Fig. 8. Argon release from KM biotite ((a) and (b)) and CPC biotite ((c) and (d)) during step-heating after the isothermal runs. Solid circles, blank squares, solid squares and blank circles represent the 400°C, 500°C, 600°C and 800°C isothermal heating runs, respectively. In (a)–(d), the original release pattern (from normal step-heating) is shown as a thick line. For comparison, the representative ${}^{39}Ar_{K}$ release patterns for a variety of trioctahedral micas with Fe/(Fe+Mg)>0.30 and <0.30, are compiled in (e) and (f), showing the compositional effects on reaction-enhanced argon release. Data sources for (e) and (f): (I) CPC and (II) KM: this study; (III) 48B and (IV) 34B: Onstott et al. (1989); P7A: Phillips and Onstott (1988).

to be inversely correlated with the Fe/(Fe + Mg) ratio of each biotite; the second pulse is centered at ~950°C for KM biotite (Fe[#] = 0.87) and at ~ 1050°C for CPC biotite (Fe[#] = 0.50).

After isothermal heating, all of the biotites were incrementally heated following a fixed temperature/ time schedule. As shown in Fig. 8a and c, after isothermal heating at 400°C and 500°C for about 44 h, the argon release patterns for both biotites still display two pulses, although the second pulse of KM biotite is shifted to a distinctly lower temperature (~ 850°C) and includes a larger proportion of gas. The release pattern of CPC biotite does not appear to be affected by the isothermal heating. Isothermal heating at 600°C and 800°C appears to result in the loss of the first pulse of gas in both biotites, although the second pulse is still present with proportionally less gas (Fig. 8b and d).

6. Argon release mechanisms

To explain the above observations, two factors must be considered: (1) the potential sites where Ar can reside in the biotite crystals, and (2) the possible mechanisms involved in releasing Ar from these sites.

6.1. Possible Ar retention sites

Given that the recoil energy of ${}^{39}\text{Ar}_{K_4}$ (from neutron irradiation) is ~ 300 keV and ${}^{40}\text{Ar}^*$ (from natural decay) is ~ 28 eV, these energies are sufficient for an argon atom to be displaced from its parent K (which is located in biotite interlayer sites) and to penetrate the biotite layer structure (Brandt and Voronovskiv. 1967: Turner and Cadogan. 1974: Onstott et al., 1995). In addition, if there are some defects (i.e., vacancies or dislocations) present in the structure, Ar atoms would preferentially occupy these defect sites (Norgett and Liaiard, 1968; Reed, 1977). Natural biotites also contain other numerous structural defects due to (1) crystal growth or deformation in the natural environment (Bell and Wilson, 1981), (2) neutron irradiation in the reactor and the natural decay of radioactive nuclides (Bonfiglioli et al., 1961; Price and Walker, 1962; Itoh and Tanimura, 1986; Tseng et al., 1995), and (3) sample preparation

(mechanical crushing and grinding) which can potentially damage the crystal structure (MacKenzie, 1953; Gerling et al., 1966; Fechtig and Kalbitzer, 1966; Meike, 1989). Thus, Ar atoms are expected to be homogeneously distributed throughout the entire crystal structure, but will preferentially concentrate in any structural defects. In addition, any atmospheric argon component is likely to be concentrated in these structural defects, since they could act as pathways for relatively rapid argon migration into the crystal.

6.2. Defect-enhanced or short-circuit diffusion

The release curves of the low-temperature isothermal runs (400°-500°C) reflect a relatively constant D/a^2 over most of the duration of the experiment with anomalously high D/a^2 values in the initial stages of heating (Fig. 7). This pattern of release is very similar to the argon released from KCl in isothermal experiments reported by Fechtig and Kalbitzer (1966), which they attributed to enhanced diffusion via structural defects. Not only are dislocations energetically favoured as traps for argon relative to the crystal structure, but they can also enhance the diffusion rate by means of fast-transport mechanisms (Yund et al., 1981; Le Claire and Rabinovitch, 1984). ³⁶Ar is the primary indicator of potential atmospheric contamination in crystals, where it would be expected to be found loosely held in extended defects and defect structures. Fig. 9 shows that most of the ³⁶Ar in the samples is released in the first 30 min to one hour and is associated with high values of D/a^2 in the initial stages of heating (Fig. 7). Thus, existing defects likely play an important role in the low-T release of Ar from biotite in vacuo.

Although the detailed transport mechanisms by which Ar moves through a crystal structure are still unknown, there are several defect-related transport mechanisms which are much more rapid than solidstate volume diffusion. More specifically, many studies (e.g., Hart, 1957; Harrison, 1961; Aifantis, 1979; Yund et al., 1981; Le Claire and Rabinovitch, 1984, and references therein) have suggested and demonstrated that extended defects (such as dislocations, micropores, microfractures, etc.) within individual crystals may serve as preferential pathways for the rapid transport of migrating species. The enhanced



Fig. 9. Fraction of 36 Ar release vs. (time) ${}^{1/2}$ for the low-temperature isothermal heating runs. Most of the 36 Ar was released during the first 30–60 min period of isothermal heating. Solid circles represent the data collected in the CPC-400 run; open circles, CPC-500; solid squares, KM-400; crosses, KM-500.

transport along any such defects may be termed "short-circuit" (SC) diffusion, and the combined interaction of solid-state volume diffusion coupled

Table 2 Multipath diffusion model parameters for low-temperature runs

with SC diffusion is known as multipath diffusion (Lee, 1993, 1995).

Lee (1993: 1995) suggested that because of the relatively large size of the Ar atom (1.9 Å) in relation to the crystal lattice spacings of most silicates, SC diffusion may be an important mode of Ar transport if extended defects are present. In addition to explaining discrepant diffusion data in the bulk Ar diffusion experiments from hornblende (Harrison, 1981) and biotite (Harrison et al., 1985). Lee (1993: 1995) demonstrated that a multipath diffusion mechanism could explain the pattern of low-temperature Ar release of hornblende in in vacuo isothermal experiments. As a result, the low-T (400 and 500°C) isothermal experiments in Fig. 7a-d were modelled using the multipath diffusion model of Lee and Aldama (1992). Input parameters to the model were derived from estimates of the volume-diffusion parameters of Ar in biotite (Giletti, 1974; Norwood, 1974: Harrison et al., 1985: Grove and Harrison, 1996), and the SC diffusion parameters of Lee (1993). The model parameters are given in Table 2 and the results of the modelling are shown in Fig. 10. In all cases, the model provides an adequate fit to the data.

There are a number of important points to note from Table 2. First, the SC diffusion coefficients

	KM biotite				CPC biotite			
	400°C		500°C	500°C			500°C	
	³⁹ Ar _K	⁴⁰ Ar*	³⁹ Ar _K	⁴⁰ Ar*	³⁹ Ar _K	⁴⁰ Ar*	Ar	
General parameters:								
Radius (µm)	96.5	96.5	96.5	96.5	108.5	108.5	108.5	
$\kappa_1 (\times 10^{-7} \text{ s}^{-1})$	0.4	0.4	0.5	0.5	_	_	0.5	
$\kappa_2 (\times 10^{-7} \mathrm{s}^{-1})$	-0.4	-0.4	-0.5	-0.5	_	_	-0.5	
f ^ā (%)	0.3	0.3	0.3	0.3	-	-	0.3	
High-diffusivity / short-circu	it (SC) paths:							
c_1 (initial) (%) ^b	3.8	2.9	4.5	4.0	< 1.0	< 1.0	6.0	
$D_{\rm sc} = D_1 (\times 10^{-10} {\rm s}^{-1})$	14	12	80	60	-	-	8	
Crystal lattice:								
c_2 (initial) (%) ^b	96.2	97.1	95.5	96.0	> 99.0	> 99.0	94.0	
$\hat{D_{v}} = D_{2} (\times 10^{-13} \text{ s}^{-1})$	2.39	2.39	16.8	16.8	1.20	1.12	16.3	

Cylindrical geometry assumed for all runs, using a fully implicit numerical scheme, 1001 spatial nodes, and 2025 time steps of 100 s each. ^aVolume fraction of high-diffusivity pathways.

^bConcentrations are normalized so that total concentration $c = c_1 + c_2 = 1$.



