The graphic method of analysis of discordant potassium-argon data

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The loss of argon from various minerals by thermal event is semi-quantitatively discussed by a graphic method based on diffusion model. The way of estimating the primary age of a rock or rock massif is presented using real samples of Kidjimitskii and Vitimkanskii complexes in Zabaikalie.

INTRODUCTION

Retention of radiogenic argon in minerals is affected by various post-crystallization alterations. The retentivity is different from mineral to mineral, and is also dependent on the extent of post-crystallization alteration.

This paper deals with the loss of argon from different minerals through thermal effect with special emphasis on the correct interpretation of K-Ar age of rocks.

Thermal influence on argon loss has been extensively investigated in both laboratory (FECHTIG and KALBITZER, 1966) and field (HART, 1964; HANSON and GAST, 1967). The term, thermal influence, may include dehydration, oxidation and phase transition due to temperature elevation. However, in this study, the loss of argon is exclusively attributed to thermally activated migration of argon. As a basis for explanation of discordant K-Ar ages of different minerals, one should accept a different retentivity of radiogenic argon for different minerals by thermal influence. Empirical sequence of retentivity can be obtained by various laboratory experiments such as argonography (MOROZOVA and ASHKINADZE, 1971) and neutron activation (LANPHERE and DALRYMPLE, 1971; BERGER, 1975).

After obtaining necessary information, the interpretation of K-Ar analysis can be given either by analytical method (LEVSKY, 1964; DAMON, 1970) or graphic method presented in this paper.

PRESENTATION OF THE MODEL

Two fundamental assumptions are necessary to put forward our discussion:

- 1) Different minerals have different retentivities with respect to radiogenic argon.
- 2) Coincident mineral ages give either the primary age or the time of intensive thermal event.

The basic idea of the graphic method is shown in Fig. 1. The apparent ages of any mineral-pair should lie on a point of the straight line, concordia (WETHERILL, 1956) in Fig. 1, when the system including the mineral-pair is a closed system from the "beginning" to the present. On the other hand, if there is any thermal event after the system becomes closed, argon loss takes place to different extents for different minerals. Let us assume that the retentivity of M_2 is higher than that of M_1 . In Fig. 1, the point "a" represents the primary age, and "b" the time of an intense thermal event. When M_1 - M_2 pair is subjected to thermal influence (e.g., being distant from a heating front), M_1 loses more fraction of radiogenic argon than does M_2 and gives a younger apparent age. On the contrary, when a pair of M_1 and M_2 undergoes an intensive thermal influence and loses radiogenic argon completely, t_{M_1} and t_{M_2} should be the same as shown by point b in Fig. 1. However, when the loss is not complete, M_2 retains more argon than does M_1 . The solid curve in Fig. 1 indicates qualitatively the situation mentioned above. The shape of the curve depends on the difference in the retentivity or more concretely the difference between the activation energy

Fig. 1. The scheme of the graphic method for analysis of age data.

of argon migration in M_1 and M_2 .

APPLICATION OF THE MODEL

Application of the model is given by the following three examples. The first example is based on the data given by DALLMEYER (1975) and shown in Fig. 2. The primary sedimentary rocks, metamorphosed regionally about 1,100 m.y. ago, were remetamorphosed about 330-350 m.y. ago with pronounced zoning. The samples were taken from the profile perpen-

Fig. 2. Application of the graphic method for metamorphic rocks. Analytical data from DALLMEYER (1975).

dicular to the zoning.

The apparent ages of biotite-amphibole pairs are plotted in Fig. 2. The steep rise of the curve is explained by a remarkable difference between activation energies of argon migration in biotite and amphibole. One can see that argon loss of $\leq 15\%$ from amphibole corresponds to practically complete loss of argon from biotite. The upper intersect of the curve with the concordia corresponds to the age of 1,050-1,100 m.y. which agrees quite well with the ^{87}Rb - ^{87}Sr isochron age of 1,060 m.y.

