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Diffusion of Geochronologically Important Nuclides in Minerals under Hydrothermal Conditions

by ALBRECHT W. HOFMANN¹⁾ and BRUNO J. GILETTI²⁾

ABSTRACT

The isotopic exchange of Rb, Sr, and K between a natural biotite and a hydrothermal solution has been studied at 550°, 650°, and 700°C and 2 kbar. Both equilibrium and kinetics have been investigated. Alteration of mica was always minor (<0.5%) and did not vary appreciably between runs buffered for oxygen fugacity (NNO or QFM) and those sealed in gold tubes with no buffer introduced. The equilibrium value $P_{Rb} = (Rb/K)_{fl}/(Rb/K)_{biot} = 0.82 \pm 0.05$ at these temperatures. Using an ideal infinite cylinder model for solid diffusion the Rb diffusivity in biotite was $D/a^2 = 2.5 \times 10^{-10} \text{ sec}^{-1}$ at 650°C, or $D = 2 \times 10^{-15} \text{ cm}^2 - \text{sec}^{-1}$ if the particle size is taken as the effective grain size. However, this may have to be corrected to a value slightly less than $0.9 \times 10^{-10} \text{ sec}^{-1}$. The diffusivity for K is approximately the same as that for Rb. The appearance of a Sr-rich phase has prevented the accurate determination of a Sr diffusivity, but that for the radiogenic Sr, as well as that for Na are similar to that for Rb within about one order of magnitude.

Introduction

One of the fundamental questions raised in all geochronological studies is whether or not the system has been open. This question has evolved from early searches for concordant systems in order to test the dating methods (e.g., ALDRICH et al., 1958) to deliberate studies of terranes which yield discordant ages. This evolution has advanced our understanding of the relative behavior of nuclides in minerals and rocks under particular natural conditions, such as the cooling of a metamorphic terrane (e.g., JÄGER et al., 1967), or the effect of contact metamorphism on isotope systems (e.g., HART, 1964). In order to relate the mobility of particular isotopes to actual temperature and other intensive parameters, however, it is desirable to have some direct experimental control. The field trip prior to this colloquium and the papers already presented serve to stress the need for experimental data in addition to field analytical results.

Numerous experimental measurements of argon release from minerals in vacuum or air have been carried out (see the summary of FECHTIG and KALBITZER, 1966), but only a few studies have been made on the Rb-Sr system. Among these are some low temperature experiments employing ion exchange on micas (GERLING and OVCHINNIKOVA, 1962; KULP and ENGELS, 1963) and two studies on Rb and Sr mobility under hydrothermal conditions (DEUSER, 1963; MCNUTT, 1964).

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The purpose of the present paper is:

- (1) To outline some of the theoretical background and experimental approach to the measurement of volume diffusion coefficients of nuclides important to Rb-Sr and K-Ar geochronology under hydrothermal conditions.
- (2) To report preliminary results on the diffusion and the equilibrium distribution of the alkalis in biotite-aqueous alkali chloride systems.

Requirements for study

In order to conduct successful measurements on volume diffusion in minerals it is important to keep several theoretical and experimental requirements in mind. Those pertaining to noble gas diffusion in solids have already been reviewed by FECHTIG and KALBITZER (1966) and by HART (1960). The present discussion refers primarily to diffusion of ionic species in solids:

(1) The mineral must be stable for the duration of the experiment with respect to its major element chemistry, its structure, and its geometry. If any of these properties undergoes significant changes during the experiment, kinetic effects other than volume diffusion will be superimposed. In this case the experimental data may not allow separation of volume diffusion effects from those of other processes, especially if the latter are dominant. While this requirement is a fairly obvious one, it has often been neglected, particularly with regard to hydrous minerals such as micas.

(2) In general, diffusion of ionic species in solids is an ion exchange process because electrical neutrality must be maintained. The only exception to this rule is when a change of oxidation state occurs simultaneously with diffusion. A consequence of this rule is that, for example, gain or loss of radiogenic Sr^{87} by a stable solid to either pure water or a vacuum is unlikely.