Fig. 10. Results of multipath diffusion modelling for low-temperature isothermal runs at 400 and 500°C. Open and solid circles represent the experimental data for ${}^{39}Ar_{K}$ and ${}^{40}Ar^{*}$, respectively. The experimental data can be explained adequately by coupling enhanced diffusion along extended defects (short-circuit diffusion) with a volume-diffusion mechanism, as proposed in a multipath diffusion model. Model parameters are given in Table 2.

used in the model are several orders of magnitude higher than the respective volume-diffusion coefficients. This is consistent with the experimental findings of several other studies of SC diffusion (e.g., Yund et al., 1981; Yurimoto et al., 1989; Lee, 1993). Second, all runs except the CPC biotite at 400°C show release patterns reflecting SC-controlled diffusion at early times followed by volume-diffusion release at later times in the same experiment. This type of behavior is consistent with the notion that any Ar trapped in SC paths will be released relatively quickly, since SC-diffusion coefficients are several orders of magnitude greater than corresponding volume-diffusion coefficients. At 400°C, the Ar release patterns from CPC biotite are consistent with release via a single diffusion mechanism (Fig. 7c), and modelling the linear segments of the curves vields diffusion coefficients consistent with those expected from Ar released via volume diffusion (Table 2). Third, the model curves require that a small fraction of the Ar must be located initially in the high-diffusivity pathways — a phenomenon which can be explained by the structural decomposition mechanisms discussed previously. At temperatures below the decomposition temperatures of the biotite samples. Fe oxidation and dehvdrogenation are still taking place. Because the oxidation of Fe^{2+} to Fe^{3+} distorts the biotite structure, defects would be expected to nucleate throughout the lattice. As suggested by Lee (1993), such defects could act as preferential trapping sites for Ar. retaining Ar atoms until either the thermal energy is high enough or times are long enough for the Ar to diffuse through a well-connected network of SC paths. Moreover, structural decomposition would also explain why the amount of Ar initially in the SC paths appears to increase with increasing temperature in both KM and CPC biotites. Although the amount of Ar initially sited in the SC paths in KM biotite ($\sim 3-4.5\%$) is identical to that estimated by Lee (1993) in the coexisting hornblende, c_1 in KM biotite is 2.9–3.8% at 400°C but 4.0-4.5% at 500°C (Table 2); a similar

trend is observed for CPC biotite. Higher temperatures would result in a greater degree of Fe-oxidation and dehydroxylation and therefore, a concomitant increase in the defect density.

One notable phenomenon from Fig. 10 is the relationship between the ³⁹Ar and ⁴⁰Ar release patterns in the same experiment. In all cases, the release patterns of both isotopes are strongly correlated. although ³⁹Ar always appears to be released faster than ⁴⁰Ar in the early steps of the experiment. Although both 39 Ar and 40 Ar are generated from K, the greater recoil distance for ³⁹Ar resulting from the 9 K(n, p)³⁹Ar reaction suggests that 39 Ar would not necessarily remain in the same lattice site as radiogenic ⁴⁰Ar (Turner and Cadogan, 1974; Onstott et al., 1995). Although the effects of neutron irradiation damage in biotite have not been studied to date, it is well known that radiation damage can enhance mass transport in solids (e.g., Borge and Dienes, 1988) and that some minerals (e.g., biotite) are particularly susceptible to artificial radiation damage (e.g., Bell and Wilson, 1977; Tseng et al., 1995). Thus, the most significant crystallographic effect of neutron irradiation on biotite is most likely to be the production of extended defects in lattice. Because of the large size of the Ar atom and concomitant energy considerations, Lee (1995) suggested that Ar will prefer to reside in structural defects. If so, then ³⁹Ar recoiled from ³⁹K may be located preferentially in irradiation-damage defects as well as defects found naturally in the crystal. From the model parameters in Table 2, both the ³⁹Ar SC diffusion coefficient (D_{sc}) and ³⁹Ar initial concentration in the SC paths (c_1) are higher than the corresponding ⁴⁰Ar SC diffusion coefficient and initial concentration at the same temperature for all samples. The higher initial concentrations and SC diffusivities of ³⁹Ar in comparison to ⁴⁰Ar agree with this idea, and indicate that neutron irradiation may influence Ar release at very low temperatures. This effect is expected to decrease significantly or disappear altogether at higher temperatures, since such defects would anneal with increasing temperature within a period of a few tens of minutes (Bonfiglioli et al., 1961; Meike, 1989). Indeed, differences between ³⁹Ar and ⁴⁰Ar release in each of the KM and CPC biotite runs are observed to be much less at 500°C than at 400°C. It should be noted that the production of small-scale defects due to Fe-oxidation and dehydroxylation (see Section 6.3) with increasing temperature may be offset eventually by the annealing of these defects (as well as irradiation-induced defects) at elevated temperatures. Although the evidence for enhanced Ar release in biotite via irradiation-induced defects is not definitive, all of the above observations are consistent with this hypothesis.

The relationship between the exchange coefficients, κ_1 and κ_2 , and the Ar partition coefficient k^* between the crystal and SC paths can be used to estimate the volume fraction f of high-diffusivity paths in the crystal, using Eq. 4.11 of Aifantis (1979). Onstott et al. (1991) estimate partition coefficients as high as 333 for Ar between a coexisting fluid and biotite. Assuming that this is probably a minimum value for Ar partitioned between voids/vacancies (i.e., the SC paths) and the crystal. the model parameters yield a maximum estimate of the volume fraction of SC paths of around 0.003, which is not unreasonable. Lee (1993) and Sletten and Onstott (1998) suggested that one important factor which may also contribute to increased defect densities is the thermal oxidation/dehvdrogenation process during heating in vacuo, which could create point/extended defects throughout the crystal lattice.

The multipath diffusion model may also explain why the calculated in vacuo volume diffusion coefficients (D_n) are 1–2 orders of magnitude higher than those of Norwood (1974), Harrison et al. (1985), and Grove and Harrison (1996). As demonstrated by Sanz et al. (1983) and Rebbert (1986), the preferential ordering of cations during thermal oxidation suggests that cations in the biotite structure are at least locally mobile, so that an increased defect density may be associated with the conversion of biotite to oxybiotite. The resultant increase in the number of SC pathways implies that SC diffusion would be the dominant diffusive process at low temperatures and would enhance the bulk Ar diffusivity in the biotite. Consequently, the volume diffusivities (D_y) calculated from the latter steps of the low-temperature isothermal runs may not be strictly representative of a true volume-diffusion process, but may be bulk diffusivities reflecting Ar release via multipath diffusion.

It is also of interest to compare the argon diffusivity of biotite in vacuo with the diffusivities derived from hydrothermal experiments on biotites with varying composition (Giletti, 1974; Norwood, 1974; Harrison et al., 1985: Grove and Harrison, 1996). In general, the argon diffusivity in biotite appears to be empirically correlated with the Fe/(Fe + Mg) ratio of the mineral (Onstott et al., 1989), as predicted in the ionic porosity model of Dahl (1994). Using the interpolation scheme proposed by Onstott et al. (1989), in which both the pre-exponential frequency factor (D_0) and the activation energy (E) of argon diffusion are functions of the Fe/(Fe + Mg) value, KM biotite (Fe[#] = 0.87) and CPC biotite (Fe[#] = 0.50) should have activation energies of 40.5 kcal/mole and 47.9 kcal/mole, respectively. The estimated D_0 for KM biotite is either 0.00052 cm²/s (by interpolating the data of Giletti (1974) and Norwood (1974) (G and N)) or 0.01938 cm^2/s (by interpolating the data of Giletti (1974). Harrison et al. (1985) and Grove and Harrison (1996) (G and H)). For CPC biotite, D_0 should be either 0.01161 cm^2/s or 0.0989 cm^2/s , respectively.

Based on these parameters, theoretical D/a^2 values were calculated at temperatures from 300–1000°C for each biotite sample, assuming various *a* values, and plotted on Arrhenius diagrams with the calculated mean D/a^2 values for the corresponding

isothermal runs (Fig. 11). From the figure, it is clear that the D/a^2 values calculated from the later stages of the low-temperature isothermal runs (as shown in Fig. 7) are about 2–4 orders of magnitude higher than those obtained from the hydrothermal diffusion data (shown as shaded areas in Fig. 11).

The most obvious cause for this discrepancy is a difference in the effective diffusion dimension *a*. Assuming this discrepancy is the sole result of *a*, then these D/a^2 values yield an effective radius of diffusion equal to $1-15 \mu$ m which is much smaller than the 64–225 μ m values reported by Norwood (1974), Harrison et al. (1985) and Wright et al. (1991). This range of *a*, however, is consistent with an increase in defect density (i.e., SC pathways) as the mineral grains are heated. With the formation of additional SC pathways and networks throughout the crystal structure, the enhanced Ar release rate would be similar to that expected from a much smaller diffusion domain.

6.3. Reaction-enhanced release of argon

In Figs. 6 and 7, it is evident that the argon released from biotites during high-temperature



Fig. 11. Comparison of D/a^2 for argon diffusion during the in vacuo low-temperature isothermal heating (circles) with D/a^2 values (shown as lines for a range of values) derived from Ar diffusion data interpolated from published experimental results. See text for discussion and the interpolation method. Solid lines utilize the D_0 value interpolated from the data of Giletti (1974), Harrison et al. (1985) and Grove and Harrison (1996), while dashed lines use D_0 values obtained from interpolating the data of Giletti (1974) and Norwood (1974). The shaded areas mark the possible ranges of the argon diffusivity of biotite with characteristic diffusion radius of 65–150 μ m, as suggested by Norwood (1974) and Harrison et al. (1985).

isothermal heating (> 600°C) is not controlled by a simple volume-diffusion mechanism, as reflected in the rapid loss of argon and the substantial decrease of D/a^2 with time. Gaber et al. (1988) observed similar features for a biotite heated at ~ 800°C in vacuo, and suggested that the rate of argon release from biotite at high-temperatures could be controlled by some process related to phase changes within the mineral. Indeed, both biotites in this study appear to have experienced complicated structural changes, as demonstrated by the HTXRD and SEM results (Figs. 2–4).