The second example is based on the analytical data obtained for the samples from Kidjimitskii complex of leucocratic granites in Zabaikalie (Table 1). The analytical technique has been described already by the authors (LEVSKY and RUBLEV, 1976). The points in Fig. 3 makes it possible to define the curve, which intersects the concordia at the age corresponding to 300 m.y. both in the cases of biotite-feldspar pair and biotite-plagioclase

Table 1. Age data for minerals of the rocks from Kidjimitskii complex

The name of a massif, sample number		K (wt.%)	$^{40}\text{Ar}_{\text{rad}}$ (10^{-9}g/g)	Age*) (m.y.)
Kidjimitskii				
2126	plagioclase	4.78	89.2	257
	microcline	8.80	159	250
	biotite	7.32	157	292
2115a	plagioclase	0.97	14.7	215
	microcline	8.47	131.5	212
	biotite	7.14	139	268
62	muscovite	8.87	210	312
Imskii				
2023	plagioclase	1.12	18.6	230
	microcline	10.30	166	223
	biotite	7.75	155	274
525	plagioclase	2.55	29.0	160
	microcline	8.75	74.6	122
	biotite	7.41	91.2	174
Itanzinskii				
2077a	plagioclase	1.10	17.6	223
	biotite	8.20	167.5	279
Djilindinskii				
2291	plagioclase	1.69	26.3	210
	microcline	9.64	161	230
	biotite	4.37	90	282
Nirokskii				
2064	plagioclase	5.49	61.2	158
	microcline	9.69	116.2	169
	biotite	7.44	136	252

*) $\sigma_t \leq 3\%$, constants used: $\lambda_e = 0.557 \cdot 10^{-10} \text{yr}^{-1}$, $\lambda_\beta = 4.72 \cdot 10^{-10} \text{yr}^{-1}$, $^{40}\text{K}/\text{K} = 1.19 \cdot 10^{-2}$ atom percent.

Fig. 3. Application of the graphic method for the rocks of Vitimkanski complex.

pair. The obtained primary age agrees with the age of muscovite from the host rocks greisen ($t_{\text{musc}} = 300 \pm 15$ m.y. by ^{87}Rb - ^{87}Sr method and $t_{\text{musc}} = 312 \pm 15$ m.y. by ^{40}K - ^{40}Ar method) and with ^{87}Rb - ^{87}Sr isochron age of Kidjimitskii massif ($t = 300 \pm 15$ m.y. Kozubova *et al.*, 1977). Such coincidence hardly occurs by chance. One should see that two curves cross the concordia at the different points in its lower part (Fig. 3, points b and b'). The reason for these scattering will be discussed later.

The data obtained on porphyritic granite of Vitimkanski complex in Zabaikalie (Table 2) enabled us to give the third example. It is to be noted that the Vitimkanski complex has been considered to belong to the early Paleozoic (SALOP, 1967). However, the new geological data indicate a middle-late Paleozoic age of the complex (LITVINOVSKII and ZANVILEVICH, 1976; GORDIENKO, 1976).

Application of the graphic method confirms the latter point of view. Both of the curves of bt-feld and bt-pl pairs cross the concordia at the age corresponding to 320 m.y. (Fig. 4). The ^{87}Rb - ^{87}Sr isochron age of Ogarinskii massif will be published by MURINA *et al.* Only one sample (2101) shows the plagioclase age of 335 m.y. Explanation of the singular point is out of the scope of this paper. However, it should be pointed out that the excess radiogenic argon in plagioclases has already been observed (MOROZOVA *et al.*, 1973). One can see in Fig. 4 the discrepancy between ages corresponding to

Table 2. Age data for minerals of the rocks from Vitimkanski complex

The name of massif, sample number		K (wt.%)	$^{40}\text{Ar}_{\text{rad}}$ (10^{-9} g/g)	Age* (m.y.)
Karskii				
500	plagioclase	0.92	20.4	300
	microcline	10.44	217	284
	biotite	7.41	172	314
2011	plagioclase	0.50	11.6	316
	microcline	11.25	241	290
	biotite	7.29	172.5	320
Ogarinskii				
546	plagioclase	0.40	7.8	268
	biotite	6.18	135.9	298
2060a	plagioclase	0.57	10.6	255
	microcline	11.45	154	188
	biotite	5.68	108.2	262
2101	plagioclase	0.49	12.3	337
	microcline	8.71	122.3	196
	biotite	7.43	118	220
Usoiskii				
131a	plagioclase	0.30	5.8	265
	microcline	11.23	162.2	201
	biotite	7.04	142.6	277

* See footnote to Table 1.