(3) Interdiffusion of two species by ion exchange is a coupled process where the effective mobility is dependent on the individual ion diffusion coefficient of each species. This may lead to fairly complicated behavior. It can be shown that this effect is negligible in most cases where diffusion of trace elements is concerned (HELFFERICH, 1962). The effect is important, however, when diffusive exchange of major elements (e.g., K-Na) occurs. Thus, it is important to measure the *individual* ion diffusivities.

One idealized experimental technique that satisfies the conditions discussed so far is a hydrothermal experiment in which the bulk chemistry of the hydrothermal solution is in equilibrium with the solid throughout the experiment and where the mobility of individual elements is measured only by isotopic exchange of stable or radioactive tracers. This technique offers the additional advantage of the migration of isotopes in opposite directions, so that the approach to equilibrium "from both sides" can be measured simultaneously. In practice, the exact equilibrium partitioning of the element under study may not be known and may be difficult to measure directly because of slow redistribution. To overcome this difficulty, a method of data evaluation has been developed which yields kinetic and equilibrium data from a single hydrothermal run that has proceeded only a fraction of the way towards isotopic equilibrium. Because of its potential usefulness to other types of experiments the method will be outlined briefly.

CRANK (1956, pp. 55–56) pointed out that the mathematical solutions of the diffusion equation, when given in terms of fractional degree of equilibration, apply both to gain and loss of the element in question. In the isotope exchange process occurring during the experiments in this report, both processes occur simultaneously. (Any isotopic fractionation will be very small and will be neglected.)

The fractional degree of equilibration is the net transport of an isotope into the fluid in the time t of the experiment, divided by the net transport that would occur if the system reached equilibrium. For those cases where diffusion is the only operative process, the following expressions (where Rb is taken as an example) may be written:

Let $^{87}\text{Rb}_{fl}^o$ = number of gram atoms of ^{87}Rb in fluid initially.

Superscripts: o = initial; t = at end of run; e = at equilibrium.

Subscripts: $_{fl}$ = fluid phase; $_{tot}$ = fluid plus solid.

$$\frac{^{87}\text{Rb}_{fl}^t - ^{87}\text{Rb}_{fl}^o}{^{87}\text{Rb}_{fl}^e - ^{87}\text{Rb}_{fl}^o} = \frac{^{85}\text{Rb}_{fl}^t - ^{85}\text{Rb}_{fl}^o}{^{85}\text{Rb}_{fl}^e - ^{85}\text{Rb}_{fl}^o} \quad (1)$$

$$\frac{^{85}\text{Rb}_{fl}^e}{^{87}\text{Rb}_{fl}^e} = \frac{^{85}\text{Rb}_{tot}}{^{87}\text{Rb}_{tot}} \quad (2)$$

Elimination of $^{85}\text{Rb}_{fl}^e$ from these equations yields:

$$^{87}\text{Rb}_{fl}^e = \frac{^{85}\text{Rb}_{fl}^o (^{87}\text{Rb}_{fl}^t - ^{87}\text{Rb}_{fl}^o) + ^{87}\text{Rb}_{fl}^o (^{85}\text{Rb}_{fl}^o - ^{85}\text{Rb}_{fl}^t)}{(^{85}\text{Rb}_{fl}^o - ^{85}\text{Rb}_{fl}^t) + (^{85}\text{Rb}_{tot} / ^{87}\text{Rb}_{tot}) (^{87}\text{Rb}_{fl}^t - ^{87}\text{Rb}_{fl}^o)} \quad (3)$$

Equation (1) is the formal statement that the fractional degree of equilibration will be the same for all isotopes of an element. Equation (2) is the condition of isotopic equilibrium. Equation (3) gives the desired equilibrium amount of one isotope in one phase in terms of quantities that can be measured directly either before or after the run. The complete details of the equilibrium distribution of an element between fluid and solid and the fraction of equilibration attained can be calculated in this way.

(4) The hydrothermal method of isotopic exchange generally requires a finite fluid reservoir. The fractional approach to equilibrium as a function of time follows a path which depends on the ratio α , which is the amount of diffusing species in the fluid reservoir to the amount in the solid at equilibrium. Solutions to this problem may be found in CRANK (1956).

