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Graphical Solutions to the Problem of Radiogenic Argon-40 Loss from Metamorphic Minerals

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ABSTRACT

Loss of radiogenic argon-40 by volume diffusion from the crystal lattices of metamorphic minerals results in discordant potassium-argon age patterns. Ar^{40}-retention ages, calculated from the measured concentration of argon-40 remaining within the mineral lattice, are termed *potassium-argon model ages*. The geologic interpretation placed on potassium-argon model ages depends on the particular diffusion model adopted. Various possible models are compared graphically using Ar^{40}-growth curves.

Where the same concentration of post-metamorphic radiogenic argon-40 has been lost from a suite of cogenetic metamorphic minerals irrespective of their potassium content, analyzed samples yield an isochron with negative intercept on an argon-40 versus potassium concentration plot. The *potassium-argon isochron age*, obtained from the slope of such an isochron, is the K^{40}-retention age which is identified with the age of metamorphic recrystallization. The concentration of argon-40 lost from the mineral suite is obtained from the negative intercept of the isochron on the argon-40 axis. Relationships between potassium-argon model ages and potassium-argon isochron ages are illustrated by means of regression lines.

Assuming that all previously held argon-40 is expelled from the whole-rock system during metamorphic recrystallization, argon isochrons with negative intercepts, obtained from previously reported analyses from the Scottish and Irish Caledonides and from the Northern Appalachians, indicate that concentrations of radiogenic argon-40 in the order of $1-3 \times 10^{-5}$ scc/gm are characteristically lost from micas during the initial postmetamorphic period. It is suggested that this concentration of argon-40 remains in the polycrystalline whole-rock system at depth, residing on grain-boundaries and that it represents the concentration necessary to "saturate" the grain-boundaries thereby inhibiting any further loss by volume diffusion from the lattice itself.

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Introduction

The radioactive isotope K^{40} decays in two modes, producing both stable Ca^{40} by beta emission and stable Ar^{40} by K-electron capture with gamma-emission. The decay constant (λ) for K^{40} decay is then given by the sum of the decay constants for beta-emission (λ_β) and electron-capture (λ_e). i.e. $\lambda = \lambda_\beta + \lambda_e$. Because of the practical difficulty of recognizing Ca^{40} in most silicate rock and mineral systems, radiometric age calculations involving K^{40} are usually based on the measured accumulation of Ar^{40} only. The total concentration of Ar^{40} accumulated is related to the remaining concentration of K^{40} by the equation:

$$Ar^{40} = \lambda_e/\lambda \cdot K^{40} (e^{\lambda t} - 1) \tag{1}$$

where λ_e/λ is the proportion of K^{40} decaying to Ar^{40} in unit time.

Solving for t, we obtain:

$$t = 1/\lambda \log_e (\lambda/\lambda_e \cdot Ar^{40}/K^{40} + 1) . \tag{2}$$

Implicit in equations (1) and (2) are the two assumptions that initially (i.e. at the time of formation of the sample dated, t_0) there was no Ar^{40} present in the system, and that after t_0 none of the radiogenic Ar^{40} subsequently produced by decay of K^{40} was lost. Because of these inherent assumptions, K^{40}-Ar^{40} ages calculated on the basis of equation (2) are here termed *potassium-argon model ages.*

More generally, the relationship between the concentration of Ar^{40} present in any mineral or whole-rock system and the concentration of K^{40} remaining should be expressed as:

$$Ar_p^{40} = \lambda_e/\lambda \cdot K_p^{40} (e^{\lambda t} - 1) + Ar_c^{40} \tag{3}$$

where Ar_p^{40} and K_p^{40} are the present (measured) concentrations of the respective isotopes in the sample, and Ar_c^{40} is the concentration of argon-40 initially present (Ar_e^{40}) minus the concentration of argon-40 subsequently lost (Ar_d^{40}).

$$\text{i.e.} \quad Ar_c^{40} = Ar_e^{40} - Ar_d^{40} . \tag{4}$$

If the concentration of argon-40 initially present (Ar_e^{40}) exceeds the total concentration subsequently lost (Ar_d^{40}), the sample will contain "excess" argon and the term Ar_c^{40} is positive. If the total concentration of argon-40 subsequently lost by diffusion from the sample exceeds the concentration initially present, the sample will be deficient in argon and the term Ar_c^{40} is negative. In either case, the potassium-argon model age, calculated on the basis of equation (2), where it is assumed that the term $Ar_c^{40} = 0$, will not be the real age of the sample. If Ar_c^{40} is positive, the potassium-argon model age will be greater than the real age of the sample, and if Ar_c^{40} is negative, the potassium-argon model age will be less than the real age of the sample.

Provided, however, that the concentration term Ar_c^{40} in equation (3) is constant for a suite of cogenetic samples irrespective of their potassium-40 contents, measured values of Ar_p^{40} plotted against K_p^{40} for each sample will generate a straight line with intercept (on the Ar^{40} axis) = Ar_c^{40}, and slope $m = (e^{\lambda t} - 1)$. Such a line is properly

called an isochron, and the K^{40}-Ar^{40} ages calculated from the slope of such an isochron are here termed *potassium-argon isochron ages.*

Potassium-argon model ages and potassium-argon isochron ages will be equivalent only in those cases where $Ar_c^{40} = 0$, i.e. when the argon isochron has zero intercept. The argon isochron have either a positive intercept or a negative intercept depending on whether the term Ar_c^{40} (equation (4)) is positive or negative (Fig. 1).

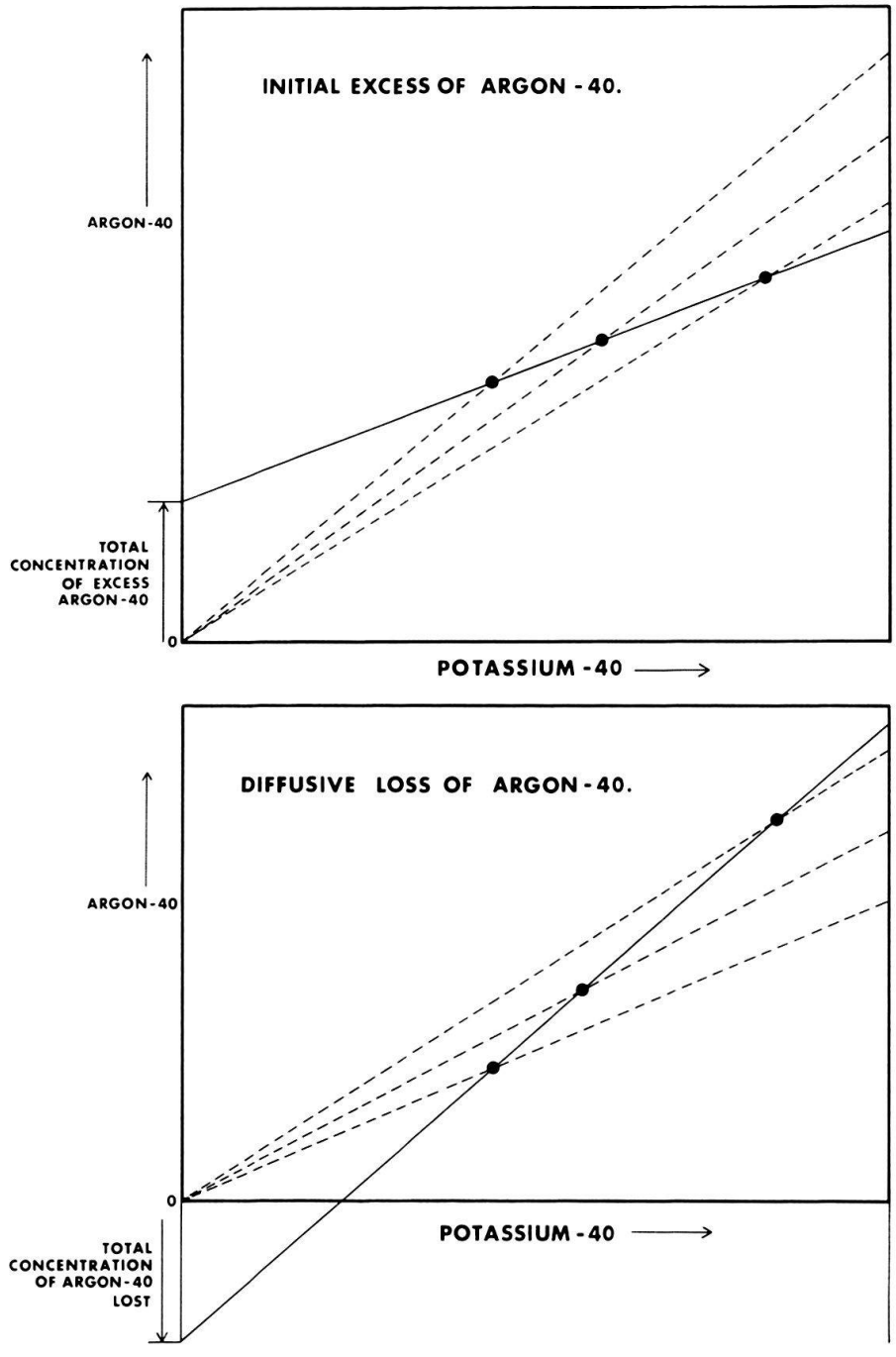

Fig. 1. Argon isochrons (solid lines) with positive and negative intercepts. Slope of broken line proportional to K-Ar model age.