The reduction of all cell parameters at elevated temperatures is consistent with the replacement of biotite with oxybiotite, through dehydrogenation, dehydroxylation and the oxidation of Fe (Wones, 1963: Ohta et al., 1982; Rebbert, 1986; Ferrow, 1987). In general, two types of oxidation are thought to occur in biotites when heated (Vedder and Wilkins, 1969; Rouxhet et al., 1972; Sanz et al., 1983; Rebbert, 1986). Thermal oxidation occurs when iron reacts with hydroxyl ions in the biotite structure due to the thermally-induced decomposition, i.e., 2Fe⁺² + $2OH^- \rightarrow 2Fe^{+3} + 2O^{-2} + H_2$. Chemical oxidation occurs when iron reacts with both free oxygen and/or the hydroxyl ions during heating, i.e., $4Fe^{+2}$ + $4OH^- + O_2 \rightarrow 2H_2O + 4Fe^{+3} + 4O^{-2}$ or $Fe^{+2} +$ $1/4O_2 \rightarrow Fe^{+3} + 1/2O^{-2}$. Thermal oxidation generally takes place at temperatures of 600-800°C and results in weight loss, whereas chemical oxidation generally takes place at lower temperatures (400-600°C) and results in weight gain (Rouxhet et al., 1972; Sanz et al., 1983). The temperature range over which the cell parameters decrease in this study (600-850°C, Figs. 2 and 3), in addition to the weight-loss data discussed previously, strongly suggests that thermal oxidation is probably the dominant process affecting biotites heated in vacuo.

Previous IR and Mössbauer studies indicate that biotite heated at elevated temperatures will experience a series of decomposition reactions, including dehydroxylation, dehydrogenation and oxidation, associated with the appearance of such decomposition products as α -Fe₂O₃ and amorphous materials (Vedder and Wilkins, 1969; Rouxhet et al., 1972; Tripathi et al., 1978; Bagin et al., 1980; Sanz et al., 1983; Ferrow, 1987). These processes usually occur in three stages: (a) release of OH⁻ groups (as H₂O)

associated with two cations and one vacancy at temperatures between 600-800°C: this becomes negligible below 600°C: (b) oxidation of Fe^{+2} to Fe^{+3} with simultaneous loss of hydrogen or hydroxyl ions from 600-800°C (thermal oxidation); and (c) loss of OH^- groups close to the octahedral sites — $3Mg^{+2}$, $2Mg^{+2}Fe^{+3}$ and $Mg^{+2}2Fe^{+3}$ — around 1000°C before or during the final decomposition of biotite. The structural changes involved in the transformation of biotite to oxybiotite include flattening of octahedral sites, rotation of tetrahedral sites and distortion of interlayer sites in the biotite structure (Hazen and Wones, 1972, 1978; Ohta et al., 1982). In addition, the generation of H₂ and H₂O after dehydroxylation and dehydrogenation, as well as the structural distortion due to Fe-oxidation, dehvdroxvlation and dehvdrogenation, will cause internal stress within the phyllosilicate structures, potentially causing the structural delamination in biotite, as observed in Fig. 4 (Vedder and Wilkins, 1969; Stucki et al., 1984; Catti et al., 1989; Wu et al., 1989).

Argon retained in the crystal is held essentially by the ionic bonds of the surrounding ions, since the Van der Waals bonds between Ar and other elements are too weak to prevent argon escape from the mica structure (Sardarov, 1961; Dahl, 1994). In this case, the irreversible destruction of the biotite structure (through the breaking of chemical bonds and subsequent delamination) could result in the rapid escape of Ar atoms from the crystal. Delamination would not only lead to the loss of argon residing in the interlayer sites, but would also result in a reduction in the characteristic dimension for argon diffusion. Consequently, even though small-scale (e.g., lattice) defects would be expected to anneal out at elevated temperatures, significantly enhanced diffusion would be expected for argon released from biotite at temperatures above its stability field due to the delamination process, as observed in Figs. 6 and 7. A similar phenomenon has also been found in hornblende and muscovite (Lee, 1993; Sletten and Onstott, 1998).

The correlation of Ar release with the decomposition of the biotite structure implies that the number of argon release pulses in a typical step-heating run should be determined by the number of octahedral environments for the OH^- ions, and the fractional loss of Ar should approximately reflect the volume fraction of biotite structure that has decomposed, i.e., Ar release at high temperatures will be a function of biotite composition and the abundance of octahedral vacancies. There are at least five possible octahedral cation configurations surrounding OH⁻ in the biotite structure: OH^--3Mg^{+2} , $OH^--2Mg^{+2}Fe^{+2}$, $OH^- Mg^{+2}2Fe^{+2}$, $OH^{-}-3Fe^{+2}$, $OH-2R^{+2}\square$ (where R represents the cation, and \Box indicates a vacancy). As discussed above, the decomposition of biotite first proceeds by the loss of OH⁻ near vacancies and Fe cations between 600-800°C, followed by the loss of the rest of the OH⁻ near $3Mg^{+2}$, $2Mg^{+2}Fe^{+3}$ and Mg⁺² 2Fe⁺³ at around 1000°C. Thus, two pulses of argon release centered around these temperature ranges (600-800°C, and ~1000°C) would be expected for the ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ step-heating of biotite. On the other hand, because there is only one type of octahedral configuration for OH⁻ in phlogopite, i.e., $OH^{-}-3Mg^{+2}$, only one argon release pulse is expected. Fig. 8 also includes a compilation of Ar release data from biotite and phlogopites obtained in other studies (Fig. 8e-f). The release patterns of the previously published biotite data and the biotite samples in this study (Fe[#] > 0.5), [which display two pulses centered at ~ 650°C and 950–1050°C (Fig. 8a-e)], in addition to the phlogopite data [which only show a single release pulse at 950-1050°C (Fig. 8f)], are consistent with this hypothesis. Thus, the loss of argon at high temperatures (> 600° C) must be controlled by the decomposition processes, i.e., reaction-enhanced diffusion.

This hypothesis may also explain why the temperature range of the second Ar release pulse for the more Fe-rich KM biotite is lower than that for the CPC biotite (Fig. 8a–d). Because the loss of $OH^$ near the Fe⁺³ rich sites is likely to be easier than the loss of OH^- near Mg⁺²-rich sites (due to the additional effects of Fe oxidation), (Vedder and Wilkins, 1969; Hazen and Wones, 1972, 1978; Ferrow, 1987), this would lower the stability field of biotite resulting in lower temperatures of Ar release.

It is well-known that the decomposition reactions of phyllosilicates are both temperature and time-dependent (Kodama and Brydon, 1968; Brindley and Lemaitre, 1987; Malhotra and Ogloza, 1989; Sletten and Onstott, 1998). With the gradual formation of oxybiotite as the biotite begins to decompose, the effect of reaction-enhanced diffusion on Ar release would be expected to decrease. This is consistent with the observation that D/a^2 values in the hightemperature isothermal runs exponentially decrease with time (Fig. 7e–f). Although it is possible that after very long times, Ar release from the partially decomposed biotite may eventually reflect a volume-diffusion process, the utility of any diffusion coefficient calculated from such data is questionable, as it characterizes argon release from a crystal structure significantly different from true biotite.

7. Implications for disturbed apparent age spectra

The above considerations can also explain some of the causes for the formation of disturbed age spectra. In the age spectra for the biotites (Fig. 5). the first few percent of ${}^{39}Ar_{K}$ released in the 400°C and 500°C runs yield young dates. By examining the corresponding D/a^2 values for ${}^{39}Ar_{\rm K}$ and ${}^{40}Ar^*$, however, the release rate of ${}^{39}Ar_{\rm K}$ during this portion of the experiment was much faster than ${}^{40}\text{Ar}^*$. although this difference diminishes with time (Figs. 7 and 10). According to volume-diffusion theory, the voung dates could result from a depletion of ⁴⁰Ar* along the grain margins. An alternative explanation, however, is that this phenomenon arises because of differences in the release of ${}^{39}Ar_{\kappa}$ residing in various defects vs. that in the crystal structure. If a biotite crystal contains a number of structural defects before neutron irradiation, argon residing in these structural defects is probably dominated by atmospheric argon with a negligible amount of radiogenic ⁴⁰Ar (e.g., Figs. 7, 9 and 10). During neutron irradiation, ³⁹Ar can be implanted into these structural defects through recoil. The argon residing in these structural defects will be first released via SC diffusion during the early stages of in vacuo heating, and will have low 40 Ar*/ 39 Ar ratios, resulting in young apparent ages.