This effect is further complicated if diffusion occurs from energetically different sites in the solid. This means that diffusion from each site follows an individual equilibration versus time path, primarily because of the energetic differences between sites, but also because the effective α value for each site depends on the amount of the diffusing species in that site.

(5) In hydrothermal experiments with natural minerals (especially when they are multicomponent solid solutions such as many micas) it may not be possible to eliminate all processes other than volume diffusion completely. Thus, minor alteration or recrystallization of thin edges may occur, because the physical and chemical conditions under which the mineral was formed cannot be reproduced perfectly. If isotope exchange due to such processes does not dominate over volume diffusion it may be

possible to correct the results to yield the desired diffusion data. The discussion of our experimental results shows one such attempt.

(6) HART (1960) has pointed out that variations in grain size will yield decreasing values of D/a^2 as the duration of the experiment is increased, because the smallest grains equilibrate faster than the larger ones. We add only that large variations in grain shape will have the same effect. Repeated careful sieving may give a sufficiently close approximation to uniformity if the grain size effective for diffusion is identical with the observable grain dimensions.

Methods employed

The systems studied were, in all cases, biotite plus an alkali chloride aqueous solution. They were sealed in gold tubing and subjected to 2000 bars external pressure at temperatures of 550, 650, and 700°C.

Reaction vessels were René 41 metal cold seal bombs with 2.5 cm inside diameter and a usable length of 7.5 cm. Temperature differences were less than 10°C between any points in this volume. The large size permits the concurrent introduction of up to seven charges, thus yielding experiments with identical pressure and temperature histories, but with different values for other parameters.

The biotite is a mica cut from a single large book derived from a pegmatite in the Spruce Pine District of North Carolina. It yields a K-Ar age of 350 m.y. and a Rb-Sr age of 370 m.y. The mica was carefully sized between 200 and 230 mesh (we shall take its mean diameter as 68 microns). Microscopic measurement revealed a range of thickness of from 0.5 to 2 microns (we shall take 1 micron as its mean thickness). Sample purity was approximately 99.9%.

The fluid consisted of water (redistilled in silica glass) with alkali chlorides added to make chloride concentrations of 0.1, 0.5, or 2.0 M. The K and Rb were usually isotopically enriched in masses 41 and 87 respectively. In addition, Sr enriched in Sr^{84} and the radioactive tracers Sr^{85} and Rb^{86} were used in some runs. Starting fluid compositions ranged from 0 to 5 in Na/K with most near 4. The starting Rb/K was usually approximately 0.002. Biotite weights ranged from 40 to 260 mg.

The biotite was found to be stable to temperatures slightly in excess of 700°C. Reaction products were less than 0.5% and appeared to be independent of run duration. The use of nickel-nickel oxide or quartz-fayalite-magnetite as oxygen fugacity buffers did not change this, and so buffering was not used.

Equilibrium determinations

The equilibrium distribution of an element between solid and fluid phases is of importance for two reasons. For the purposes of this study, knowledge of the equilibrium parameters is essential to permit calculation of diffusion constants. Of more general importance, however, is the fact that net transport of an element into or out of a solid phase depends both on the value of the diffusion constant and on the intensive and extensive properties of its surroundings.

In the present study, deviations from the case where only diffusion occurred were observed. Where large fluid/solid ratios were prepared, measurable dissolution of the biotite occurred. (It may be that the process was not dissolution, but the apparent

effect was the same.) It was found that the equations can be modified to take this effect into account, but then the results of at least two charges must be used to obtain a unique solution.

We define:

$$P_{\text{Rb}} = \frac{(\text{Rb/K})_{\text{fluid}}}{(\text{Rb/K})_{\text{biot}}}$$

as the partitioning constant for Rb in this system. The following are the values for P_{Rb} obtained:

T °C	P_{Rb}
550	0.81 ± 0.05
650	0.82 ± 0.05
700	0.83 ± 0.05

Biotite, therefore, records a Rb/K ratio which is very similar to that in a coexisting aqueous fluid. The Rb displays a slight preference for the solid. These results apply only for low Rb/K ratios as no charges contained Rb as a major constituent. The data are in general agreement with those of BESWICK and EUGSTER (1968) who studied the complete solid solution system K-phlogopite–Rb-phlogopite.

