RADIOGENIC ARGON DIFFUSION STUDIES ON TWO HAWAIIAN BASALTS

A Senior Honors Thesis

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by

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To Dr. B, whose patient guidance made it possible

TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES

LIST OF FIGURES

I. Introduction

A. Potassium-Argon Dating Method

The potassium-argon dating technique is based on the fact that one of the three isotopes of potassium, K-40, naturally decays to Ca-40 by β-emission and to Ar-40 by electron capture. Because the rate of decay is known, the time elapsed since the formation of a rock or mineral can be found by knowing the quantities of the parent and the daughter it contains.

This dating technique is successful because potassium is found in nearly all rocks, either as an essential constituent of the rock minerals or as a substituent or replacement atom in the lattice structure. Actually, the decay scheme to Ca-40 is not used for the age calculation because there is no convenient way to distinguish the radiogenically produced Ca-40 from the very common natural Ca-40. On the other hand, the radiogenic Ar-40 (hereafter referred to as Ar-40*) can be distinguished from the Ar-40 present in the air, as explained below.

With a knowledge of the rate of decay of K-40 to Ar-40 and Ca-40 and knowing the amounts of K-40 and Ar-40* in a sample, the following equation can be used to determine the time elapsed since the formation of a rock or mineral[1]:

$$t = \frac{1}{\lambda_\gamma + \lambda_\beta} \ln\left[1 + \frac{\text{Ar-40}}{\text{K-40}}\left(\frac{1+R}{R}\right)\right]$$

where t is the age of the mineral, λ_γ and λ_β are decay constants for electron capture and β-decay, respectively, and R is $\lambda_\gamma/\lambda_\beta$, the branching ratio.

1. Introduction

A. Potassium-Argon Dating Method

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This dating technique is successful because potassium is found in nearly all rocks, either as an essential constituent of the rock minerals or as a substituent or replacement atom in the lattice structure. Normally, the decay scheme to Ca^{-40} is not used for the age calculation because there is no convenient way to distinguish the radiogenically produced Ca^{-40} from the very common natural Ca^{-40}. On the other hand, the rare isotope Ar^{-40} (presently referred to as Ar^{*40}) can be distinguished from the Ar^{-40} present in the air, as explained below.

With a knowledge of the rate of decay of K^{-40} to A^{-40} and Ca^{-40} and knowing the amounts of K^{-40} and A^{*40} in a sample, the following equation can be used to determine the time elapsed since the formation of a rock or mineral[1]:

$$t = \frac{1}{\lambda_e + \lambda_\beta} \ln\left[1 + \frac{\lambda_e + \lambda_\beta}{\lambda_e} \left(\frac{A^{*40}}{K^{-40}}\right)\right]$$

where t is the age of the mineral, λ_e and λ_β are decay constants for electron capture and β^--decay, respectively, and $\lambda = \lambda_e + \lambda_\beta$ is the branching ratio.

B. Background of Problem

From the age equation given above, rocks from the Precambrian period, as old as 2000 million years (my), have been dated(1). These rocks contain large amounts of radiogenic argon as compared with relatively young rocks, for example, those of the Hawaiian Islands. The latter date from those newly formed (Kilauea is currently erupting) to 20 my old.

Using the age equation, the approximate amount of Ar-40* contained in a sample of a Hawaiian rock with a potassium concentration of 2% and an age of 10 my, was calculated to be 10^{-7} cc/gm(2). This quantity is very small but not inordinately difficult to measure with the mass spectrometric techniques now available.

The problem arises from the fact that air contains 0.934 mole percent argon with the relative isotopic abundances of 0.337 mole percent of Ar-36, 0.063 mole percent of Ar-38 and 99.600 mole percent of Ar-40(3). It must be remembered that all substances exposed to the atmosphere adsorb air on their surfaces and in any cracks or imperfections on these surfaces. Rocks are no exception. Thus, when the rocks are heated both the radiogenic argon and the contaminating air argon are released and the Ar-40 measured is made up of both, the two parts being, of course, indistinguishable. However, knowing the ratios of the argon isotopes in air and given the fact that Ar-36 and Ar-38 occur only in the air argon, it is possible to correct for the contamination. The amount of Ar-36 which the sample contains is measured and multiplied by a factor of 296, the ratio of Ar-40 to Ar-36 in air. This means that any error in measuring the amount of Ar-36 is multiplied about 300

times.

By using the equation[4]:

$$E = \frac{ef}{100 - f}$$

where E equals percentage error in the quantity of Ar-40* due to error in Ar-36/Ar-40, e equals percentage error in Ar-36/Ar-40, and f equals percentage atmospheric argon in the sample, Funkhouser[4] has shown that with 95% air argon contamination of a young rock with very little radiogenic Ar-40, a 57% error could result in the determination of the radiogenic Ar-40. Air contamination in Hawaiian rocks is commonly in the range of 70 to 90%[4,5,6].

Much effort has been exerted to discover methods which might decrease the air contamination. Extensive diffusion studies have been undertaken by Amirkhanov[7], Evernden[8], Fechtig[9] and others. These workers suggest preheating the sample at about 150°C to drive off as much air argon as possible without loss of a significant amount of radiogenic argon. This procedure is not entirely satisfactory because even when it was followed, the air contamination of Hawaiian rocks was still found to be from 70 to 90% by workers at the University of Hawaii[4,5].

A technique has been suggested by Naughton[10] which might be a useful method for more accurate Ar-40* determinations. Naughton proposed irradiating a silicate glass to produce a known quantity of Ar-39 (an isotope not found in air) and then mixing this glass with the sample to be dated. A rigorous preheating could then be used to drive off as much air argon as possible even to the extent of losing some radiogenic argon. The amount of

radiogenic argon lost could be found from the amount of Ar-39 lost by standard isotopic dilution equations. The basic assumption made in this method is that the rate of diffusion of argon from the silicate glass is similar to that of the natural rock.

An object of this research was to determine whether this assumption is reasonably valid. No diffusion measurements had yet been made on Hawaiian basalts so it was not known whether or not the diffusion rates of the Hawaiian samples are similar to those of the artificial glasses. The diffusion parameters for the artificial, irradiated silicate rocks have been previously determined(2). The two natural (Hawaiian) samples used in this study are discussed below.

C. Diffusion Processes

Diffusion is an irreversible process by which differences in concentration are smoothed out by a flow of particles toward the area of low concentration. The basic description of the diffusion phenomenon is given by Fick's law:

$$J = -D\, dc/dx$$

where J is the flow, or diffusion current, D the diffusion coefficient and dc/dx, the concentration gradient. This relation is dependent on temperature and on the structure of the substance being studied.

By making certain assumptions, the Fick's law equation can be solved for certain physical situations. Let the structure of the substance be a sphere and the amount of argon at time zero be homogeneously distributed. Also, let the concentration of argon

outside the sphere equal zero. This condition can be met experimentally by adsorbing the gases released during a diffusion run on charcoal in a glass finger around which liquid nitrogen had been placed. Then the exact solution of the equation for this system is(1,11):

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 Bt)$$

where F is the fraction of argon lost, B is equal to $\pi^2 D/a^2$, t is time, D, the diffusion coefficient, and a the radius of the sphere.

The solution above is for high losses. A more practical (approximate) solution for low losses was found by Reichenburg(12). For values of F up to 0.85, the solution becomes,

$$F = \frac{6}{\pi^{3/2}} (Bt)^{\frac{1}{2}} - \frac{3}{\pi^2} (Bt)$$

or

$$Bt = 2\pi - \frac{\pi^2 F}{3} - 2\pi (1 - \pi/3\ F)^{\frac{1}{2}}$$

$$= 6.28318 - 3.2899F - 6.28318\ (1 - 1.0470F)^{\frac{1}{2}}$$

Some complications result when a natural sample is considered. First, the shapes of naturally occurring crystals are usually only approximately spheres(1). Second, when the sample is heated at different temperatures, the simple profile is disturbed, as shown by Carslaw and Jaeger(11). Third, natural samples contain a variety of grain sizes. The grain size of a sample is usually not the sieve size and therefore if small grains, which rapidly lose their gas content, comprise a significant amount of the sample, the diffusion constants calculated would be too low(1,13).