Similarly, if there was excess argon present in these structural defects, the resulting age spectra should exhibit anomalously old dates in the early heating steps. This might explain the age spectrum of a hydrothermally treated biotite (Cooma biotite) reported by Harrison et al. (1985). Before hydrothermal treatment, the biotite separate yielded a flat age spectrum with a plateau date consistent with the K–Ar date (399.8 Ma), indicating a homogeneous distribution of 40 Ar* in the original biotite. After being placed in a hydrothermal bomb (for 9.05 days with 5–20% water at 700°C), the age spectrum of the biotite displayed a rapid decrease from initially

old dates (1275 Ma) down to a plateau (at 234 Ma) extending over the last 80% of the total ³⁹Ar released. Harrison et al. (1985) attributed the shape of this age spectrum to an artifact of the vacuum extraction technique, resulting from the dehydroxylation of the biotite. It seems very unlikely, however, that any



Cumulative fraction lost

Fig. 12. (a) Fractional loss for a cylindrical crystal according to Eq. (1) using the first 20 terms of the exact solution (I), and the approximation equations (II and III) (Eqs. (2) and (3), in text). If only the first two terms of Eq. (2) are used, the fraction lost is shown as (IV). (b) Underestimated and overestimated D/a^2 (shown as percent of deviation from the true value) caused by using the approximation equations (Eqs. (4) and (5), in text). The percent deviation is a function of the cumulative fraction lost and D/a^2 . The curves in the upper part of the diagram represent D/a^2 calculated from Eq. (5) in the text, whereas those in the lower part represent D/a^2 calculated from Eq. (4). In general, a value of F = 0.6 has been used to mark the transition between the use of either Eq. (4) or Eq. (5).

dehydroxylation process can cause anomalously old dates in a biotite age spectrum. Instead, these dates could be the result of the rapid release of an excessargon component residing in structural defects in the mineral. When the biotite was heated in the hydrothermal bomb, the ${}^{40}\text{Ar}^*$ lost from the biotite would increase the ${}^{40}\text{Ar}/{}^{36}\text{Ar}$ ratio in the surrounding fluid. This "excess" argon component could



Fig. 13. The distribution of diffusion radii (shown in (a)) used in modelling the effect of a distribution of diffusion radii on the estimation of D/a^2 (shown in (b)). Curves (I) and (II) represent normal distributions of diffusion radii with a mean value of 100 µm but with different standard deviations: 20 µm for (I) and 50 µm for curve (II). Curves (III) and (IV) represent lognormal and inverse-lognormal distributions, respectively, with a same mean diffusion radius and standard deviation as (II). The curves were constructed by assuming that the argon lost from a bulk sample with the grain size distribution shown in (a) was controlled by volume diffusion with a constant D value $(10^{-12} \text{ cm}^2 \text{ s}^{-1})$.

have been trapped easily in the structural defects and subsequently released via SC diffusion in the low-temperature steps of the 40 Ar/ 39 Ar step-heating experiment, yielding anomalously old dates.

From the above discussion, the structural defects play an very important role in the Ar released in the low-temperature steps of an 40 Ar/ 39 Ar step-heating experiment. When interpreting the age spectra of natural biotites, two things must be considered. First, any argon (including argon contamination such as excess argon) residing in the structural defects might not be easily detected and SC diffusion is so fast relative to volume diffusion that the Ar in these defects can be rapidly exchanged. Secondly, most of the temperature steps utilized in typical step-heating experiments are generally higher than the decomposition temperature of biotite (which starts as low as 600°C). At these temperatures, argon release is strongly correlated with the decomposition process. This could homogenize any age gradients, potentially leading to plateau profiles, regardless of the spatial distribution of argon in the crystal. Several examples of biotite plateaus, for samples known either to contain excess argon or to have experienced argon loss (e.g., Berger, 1975; Dallmeyer, 1975; Hanson et al., 1975; Foland, 1983), appear to reflect this phenomenon. Consequently, in 40 Ar/ 39 Ar step-heating experiments, accurate information on the spatial distribution of Ar within biotite will only be obtained from using a temperature schedule that includes more low-temperature steps of longer duration (for T <600°C) and only if SC diffusion and recoil effects are well-constrained. In certain circumstances, however, such low-T steps may serve as sensitive indicators of the existence of non-radiogenic (e.g., unsupported, excess) ⁴⁰Ar within biotite, since this type of Ar will preferentially reside in SC pathways. For example, if the ages are obtained in the low-T steps of a step-heating run are lower than those in subsequent high-T steps, then this suggests that excess Ar may not be an influential component of any dates derived from the experiment. In general, however, it is clear that the most definitive means to evaluate the intragrain spatial distribution of argon in biotite is by using a spot-fusion (laser microprobe) technique.

Many authors have attributed the disturbed age spectra from biotite to be the result of biotite phase changes at high temperature during 40 Ar/ 39 Ar in

vacuo heating (Berger, 1975; Hanson et al., 1975; Harrison et al., 1985; Hess et al., 1987). From results of the present study, as well as those from Lo and Onstott (1989), phase changes in biotite during 40 Ar/ 39 Ar step-heating are unlikely to induce any perturbations in the age spectra at high temperatures ($T > 600^{\circ}$ C); indeed, the decomposition of biotite would probably have the opposite (homogenizing) effect. Consequently, any disturbances reflected in the high-temperature steps of a biotite age spectrum are therefore likely to be caused by effects other than phase changes, e.g., the outgassing of mineral impurities or the artifacts of experimental procedures (e.g., improper blank corrections, uneven heating of the sample, etc.).

The importance of both short-circuit (SC) diffusion and ³⁹Ar recoil in step-heating experiments may have fundamental implications for the volume-diffusion interpretation of spatial distributions of Ar in other minerals using a 40 Ar/ 39 Ar step-heating technique (e.g., Lovera et al., 1993). From the biotite degassing experiments, the amount of ³⁹Ar that can recoil into extended defects is measurable and nontrivial, confirming the theoretical predictions of Onstott et al. (1995) and Villa (1997). That these defects exist in many minerals and can serve as highdiffusivity pathways throughout individual crystals during the low-T steps of a step-heating run means that an accurate determination of the spatial distribution of ages within mineral grains with the ultimate intent of deriving temperature-time histories from such models is not possible using the data from these steps.

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Appendix A.	⁴⁰ Ar/ ³⁹ Ar	analytical d	lata							
Step no.	<i>T</i> (°C)	Time (min)	^{36}Ar (×10 ⁻¹⁰)	$^{37}\text{Ar}_{\text{Ca}}$ (×10 ⁻⁹)	$^{38}\text{Ar}_{\text{Cl}}$ (×10 ⁻⁹)	$^{39}\text{Ar}_{\text{K}}$ (×10 ⁻⁸)	$^{40}\text{Ar}^{*}$ (×10 ⁻⁷)	$^{39}Ar_{K}$ Cum.	40 Ar* Cum.	Apparent age (Ma)
VIAND:	(1,	1	CCNTP	CCNTP	CCNTP	CCNTP	CCNTP	loss (%)	loss (%)	
KM-N Biotite	(normal stej 550	<i>p-neating ru</i> 30	n) 15 35	0.80	2 97	6.02	931	4 62	4.05	85.0 ± 1.8
2	580	60	2.81	0.36	2.97	6.02	11 11	9.43	8.89	97.2 ± 1.0
3	610	90	2.60	0.18	3.80	8.67	15.24	16.07	15 52	964 ± 0.9
4	640	120	1.68	0.42	5.00	11 47	20.41	24.87	24 40	97.5 ± 1.0
5	670	150	0.94	0.12	4 86	11.09	19.88	33 38	33.05	983 ± 10
6	700	180	0.67	0.28	4 01	9.23	16.49	40.46	40.23	97.9 ± 1.0
7	750	210	1 22	0.30	3.09	6 94	12.20	45 77	45 54	965 ± 14
8	800	240	1.54	0.50	3.04	6.87	12.20	51.04	50.80	96.5 ± 1.7
9	840	270	1.18	0.70	2.01	4.30	7.57	54.34	54.09	96.4 ± 1.2
10	880	300	1.08	0.64	2.74	6.02	10.77	58.96	58.78	98.0 ± 1.3
11	907	330	1.42	0.21	3.62	8.16	14.50	65.21	65.09	97.4 ± 1.0
12	932	360	2.00	0.48	0.52	11.74	20.88	74.22	74.18	97.5 ± 1.0
13	957	390	1.89	0.47	3.34	7.37	12.98	79.87	79.83	96.6 ± 1.1
14	1000	420	2.87	0.57	4.36	9.71	17.12	87.32	87.28	96.7 ± 1.2
15	1040	450	2.33	0.49	2.93	6.51	11.52	92.31	92.29	97.0 ± 1.0
16	1090	480	3.88	0.27	3.30	7.23	12.88	97.85	97.90	97.7 ± 1.0
17	1150	510	5.60	0.40	1.37	2.81	4.83	100.00	100.00	94.5 ± 1.1
Mass = 0.150)2 g					J-value = 0.0	003123 + 0.00002	29		
Integrated dat	te = 96.6 + 0	.9 Ma				Plateau date	$= 97.2 \pm 0.9$ Ma	(steps 2–17)		
8										
KM-400 Biota	ite (400°C is	othermal rui	n)							
1	400	5	9.84	0.22	0.96	0.44	0.32	0.41	0.14	32.1 ± 3.8
2	400	15	6.11	0.08	0.66	0.47	0.53	0.85	0.36	49.8 ± 1.2
3	400	30	5.03	0.24	0.39	0.62	0.91	1.42	0.74	64.5 ± 3.4
4	400	50	3.64	0.26	0.30	0.62	1.18	1.99	1.24	83.6 ± 2.8
5	400	80	3.61	0.35	0.31	0.65	1.27	2.59	1.78	85.8 ± 1.5
6	400	130	3.80	0.14	0.30	0.70	1.36	3.25	2.36	84.7 ± 2.7
7	400	220	3.68	0.14	0.33	0.78	1.62	3.97	3.04	90.5 ± 2.1
8	400	370	3.36	0.07	0.34	0.89	1.86	4.80	3.83	91.3 ± 3.1
9	400	610	2.78	0.06	0.34	0.91	1.90	5.64	4.64	91.7 ± 2.9
10	400	850	1.59	0.18	0.23	0.63	1.33	6.23	5.20	91.9 ± 3.5
11	400	1150	0.98	0.15	0.18	0.61	1.36	6.79	5.78	98.1 ± 1.5
12	400	1580	1.02	0.17	0.20	0.67	1.51	7.42	6.42	97.7 ± 1.7
13	400	2170	0.82	0.07	0.24	0.69	1.55	8.06	7.08	98.4 ± 2.3
14	400	2800	0.64	0.04	0.22	0.60	1.35	8.62	7.65	97.8 ± 2.2
15	550	2830	1.04	0.06	1.02	2.70	6.01	11.12	10.20	97.2 ± 1.1
16	581	2860	0.69	0.45	1.58	4.22	9.55	15.04	14.25	98.7 ± 0.8
17	610	2890	0.86	0.15	2.38	6.07	13.45	20.68	19.95	96.7 ± 0.7
18	641	2920	0.88	0.06	2.65	7.06	15.48	27.24	26.52	95.8 ± 0.7