Diffusion constant determinations

The advantage gained in the use of isotopically enriched tracers in the fluid phase lies in the possibility of determining both equilibrium and diffusion data from the same charges in a single experiment. Also, this method yields individual ion diffusivities rather than the more complex interdiffusion behavior characteristic for the diffusive exchange of chemically different species. The results for K and Rb will be given. It is useful to consider briefly the diffusion model used.

Two idealized geometries are examined. The first is that for an infinite slab in which diffusion occurs such that net transport is perpendicular to the plane of the slab. This will be called the plate model and will refer to net transport parallel to the mica C-axis. The second geometry is that of an infinite cylinder, in which net diffusional transport occurs radially in all directions perpendicular to the cylinder axis. This will be called the cylindrical model and refers to transport parallel to the mica layers. The following is an example of how the calculated diffusion coefficient will differ when the same experimental data are evaluated in terms of the two models.

Cylindrical Model: $D/a^2 = 3.3 \times 10^{-10} \text{ sec}^{-1}$
 $D = 3.8 \times 10^{-15} \text{ cm}^2\text{-sec}^{-1}$
 where $a = \text{radius} = 0.0034 \text{ cm}$.

Plate Model: $D/l^2 = 13.7 \times 10^{-10} \text{ sec}^{-1}$
 $D = 3.4 \times 10^{-18} \text{ cm}^2\text{-sec}^{-1}$
 where $l = \text{half-thickness} = 0.00005 \text{ cm}$.

It should be added that while there are considerable differences in the diffusion coefficients, the temperature dependence or activation energies will vary only insignificantly. It is assumed that the particle dimensions are the effective dimensions for the solid diffusion.

The results will be reported for the cylindrical model. However, although HART'S (1964) work suggests this geometry, the mica flakes are so thin that further work is needed to permit a clear choice of model. It may be that both transport directions contribute significantly for this radius/thickness ratio.

The calculation of the diffusion constant was made for the case where the amount of the diffusing species in the fluid is finite and changes as a result of diffusion in the solid (for details see CRANK, 1956, pp. 70–73).

Table 1 gives the calculated D/a^2 values based on the assumption that all transport was the result of diffusion. Clearly, all the results do not agree. Figure 1 shows a plot for Rb of the variation of calculated D/a^2 as a function of the fluid/solid weight ratio

Table 1. Apparent D/a^2 values calculated assuming a simple volume diffusion process only.

Temperature °C	Run Duration (in 10^6 secs.)	Weight fluid Weight biotite		D/a^2 (in 10^{-10} sec. ⁻¹)	
				Rb	K
700	1.622	3.18		6.99	
		11.48		24.5	
650	0.396	0.901		12.5	
		14.24		44.1	
	1.804	1.052		4.68	
		1.517		5.01	
		1.715		4.47	
	3.520	1.037		2.51	2.88
		1.470		3.19	3.58
		1.651		3.06	3.48
15.16			14.5	16.72	
550	4.227	0.819		0.639	0.66
		4.84		1.03	
		14.10		3.45	6.86
		1.81		0.53	
	5.84	1.09		0.275*	
		1.74		0.25*	

* These early data were obtained not by isotopic exchange of Rb, but by exchange of biotite Rb for fluid K. They are, thus, somewhat less reliable than the other diffusion data in the table.

for the longest duration runs made at each temperature. The effect suggests that some dissolution of biotite occurs, as already noted in the discussion of the equilibrium calculation. Figure 2 shows the equivalent results for potassium.

The value most closely corresponding to the case where diffusion is the only mechanism will be that where the amount of "dissolution" is least. This is the zero fluid/solid intercept.

The three zero intercepts obtained in Figure 1 are plotted in Figure 3 to give an estimate of this behavior as a function of temperature. This Arrhenius plot is tentative at present despite the excellent linearity obtained. The K data zero intercepts are also plotted in Figure 3. No difference in behavior between K and Rb may be inferred from these results.