In this study, the above were not considered to be of great significance since only relative quantities were desired. That is, the information sought was the apparent radiogenic argon loss of a typical Hawaiian rock, as compared with that of artificial silicate glasses. In addition, the grain sizes of the minerals in many Hawaiian rocks are similar. It was, however, considered important to attempt to run the diffusion analyses in a manner similar to that used for the diffusion studies of the silicate glasses[2]. The same method of heating the samples for set periods of time at known temperatures was used and the results of this study are compared with those obtained, with the hope that the data would be applicable to future work in geochronology.

II. Experimental

A. Description of Samples

The first sample used in this study was labeled HK 121 and is a hornblende-biotite rhyodacite from a quarry at the southwest end of Mauna Kuwale ridge, Waianae Range, Oahu. It is a massive, dark gray rock containing oligoclase phenocrysts and crystals of biotite, basaltic hornblende and magnetite in a fine-grained groundmass[4]. A detailed petrographic description has been published[14,16] and a chemical analysis is reported by the Geological Survey of the United States Department of the Interior[15]. Funkhouser[4] has done much work on HK 121 and shows photographs of fluid and multiple-phase inclusions contained in the rock.

Stearns and Vaksvik[21] believed that this rhyodacite represented the remains of the summit of an ancient volcano. McDougall[6] found support for this idea when his K-Ar dating experiments resulted in an age of 8.36 my for the rock while other rocks from the surrounding area were found to be only 2.7-3.4 my old. However, Funkhouser, after K-Ar dating of the whole rock as well as its mineral fractions, concluded that the rock is 2.3 my old and therefore contemporaneous with the rocks of the upper Waianae series, or the post-caldera flows of the Waianae range. He contended that the older age found by McDougall resulted from excess argon contained in the mineral inclusions.

This rock was selected because much work had been done on it and the total Ar-40* content was known.

The Palolo sample (HIGS-4), a coarse grained basalt, is

from the contact area of an intrusive body on the east face of the Palolo Quarry (Oahu) wall. A more detailed petrographic description has been published[14], as has a chemical analysis[15]. As far as is known, no attempt to apply K-Ar dating techniques to this material has been made. This rock was selected because it is fresh and is composed of large crystals representative of the usual minerals found in Hawaiian rocks. It was believed that diffusion in these minerals would be well-defined and easily measured.

Both samples were ground to 40-60 mesh and about one-half gram was used for diffusion studies and for melting the sample in order to determine the total Ar-40* content.

B. Instrumentation

The instrumentation used in the experiments described here consisted essentially of two parts. A small all-glass, bakeable vacuum system and an all-glass mass spectrometer. Both of these have been used by many investigators and a large number of references to them may be found in the literature[1,4,5,18,19]. For this reason, a detailed description is not given but the sections are described briefly for the benefit of those completely unfamiliar with this type of equipment. A schematic diagram of the system is included as Figure 1.

The vacuum system was constructed of Pyrex tubing supported with small stainless steel clamps attached to a network of $\frac{1}{2}$ inch stainless steel rod. This grid was supported on an insulating top of Maranite (Johns Mansville & Co.). Beneath this top were

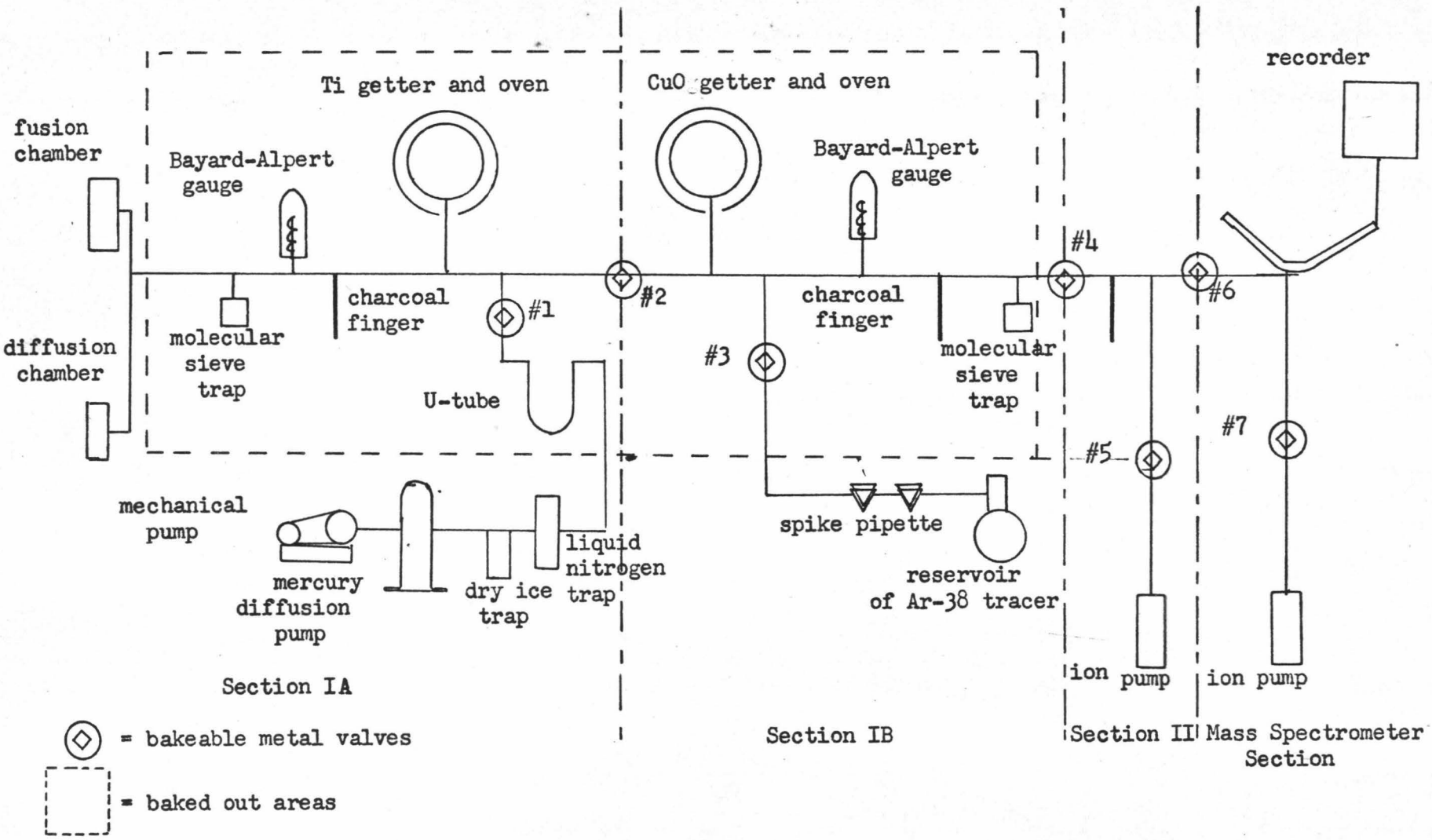


FIGURE 1 Diagram of Gas Extraction, Purification and Analysis System

a roughing pump, a mercury diffusion pump and suitable cold traps. The Ar-38 tracer addition system, similar to that described by Dalrymple[22] was also located below the table top.

Attached to the upper system were vacuum gauges, charcoal traps to transport the gases within the system, Ti and CuO getters for chemical purification of the gases, and molecular sieve zeolite (5A°) traps for selective adsorption of extraneous gases. All-metal, bakeable, high vacuum valves (Granville-Phillips Co., Type C) were used to isolate various sections. This part of the upper section could be baked out at temperatures of up to 480°C.

The quartz chamber for diffusion studies and the quartz, water-jacketed fusion chambers for melting the samples were also located above the top. As explained in II.C., this section was baked out separately from the upper section described above.

The mass spectrometer used was a 4.5 inch radius, single sector, 60° magnetic deflection instrument commonly referred to as a "Reynolds-type." The entire instrument with the exception of the source and collector parts is constructed of glass with the inner surfaces of the flight tube coated with tin oxide for electrical conduction. Good detailed descriptions of this type of instrument have been published[1,17].

In this particular instrument, the various voltages were held constant and the magnetic field varied to bring to focus on the collector slit, the ion beam of the various isotopic masses. The operating parameters used were the same as those used by Noble[5]:

High voltage	2 kilovolts

Trap current	26 microamps
Filament current	3.9 amps
Case voltage	48 volts
Case current	1.0 milliamps
Trap voltage	147 volts

C. Gas Extraction, Purification and Analysis

The procedure used maybe summarized as follows:

1. Prepared samples were placed into the quartz reaction chambers

2. Adsorbed atmospheric gases in the extraction and purification system were removed by baking out overnight under vacuum, after the reaction chambers had been attached.