Potassium-argon Model Ages and Ar^{40}-growth Curves

Metamorphic rocks, particularly those from regionally metamorphosed areas, are frequently characterized by discordant isotopic age patterns. K^{40}-Ar^{40} model ages obtained from metamorphic mineral separates are generally lower than either Rb^{87}-Sr^{87} whole-rock isochron or Pb^{206}-U^{238} v's Pb^{207}-U^{235} concordia ages, implying that a deficiency of radiogenic Ar^{40} exists in potassium-bearing minerals, relative to the radiogenic strontium or lead contents of cogenetic systems (e.g. MOORBATH, 1967). Conversely, many recent studies have demonstrated that volcanic (basaltic) materials contain excess argon-40 and give anomalously high K^{40}-Ar^{40} model ages (e.g. DAMON et al., 1967; DALRYMPLE et al., 1968; NOBLE et al., 1968; FUNKHOUSER et al., 1968).

In the early 1950's the consistently low K^{40}-Ar^{40} model ages obtained from plutonic potassium feldspars were seen to imply a necessary correction to the decay constants for K^{40} disintegration. Specifically, an adjustment was deemed necessary to the physically determined branching ratio λ_e/λ_β, a measure of the proportion of existing K^{40} atoms decaying in unit time to Ar^{40} relative to the proportion decaying to Ca^{40}. The apparent argon-40 deficiency (i.e. the low K^{40}-Ar^{40} model ages) could be "corrected" by assuming that in the plutonic environment, contrary to the laboratory evidence, a smaller proportion of the K^{40} atoms decaying in unit time were decaying to Ar^{40} and a larger proportion were decaying to Ca^{40}. In other words an empirical decrease in the value of the branching ratio for K^{40} decay (λ_e/λ_β) could be made to eliminate any discordancy between K^{40}-Ar^{40} model ages and isotopic ages calculated on the basis of other time dependent isotopic systems.

This artificial procedure was soon found to be invalid when coexisting (cogenetic) potassium feldspars and micas were shown to have different Ar^{40}/K^{40} ratios (WETHERILL et al., 1955; FOLINSBEE et al., 1956). Arbitrarily decreasing the proportion of K^{40} atoms that should be disintegrating to Ar^{40} in unit time might therefore bring the calculated potassium argon model age for feldspar into concordancy with ages determined by other methods, but then the calculated argon model ages for the coexisting micas become discordantly high.

It thus became clear that loss by diffusion of a proportion of the radiogenic argon-40 produced in situ in potash-bearing minerals was the reason for the low Ar^{40}/K^{40} ratios measured in certain minerals, particularly the potash feldspars, rather than some universal decrease in the rate of radiogenic Ar^{40} production in plutonic rocks. Consequently, potassium-argon dating became restricted to the more "retentive" minerals such as muscovite, biotite and hornblende, and current interpretations of potassium-argon model age patterns in metamorphic regions are based on temperature dependent models involving either episodic or continuous loss of radiogenic argon-40 by diffusion (e.g. BROWN et al., 1965; ARMSTRONG, 1966; MOORBATH, 1967; HARPER, 1967a). The particular diffusion model adopted essentially controls the geologic interpretation placed on the radiometric age data, and significantly different geologic interpretations are obtained when the same set of K^{40}-Ar^{40} measurements are fitted to different argon-diffusion models.

Various possible argon-diffusion models appropriate for the interpretation of potassium-argon model ages are most conveniently compared by means of diagrammatic *growth curves* (Figs. 2 and 3). The growth curves illustrated are applicable over

time intervals which are small compared to the half-life of K^{40} so that constant, rather than exponential, rates of radiogenic Ar^{40} production may be assumed. The curves illustrate possible relationships between the rate of radiogenic production and the rate of loss by diffusion, which together control the net rate of argon-40 accumulation in any system. The rate of radiogenic production is controlled by the concentration of radioactive K^{40} and λ_e, the decay probability via electron capture. The rate of accumulation of argon-40 in the system will then depend on the difference between the rates of Ar^{40}-production and Ar^{40}-diffusion. DAMON (1968a, 1968b) has expressed this in terms of a linear differential equation of the first order:

$$d(Ar^{40})/dt = \lambda_e K^{40} - \lambda_d Ar^{40}$$

the Ar^{40} escape probability being expressed in terms of a constant λ_d. We may assume that once the concentration of potassium-40 becomes fixed in any system under consideration, the resulting radiogenic argon-40 production rate will not be influenced by environmental conditions. The radiogenic argon-40 diffusion rate will, however, vary considerably according to the nature of the environment.

Model 1 (Fig. 2):

In the first model, a K^{40}-bearing system formed at time t_1 years ago looses Ar^{40} as fast as it is produced from the decay of K^{40} present in the system. i.e. the rate of diffusion equals the rate of radiogenic production and the net accumulation in zero. The total amount of Ar^{40} produced from time t_1 to the present equals the total amount of Ar^{40} lost by diffusion, the system remains "open" with respect to Ar^{40} throughout its whole life-time, and its potassium-argon model age is zero.

Model 2 (Fig. 2):

This is the fast cooling or overprinting model. Here, a system formed at time t_1 years ago begins to retain quantitatively all the radiogenic Ar^{40} produced in situ from the decay of K^{40} after a negligible time interval $t_1 - t'_1$. At some later time, t_2, a thermal event of short duration causes a loss by diffusion of all previously accumulated Ar^{40}. The net accumulation to the present represents, therefore, only the amount retained since t_2. The calculated argon model age, calculated on the basis of net Ar^{40} accumulation, will give the age of the thermal event t_2 which has effectively "overprinted" the original formation event t_1. Note that a spread of model age values will result if the expulsion of Ar^{40} is not complete at t_2. Individual mineral systems may, for instance, retain various proportions of the radiogenic Ar^{40} produced during the time interval $t_1 - t_2$ and will consequently give model ages intermediate between t_1 and t_2. Such intermediate model age values have no geological significance, except the highest, which will represent a minimum estimate of t'_1, and the lowest, which should approximate the age of the overprinting event t_2.

Model 3 (Fig. 2):

The slow cooling, or refrigeration model. In this model, the time elapsed between the time of formation of the system (t_1) and the time when quantitative Ar^{40} retention begins (t_2) is no longer negligible, and the system remains open to Ar^{40} diffusion during a considerable time interval $t_1 - t_2$. At time t_2, closure is rapid, and the system retains radiogenic Ar^{40} quantitatively from time t_2 to the present. Calculated argon model ages will therefore give the time of closure t_2. The difference between the age

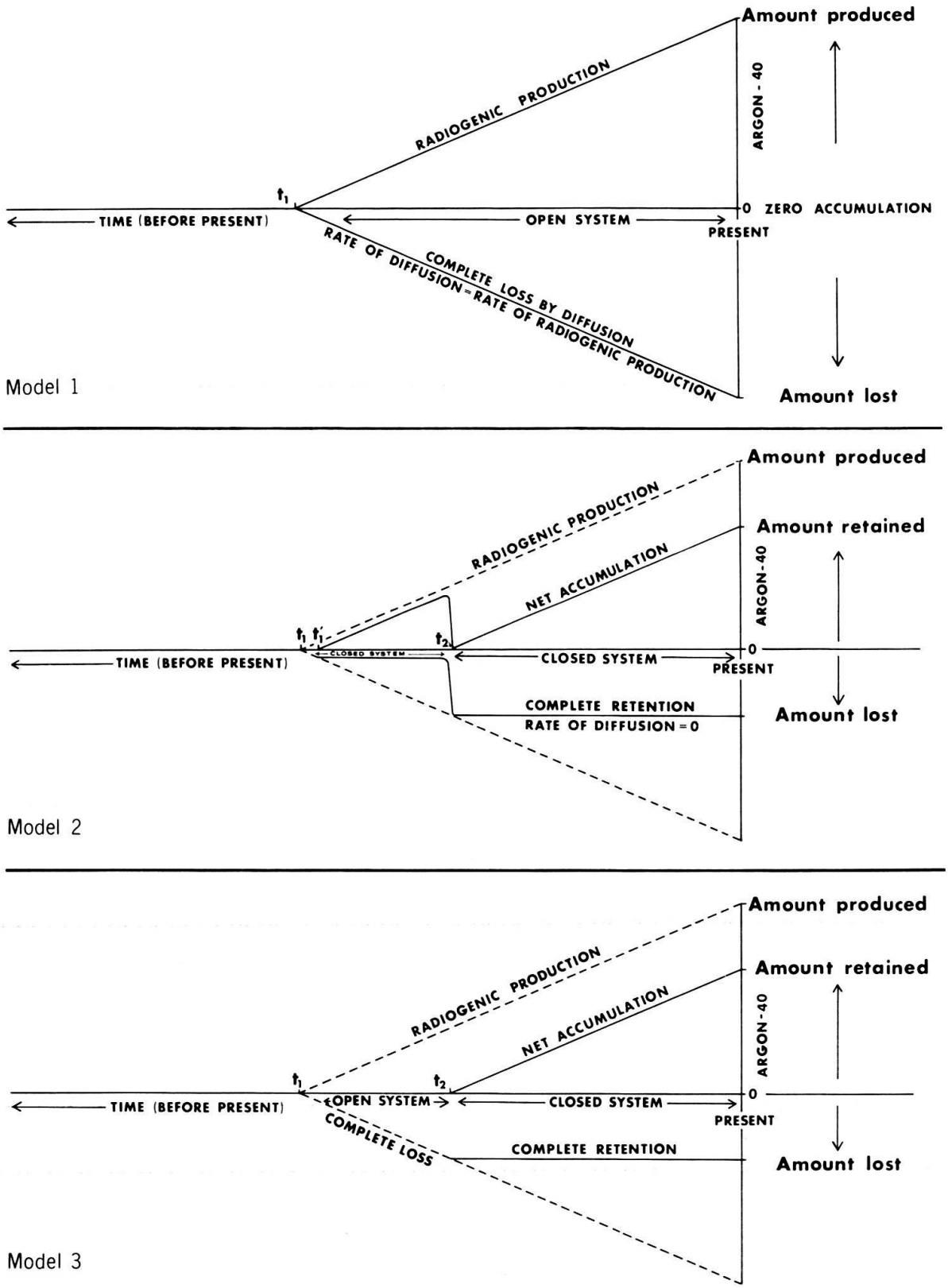

Fig. 2. Argon-40 growth curves
(t_1 is the time of formation of a K^{40}-bearing system, t_2 is its K-Ar model age, see text).