The Arrhenius plot is subject to change because, so far, the effect of run duration has been neglected. Figure 4 shows the apparent diffusivities for three runs made at

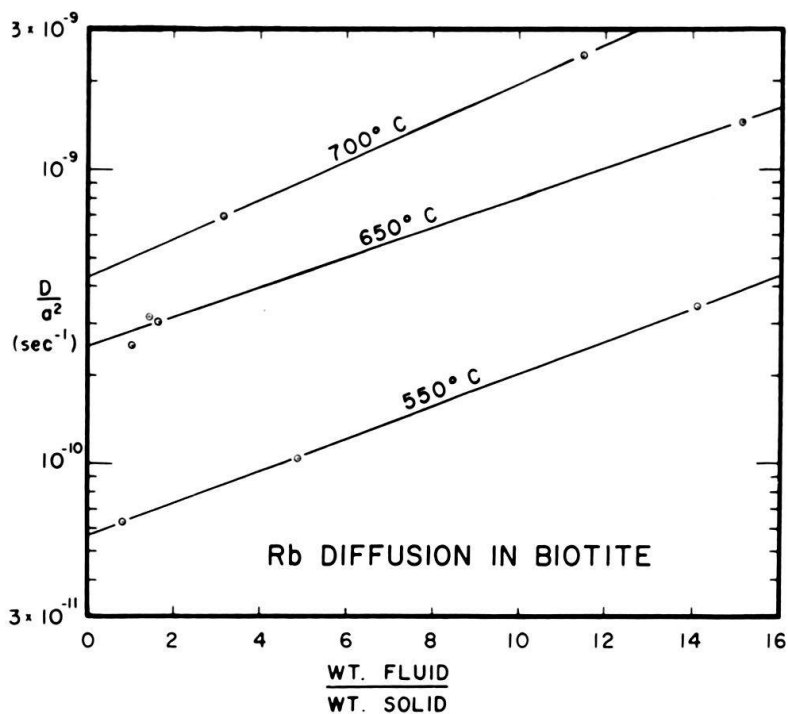


Fig. 1. Dependence of D/a^2 for Rb, calculated for a simple cylindrical diffusion model, on fluid/solid ratio in charge.

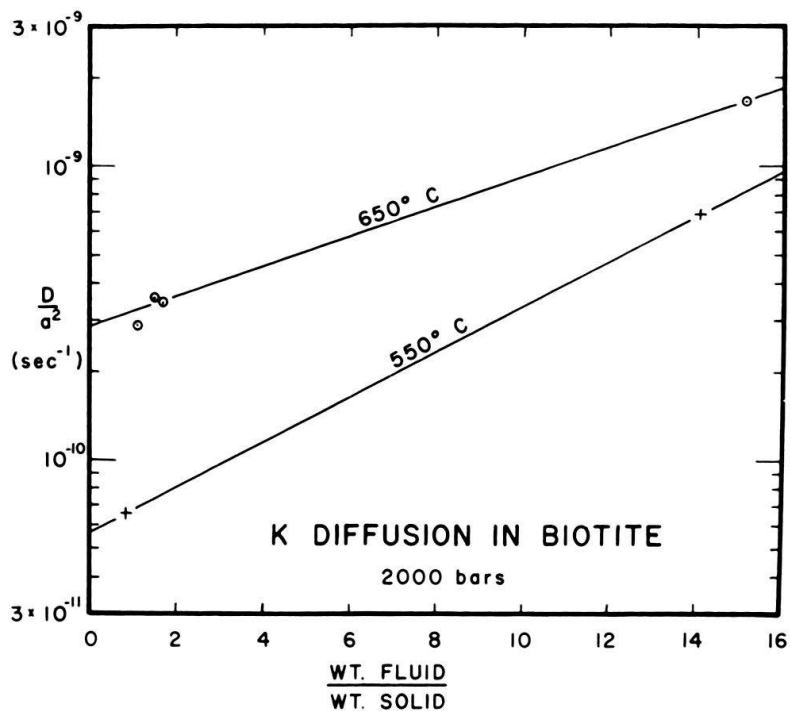


Fig. 2. Dependence of D/a^2 for K, calculated for a simple cylindrical diffusion model, on fluid/solid ratio in charge.