3. A known amount of Ar-38 tracer was introduced into the extraction system.

4. The sample was heated for a pre-determined time and temperature for diffusion, or melted by induction heating to determine the total radiogenic Ar-40 content.

5. Released gases were purified by gettering.

6. Extracted and purified gases were analyzed mass spectrometrically.

In detail, the procedure is as follows.

For diffusion studies, the ground and weighed sample was put into the quartz diffusion chamber. For fusion work the ground and weighed samples were wrapped in aluminum foil and put into the sidearms of the reaction chambers. The chambers were glassblown onto the system and a mechanical pump was used to create a partial vacuum in order to check for leaks with a Tesla coil. If no leaks were apparent, Sections IA and IB (see Figure 1) were baked out

overnight at about 400°C. After degassing the molybdenum crucibles in the fusion chambers with low-level induction heating, the entire chamber was enclosed in an oven and heated to 200-330°C. The samples in the sidearm and in the diffusion chamber were heated only to 150°C, to minimize Ar-40* loss. The Ti getter was degassed at about 840°C. Bakeout was continued for 12-16 hours. During the last hour of bakeout, the exposed sections of tubing were degassed with a softflame from a gas torch. After the ovens had cooled and been removed, the pressure was checked. Usually after bakeout, the pressure was about 4×10^{-7} torr.

Before a run, liquid nitrogen was placed on the U-tube in IA, while the Ar-38 tracer pipette was opened to the pump for 5 minutes to make certain it was clean. Then the Bayard-Alpert gauge in IB was degassed and if the pressure in the system was below 3×10^{-6} torr, valve 2 was closed for 10-15 minutes. If the pressure remained low, without substantial rise, which was an indication that the system was leak-free, a known amount of Ar-38 was introduced from the pipette. After allowing one hour to draw the spike onto the charcoal finger in IB with liquid nitrogen, valve 3 was closed and warm water (approximately 60°C) was placed around the finger.

For diffusion studies, the next step was to place a nichrome resistance wire furnace around the quartz chamber along with a chromel-alumel thermocouple for temperature measurements. Pyrex glass wool was used to cover the open ends of the furnace to prevent excessive heat loss. Air guns were used to blow cool air across the top of the diffusion furnace to prevent the quartz-to-pyrex seal from

overheating and collapsing. While the sample in the diffusion chamber was being heated, liquid nitrogen was placed on the charcoal finger in IA and allowed to remain on for 20 minutes after the heating period was completed in order to catch any gas released while the sample was cooling.

The heating schedule used for the diffusion studies was similar to that used by Barnes[2]. The sample was heated for three one-hour, a two-hour and a five- to six-hour periods at 400°, 600°, 700°, and 800°C. The total time that a sample was heated at a given temperature was about 11 hours. Modifications to the schedule were made when necessary.

For fusion of a sample, a small iron bar was manipulated by a magnet to cause the foil-wrapped sample to fall into the molybdenum crucible. Then an induction coil was placed around the quartz chamber. Air was passed through the jacket of the chamber to prevent the quartz walls from overheating and air guns were used to blow cool air on the induction coils. Induction heating was continued for about six minutes at the temperature needed to melt the sample. Liquid nitrogen was placed on the charcoal finger in IA during the heating to prevent excessive buildup of gases which cause glow discharges during the heating.

After diffusion or fusion heating was completed, valve 1 was closed and the charcoal finger in IA was warmed to release the adsorbed gases. Then the Ti getter was heated for one hour at its operating temperature, 800°C. Titanium getters H_2 at 400°C and below, so valve 1 was kept closed to protect the CuO getter in IB while the Ti getter was on[4,5]. After the Ti getter had

cooled to below 350°C, valve 1 was opened to expose the gases to the CuO getter. About 20 minutes later, the pressure of the gas sample was rapidly checked (in about 5 seconds) with the Bayard-Alpert gauge in IB. If the gauge were kept on longer, it would act as a pump and discriminately remove argon isotopes[2,5]. If the pressure was below 2×10^{-5} torr, the sample was drawn into II with liquid nitrogen on the charcoal finger in II. During the half hour allowed for this, the gaussmeter was calibrated by referencing it to mass 28 ($CO + N_2$), which was always present in the mass spectrometer, and the instrumental background in the region of interest was run.

When the half hour had elapsed, valve 4 was closed, the finger in II was warmed for five minutes, then valve 7 was closed and valve 6 opened for four minutes to introduce the sample into the mass spectrometer. After valve 6 had been closed for one minute to equilibrate the system, the mass spectrometric analysis was begun.

The accelerating voltage was turned on and the peaks for Ar-40, Ar-38, and Ar-36 were found and monitered for one-half to one minute intervals. Two peaks for each isotope were used to extrapolate back to zero-time in order to compensate for the "memory effect" of the instrument, which either caused the peak height to decrease or increase with time.

The time involved for the above procedure, not including the bakeout, is approximately as follows:

Physical preparation of sample	1 hour
Addition of Ar-38 tracer	1

Argon extraction	1 - 7
Gas purification	4
Gas analysis by mass spectrometer	1
Computation	1
	9 - 15 hours

The time schedule given above is for a single time interval at one temperature. Such a schedule was repeated about 20 times each for both samples. Suggestions for reduction of this time are given below.

III. Results and Discussion

As described in the introduction and experimental sections, the sample was heated at pre-determined time intervals and temperature settings. After each run, the amount of Ar-40* lost was calculated from the chart printed out by the recorder of the mass spectrometer. To find F, the sum of the Ar-40* lost during the current run and the amount lost during previous runs was divided by the total amount of Ar-40* present in the sample. The total Ar-40* content in HK 121 was found to be 2.667×10^{-7} cc/gm by Funkhouser[4]. Because no previous work had been done on the Palolo rock, a sample was melted and the total Ar-40* content was found to be 1.022×10^{-7} cc/gm.

From the approximation[12]:

$$Bt = 6.28318 - 3.2899F - 6.28318\ (1 - 1.0470F)^{\frac{1}{2}}$$

the quantity Bt was found. A short computer program was written for this calculation. Tables 1 and 2 summarize the results of the experiments.

From the data in Tables 1 and 2, plots of F vs. t (time) were made. (See Figures 2 and 3) The plots for both HK 121 and Palolo show that there was a rapid loss of Ar-40* during the first three hours of heating at each temperature, after which the amount lost with time increased at a much slower rate. This rapid loss during the first few hours of heating is believed to be non-volume diffusion from at or near the surfaces, surface irregularities, grain boundaires, or structural defects. A rapid initial loss is apparent at each temperature increment probably because a rapid depletion of near surface gas takes place at the new, higher

Table 1

Data for Ar-40* Released from HK 121

Temperature (°C)	Time (hours)	Ar-40* Released (10-7 cc)	Cumulative Ar-40* Released (10-7 cc)	F, Fraction Released (10^{-2})	Bt (10^{-3})
400	1	*0.023	0.023	1.60	0.210
	2	0.0256	0.0486	3.37	0.975
	3	0.0277	0.0763	5.29	2.44
	5	0.0257	0.102	7.07	4.43
	11	0.0925	0.194	13.5	16.8
600	1	0.0649	0.259	18.0	30.7
	2	0.0258	0.285	19.8	37.6
	3	0.0661	0.351	24.4	58.7
	5	0.0390	0.390	27.1	73.8
	11	0.0657	0.456	31.6	104
700	1	0.0538	0.510	35.4	134
	2	0.0269	0.537	37.2	150
	3	0.0367	0.573	39.8	175
	5	*0.39	0.612	42.5	204
	10	0.0612	0.674	46.7	255
800	1	0.0231	0.697	48.3	277
	2	0.0264	0.723	50.2	303
	3	0.0788	0.802	55.6	393
	5	0.0396	0.842	58.4	445
	11	0.0808	0.922	64.0	568

Samples marked with asterisks were probably contaminated because the amount of Ar-40 released was measured to be larger than the total Ar-40* content of the sample itself. Therefore, the amounts in the table were estimated from the samples taken at similar time intervals so that the cumulative amount of Ar-40* lost would be closer to the actual amount lost.