of formation (t_1) and the model age (t_2) will be a function of both the system's critical blocking temperature for argon diffusion and the rate of cooling. Rapidly cooling mineral systems with high argon blocking temperatures will give model ages most closely approximating the real age of formation, t_1. A spread of model age values will be expected from minerals having different blocking temperatures, and from minerals with the same blocking temperature situated at different structural levels in a metamorphic environment where temperatures reached during the metamorphic peak, and the rate of cooling, may be variable. The spread of calculated argon model ages will, in terms of model 3, be related to the cooling history of the metamorphic region. The highest model age values will here, as in model 2, represent minimum estimates of t_2, but the lowest model age values will have, according to model 3, no geological significance whatsoever other than indicating the latest time of closure for Ar^{40} diffusion for all systems analyzed.

The geologic interpretation placed on low argon model age values is thus quite different depending on whether the interpretation of a measured spread of model age values is based on model 2 (fast cooling) or on model 3 (slow cooling), e.g. BROWN et al., 1965. In the first case (fast cooling), low argon model ages can be identified with a real metamorphic event, the thermal overprinting event. In the second case (slow cooling), low argon model ages may be of mineralogical interest but they cannot be identified with any specific metamorphic event.

Three other possible argon-diffusion models (Fig. 3) which might be appropriate for the interpretation of potassium-argon model ages should also be briefly considered.

Model 4 (Fig. 3):

The continuous diffusion model. In this model, loss of radiogenic argon-40 by continuous diffusion occurs throughout the whole life-time of the system under consideration, from t_1 until the present. The rate of loss by diffusion is, however, smaller than the rate of radiogenic production so that there is a net accumulation of Ar^{40} in the system (c.f. model 1). Because the system remains partially open throughout its whole history, the calculated argon model age, t_2, is again only a minimum estimate of the true age of formation t_1. Because the rate of radiogenic Ar^{40} production varies as a function of K^{40} concentration, a spread of calculated argon model ages would be apparent if a constant rate of diffusion were applicable to minerals having different potassium contents. Minerals with high rates of radiogenic Ar^{40} production (i.e. high K-contents) such as potash feldspar should then give higher argon model ages than minerals with low rates of radiogenic Ar^{40} production (i.e. low K-contents) such as hornblende. This is quite contrary to experience, and it would seem doubtful if model 4 is applicable to natural systems. If it were applicable, the amount of argon-40 lost and the age discrepancy ($t_1 - t_2$) between the real age and the measured potassium-argon model age, would increase in proportion to the real age of the system.

Model 5 (Fig. 3):

In model 5, the rate of loss by diffusion of radiogenic Ar^{40} gradually decreases (i.e. the system gradually closes) over a significantly long period of time $t_1 - t_2$. No potassium-argon model ages calculated on the basis of net Ar^{40} accumulation would, in this case, bear any relation to a specific geological event. There is no rapid change, involving only a short time interval, between total loss and total retention of Ar^{40},

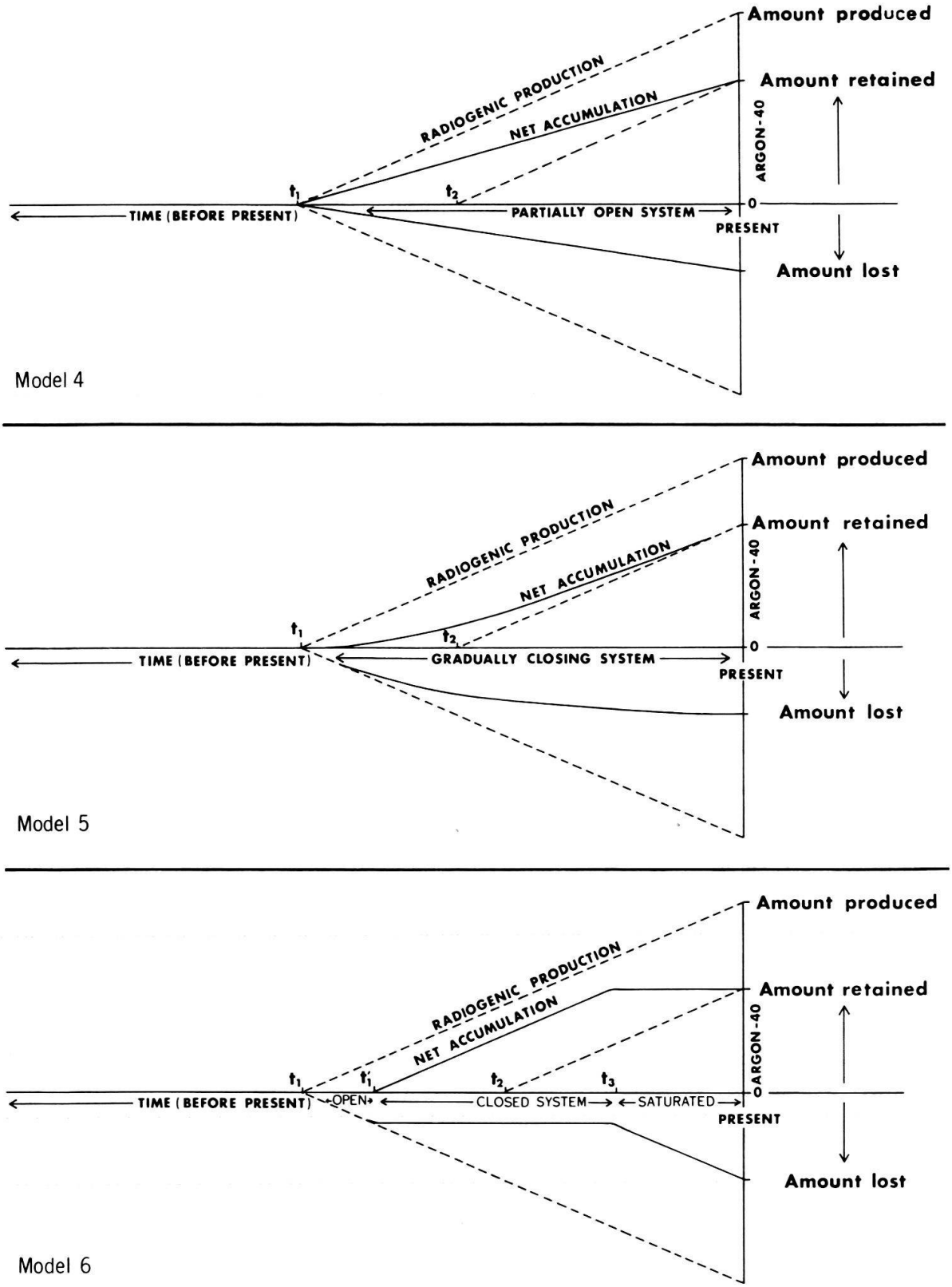

Fig. 3. Argon-40 growth curves
(t_1 is the time of formation of a K^{40}-bearing system, t_2 is its K-Ar model age, see text).

as is implied in model 3. Model 5 would therefore be appropriate for the interpretation of model ages where the rate of cooling through a critical blocking temperature was extremely slow.

Model 6 (Fig. 3):

The Ar^{40} growth curve illustrated in model 6 has some interesting implications relating to the interpretation of potassium-argon model ages. A system formed at time t_1 remains open and does not begin to retain radiogenic Ar^{40} until some later time t'_1, when it begins to retain Ar^{40} quantitatively. At a much later time t_3, the system becomes "saturated" with respect to Ar^{40}, so that after t_3 no more radiogenic Ar^{40} can be retained within the system, and all subsequently produced radiogenic Ar^{40} is lost. The concentration of Ar^{40} would thus build up to a level beyond which no further Ar^{40} could be accomodated in the system. Once this saturation level is reached, all subsequent Ar^{40} generated within the system displaces an equal amount of Ar^{40} present, so that further net accumulation within the system is zero. In this case, if t'_1 is the time of initial closure, and t_2 is the potassium-argon model age calculated on the basis of net Ar^{40} accumulation, then the time interval $t'_1 - t_2$ (the argon age discrepancy) increases with time, in spite of the fact that the time intervals $t_1 - t'_1$ and $t_1 - t_3$ remain constant. The concept of an "age barrier" would here be applicable. The presence of an Ar^{40} saturation level in this case ensures that argon model ages greater than t_2 could not be measured in the system.