KM-400	Biotite (400°C i	sothermal rur	ı)							
19	670	2950	0.74	0.07	3.55	9.36	20.50	35.93	35.22	95.6 ± 0.7
20	700	2980	0.44	0.19	2.44	6.57	14.34	42.03	41.30	95.3 ± 1.1
21	750	3010	0.58	0.08	3.16	8.45	18.53	49.88	49.16	95.7 ± 0.7
22	800	3040	0.78	0.07	3.30	8.35	18.34	57.63	56.94	95.9 ± 0.7
23	840	3070	1.52	0.77	5.02	13.09	29.33	69.79	69.38	97.8 ± 0.8
24	880	3100	1.39	0.83	4.49	11.79	26.04	80.74	80.43	96.5 ± 0.7
25	907	3030	1.45	0.42	4.78	12.55	27.66	92.40	92.16	96.2 ± 0.7
26	932	3160	0.33	0.06	1.67	4.41	9.75	96.49	96.29	96.6 ± 0.9
27	957	3190	0.04	0.07	0.75	1.92	4.37	98.27	98.15	99.2 ± 0.8
28	1000	3220	0.59	0.46	0.36	1.08	2.42	99.27	99.18	97.9 ± 2.2
29	1041	3250	1.12	0.50	0.23	0.63	1.40	99.86	99.77	97.5 ± 4.4
30	1090	3280	1.34	1.10	0.00	0.08	0.29	99.93	99.90	158.4 ± 41.5
31	1150	3310	1.42	0.06	0.00	0.07	0.25	100.00	100.00	145.0 ± 58.8
Mass = 0).1364 g					J-value = (0.002486 ± 0.0000	017		
Integrate	d date = 95.6 ± 0	0.7 Ma				Plateau dat	$e = 96.2 \pm 0.7 Ma$	a (steps 4–29)		
KM-500	Biotite (500°C i	sothermal rui	1)							
1	500	7	7.28	0.18	0.60	1.14	1.63	1.12	0.72	63.1 ± 1.6
2	500	27	9.78	0.29	0.98	2.07	4.13	3.14	2.54	87.3 ± 1.4
3	500	61	4.12	0.30	0.74	1.70	3.69	4.81	4.17	94.7 ± 1.5
4	500	105	1.00	0.07	0.22	0.68	1.49	5.47	4.83	96.2 ± 2.1
5	500	206	1.81	0.06	0.68	1.67	3.70	7.10	6.46	96.9 ± 1.6
6	500	344	1.33	0.01	0.52	1.46	3.18	8.53	7.87	95.4 ± 1.4
7	500	564	0.52	0.06	0.35	1.05	2.36	9.56	8.91	97.8 ± 2.1
8	500	879	0.73	0.05	0.59	1.58	3.47	11.10	10.44	96.1 + 1.0
9	500	1258	0.58	0.03	0.48	1.35	2.90	12.42	11.72	93.8 ± 2.4
10	500	1750	0.08	0.03	0.51	1.53	3.46	13.92	13.25	98.9 ± 1.6
11	500	2222	0.07	0.05	0.37	1.06	2.31	14.95	14.27	95.5 ± 2.3
12	500	2670	0.04	0.44	0.31	0.96	2.08	15.89	15.19	94.3 ± 3.0
13	549	2700	0.06	0.05	0.34	0.94	1.96	16.81	16.05	91.1 ± 2.2
14	580	2730	0.08	0.06	0.85	2.28	5.02	19.04	18.27	96.2 ± 1.1
15	610	2760	0.45	0.01	1.83	4.74	10.37	23.68	22.85	95.6 ± 0.8
16	641	2790	0.49	0.08	2.73	7.00	15.36	30.53	29.63	95.8 ± 0.8
17	670	2820	0.61	0.05	3.35	8.58	18.83	38.93	37.94	95.8 ± 0.7
18	700	2850	0.12	0.46	2.41	6.27	13.72	45.06	44.00	95.6 ± 0.8
19	752	2880	0.87	0.45	3.26	8.15	18.26	53.03	52.06	97.8 ± 1.4
20	800	2910	1.00	0.60	4.19	10.40	23.47	63.20	62.42	98.5 ± 0.8
21	840	2940	1.63	0.27	5.16	13.21	29.65	76.13	75.51	98.0 ± 0.8
22	880	2970	1.36	0.23	5.11	12.64	28.85	88.50	88.25	99.6 ± 1.1
23	907	3000	0.70	0.35	2.43	6.48	14.26	94.84	94.55	96.1 ± 1.0
24	932	3030	0.20	0.34	1.04	2.73	6.27	97.51	97.31	100.2 ± 1.3

Appendix A	. (continued)									
Step no.	<i>T</i> (°C)	Time	³⁶ Ar	³⁷ Ar _{Ca}	³⁸ Ar _{Cl}	³⁹ Ar _K	⁴⁰ Ar*	³⁹ Ar _K	$^{40}\text{Ar}^*$	Apparent
		(min)	$(\times 10^{-10})$	$(\times 10^{-9})$	$(\times 10^{-9})$	$(\times 10^{-8})$	$(\times 10^{-7})$	Cum.	Cum.	age (Ma)
			CCNTP	CCNTP	CCNTP	CCNTP	CCNTP	loss (%)	loss (%)	
KM-500 Bion	tite (500°C is	othermal run	ı) 0.10	0.27	0.45	1.16	0.67	00.65	00.40	100.0 + 2.1
25	957	3060	0.10	0.37	0.45	1.16	2.67	98.65	98.49	100.0 ± 3.1
26	1000	3090	0.10	0.84	0.20	0.67	1.56	99.30	99.18	101.6 ± 4.7
27	1039	3120	0.26	0.09	0.13	0.45	1.18	99.74	99.70	113.7 ± 4.9
28	1100	3150	1.88	0.60	0.02	0.07	0.22	99.81	99.80	132.4 ± 21.6
29	1190	3180	3.26	0.20	0.08	0.19	0.46	100.00	100.00	105.0 ± 10.9
Mass = 0.16	13 g					J-value = 0.0	002486 ± 0.00001			
Integrated da	$te = 96.8 \pm 0$./ Ma				Plateau date	$= 9/.1 \pm 0.7$ Ma	(steps 3–26)		
KM-600 Biot	tite (600°C is	othermal run	1)							
1	600	5	42.29	3.45	5.28	8.29	16.06	7.55	6.72	84.9 ± 0.7
2	600	12	4.13	1.56	0.95	1.96	3.98	9.33	8.39	89.1 ± 1.9
3	600	30	8.90	1.46	3.25	7.71	16.40	16.36	15.26	92.9 ± 0.8
4	600	50	1.86	0.43	1.64	4.23	9.15	20.21	19.09	94.5 ± 1.3
5	600	80	0.83	0.00	1.74	4.40	9.74	24.22	23.17	96.6 ± 1.1
6	600	120	0.95	0.25	1.64	4.24	9.26	28.08	27.05	95.4 ± 0.9
7	600	147	0.05	0.08	0.91	2.44	5.38	30.31	29.30	96.1 ± 1.2
8	600	198	0.05	0.29	1.32	3.60	7.97	33.59	32.63	96.6 ± 1.1
9	600	257	0.05	0.08	1.23	3.37	7.41	36.66	35.74	96.0 ± 0.9
10	600	337	0.04	0.09	1.35	3.54	7.77	39.88	38.99	96.0 ± 0.9
11	600	440	0.05	0.07	1.40	3.73	8.17	43.28	42.41	95.7 ± 0.9
12	600	537	0.04	0.07	1.11	2.84	6.27	45.86	45.04	96.5 ± 1.9
13	600	657	0.07	0.06	1.16	3.23	7.14	48.80	48.02	96.4 ± 1.0
14	600	810	0.03	0.00	1.21	3.21	7.12	51.73	51.00	96.7 ± 0.9
15	600	960	0.02	0.02	0.91	2.58	5.69	54.08	53.38	96.2 ± 1.5
16	600	1165	0.03	0.00	0.99	2.79	6.15	56.62	55.96	96.3 ± 1.1
17	600	1486	0.01	0.02	1.31	3.55	7.79	59.85	59.22	95.7 ± 0.9
18	600	1966	0.29	0.09	1.53	4.30	9.49	63.77	63.19	96.4 ± 1.3
19	600	2366	0.07	0.10	0.83	2.41	5.24	65.96	65.39	95.0 ± 1.8
20	600	2796	0.03	0.08	0.67	2.01	4.39	67.79	67.22	95.5 ± 1.2
21	611	2826	0.02	0.08	0.00	0.14	0.27	67.92	67.34	83.6 ± 5.1
22	641	2856	0.03	0.08	0.09	0.46	0.94	68.34	67.73	89.5 ± 5.6
23	670	2886	0.05	0.05	0.36	1.17	2.53	69.40	68.79	94.2 ± 2.7
24	700	2916	0.05	0.03	0.69	2.00	4.47	71.23	70.66	97.5 ± 2.1
25	750	2946	0.41	0.07	1.61	4.24	9.32	75.09	74.56	96.0 ± 1.0
26	800	2976	1.05	0.16	2.07	5.36	11.86	79.96	79.53	96.7 ± 0.9
27	840	3006	1.08	0.08	2.44	6.55	14.38	85.93	85.55	95.8 ± 0.7
28	880	3036	1.39	0.09	2.44	6.52	14.07	91.87	91.44	94.3 ± 1.1
29	907	3066	0.01	0.07	1.07	3.16	7.10	94.75	94.41	98.0 ± 1.0
30	932	3096	0.45	0.06	0.71	2.03	4.61	96.60	96.34	99.1 ± 2.1