Table 2

Data for Ar-40* Released from Palolo

Temperature (°C)	Time (hours)	Ar-40* Released (10^{-7} cc)	Cumulative Ar-40* Released (10^{-7} cc)	F, Fraction Released (10^{-2})	Bt (10^{-3})
400	1	0.0182	0.0182	2.08	0.361
	2	0.0359	0.0541	6.18	3.35
	3	0.0400	0.0941	10.7	10.5
	5	0.0175	0.112	12.7	14.9
	10	0.0133	0.125	14.3	18.9
600	1	0.0521	0.177	20.2	39.3
	2	0.0266	0.204	23.2	53.1
	3	0.0398	0.243	27.8	78.2
	5	0.0114	0.255	29.1	86.5
	10	0.0000	0.255	29.1	86.5
800	1	0.0379	0.293	33.4	118
	2	0.0377	0.330	37.7	155
	3	0.0385	0.369	42.1	200
	7	0.0376	0.406	46.4	252

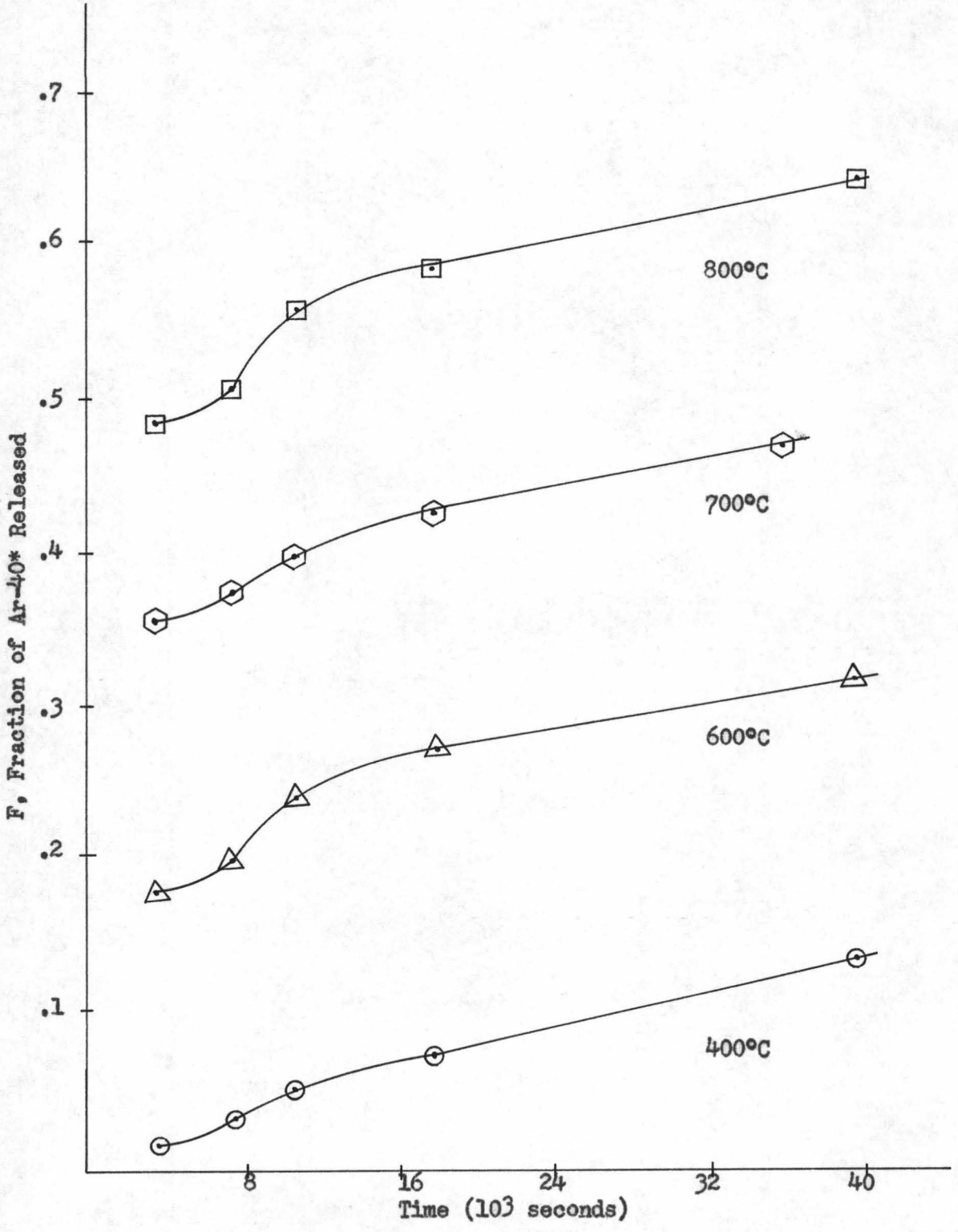


FIGURE 2 - Plot of Fraction Released vs Time for HK 121 at 400°, 600°, 700° and 800°C