Potassium-argon Isochron Ages: Regression Lines and Isochrons

Because of present uncertainties regarding the exact argon diffusion mechanism operating in the metamorphic environment, any number of possible argon-40 growth curves might be considered. In general, however, possible growth curves could result in either an accumulated concentration of argon-40 equal to that produced radiogenically from the decay of K^{40} within the metamorphic system under consideration, or in an accumulated concentration of argon-40 in excess of that produced radiogenically within the system, or in a net radiogenic argon-40 deficiency within the system.

In each case, whatever the growth curve followed, if a suite of three or more cogenetic samples are analyzed for both Ar^{40} and K^{40} concentrations, three or more *regression lines* may be drawn from the measured Ar^{40} concentrations with slopes proportional to the respective K^{40} concentrations measured. The concentration of Ar^{40} is plotted on the ordinate, with time (as the function, $e^{\lambda t} - 1$) on the abscissa. Such a plot represents a graphical solution to equation (1), where $y = Ar^{40}$ concentration, $x = (e^{\lambda t} - 1)$, and the slope of the regression line $m = \lambda_e/\lambda\ K^{40}$. This slope will be similar for all samples having the same potassium contents. On a regression diagram, real time (as $e^{\lambda t} - 1$) is plotted on the x-axis, with $x > 0$ for time future, $x = 0$ for time present, and $x < 0$ for time past. Inspection of equation (1) shows that the slope of the regression line $m = y/x = Ar^{40}/(e^{\lambda t} - 1)$ is not constant for samples having different ages, so that plotting values of Ar^{40} concentration simply against time t, rather than against the function $(e^{\lambda t} - 1)$ would result in an exponential curve, not a straight line. Ar^{40} concentration is a linear function of time t only over time intervals which are small relative to the half-life of K^{40}, when $(e^{\lambda t} - 1) \simeq \lambda t$.

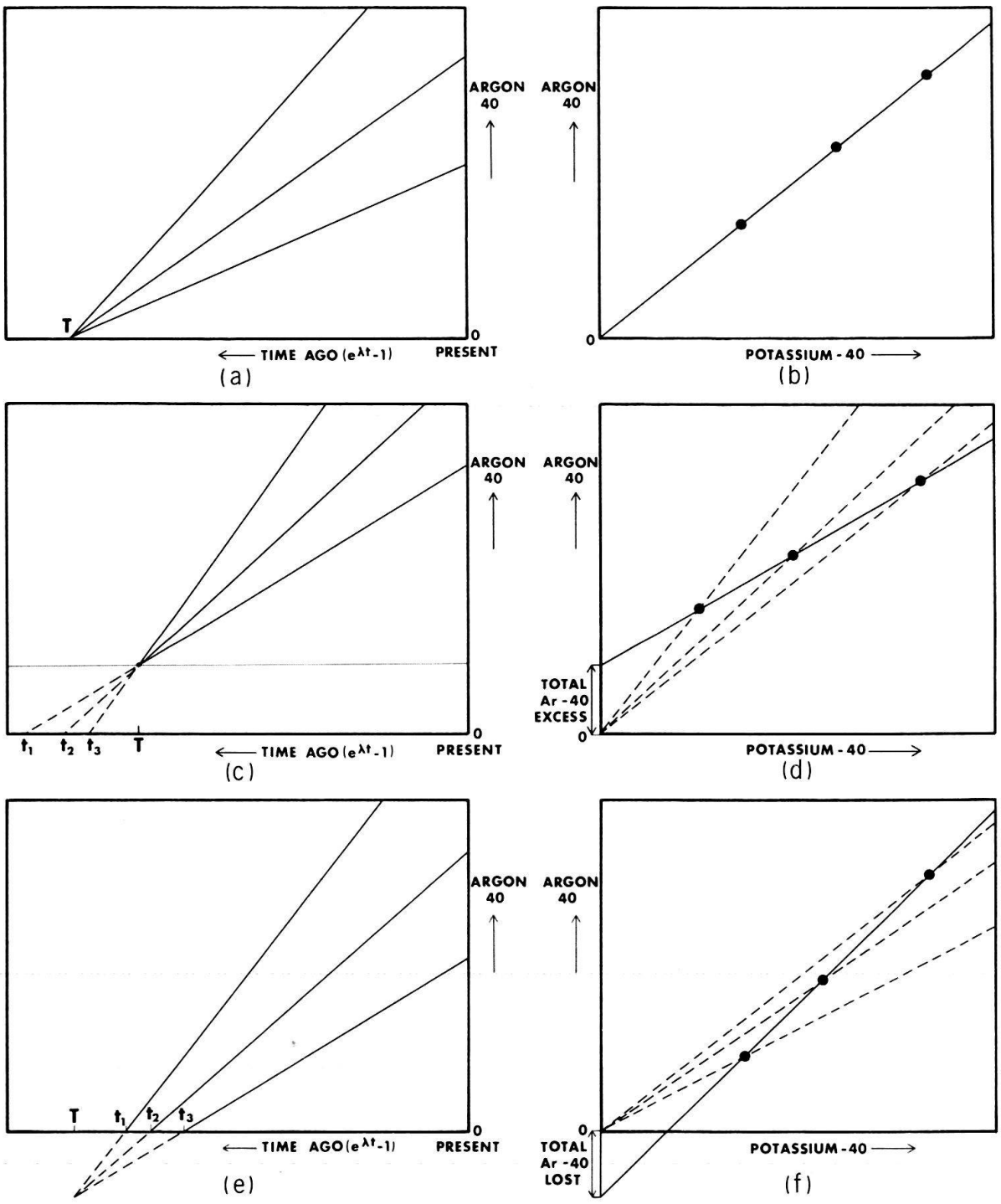

Fig. 4. Graphical solutions of the potassium-argon age equation. Linear regression lines (a, c, e) and isochrons (b, d, f). The real age (T) of a K^{40}-bearing system may be obtained from the intersection of the regression lines or from the slope of the isochrons. The position of the intersection point (regression lines) or intercept (isochrons) is indicative of the presence or deficiency of Ar^{40} at the time of, or subsequent to, formation of the system.

For cogenetic samples with different potassium concentrations, linear regression lines with slopes proportional to the measured K^{40} values will, when projected from the measured values for Ar^{40} concentration plotted on the y-coordinate, intercept

the x-coordinate at the appropriate value of $(e^{\lambda t} - 1)$, where the exponent t is the potassium-argon *model* age (Fig. 4a, c, e). The point of intersection of the regression lines themselves gives the potassium-argon *isochron* age (Fig. 4b, d, f). The regression lines will intersect exactly on the x-coordinate (Fig. 4a) only if the potassium-argon model age equals the potassium-argon isochron age (T). The point of intersection of the regression lines will lie above the x-coordinate (Fig. 4c) if the potassium-argon model ages (t_1, t_2, t_3) are greater than the potassium-argon isochron age (T), and there is the same concentration of argon-40 in excess of that produced radiogenically in each sample. The point of intersection of the regression lines will lie below the x-coordinate (Fig. 4e) if the potassium-argon model ages (t_1, t_2, t_3) are less than the potassium-argon isochron age (T), and there has been an equal concentration of radiogenic argon-40 lost from each sample.

The intersection point of the linear regression lines obtained from any suite of cogenetic samples thus defines the potassium-argon isochron age and the height of the intersection point above or below the x-axis defines the total concentration of argon-40 in excess or lost from each of the samples in the suite.

In cases where excess argon-40 is present, provided only that the same concentration of excess argon was incorporated at the same time into a suite of samples irrespective of their potassium content, measured values of Ar^{40} concentration plotted against potassium concentration on an *isochron diagram* (Fig. 4d) will generate a straight line with slope proportional to $(e^{\lambda t} - 1)$ where t in this case defines the potassium-argon isochron age, equivalent to the time of incorporation of the excess argon. The positive intercept of this isochron on the Ar^{40} axis gives the concentration of excess Ar^{40} incorporated at time t. Potassium-argon *model* ages, calculated for the individual samples in the suite on the basis of equation (1), will in this case be greater than the potassium-argon isochron age, but will *decrease with increasing potassium content.*

Assuming that no "detrital" argon-40 (inherited by the crystal lattice from time prior to crystallization due to incomplete outgassing) is present, the excess argon-40 indicated by an argon isochron with positive intercept may either have been incorporated into the mineral at the time of crystallization, residing for instance in fluid inclusions, or, it may have been occluded into the mineral lattice at some time subsequent to crystallization under conditions of very high pressure.

In cases where there has been a net loss of argon-40 through diffusion, provided that the same concentration of argon-40 has been lost from a suite of cogenetic samples irrespective of their potassium content, measured values of Ar^{40} concentrations plotted against potassium concentration on an isochron diagram (Fig. 4f) will generate a straight line with slope proportional to $(e^{\lambda t} - 1)$, where t again defines the potassium-argon isochron age. The potassium-argon isochron age will in this case be equivalent to the time of K^{40}-retention, i.e. to the time of crystallization. The negative intercept of this isochron on the Ar^{40} axis gives the total concentration of argon-40 lost by diffusion since the time of crystallization. Potassium-argon *model* ages for each of the samples in the suite will in this case be less than the potassium-argon isochron age, but will *increase with increasing potassium content.*

In metamorphic environments, where loss of argon-40 by diffusion from individual mineral lattices may be effected by the external partial pressure of argon within the whole-rock system, similar concentrations of argon-40 may be lost from minerals having similar lattice structures. Where this occurs, argon isochrons with negative intercepts should be obtained from cogenetic suites of minerals having similar lattice structure but different potassium concentrations. The slope of such an isochron, i.e. the potassium-argon isochron age, would then give the time of K^{40}-retention which would be equivalent to the metamorphic age of the minerals. The potassium-argon model ages, measured for each sample on the basis of equation (1), would be indicative of the times of Ar^{40}-retention for each mineral.