Fig. 4. Application of the graphic method for the rocks of Vitimkanski complex.

the lower crossing point for two curves. The geological meaning of these ages depends on the model of argon migration in minerals.

DISCUSSION

The above mentioned approach is phenomenological in character. However, it is in

order to determine analytical shape of the age curve and to understand the physical meaning of "b" in Figs. 3 and 4, necessary to inquire into account certain mechanism of radiogenic argon migration in minerals.

In the following we will discuss the loss of argon from a mineral by assuming that the loss of argon is the first-order rate process (LEVSKY, 1964; MOROZOVA and ASHKINADZE, 1971).

In such a case it is more convenient to study the retentivity of radiogenic argon in minerals by means of the argonographic method (the linear heating under constant rate of temperature rise (MOROZOVA and ASHKINADZE, 1971; ZIMMERMANN, 1970; FRICK *et al.*, 1973). Argonograms* of minerals can be characterized by the following parameters:

- number of maxima for radiogenic argon release rate (energetic position),
- argon population in different lattice site,
- diffusion parameter E (activation energy) and C (frequency factor) values.

The experimental values of activation energy and other special features of the argonograms make it possible to explain the empirical series of mineral stability against radiogenic argon loss and enable us to calculate the argon loss curves through alteration by thermal influence.

A result of model calculation for biotite, microcline and amphibole with the primary age of 300m.y. is presented in Fig. 5, where apparent age is taken as an ordinate instead of argon loss. In this calculation, it is assumed that the residing site of argon in the lattice of amphibole is single and two-fold (see Fig. 7) for biotite and microcline. It is further assumed that the ratio of argon population for both sites of biotite is one and that for microcline is two (more retentive site accommodates twice as much argon as in the other site). The diffusion parameters are taken as follows (MOROZOVA and ASHKINADZE, 1971):

amphibole	: $E = 120\text{KCal/mol}$, $C = 10^{11}\text{sec}^{-1}$
biotite	: $E_1 = 50\text{KCal/mol}$, $C_1 = 10^6\text{sec}^{-1}$: $E_2 = 70\text{KCal/mol}$, $C_2 = 5 \times 10^7\text{sec}^{-1}$
microcline	: $E_1 = 35\text{KCal/mol}$, $C_1 = 3 \times 10^4\text{sec}^{-1}$

Fig. 5. The diagram for estimation of argon losses in minerals at thermal influence, a)-continuous losses, b)-impulse losses.

$$: E_2 = 100\text{KCal/mol}, \\ C_2 = 10^9\text{sec}^{-1}$$

The calculation is made for two cases, a) continuous loss and b) catastrophic loss (LEVSKY, 1964). In the latter case the thermal event has been assumed to occur lately with the duration of 10m.y. against the primary age of 300m.y.

The result of model calculation agrees basically with the observed results on intrusive exocontact of Eldora stock given by HART (1964), and in particular the cross-over of apparent ages for biotite and microcline with the distance from the heat-front was really found. This agreement supports our assumption that major loss of argon from a crystal is attributed to migration by heating.

The diagram represented in Fig. 6 approximates, to a considerable extent, the natural situation. The apparent ages are shown in the diagram *versus* L , the "influence operator" which is a function of time and temperature (for impulse losses: $L \sim \exp[-Ct] (\exp -E/RT [t])$ (LEVSKY, 1964).

According to Fig. 6, the age difference between biotite and microcline (Δt) increases with the rise in thermal influence, reaches the maximum and then decreases to zero (point b). Beyond point b, inversion of apparent ages takes place. The similar situation can be seen for the biotite-amphibole pair. On these bases, we can derive following criteria which are useful for the interpretation of discordant mineral ages.