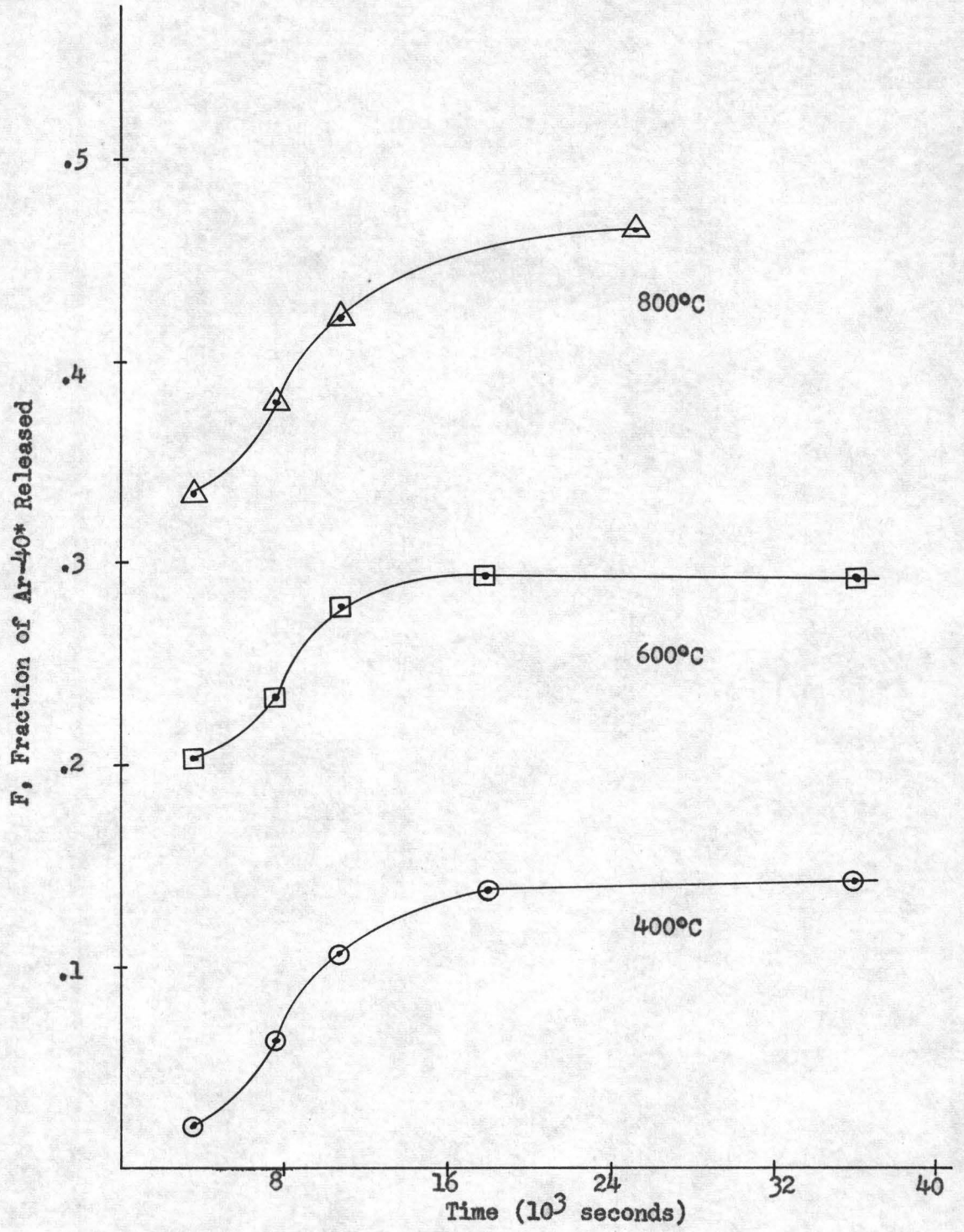


FIGURE 3 - Plot of Fraction Released vs Time for Palolo at 400°, 600° and 800°C

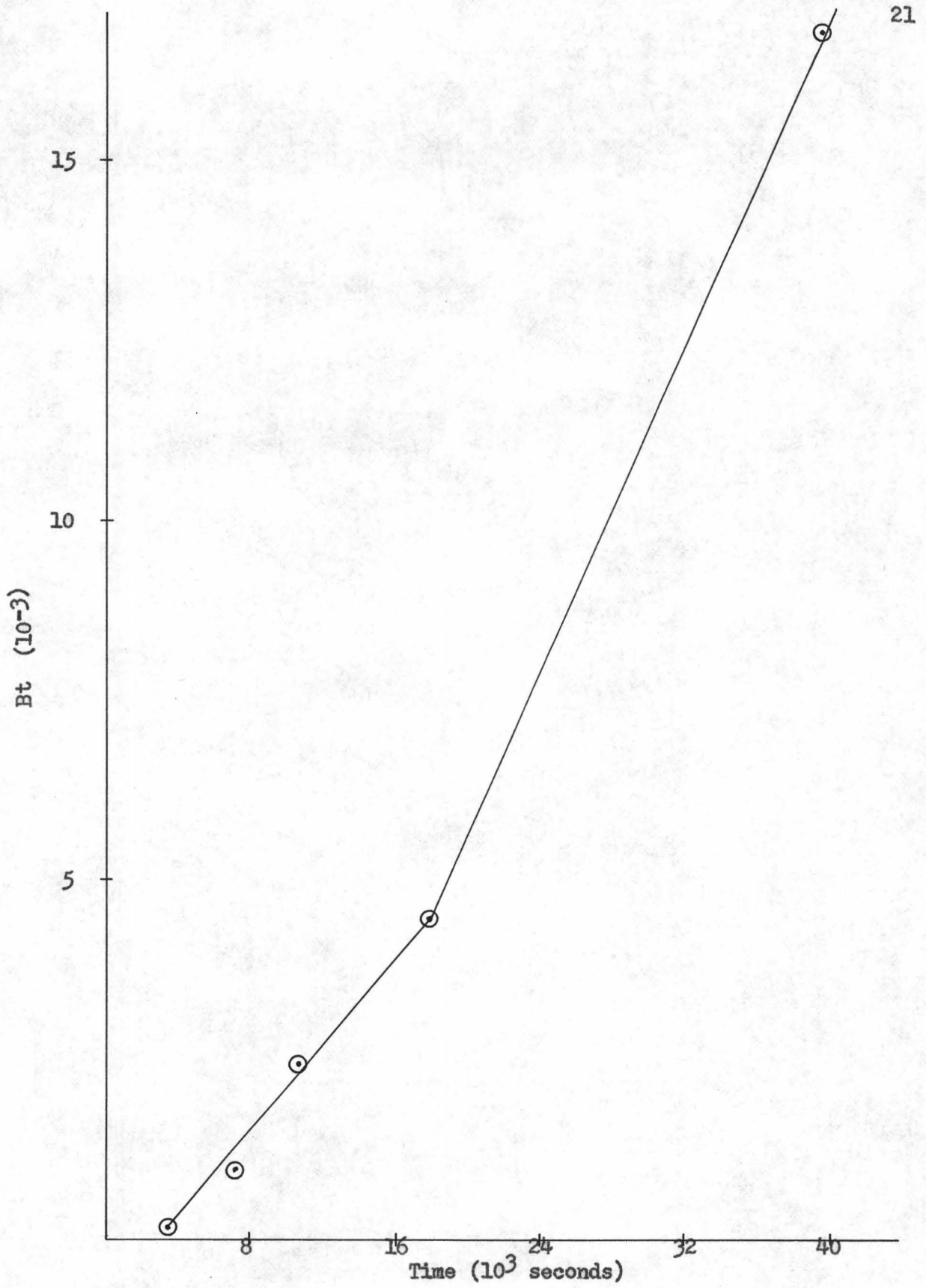
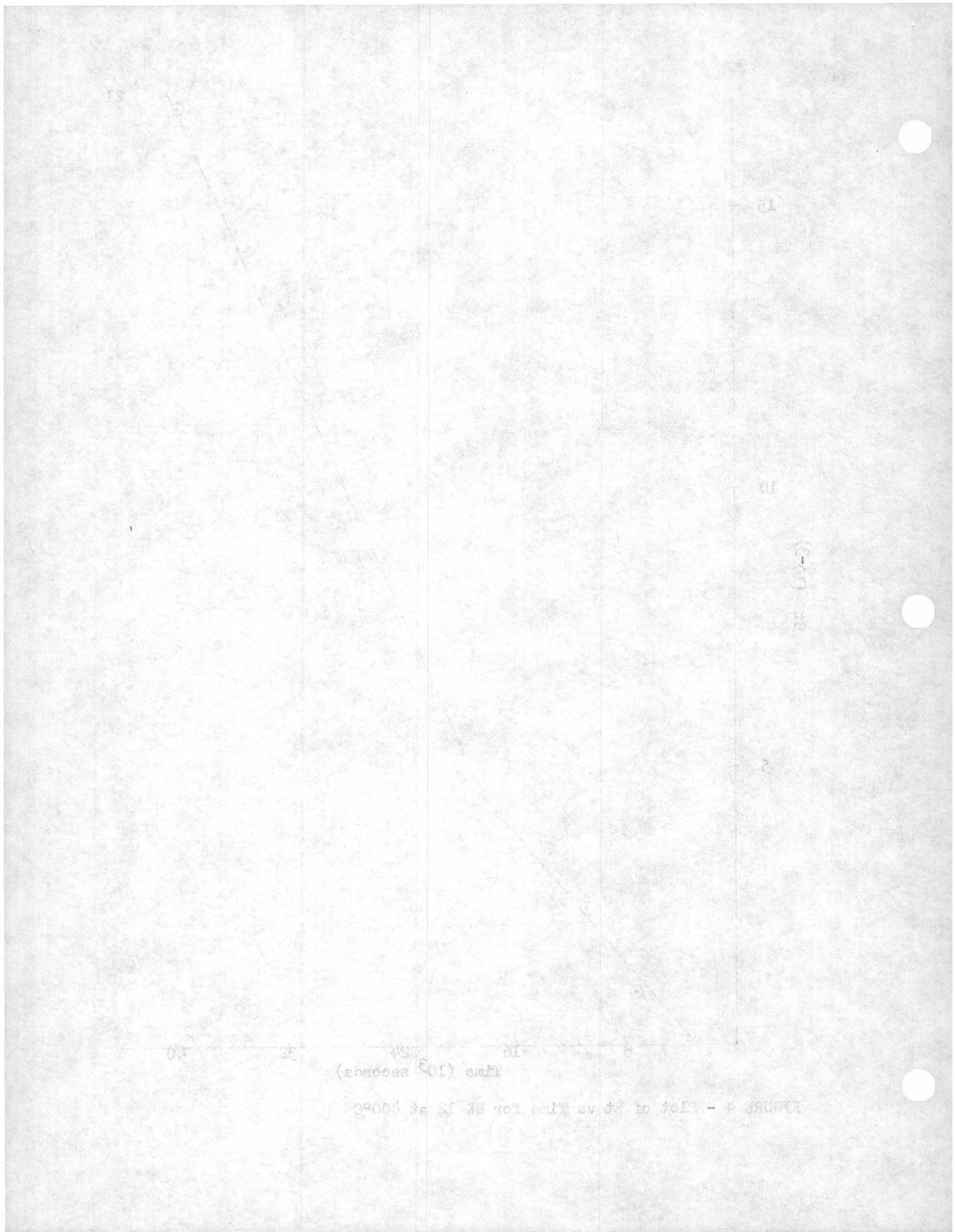