Argon Isochrons with Negative Intercepts

From the considerable volume of K^{40}-Ar^{40} data now available in the literature, previously reported analyses from three different Phanerozoic metamorphic areas familiar to the author have been plotted on isochron diagrams (Figs. 5–9). Although the scatter of data is in some cases more than desirable, the results do illustrate the feasibility of using isochron-type plots for K^{40}-Ar^{40} data presentation as has been variously suggested by HARPER (1965), LIVINGSTON et al. (1967), MAUGER et al. (1968), MCDOUGAL et al. (1969) and YORK et al. (1969). The new isochrons shown here, however, demonstrate the possibility of obtaining a direct measure of the concentration of argon-40 lost from a suite of metamorphic minerals, together with their real metamorphic age, in cases where the argon-isochron has a negative intercept.

The potassium-argon data discussed below are summarized on Table 1. In most instances, estimates of the slope and intercept of the isochrons obtained graphically are compared with the "best" isochron computed according to the least squares cubic method described by YORK (1966, 1967). In cases where both have been applied, eyeball and computer are in agreement with one another.

Scottish Caledonides (Figs. 5, 6):

The interpretation of potassium-argon model ages from the Scottish Caledonides has been the subject of some controversy (e.g. BROWN et al., 1965; HARPER, 1967). In Figure 5, K^{40}-Ar^{40} analyses reported by HARPER (1967, Table 3) from Upper Dalradian slates giving model argon ages in the range 508–500 m.y., averaging 503 m.y., are plotted on an isochron diagram and yield a 500 m.y. isochron with zero intercept. On the same diagram (Fig. 5) are also plotted ten analyzed mica samples reported by HARPER (1967, Table 1). These latter lie close to a second isochron, parallel to the 500 m.y. isochron given by the slate samples, but with a negative intercept indicating a loss of argon-40 from each of the analyzed micas in the order of 1.3×10^{-5} scc/gm.

From these results it is apparent that both slates and micas have the same potassium-argon isochron age, and so they must have both recrystallized at the same time some 500 m.y. ago. The age of crystallization being given by the potassium-argon isochron age. The micas, however, lost (during a post-metamorphic period) approximately 1.3×10^{-5} scc/gm of their radiogenic argon-40 before lattice closure occurred, and consequently they have a much wider variation in measured potassium-argon

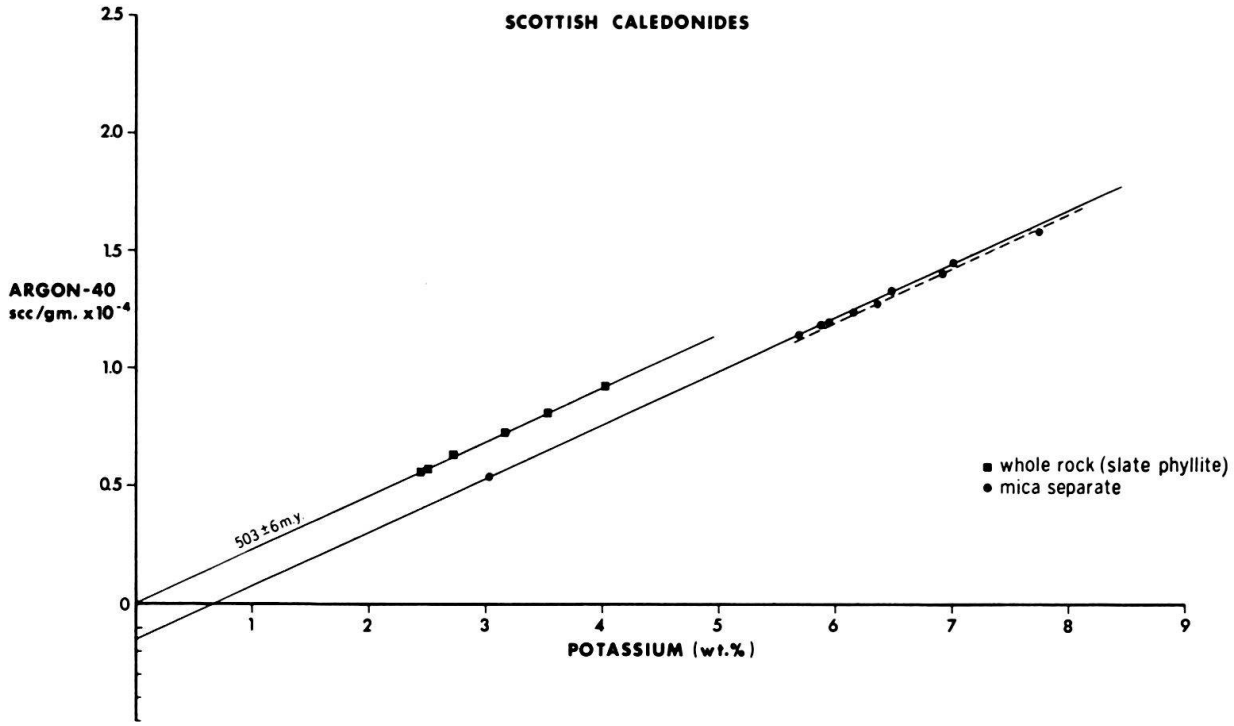

Fig. 5. Potassium-argon isochron data for the Scottish Caledonides. Average model age of slates, 503 ± 6 m.y. Mica isochron age, 489 ± 9 m.y., intercept (Ar^{40}-loss) − 1.31 ± 0.25 scc/gm × 10^{-5}. K-Ar analyses, HARPER (1967).

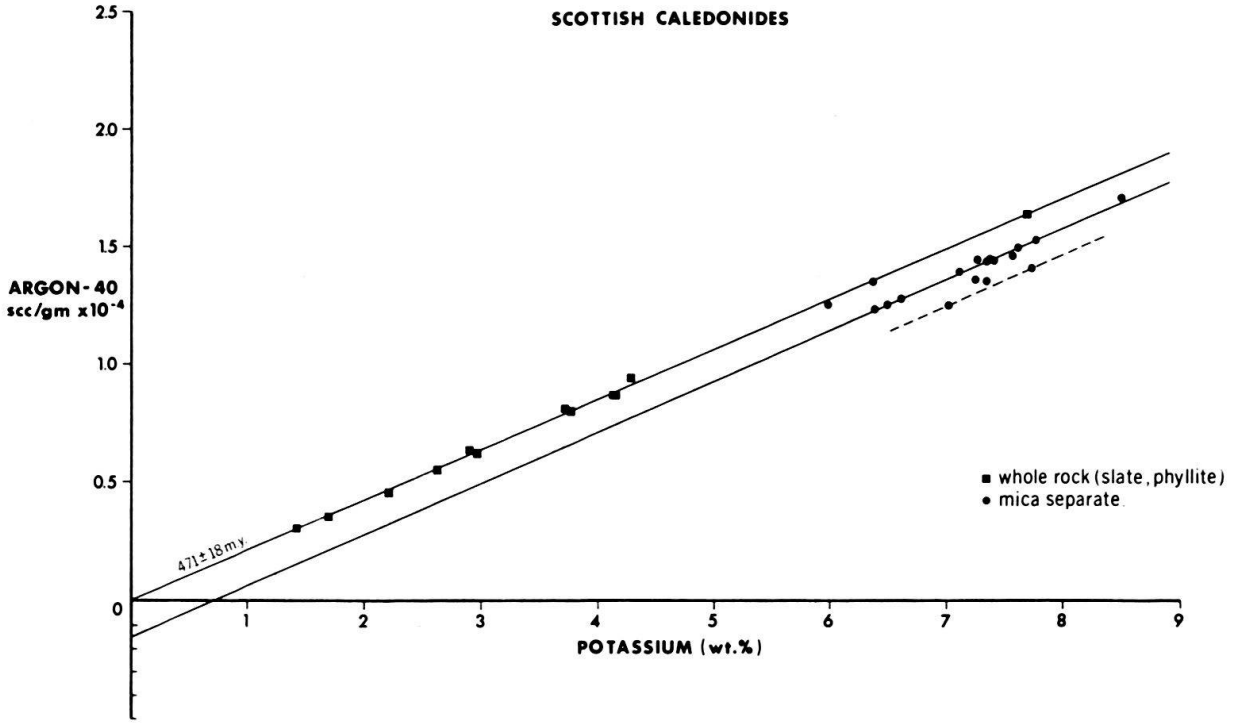

Fig. 6. Potassium-argon isochron data for the Scottish Caledonides. Average model age of slates 471 ± 18 m.y. Mica isochron age, 477 ± 32 m.y., intercept (Ar^{40}-loss) − 1.47 ± 1.17 scc/gm × 10^{-5}. K-Ar analyses, HARPER (1967).

model age than the whole-rock slate samples. Low potash micas give the youngest model argon ages and high potash micas the oldest.