650°C for durations of 5, 21, and 41 days respectively. The data points are shown as a function of fluid/solid ratio. It can be seen from these data and those of Figure 1 that the slopes of the lines are all approximately the same. It was assumed that the data for 21 days followed the same behavior pattern, and the dashed line was drawn with a slope intermediate between the slopes of the other two curves.

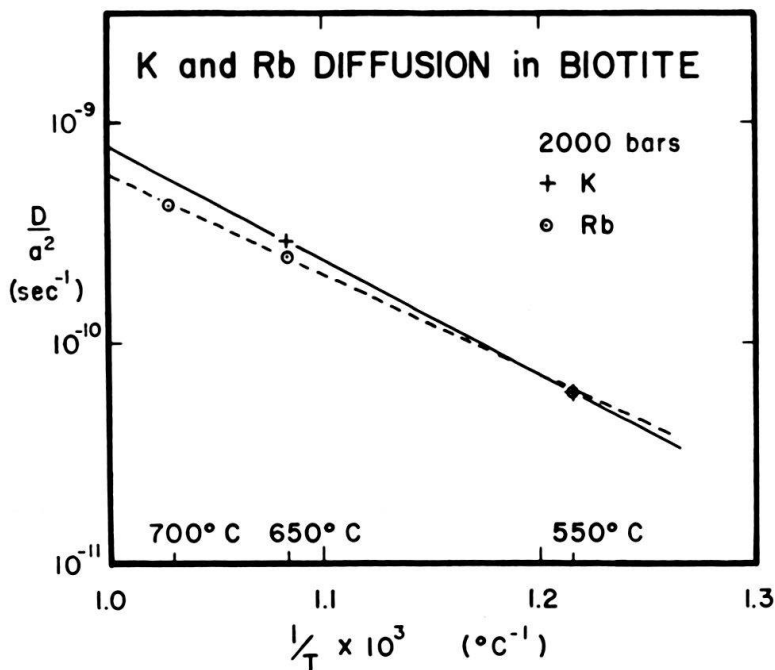


Fig.3. Arrhenius plot of diffusion data using the zero fluid/solid ratio intercepts of Figs. 1 and 2.

If diffusion were the only mechanism operating, and it were by one mechanism, the three curves should be coincident. The fact that they yield apparent diffusion coefficients which increase with decreasing run duration suggests that there is some initial perturbation which produces high apparent diffusion rates. This can be seen if a plot of apparent Dt/a^2 vs. t is made as in Figure 5. (For a discussion of this type of plot see HART, 1960.) The slope of this line is D/a^2 . If only one diffusion mechanism

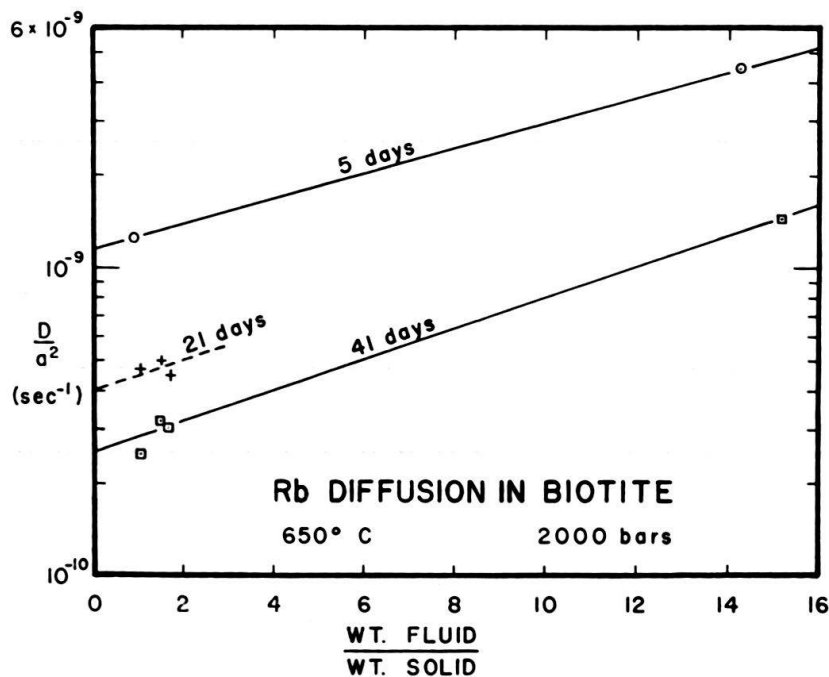


Fig.4. Comparison of D/a^2 values obtained 650°C for runs of different duration, plotted as a function of fluid/solid ratio.