FIGURE 4 - Plot of Bt vs Time for HK 12 at 400°C



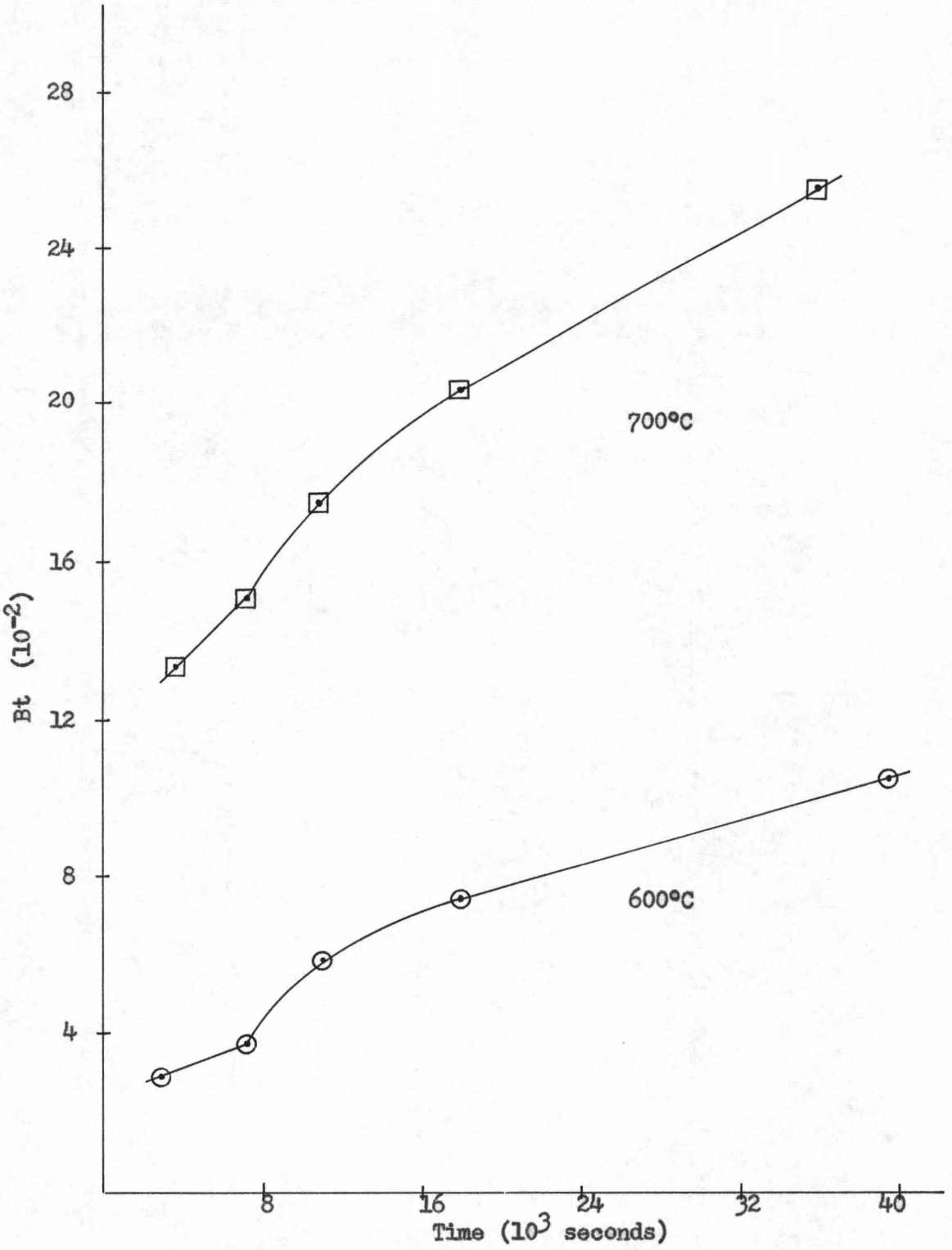


FIGURE 5 - Plot of Bt vs Time for HK 121 at 600° and 700°C

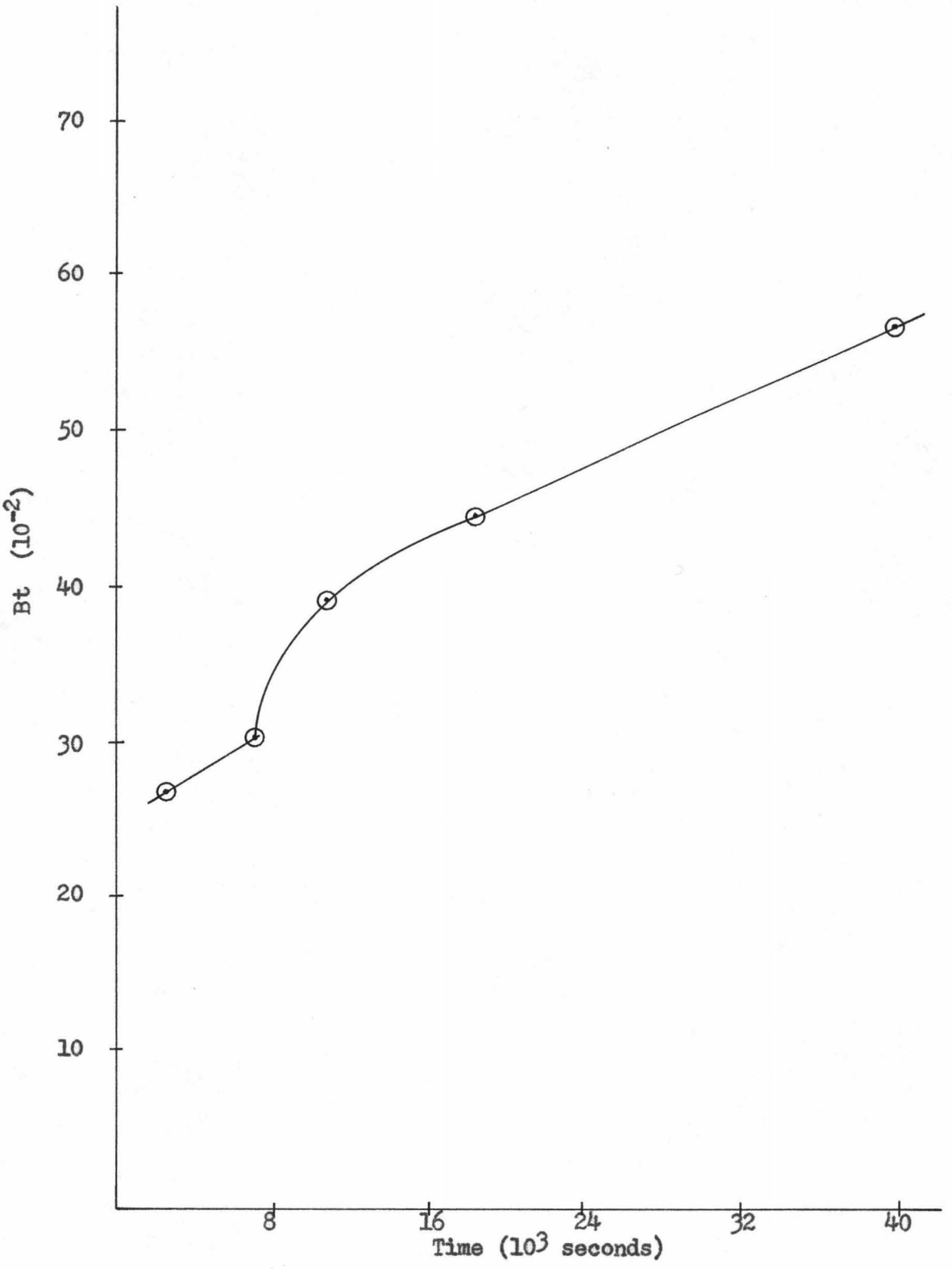


FIGURE 6 - Plot of Bt vs Time for HK 121 at 800°C

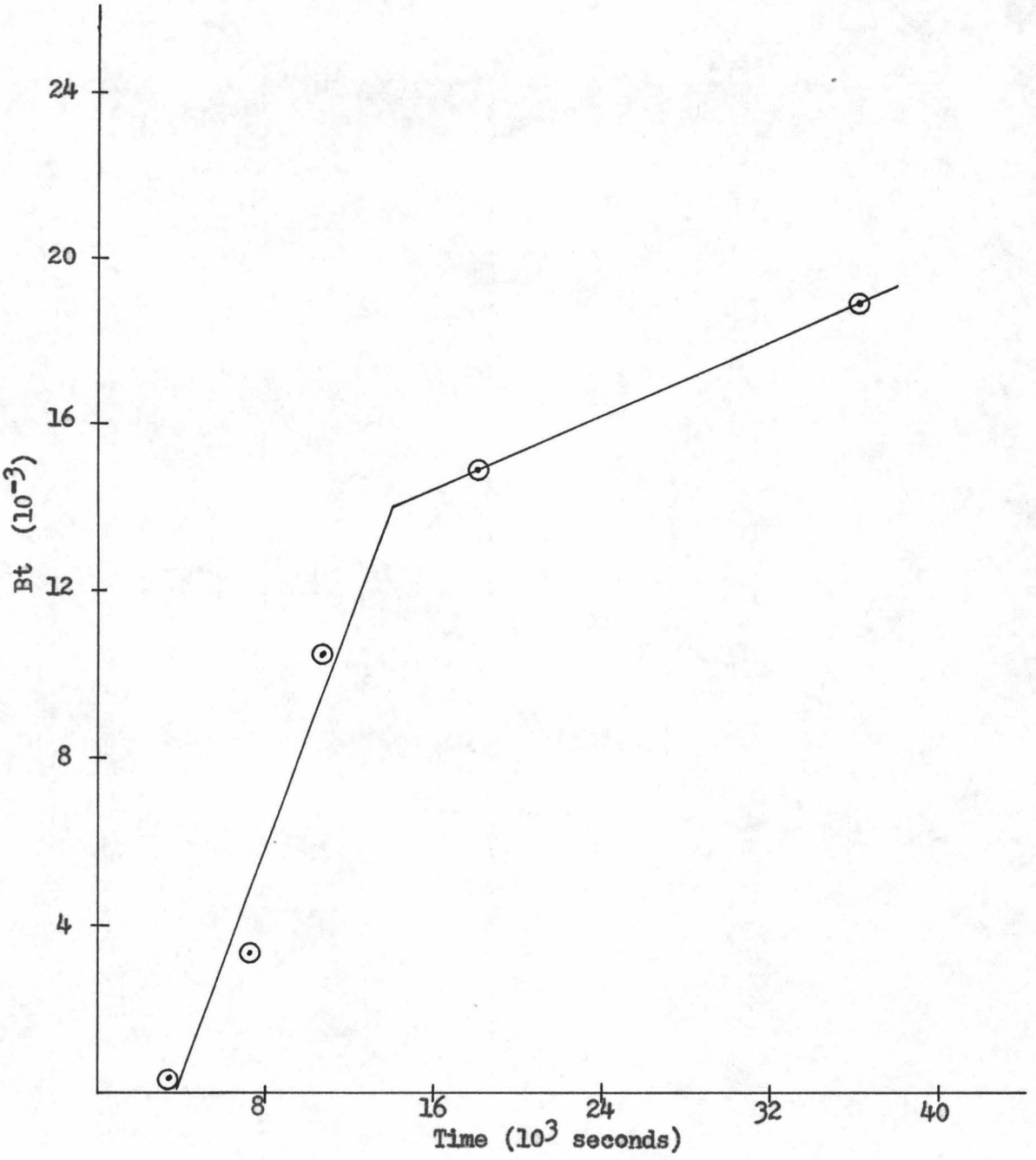


FIGURE 7 - Plot of Bt vs Time for Palolo at 400°C

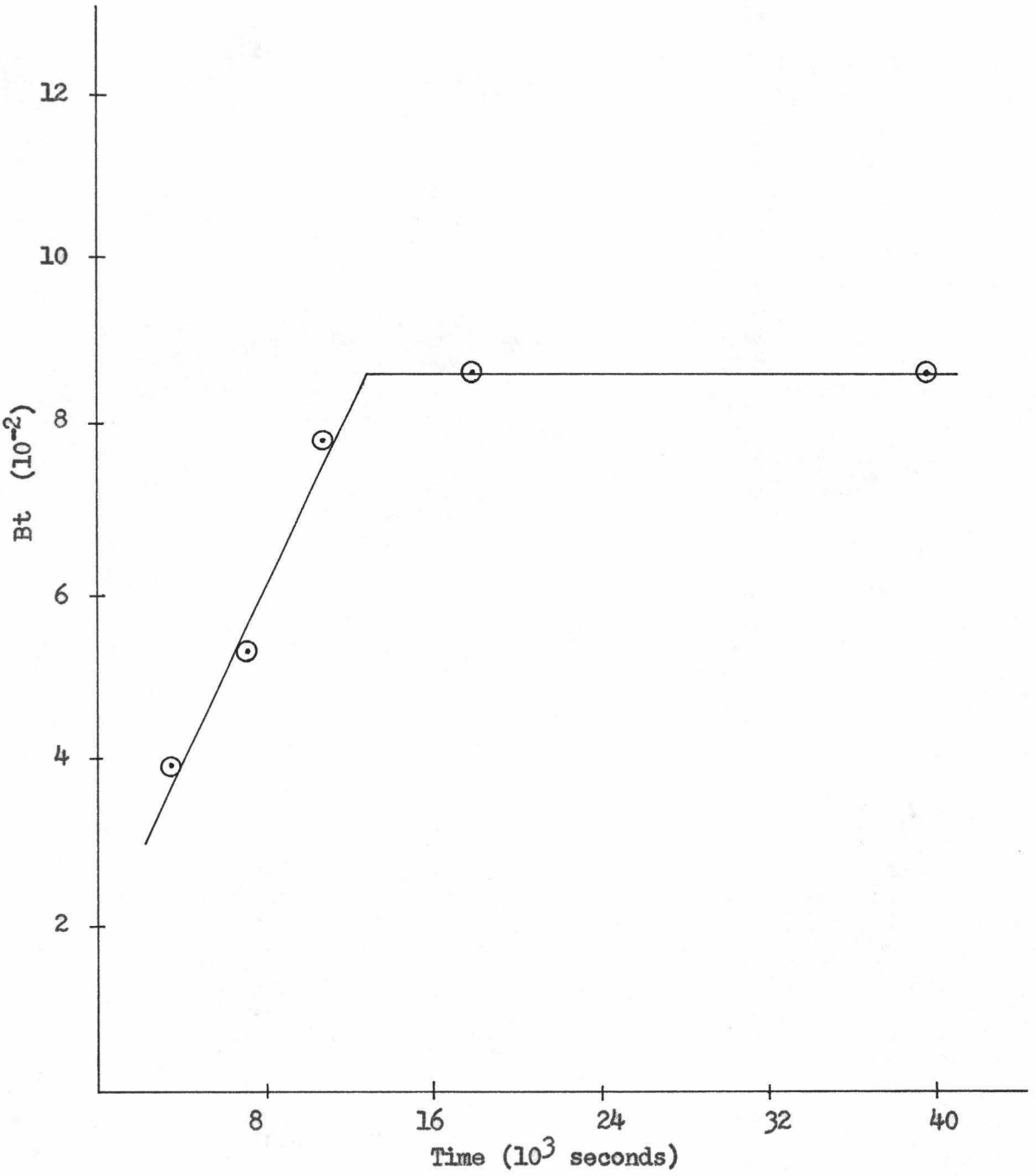


FIGURE 8 - Plot of Bt vs Time for Palolo at 600°C

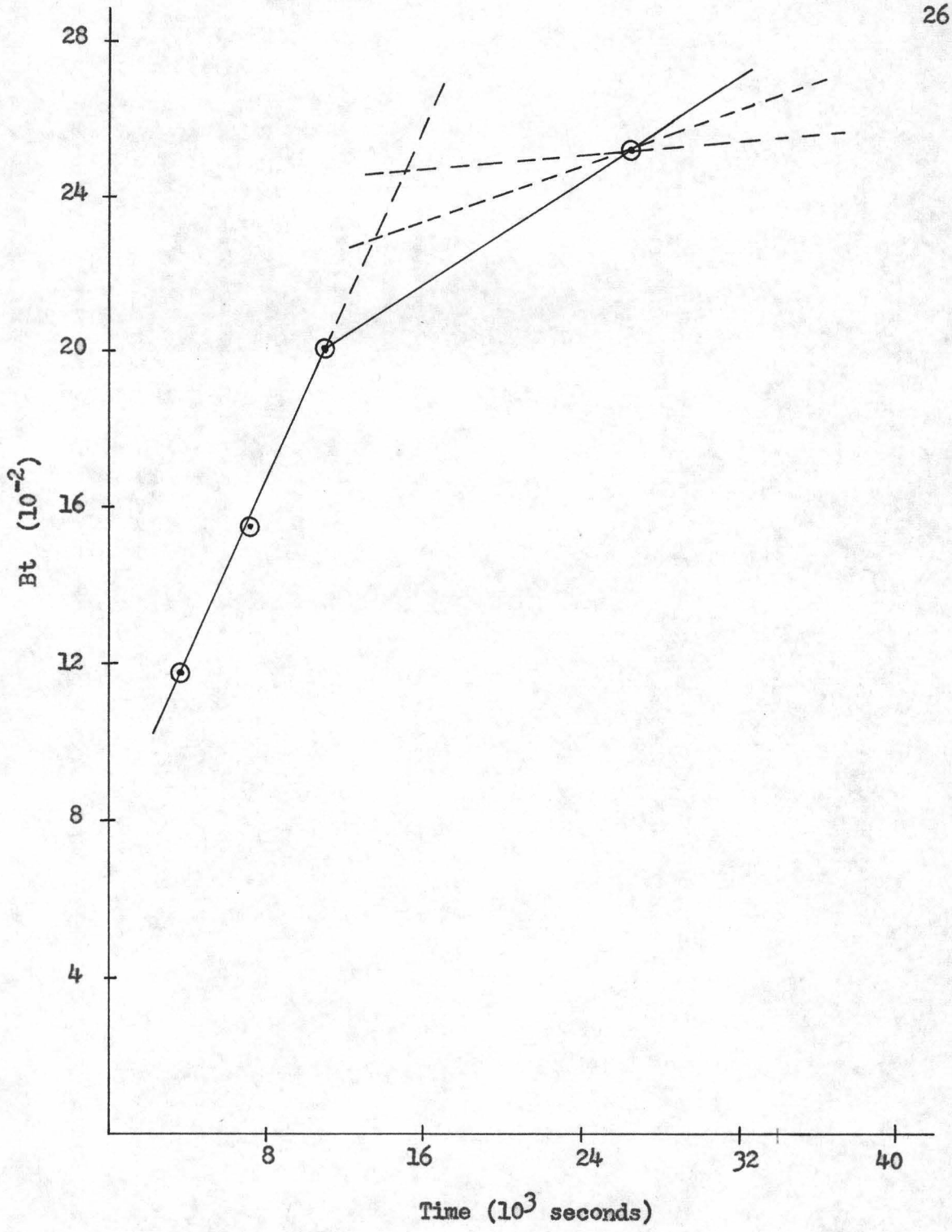


FIGURE 9 - Plot of Bt vs Time for Palolo at 800°C

temperature. When the amount of Ar-40* lost per unit time began to decrease, it appeared as a plateau on the F vs. t plots. At this stage, the Ar-40* was probably being lost by volume diffusion. All of the F vs. t plots indicate that the transition from non-volume diffusion is gradual. This is to be expected with any such natural situation where there is no sharp differentiation between diffusion from "near surface" or "volume" sites.

Figures 4 to 9, plots of Bt vs. t, were also made from the data in Tables 1 and 2. If volume diffusion were the sole type of mass transport, then these graphs would be straight lines. However, in the case of natural rock samples such as the ones used in this study, this is not to be expected. Figure 4, of HK 121 heated at 400°C, indicates that Ar-40* was probably lost in two different ways. The first segment is believed to be due to non-volume diffusion because Figure 2 shows a rapid initial Ar-40* loss characteristic of non-volume diffusion. Figures 5 and 6 of HK 121 are similar, indicating as in Figure 2, initial non-volume diffusion followed by a transition stage to volume diffusion.

Figures 7 and 8 of the Palolo sample also indicate two types of diffusion, the first probably non-volume diffusion and the second, volume diffusion. The dotted lines were drawn in Figure 9 because there was not enough data to establish exactly where the second segment lies[23]. As can be seen from Figures 7 and 8, volume diffusion began somewhere between the third and fifth hours of heating and a data point taken after a longer heating period (e.g., 11 hours) would be necessary to show where the line actually is located. Judging from Figures 7 and 8, one of the two dotted lines