The same effect is apparent in Figure 6. Here, twelve Upper Dalradian slates giving whole-rock model argon ages in the range 485–455 m.y. averaging 471 m.y. (as reported by HARPER, 1967, Table 3) lie close to a 470 m.y. isochron with zero intercept. Twelve other micas (HARPER, 1967, Table 1) plot close to a parallel isochron with negative intercept indicating a loss of 1.5×10^{-5} scc/gm of argon-40 from each of the analyzed mica samples. A second metamorphic event occurring 470 m.y. ago, which effected both slates and micas is apparently confirmed by the similar potassium-argon isochron ages obtained from both slate and mica samples. The 470 m.y. micas from Figure 6, and the 500 m.y. micas from Figure 5 both appear to have lost similar concentrations of radiogenic argon-40 subsequent to their formation.

Although most of the micas plotted in Figure 6 appear to have lost the same concentration of argon-40 (and so cluster close to a single isochron with negative intercept) two micas appear to have retained nearly all their radiogenic-argon-40 subsequent to the 470 m.y. event and these lie very close to the 470 m.y. isochron with zero intercept. A few micas have lost significantly more argon than 1.5×10^{-5} scc/gm and these lie below the 470 m.y. isochron with -1.5×10^{-5} intercept.

The two groups of micas shown respectively in Figures 5 and 6 each have different isochron ages, reflecting different times of K^{40}-retention. However, the two groups appear indistinguishable on the basis of either stratigraphic, structural or geographic criteria. Micas having 500 m.y. argon isochron ages from the Scottish Caledonides do on average have slightly lower potassium-contents, but this would not appear to be significant, and preservation of these older K^{40}-retention (argon isochron) ages appears to be quite fortuitous.

Irish Caledonides (Fig. 7):

Potassium-argon model ages have been reported from a number of micas separated from schists collected in Western Ireland by MOORBATH et al. (1968). When plotted on an isochron diagram (Fig. 7) the analysed Irish samples fall on two distinct isochrons with negative intercepts, indicating larger argon-40 losses in the order of 2.0 and 3.0×10^{-5} scc/gm respectively. The slopes of the two isochrons are similar and indicate a potassium-argon isochron age of 530 m.y. Micas with low potassium contents (less than 6%) have lost less radiogenic argon-40 than micas with potassium contents in excess of 6% by weight.

This 530 m.y. K-Ar isochron age from the Irish Caledonides has no counterpart in the Scottish Caledonides, although K-Ar model ages of 516, 507 m.y. have been reported from the Torridonian slates (HARPER, 1967). Interpretation of the 530 m.y. K-Ar mineral isochron age from Ireland as a metamorphic age is supported by the post-metamorphic Rb-Sr whole-rock isochron age of 510 m.y. reported from the Oughterrard granite at Connemara (LEGGO et al., 1966).

Northern Appalachians (Figs. 8, 9):

A 470 m.y. event, similar to that recorded in the Scottish Caledonides, is revealed by isochron analysis of the potassium-argon data recently reported from the Taconic slates and Green Mountain schists of Vermont (HARPER, 1968, Table I). However, in the western Vermont region the 470 m.y. event has been severely overprinted by a

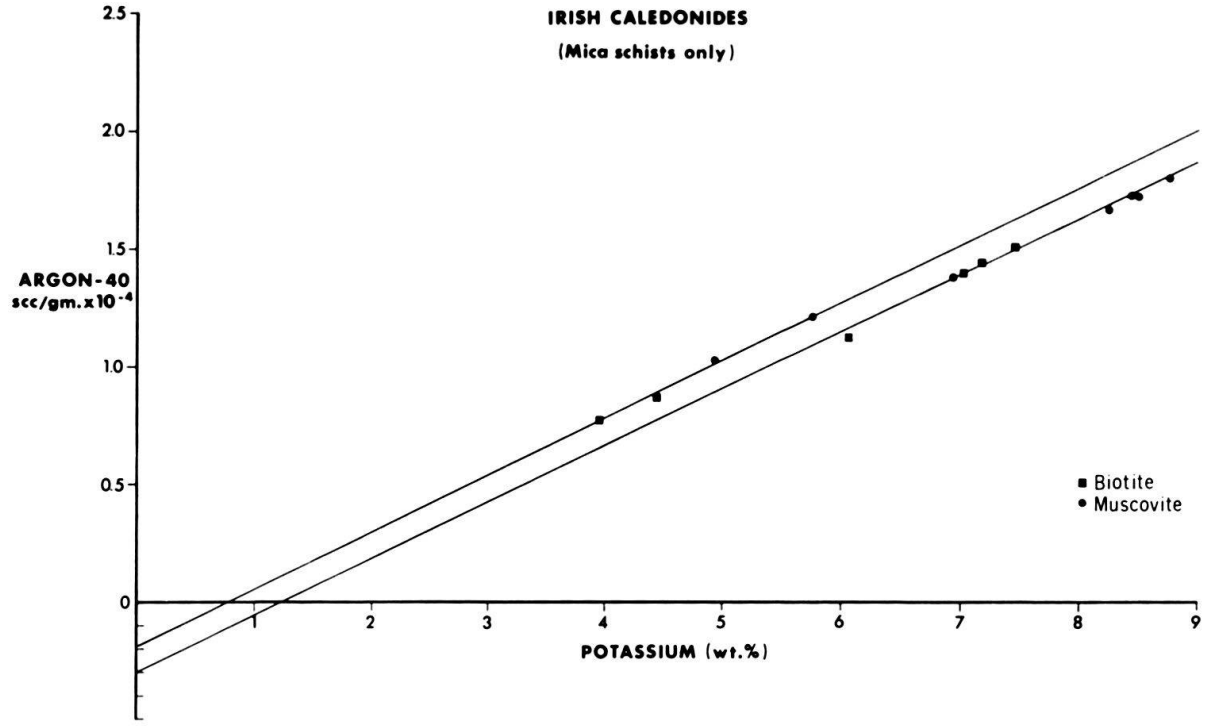

Fig. 7. Potassium-argon isochron data for the Irish Caledonides. Mica isochron ages, 532 ± 33 m.y. and 530 ± 25 m.y. Intercepts (Ar^{40}-loss) 2.06 ± 0.82 and 3.38 ± 1.00 scc/gm × 10^{-5} respectively. K-Ar analyses, MOORBATH et al. (1968).

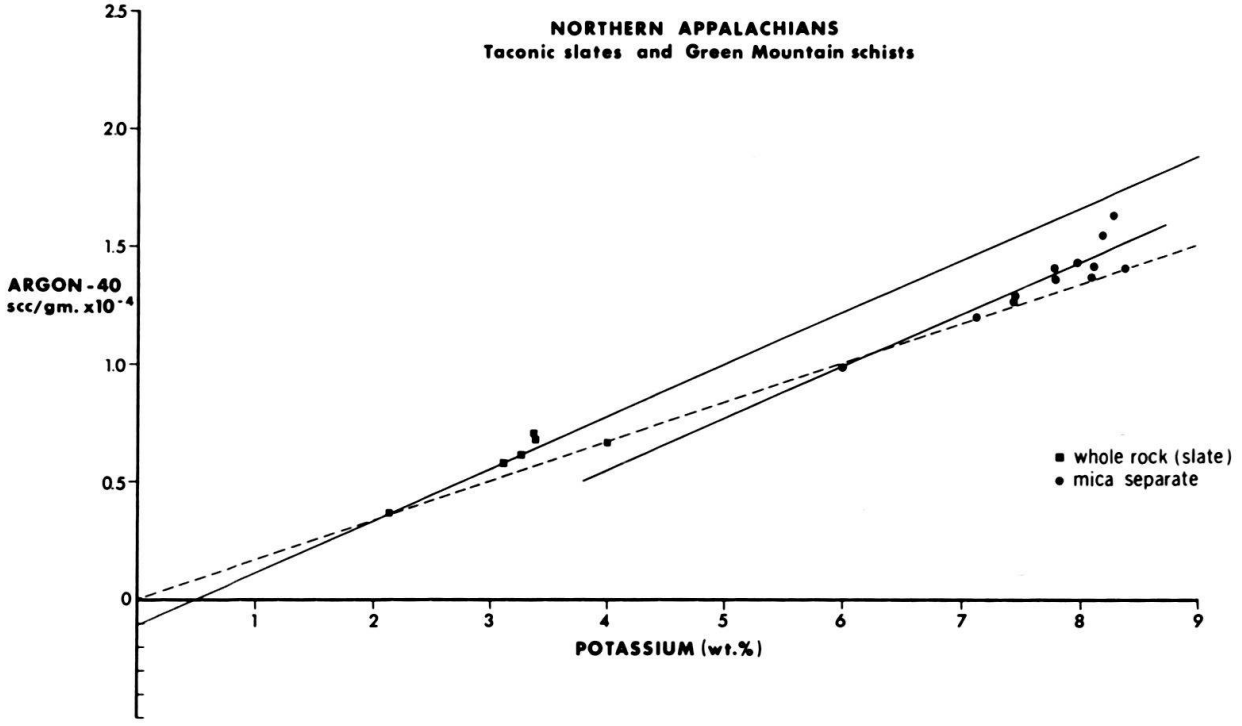

Fig. 8. Potassium-argon isochron data for the Northern Appalachians. Slates and micas give isochron ages (solid lines) of 475 ± 24 m.y. and 480 ± 30 m.y. respectively. Data indicates overprinting by a 380 m.y. event (broken line). K-Ar analyses, HARPER (1968).