were operating, the line should be straight and should pass through the origin. The plot suggests that there is some marked effect at first. This may be due to volume diffusion from an energetically different site or it may be some process other than volume diffusion. The slope of the line joining the two long duration runs yields a D/a^2 of $0.9 \times 10^{-10} \text{ sec}^{-1}$. This should be compared with the value of $2.5 \times 10^{-10} \text{ sec}^{-1}$ obtained by means of the fluid/solid ratio plot for the longest duration run.

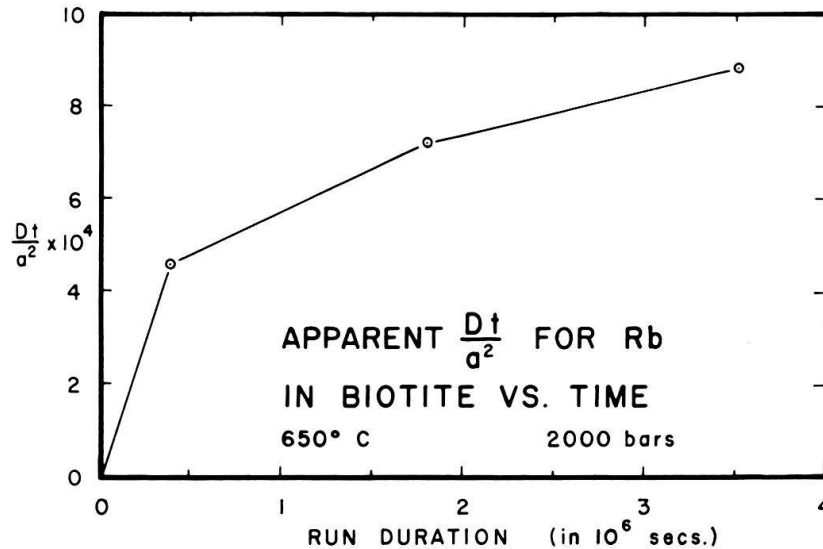


Fig. 5. Apparent Dt/a^2 plotted as a function of run duration, t .

Clearly, the reduction in value for D/a^2 is significant and further work is needed in order to determine the exact diffusivity at 650°C. It is likely that the D/a^2 will be somewhat less than $0.9 \times 10^{-10} \text{ sec}^{-1}$. This result further suggests that all the values plotted on the Arrhenius curve will be lowered. This could have a significant effect on the slope of the curve and the corresponding "activation energy", which in Figure 3 is 21 kcal/gm-atom.

It is important to note that extrapolation to lower temperatures will be essential in order to apply this data to geological settings, particularly to cooling histories. Using a $1/T$ linear plot, however, results in a very long extrapolation. Thus, while the absolute magnitude of the D/a^2 is probably known sufficiently for calculation at the temperatures at which it was measured, the slope of the line is not yet determined and requires further refinement prior to calculation of low temperature behavior.

Early results on the diffusion of Na and radiogenic Sr^{87} suggest that the D/a^2 values will not differ from those of K and Rb by more than one order of magnitude. The Na diffuses faster than K or Rb.

Conclusions

Preliminary results suggest that the P_{Rb} for the biotite water systems in the temperature range 550 to 700°C is 0.8. The diffusion constants are shown to depend on the fluid/solid weight ratio and a correction for this was made. A further correction is needed in order to eliminate an initial, transient effect. When this is done, the value for D/a^2 based on a cylindrical model is somewhat less than $0.9 \times 10^{-10} \text{ sec}^{-1}$.

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