better approximates the volume diffusion segment than the line drawn with only the last two data points.

The quantity B is related to the diffusion coefficient by $B = \pi^2 D/a^2$. If a, the effective radius of the particle were known, D could easily be found. However, there is much uncertainity in this quantity, therefore D/a^2 is usually used. From Bt found above, B was calculated:

$$\frac{Bt}{t} = \frac{D}{a^2}$$

where t is the time interval over which the sample was heated. The quantities calculated are presented in Tables 3 and 4 and in Figures 10 and 11.

The curves from 600°, 700°, and 800°C in Figure 10 are similar in shape and indicate a rapid loss with the characteristically high D/a^2 rates of non-volume diffusion when the sample was first heated at a higher temperature. After this easily-lost material was released, volume diffusion became apparent.

On the other hand, the curve for 400°C began with a low D/a^2 rate which rose as heating was continued, then fell and began rising again, this time more slowly. The unusual shape of this curve could result if one or more of the data points were wrong. However, this initial rise in the rate of D/a^2, a subsequent fall, then a gradual rise also appears in Figure 11 for the Palolo sample. Both curves are for the first temperature setting. Therefore it is believed that there might be a logical explanation for this phenomena. As explained above, it is believed that non-volume diffusion takes place during the first few periods at all

better approximates the volume diffusion segment than the line drawn with only the last two data points.

The quantity B is related to the diffusion coefficient by $B = \pi^2 D/a^2$. If a, the effective radius of the particle were known, D could easily be found. However, there is much uncertainty in this quantity, therefore B/a^2 is usually used. From Bt found above, a was calculated by