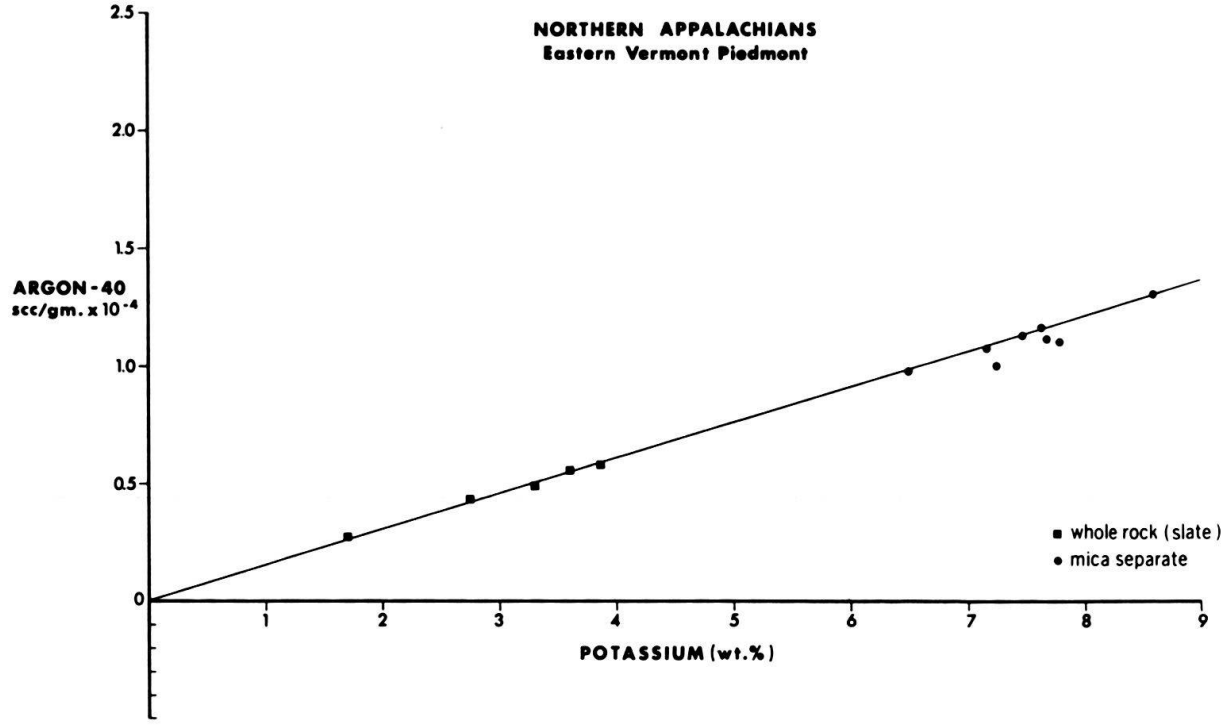

Fig. 9. Potassium-argon isochron data for the Northern Appalachians indicative of a 345 m.y. event effecting the Eastern Vermont Piedmont without subsequent loss of radiogenic argon. K-Ar analyses, HARPER (1968).

much later event occurring around 380 m.y. ago in Lower Devonian times. Consequently, much of the K-Ar data obtained from the Taconic slates and from mica separates from the schists now outcropping along the Green Mountain anticline trend towards a 380 m.y. isochron with zero intercept (Fig. 8). However, "residual" isochrons with slopes approximating 470 m.y. are still apparent. Both the Taconic slates and the Paleozoic schists of western Vermont would therefore appear to have originally crystallized some 470 m.y. ago and to have been later affected by a Lower Devonian thermal event of considerable severity.

In eastern Vermont on the other hand, K-Ar data reported by HARPER (1968, Table II) from a variety of slates and metamorphic mineral separates from schists and gneissic domes all lie on a single isochron with zero intercept (Fig. 9), indicating that a major event occurred to the east some 345 m.y. ago between the Upper Devonian and Lower Carboniferous. The zero intercept given by the isochron, indicating no radiogenic argon-40 loss from the analyzed samples subsequent to the 345 m.y. event, suggests rapid lattice closure at this time. The nature of this event has been discussed elsewhere (HARPER, 1968, p. 54).

Proposed Mechanism for Argon Loss and Retention in Metamorphic Mineral Systems

The occurrence of argon isochrons with negative intercepts may be readily explained if a pressure dependent mechanism governing the diffusive loss and retention of radiogenic argon-40 is effective in metamorphic environments.

Table 1. Potassium-argon Isochron Age Data

Locality	Text-figure	Samples	Number of points on isochron	K-Ar model ages (m.y.)	K-Ar isochron age (m.y.)	Ar^{40}-loss[a] ($scc/gm \times 10^{-5}$)
Irish Caledonides	7	Mica	4	462–435	530	1.90
					532 ± 33[b])	2.06 ± 0.82
Irish Caledonides	7	Mica	9	454–438	530	3.00
					530 ± 25[b])	3.38 ± 1.00
					(Middle Cambrian)	
Scottish Caledonides	5	Slate (WR)	6	508–500	500	Zero
					499 ± 22[b])	(+ 0.06 ± 0.33)
Scottish Caledonides	5	Mica	10	458–399	500	1.50
					489 ± 9[b])	1.31 ± 0.25
					(Lower Ordovician)	
Scottish Caledonides	6	Mica	12	448–431	470	1.55
					477 ± 32[b])	1.47 ± 1.17
Scottish Caledonides	6	Slate (WR)	12	484–455	470	Zero
					474 ± 6[b])	(− 0.06 ± 0.08)
Northern Appalachians	8	Slate (WR)	3	420–388	470	1.10
					475 ± 24[b])	0.96 ± 0.33
Northern Appalachians	8	Mica	8	407–374	470	3.50
					480 ± 30[b])	3.35 ± 1.14
					(Mid Ordovician)	
Northern Appalachians	8	Mica, Slate (WR)	6	388–374	380	Zero
					(Lower Devonian)	
Northern Appalachians	9	Mica, Slate (WR)	10	362–334	345	Zero
					339 ± 4[b])	(+ 0.16 ± 0.07)
					(Upper Devonian – Lower Carboniferous)	

[a]) Indicated by negative intercept. [b]) Computed values errors quoted are 1 σ.

During metamorphism it may be assumed that all previously accumulated radiogenic argon-40 is expelled from the lattices of recrystallizing minerals and is lost from the whole-rock system. Once crystallization is complete (at time t_0) potassium-40 becomes fixed in the crystal lattices of appropriate minerals along with other ionic radioactive parents such as rubidium-87, uranium-238, uranium-235, and thorium-232.

From time t_0 onwards, the ionic daughter products of potassium, rubidium, uranium and thorium decay (calcium, strontium and lead) will be retained in individual mineral or whole-rock systems and will there begin to accumulate. More generally, however, the same system may become closed to different isotopes at different times. One of the daughter products of potassium-40 decay, argon-40, cannot form ionic bonds within crystal lattices because it acquires the extra-nuclear electronic configuration of an inert gas. Consequently, it is not fixed ionically in any crystal lattice or whole-rock system at t_0. The potassium-argon decay scheme thus represents a two-phase scheme, where the potassium-retention age (given by the K^{40}-Ar^{40} isochron age) may be different from the argon retention age (given by the K^{40}-Ar^{40} model age).

Newly formed metamorphic mineral assemblages, particularly those situated at elevated temperatures in the metamorphosed orogen, will thus continue to loose radiogenic argon-40 from their lattices by volume diffusion after crystallization. However, at depth (i.e. under elevated pressure) the argon-40 lost from the crystal lattice will tend to be retained in the whole rock system. Where this occurs, the argon-40 lost by volume diffusion from the lattice will accumulate along grain-boundaries and lattice defects within the polycrystalline whole-rock system. Consequently, the partial pressure of argon surrounding the crystal lattice must increase until it finally reaches a level sufficient to inhibit further loss of radiogenic argon from the lattice. The mineral system then becomes "closed" to any further argon loss. The time of argon-closure for any particular mineral (i.e. the K^{40}-Ar^{40} model age) will depend, therefore, not so much on the *temperature* of the metamorphic environment, as on the *partial pressure* of argon-40 along the grain-boundaries and lattice defects of the mineral in question.

A mineral's "retentivity" for argon-40 in a metamorphic environment should thus be regarded as a function of a thermally controlled balance between the internal partial pressure of argon inside the crystal (caused by the continual formation of radiogenic argon within the lattice) and the external partial pressure on grain-boundaries (caused by the build-up along available grain-boundaries of radiogenic argon-40 diffusing from the crystal lattice).