KM-600 E	Biotite (600°C is	sothermal ru	n)											
31	957	3126	0.67	0.10	0.40	1.34	2.98	97.83	97.59	96.7 ± 2.4				
32	1000	3156	1.03	0.41	0.52	1.66	3.71	99.33	99.14	97.8 ± 2.3				
33	1040	3186	1.16	0.06	0.19	0.62	1.49	99.90	99.77	105.1 ± 5.5				
34	1090	3216	1.65	0.07	0.00	0.04	0.32	99.93	99.90	328.5 ± 65.8				
35	1160	3246	3.49	0.09	0.00	0.07	0.24	100.00	100.00	137.3 ± 24.8				
Mass = 0.	1156 g					J -value = 0.002486 ± 0.000017								
Integrated	date = 95.1 ± 0).7 Ma				Plateau dat	$e = 95.8 \pm 0.7 \text{ M}$	a (steps 2–33)						
KM-800 E	Biotite (800°C is	sothermal ru	n)											
1	650	30	51.48	0.46	14.19	33.83	73.16	29.93	29.22	94.5 ± 0.8				
2	750	60	5.76	0.56	11.46	30.37	67.91	56.80	56.34	97.6 ± 1.2				
3	800	65	2.92	0.96	2.92	7.46	16.26	63.40	62.83	95.2 ± 1.0				
4	800	77	0.24	0.46	0.79	1.99	4.44	65.16	64.60	97.5 ± 0.7				
5	800	90	0.60	0.49	1.64	4.38	9.84	69.03	68.53	98.0 ± 0.8				
6	800	116	0.17	0.16	0.90	2.36	5.27	71.12	70.64	97.5 ± 1.7				
7	800	136	0.43	0.19	1.19	3.11	6.85	73.87	73.37	96.1 ± 1.0				
8	800	167	0.06	0.06	0.80	2.21	4.89	75.83	75.32	96.5 ± 1.1				
9	800	207	0.06	0.06	0.78	2.21	4.90	77.79	77.28	96.6 ± 1.6				
10	800	257	0.07	0.05	0.79	2.24	4.95	79.77	79.26	96.7 ± 1.1				
11	800	317	0.08	0.07	0.69	1.95	4.32	81.49	80.98	96.9 ± 1.1				
12	800	397	0.08	0.06	0.63	1.80	4.00	83.08	82.58	96.8 ± 1.3				
13	800	497	0.53	0.06	0.57	1.64	3.65	84.54	84.04	97.2 ± 1.9				
14	800	597	0.13	0.05	0.40	1.26	2.81	85.65	85.16	97.5 ± 1.6				
15	800	717	0.07	0.05	0.42	1.17	2.69	86.69	86.24	100.3 ± 2.0				
16	800	870	0.07	0.07	0.33	1.11	2.57	87.67	87.26	100.8 ± 1.4				
17	800	1020	0.06	0.05	0.25	0.81	1.86	88.38	88.01	100.9 ± 1.9				
18	800	1240	0.44	0.04	0.27	0.91	2.11	89.19	88.85	100.8 ± 1.9				
19	800	1580	0.94	0.04	0.33	0.95	2.18	90.03	89.72	100.2 ± 2.5				
20	841	1610	0.04	0.04	0.00	0.10	0.23	90.12	89.81	96.9 ± 4.3				
21	881	1640	0.06	0.02	0.35	1.14	2.53	91.13	90.82	96.8 ± 3.1				
22	908	1670	0.07	0.02	0.56	1.62	3.69	92.56	92.29	99.3 ± 1.7				
23	935	1700	0.01	0.01	1.01	2.72	6.10	94.97	94.73	98.0 ± 1.5				
24	957	1730	0.02	0.06	0.72	1.93	4.39	96.68	96.48	98.9 ± 1.5				
25	1002	1760	0.10	0.07	0.59	1.71	3.84	98.19	98.01	98.2 ± 1.6				
26	1040	1790	0.83	0.56	0.69	1.88	4.29	99.85	99.73	99.6 ± 1.8				
27	1100	1820	1.35	0.68	0.00	0.05	0.36	99.90	99.87	273.9 ± 38.5				
28	1190	1850	2.92	0.05	0.00	0.11	0.33	100.00	100.00	123.0 ± 18.7				
Mass = 0.1683 g						J-value = 0	J -value = 0.002486 ± 0.000017							

Integrated date = 96.7 ± 0.7 Ma

Plateau date = 96.6 ± 0.7 Ma (steps 1–26)