* The argonogram is the radiogenic argon release rate $\frac{d^{40}\text{Ar}}{dt} = f(T)$ on heating the sample with constant rate of temperature rise.

Fig. 6. The diagram for argon losses in minerals applied to the interpretation of discordance (explanation in the text).

- 1), If there is no difference in mineral ages,
 - a) the measured value corresponds to the time of crystallization (point a, in Fig. 6), the primary age.
 - b) the measured value corresponds to the time of the heaviest thermal event (point c).
- a) and b) can be discriminated in most cases by other geological information.
- 2), If $t_{bt1} > t_{bt2}$ and $\Delta t_1 < \Delta t_2$ (refer to Fig. 6), the thermal effect after the primary crystallization is slight, and the primary age of the rock is almost equal to or slightly higher than t_{bt1} . In such a case t_{amph} should be the same as the primary age.
- 3), If $t_{bt3} > t_{bt4}$ and $\Delta t_3 > \Delta t_4$, the intensity of the thermal event is much more than that of the former case. In this case, t_{amph} should be slightly lower than the primary age.
- 4), If $t_{bt} < t_{feld}$, the thermal effect is most intensive. In this case, t_{amph} should be also significantly lower than the primary age. The time of thermal event may be close to t_{bt} .
- 5), For biotite-microcline (or biotite-plagioclase) pair, the cross-over of apparent ages took place when the thermal effect was intensive. However, point b in the insert of Fig. 6 has no geological meaning.

Let us now examine the analytical data given in Table 1. In all the cases, t_{bt} is higher than t_{feld} , which indicates that the thermal effect exerted to Kidjimitskii complex was moderate. In order to specify the time of primary crystallization, one has to examine the relationship between t_{bt} and Δt . For this purpose, we use the data for samples 2126, 2115a, 525 and 2064 in Table 1. One can see from the data,

Fig. 7. The biotite argonograms obtained on rocks of Kidjimitskii complex.

Δt increases from 2126 to 2115a and further to 2064, whereas t_{bt} decreases in this order. This example exactly corresponds to the case 2) mentioned already. Therefore, the primary age of the complex should be close to t_{bt} of 2126, i.e., 290 m.y. On the other hand, when the data of 525 is taken into account, t_{bt} is very low and t is close to that of 2115a, which indicates that 525 was subjected to more intensive thermal effect than others (case 3).

It is interesting to inspect the argonograms of above four samples shown in Fig. 7. A consecutive decrease in the first peak is observed from 2126 through 2064. The ratios of areas of first and second peaks (S_1/S_2) are 0.78, 0.66 and 0.55 for 2126, 2115a and 2064, respectively. When S_1/S_2 ratios of 2115a and 2064 are normalized to 0.78 and then content of radiogenic argon is corrected for, the readjusted age gives around 290 m.y. for these two samples.

The first peak appearing in the lower temperature side in Fig. 7, corresponds to the site where the rate of loss of argon is more than that of the other site. However, even after the destruction of both sites through an intensive thermal event, partial or complete restoration may be possible for the original two-site structure. The sample 525 may be regarded as an example of such a case (MOROZOVA *et al.* paper will be published).

Let us extend the applicability of the proposed graphic method to the case where the number of rock samples is not enough to cover a wide range of apparent ages of minerals. Suppose that only two samples, 2126 and 2064 are available (refer to Fig. 3). It is still

possible to estimate the range of the primary age of the rock in the following way; the maximum value can be estimated by drawing a straight line connecting dots of the feld-bt ages and the intersect of the line with the concordia gives the maximum age. In this particular case, it is 330 m.y. Since the angle, α between the line and the abscissa is smaller when the thermal event is more intensive, a larger value of maximum age is obtained when the thermal influence is heavier. On the other hand, the minimum age can be estimated by drawing a straight line parallel to the ordinate from the point of 2126, and the cross of this line with the concordia gives the minimum age.

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