Relationships between the rate of radiogenic argon-40 production, and the rate of argon-40 accumulation on grain-boundaries and within the crystal lattice itself are shown in Figure 10. The rate of radiogenic argon-40 production is a function of potassium content (Fig. 10a). Initially, after metamorphic recrystallization at time t_0, much of the radiogenic argon-40 produced within the crystal lattices of potassium-bearing phases making up the whole-rock system diffuses from the lattice and accumulates, under elevated temperature and pressure, along grain-boundaries separating individual lattices. After a certain time interval, a "saturation-level" will be reached when the partial pressure of argon on the grain-boundaries has increased to the point where further volume diffusion to the grain-boundaries is inhibited (Fig. 10b). All the

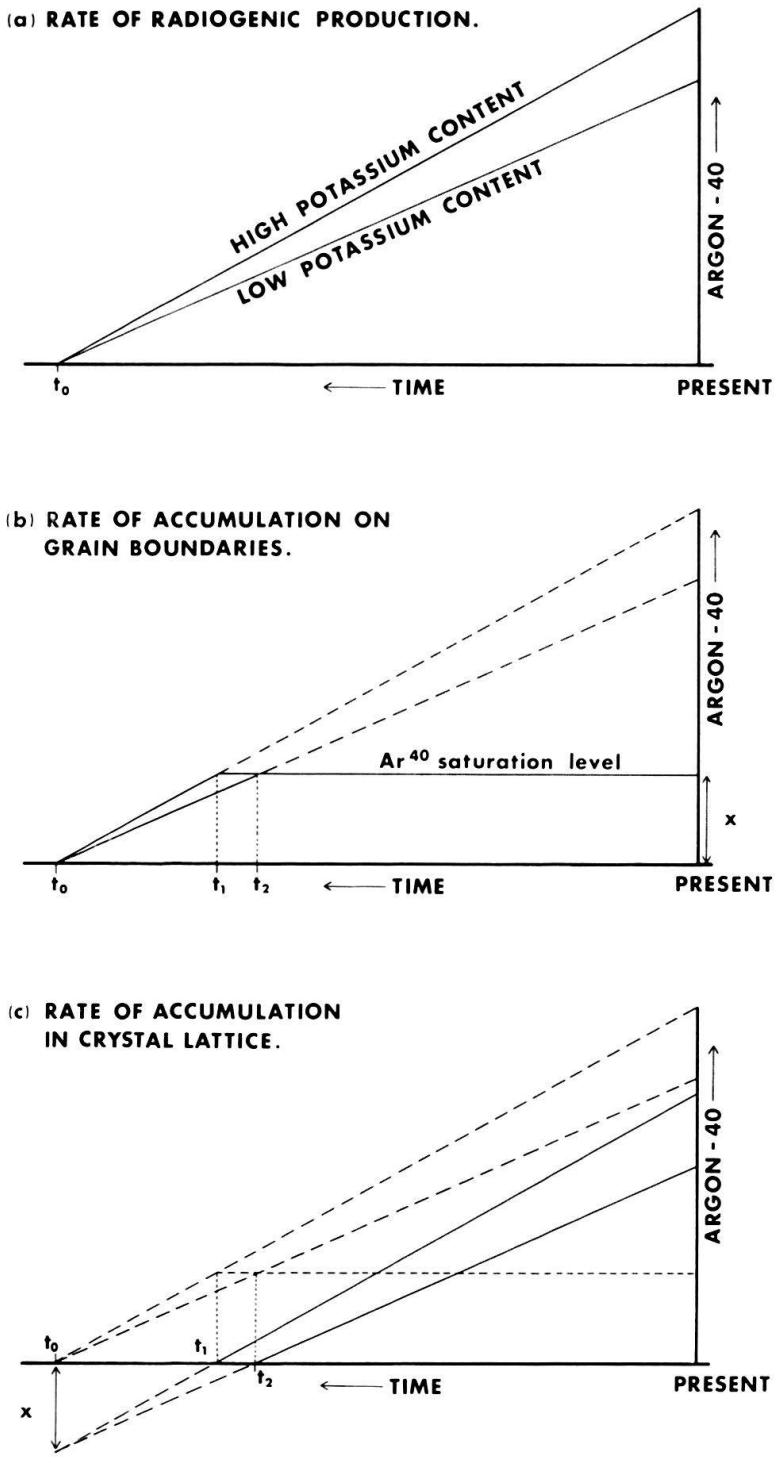

Fig. 10. Relationships between rate of radiogenic Ar^{40} production and accumulation. t_0 is the time of formation of a metamorphic mineral system, t_1 and t_2 are times of lattice closure (K-Ar model ages) for minerals with different potassium contents. x is the concentration of Ar^{40} lost by volume diffusion from crystal lattice to grain boundaries. Rates of accumulation given by solid lines.

radiogenic argon-40 subsequently produced by the mineral is then retained within the lattice (Fig. 10c).

Potassium-argon model ages (t_1 and t_2, Fig. 10) are, however, calculated solely on the basis of the measured proportion of radiogenic argon-40 remaining within the

crystal lattice. The proportion of radiogenic argon-40 which initially accumulates on grain-boundaries under elevated temperatures and pressures is likely to be lost from the whole-rock system by grain-boundary diffusion upon release of pressure during uplift and erosion. Renewed volume diffusion would at this time be unlikely because of the lower temperatures prevailing. Any argon-40 that did remain on grainboundaries would most probably be lost during the mineral extraction and bakeout procedures normally adopted in K-Ar dating. Thus, the concentration of argon-40 (x in Fig. 10) necessary to locally saturate the grain-boundary before lattice closure is equal to the total concentration of radiogenic argon-40 effectively lost from the crystal lattice.

The commonly observed potassium-argon model age patterns in metamorphosed regions indicate that the argon-40 saturation level required for lattice closure of minerals under elevated PT conditions is a function of mineral structure. Amphiboles apparently have lower saturation levels than micas, which in turn have lower saturation levels than potash-feldspars. The corresponding loss of lattice argon is minimal for metamorphic hornblende and a maximum for metamorphic potash-feldspar.

The length of time it takes a given mineral, such as a phyllosilicate mica, to reach the required local grain-boundary saturation level appropriate for its structure, is a function of the rate of radiogenic argon-40 production within the lattice. That is to say the magnitude of the time interval between metamorphic recrystallization and lattice closure, during which radiogenic argon-40 diffuses from the lattice to the grain-boundary, depends on the potassium content of the mica. Potassium-poor micas, because they take a longer time to build up along their grain-boundaries the saturation level of argon-40 necessary for lattice closure, will have younger K^{40}-Ar^{40} model ages than potassium-rich micas with similar lattice structure. Nevertheless, under similar PT conditions, providing the grain-boundary thickness and the ratio of grain interfacial area to grain volume remains relatively constant, the same concentration of radiogenic argon-40 will be lost by volume diffusion from the crystal lattices of minerals with similar lattice structure irrespective of their potassium-contents.

Argon isochrons with negative intercepts are now readily explained. All mineral samples lying on such an isochron, irrespective of their potassium content, must have lost the same concentration of argon-40 by volume diffusion from the mineral lattice to grain-boundaries. The concentration of lattice argon-40 lost from each of the minerals simply represents the concentration required to close the lattice to any further loss of argon through volume diffusion by locally saturating the grain-boundaries and lattice defects with argon-40 under elevated PT conditions. The times of lattice closure with respect to volume diffusion of argon-40 (i.e. the K^{40}-Ar^{40} model ages) are then proportional to the potassium contents of the individual minerals. The time of lattice closure with respect to potassium-40 diffusion will be the same for all minerals lying on the isochron and is given by the K^{40}-Ar^{40} isochron age obtained from the slope of the isochron with negative intercept. The concentration of lattice argon-40 lost to the grain-boundaries, and ultimately from the whole-rock system, is given by the negative intercept itself.

Conclusions

Graphical solutions to the problem of radiogenic argon-40 loss from metamorphic minerals are effective provided only that the same concentration of argon-40 is lost

from a suite of cogenetic minerals irrespective of their potassium contents. Where this occurs, analyzed samples will yield an isochron with negative intercepts on an argon-40 versus potassium concentration plot. The potassium-argon *isochron* age, obtained from the slope of such an isochron is the K^{40}-retention age which can be identified with the age of metamorphic recrystallization. The concentration of argon-40 lost by volume diffusion from each of the mineral samples lying on the isochron is given by the negative intercept of the isochron on the argon-40 axis. This concentration lost is a measure of the amount necessary to locally saturate available lattice defects and grain-boundaries surrounding the mineral with radiogenic argon-40 to a level where further loss by volume diffusion from the lattice is inhibited.

Argon isochrons with negative intercepts obtained from metamorphic micas of various ages indicate that in the metamorphic environment concentrations of radiogenic argon-40 in the order of $1-3 \times 10^{-5}$ scc/gm are lost from phyllosilicate lattices before quantitative lattice-retention begins.

Potassium-argon ages, calculated only from the measured proportion of radiogenic argon-40 retained within the mineral lattice, are here termed potassium-argon *model* ages, and are equivalent to the Ar^{40}-retention age. In cases where the same concentration of radiogenic argon-40 has been lost from a cogenetic suite of minerals irrespective of their potassium content, measured potassium-argon model ages are proportional to the potassium-contents of the minerals analyzed, and have no geological significance.

Previous interpretations of Ar^{40}-retention ages based on temperature dependent models involving either episodic or continuous loss of radiogenic argon-40 from the lattice by volume diffusion may thus be over-simplified. Lattice retention of radiogenic argon-40 appears to be a function not only of temperature, but also of pressure, specifically, the partial pressure of argon-40 on grain-boundaries within the polycrystalline whole-rock system.

The presence of granitic or basaltic melts in the metamorphic environment may further complicate the pattern of argon-40 mobility. The presence of a melt would act as a "sink" for the argon-40 situated along the crystalline grain-boundaries within any whole-rock system (c.f. KIRSTEN, 1968; FYFE et al., 1969). Most metamorphic rocks are indeed characterized by a deficiency of radiogenic argon-40 in their constituent potash-bearing minerals (MOORBATH, 1967), while many igneous rocks appear to have crystallized in the presence of excess argon-40 (DAMON et al., 1967). Because the diffusivity of radiogenic argon produced during the initial post-metamorphic period may be controlled by segregation of argon-40 at grain-boundaries, studies of relationships between argon-retentivity and the microstructure of polycrystalline metamorphic rocks would appear to be warranted. The kinetics of most solid-state processes in polycrystalline solids are known to be effected by grain-boundaries (WESTBROOK, 1964).

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