Appendix A	. (continued))								
Step no.	T (°C)	Time	³⁶ Ar	³⁷ Ar _{Ca}	³⁸ Ar _{Cl}	³⁹ Ar _K	$^{40}Ar^{*}$	³⁹ Ar _K	$^{40}Ar^{*}$	Apparent
		(min)	$(\times 10^{-10})$	$(\times 10^{-9})$	$(\times 10^{-9})$	$(\times 10^{-8})$	$(\times 10^{-7})$	Cum.	Cum.	age (Ma)
			CCNTP	CCNTP	CCNTP	CCNTP	CCNTP	loss (%)	loss (%)	
CPC-N Bioti	te (normal st	tep-heating ri	un)	0.05	•		1.00			
1	550	30	8.40	0.35	2.68	4.04	4.90	3.39	3.22	53.6 ± 0.7
2	580	60	1.83	1.79	4.04	6.47	8.26	8.83	8.66	56.4 ± 0.5
3	609	90	2.30	2.09	7.19	11.51	14.60	18.49	18.26	56.0 ± 0.5
4	640	120	1.41	3.16	8.82	14.44	18.47	30.62	30.41	56.5 ± 0.4
5	6/0	150	0.77	2.54	9.29	15.21	19.46	43.40	43.21	56.5 ± 0.4
6	700	180	0.35	1.17	7.07	11.46	14.61	53.02	52.82	56.3 ± 0.4
/	/50	210	0.08	1.30	3.78	0.13	1.82	58.18	57.96	56.3 ± 0.4
8	800	240	0.19	0.66	2.01	3.22	4.15	60.88	60.69	56.8 ± 0.5
9	841	270	0.78	0.85	2.44	3.93	5.06	64.19	64.01	56.7 ± 0.8
10	880	300	1.15	0.90	2.92	4.69	6.08	68.13	68.01	57.2 ± 0.9
11	907	330	1.88	0.39	2.90	4.69	5.94	72.06	71.92	56.0 ± 0.6
12	932	360	0.50	0.40	2.48	3.96	5.07	75.39	75.25	56.5 ± 0.7
13	958	390	1.20	0.09	2.99	4.79	0.18	79.42 85.26	79.32	56.9 ± 0.7
14	1000	420	2.36	1.31	4.16	6.96	8.82	85.26	85.12	56.0 ± 0.4
15	1040	450	3.40	2.03	4.31	0.58	8.40	90.79	90.65	56.4 ± 0.5
16	1091	480	3.85	2.00	4.32	7.34	9.28	96.95	96.76	55.9 ± 0.5
17	1150	520	7.31	2.05	2.20	3.55	4.63	99.94	99.80	$5/.5 \pm 1.0$
18	1190	550	2.83	0.19	0.03	0.07	0.30	100.00	100.00	$1/4.3 \pm 24.1$
Mass = 0.13	14 g					J-value = 0.0	102486 ± 0.00001	(1 2 17)		
Integrated da	$te = 56.4 \pm 0$	0.4 Ma				Plateau date	$= 56.4 \pm 0.4$ Ma	(steps $2-17$)		
CPC-400 Bid	otite (400°C i	isothermal ru	un)							
1	400	5	6.72	0.20	0.47	0.33	0.32	0.25	0.19	42.6 ± 3.7
2	400	15	2.78	0.07	0.20	0.16	0.16	0.38	0.28	42.7 ± 3.3
3	400	30	1.57	0.02	0.15	0.12	0.12	0.47	0.35	44.7 ± 2.7
4	400	50	0.49	0.03	0.06	0.06	0.06	0.52	0.39	44.2 ± 3.9
5	400	80	0.48	0.04	0.05	0.08	0.09	0.58	0.44	48.0 ± 6.2
6	400	130	1.26	0.05	0.12	0.13	0.14	0.68	0.52	47.6 ± 5.5
7	400	220	0.92	0.04	0.11	0.17	0.18	0.80	0.62	47.0 ± 3.0
8	400	400	0.71	0.06	0.10	0.21	0.25	0.96	0.77	54.4 ± 3.8
9	400	700	1.44	0.05	0.26	0.43	0.53	1.29	1.08	54.3 ± 2.2
10	400	1070	1.39	0.07	0.29	0.47	0.60	1.65	1.43	55.7 ± 2.6
11	400	1550	1.09	0.05	0.32	0.51	0.65	2.04	1.81	56.3 ± 1.2
12	400	2090	0.78	0.03	0.23	0.41	0.50	2.35	2.11	54.5 ± 4.8
13	400	2800	1.26	0.08	0.34	0.56	0.68	2.78	2.51	54.0 ± 4.1
14	550	2830	5.21	0.09	3.70	5.69	7.29	7.12	6.78	56.6 ± 0.4
15	580	2860	2.54	0.00	4.67	7.31	9.55	12.70	12.38	57.7 ± 0.4
16	610	2890	2.90	0.15	7.16	11.16	14.56	21.23	20.92	57.6 ± 0.4
17	640	2920	2.10	0.14	8.78	13.88	18.09	31.83	31.54	57.5 ± 0.4
18	670	2950	1.65	0.10	9.35	14.78	19.21	43.12	42.81	57.4 ± 0.4
19	700	2980	0.58	0.09	7.04	11.12	14.52	51.61	51.33	57.6 ± 0.4

CPC-40	0 Biotite (400°C	isothermal r	un)							
20	750	3010	0.77	0.06	4.24	6.68	8.72	56.71	56.45	57.6 ± 0.5
21	800	3040	0.88	0.15	2.64	4.19	5.55	59.92	59.70	58.4 ± 0.5
22	840	3070	0.85	0.10	2.53	3.99	5.26	62.96	62.79	58.2 ± 0.5
23	880	3100	1.83	0.36	3.68	5.70	7.53	67.32	67.20	58.3 ± 0.4
24	907	3130	1.36	0.04	3.17	4.97	6.52	71.12	71.03	57.8 ± 0.4
25	932	3160	1.31	0.07	3.05	4.80	6.21	74.78	74.67	57.1 ± 0.4
26	957	3190	1.50	0.10	3.37	5.33	6.90	78.86	78.71	57.1 ± 0.5
27	1000	3220	1.98	0.10	5.42	8.41	11.03	85.28	85.19	57.9 ± 0.4
28	1040	3250	1.92	0.15	4.46	6.70	8.77	90.40	90.33	57.8 ± 0.4
29	1090	3280	3.26	0.12	5.81	9.01	11.77	97.28	97.24	57.7 ± 0.4
30	1149	3310	4.25	0.12	2.28	3.46	4.51	99.92	99.88	57.6 ± 0.5
31	1188	3340	4.51	0.04	0.15	0.10	0.20	100.00	100.00	82.9 ± 6.9
Mass =	0.1808 g					J-value = (0.002486 ± 0.0000	017		
Integrate	ed date = 57.5 ± 0	0.4 Ma				Plateau dat	$te = 57.1 \pm 0.4 \text{ Ma}$	a (steps 1–30)		
an a	0 D (5000 G									
CPC-50	0 Biotite (500°C	isothermal r	un)	0.07	1.16	0.71	0.71	0.54	0.42	12.0 + 2.1
1	500	5	14.10	0.07	1.16	0.71	0.71	0.56	0.43	43.9 ± 2.1
2	500	15	6.59	0.38	0.75	0.74	0.83	1.14	0.94	49.3 ± 2.0
3	500	30	2.40	0.09	0.49	0.69	0.81	1.68	1.44	52.1 ± 2.6
4	500	50	2.19	0.05	0.61	0.92	1.09	2.40	2.11	52.1 ± 1.5
5	500	80	2.03	0.05	0.73	1.12	1.35	3.27	2.94	53.3 ± 2.0
6	500	110	1.21	0.12	0.57	0.94	1.18	4.00	3.66	55.2 ± 1.5
7	500	170	1.50	0.02	0.90	1.46	1.86	5.14	4.80	56.2 ± 0.8
8	500	250	1.25	0.03	0.87	1.50	1.89	6.31	5.96	55.7 ± 0.9
9	500	365	1.16	0.04	0.96	1.58	2.02	7.54	7.20	56.4 ± 1.2
10	500	500	0.77	0.04	0.83	1.40	1.76	8.64	8.28	55.4 ± 1.3
11	500	740	0.99	0.05	1.17	1.95	2.44	10.16	9.78	55.4 ± 1.0
12	500	880	0.28	0.05	0.72	1.22	1.61	11.11	10.77	58.3 ± 1.6
13	500	1180	0.28	0.00	0.86	1.46	1.89	12.25	11.93	57.1 ± 0.8
14	500	1580	0.14	0.05	0.80	1.39	1.81	13.34	13.04	57.3 ± 0.7
15	500	2080	0.20	0.03	1.02	1.72	2.24	14.68	14.41	57.5 ± 1.0
16	500	2670	0.28	0.03	1.00	1.84	2.36	16.12	15.86	56.7 ± 1.3
17	550	2700	0.02	0.03	0.66	1.16	1.47	17.02	16.77	56.2 ± 1.4
18	580	2730	0.14	0.03	1.85	3.10	3.95	19.44	19.20	56.4 ± 0.6
19	610	2760	0.53	0.04	4.19	6.86	8.76	24.80	24.58	56.4 ± 0.5
20	640	2790	0.52	0.05	7.20	11.65	14.93	33.89	33.76	56.6 ± 0.4
21	668	2820	0.63	0.02	8.39	13.64	17.37	44.55	44.43	56.3 ± 0.4
22	700	2850	0.28	0.05	7.33	11.99	15.32	53.91	53.84	56.4 ± 0.4
23	752	2880	0.47	0.04	3.51	5.84	7.33	58.47	58.34	55.4 ± 0.5
24	800	2910	0.15	0.22	1.52	2.53	3.30	60.44	60.37	57.7 ± 0.9
25	840	2940	0.76	0.43	1.97	3.27	4.13	63.00	62.91	55.7 ± 0.7
26	880	2970	0.66	0.36	2.29	3.74	4.88	65.92	65.91	57.7 ± 0.6
27	907	3000	0.86	0.15	2.74	4.45	5.69	69.39	69.41	56.5 ± 0.6
28	933	3030	0.77	0.05	2.69	4.46	5.63	72.87	72.87	55.7 ± 0.4
29	957	3060	0.64	0.04	2.96	4.91	6.20	76.71	76.67	55.8 ± 0.4
-										

Appendix	A. (continued))								
Step no.	<i>T</i> (°C)	Time (min)	^{36}Ar (×10 ⁻¹⁰)	$^{37}\text{Ar}_{\text{Ca}}$ (×10 ⁻⁹)	$^{38}\text{Ar}_{\text{Cl}}$ (×10 ⁻⁹)	$^{39}\text{Ar}_{\text{K}}$ (×10 ⁻⁸)	$^{40}\text{Ar}^{*}$ (×10 ⁻⁷)	³⁹ Ar _K Cum.	⁴⁰ Ar* Cum.	Apparent age (Ma)
			CCNTP	CCNTP	CCNTP	CCNTP	CCNTP	loss (%)	loss (%)	age (Ma)
KM-600 B	iotite (600°C is	othermal ru	n)	0.26	4.05	7 70	0.00	82.70	00.75	561+04
30	1000	3090	0.91	0.36	4.85	7.79	9.89	82.79	82.75	56.1 ± 0.4
31	1040	3120	0.91	1.65	5.53	8.58	10.93	89.49	89.47	56.2 ± 0.4
32 22	1090	2190	1.58	0.95	0.44	10.41	13.21	97.62	97.58	56.0 ± 0.4
33 24	1151	2210	1.42	1.11	1.80	2.99	3.85	99.96	99.94	50.0 ± 0.4
$M_{\text{mass}} = 0.1$	1190	5210	2.55	0.50	0.06	0.05	0.10	7	100.00	87.2 ± 30.7
Integrated	doto = 56.1 + 0) 4 Ma				J-value = 0.0	-56.1 ± 0.4 Me	(stops 1 22)		
Integrated	date = 56.1 ± 0	.4 Ma				Plateau date	$= 30.1 \pm 0.4$ Ma	(steps 1–55)		
CPC-800 I	Biotite (800°C i	isothermal ri	un)							
1	650	30	28.94	0.03	29.77	45.14	57.53	34.72	34.45	56.3 ± 0.4
2	750	60	3.83	0.88	15.33	24.25	31.22	53.37	53.14	56.8 ± 0.4
3	800	65	1.77	0.16	2.30	3.32	4.28	55.93	55.70	56.9 ± 0.6
4	800	80	1.83	0.20	2.49	3.46	4.64	58.59	58.48	59.1 ± 2.1
5	800	90	0.24	0.12	0.28	0.38	0.51	58.88	58.79	58.9 ± 1.7
6	800	110	0.42	0.08	1.07	1.76	2.30	60.24	60.17	57.8 ± 0.9
7	800	140	0.36	0.08	0.97	1.57	2.09	61.44	61.42	58.8 ± 1.2
8	800	170	0.60	0.13	0.71	1.19	1.49	62.36	62.31	55.1 ± 1.7
9	800	230	0.48	0.11	1.09	1.77	2.32	63.72	63.70	57.8 ± 1.5
10	800	310	0.86	0.02	1.11	1.78	2.23	65.09	65.03	55.2 ± 1.4
11	800	425	0.93	0.00	1.18	1.89	2.39	66.54	66.46	56.0 ± 1.0
12	800	560	0.77	0.11	1.01	1.58	1.98	67.76	67.65	55.3 ± 1.1
13	800	710	0.78	0.21	0.84	1.35	1.66	68.80	68.65	54.6 ± 1.3
14	800	940	0.66	0.03	1.06	1.70	2.17	70.10	69.95	56.4 ± 1.1
15	800	1240	0.50	0.00	1.13	1.74	2.21	71.44	71.27	55.9 ± 1.3
16	800	1640	0.01	0.02	1.16	1.81	2.24	72.83	72.61	54.6 ± 1.2
17	800	2140	0.20	0.00	1.18	1.80	2.25	74.22	73.96	55.1 ± 0.9
18	800	2730	0.22	0.11	1.13	1.71	2.11	75.53	75.22	54.5 ± 1.1
19	840	2760	0.10	0.08	0.06	0.21	0.28	75.70	75.38	58.3 ± 1.7
20	880	2790	0.35	0.08	0.51	0.89	1.22	76.38	76.11	60.5 ± 0.6
21	907	2820	0.53	0.10	1.00	1.61	2.21	77.62	77.43	60.3 ± 1.3
22	933	2850	1.24	0.10	1.76	2.78	3.65	79.76	79.62	58.0 ± 0.6
23	957	2880	0.65	0.06	1.54	2.50	3.29	81.68	81.59	58.1 ± 1.2
24	1000	2910	2.04	0.07	3.40	5.36	6.91	85.79	85.73	57.0 ± 0.4
25	1040	2940	1.77	0.13	3.68	5.64	7.27	90.13	90.08	56.9 ± 0.4
26	1090	2970	2.64	0.40	5.30	8.17	10.61	96.42	96.43	57.3 ± 0.4
27	1150	3000	4.38	0.23	2.92	4.62	5.85	99.97	99.93	55.9 ± 0.9
28	1190	3030	3.88	0.06	0.06	0.04	0.12	100.00	100.00	131.0 ± 72.2
Mass = 0.1	495 g					J-value = 0.0	002486 ± 0.00001	7		

Mass = 0.1495 g Integrated date = 56.7 ± 0.4 Ma

Plateau date = 56.7 ± 0.4 Ma (steps 1–27)

Appendix B. Evaluation of approximation equations in D/a^2 calculations

As stated by Trull (1989), the calculation of D/a^2 using the approximation equations [e.g., Eqs. (4) and (5)] may result in significant deviations from the exact D/a^2 values, because F is a exponential function of D/a^2 (Eq. (1)). Consequently, a comparison of theoretical F values derived by using a 20-term series of Eq. (1) with those calculated from the approximation equations [Eqs. (2) and (3)] is shown in Fig. 12a. In general, the approximation Eqs. (2) and (3) are consistent with the 20-term series of Eq. (1) over their respective ranges of F. However, depending on F and the corresponding D/a^2 values. Eqs. (4) and (5) could yield significant deviations of the calculated D/a^2 from the exact value over a range of F values from 0.3-0.75. As shown in Fig. 12b. Eq. (4) could underestimate D/a^2 by about 2% for large D/a^2 values near an F value of 0.6, while Eq. (5) will overestimate D/a^2 in the same region. Thus, any calculation of D/a^2 according to the approximation equations needs to be corrected for these deviations in the F value range between 0.3 and 0.75.

Since the fraction lost (F) is a function of the dimensionless parameter (Dt/a^2) , as shown in the above equations, grains with a small radius of diffusion (a) would be expected to lose much more of their argon than grains with larger a under the same temperature/time conditions, due to the D/a^2 dependence [Eq. (1)]. This could: (a) potentially cause staircase-shaped age spectra characterized by young dates in the first few steps which then climb to a plateau, as observed in natural feldspar (e.g., Lovera et al., 1989), and (b) also result in the underestima-

tion of the activation energy for noble gas diffusion (Fechtig and Kalbitzer, 1966; Trull, 1989).

To examine this effect, the argon diffusion loss from a theoretical bulk sample was modelled with a continuous distribution of diffusion radii, and the calculated fraction lost from the sample was used to derive the corresponding D/a^2 value according to Eqs. (4) and (5). In this model, the total fraction lost (F) for the whole sample during each time interval is given by:

$$F = \sum_{i=1}^{n} Q_i G_i \tag{6}$$

where Q_i represents the fraction loss of argon from *i*th domain in this period of time, as given by Eq. (1); and G_i is the fraction of the square of the radius for *i*th size domain. The fraction of the square of the radius can be used instead of the volume fraction in Eq. (6) because the geometry of diffusion for argon in biotite is assumed to be an infinite cylinder and the volume fraction for such a geometry is independent of the cylinder's height.

By using normal and lognormal distributions of a range of effective diffusion radii (Fig. 13a), the effects on the calculation of D/a^2 are shown in Fig. 13b. A value of $D = 10^{-12}$ cm²/s was assumed, and all of the distributions have a mean $a = 100 \,\mu\text{m}$ with a standard deviations of either 20 μm or 50 μm . As a result of a range of diffusion radii, D/a^2 can be underestimated for high *F* values and overestimated for low *F* values for a lognormal distribution (Fig. 13b). In contrast, D/a^2 values will always be underestimated for low *F* values in normal and inverse-lognormal distributions. More generally, a distribution of effective diffusion radii may result in

Notes to Appendix A:The apparent age is obtained according to: t (apparent age) = $(1/\lambda) \ln (({}^{40}\text{Ar}^*/{}^{39}\text{Ar}_{K})_s J + 1)$. J-value: Weighted mean of three fusions of irradiation standard P-207 muscovite, utilizing the K–Ar age of 82.6 ± 1.0 Ma (Dalrymple et al., 1981); except that for the normal step-heating run for KM-800 biotite, which J was obtained by using standard MMHb-1 hornblende (520.4 ± 1.4 Ma) (Sampson and Alexander, 1987) as a monitor. J-value is obtained according to $J = (e^{\lambda tm} - 1)/({}^{40}\text{Ar}^*/{}^{39}\text{Ar}_{K})_m$; where "m" is quoted for the standard and "s", the sample.Date (Ma) = the date calculated using the following decay constants: $\lambda = \lambda_{\varepsilon} (0.581 \times 10^{-10} \text{ yr}^{-1}) + \lambda_{\beta} (4.961 \times 10^{-10} \text{ yr}^{-1})$; ${}^{40}\text{K/K} = 0.01167$ atom %.The quoted error is one standard deviation and does not include the standard error and the errors in the interference corrections.Integrated date = the date and error calculated from the sum total gas from those steps, the ages of which fall within 2 S.D. of each other. $T(^{\circ}\text{C}) =$ temperature has an uncertainty of $\pm 2^{\circ}\text{C}$.

either an under- or overestimate of D/a^2 , the deviation increasing with increasing *F* (Fig. 13b). If F < 0.4, however, this deviation is typically less than 1.5% (Fig. 13b).

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