$$\frac{Bt}{a^2} = \frac{Dt}{a^2}$$

where t is the time interval over which the sample was heated. The quantities calculated are presented in Tables 3 and 4 and in Figures 10 and 11.

The curves from 600°C, 700°C, and 800°C in Figure 10 are similar in shape and indicate a result that the observed relatively high D/a^2 value of non-volume diffusion when the sample was first heated at a higher temperature. After this easily-lost material was released, volume diffusion became apparent.

On the other hand, the curve for 900°C began with a low D/a^2 value which rose as heating was continued. When cool and began heating again, this time more slowly. The normal shape of this curve could result if one or more of the data points were wrong. However, this initial rise on the curve of 1/T, a subsequent fall, then a normal rise also appears in Figure 11 for the Lafolo sample. Both curves are for the first temperature cycling. Therefore it is believed that there might be a logical explanation for the phenomena. As explained above, it is believed that non-volume diffusion takes place during the first few periods at all

Table 3

Data for Diffusion Curves for HK 121

Temperature (°C)	Cumulative time (hours)	D/a^2	Log D/a^2
400	1	5.90×10^{-9}	-8.229
	2	1.37×10^{-8}	-7.863
	3	2.29×10^{-8}	-7.640
	5	1.25×10^{-8}	-7.904
	11	4.29×10^{-8}	-7.367
600	1	8.64×10^{-7}	-6.063
	2	5.28×10^{-7}	-6.277
	3	5.51×10^{-7}	-6.259
	5	2.08×10^{-7}	-6.682
	11	2.66×10^{-7}	-6.575
700	1	3.76×10^{-6}	-5.425
	2	2.11×10^{-6}	-5.675
	3	1.64×10^{-6}	-5.785
	5	5.74×10^{-7}	-6.241
	11	6.78×10^{-7}	-6.169
800	1	7.80×10^{-6}	-5.108
	2	4.27×10^{-6}	-5.370
	3	3.68×10^{-6}	-5.434
	5	1.25×10^{-6}	-5.903
	11	1.45×10^{-6}	-5.838

Table 4

Data for Diffusion Curves for Palolo

Temperature (°C)	Cumulative time (hours)	D/a^2	Log D/a^2
400	1	1.02×10^{-8}	-7.992
	2	4.72×10^{-8}	-7.326
	3	9.82×10^{-8}	-7.008
	7	6.63×10^{-8}	-7.178
600	1	1.11×10^{-6}	-5.956
	2	7.47×10^{-7}	-6.126
	3	7.34×10^{-7}	-6.134
	7	3.48×10^{-7}	-6.458
800	1	3.31×10^{-6}	-5.480
	2	2.18×10^{-6}	-5.661
	3	1.88×10^{-6}	-5.727
	7	1.01×10^{-6}	-5.996

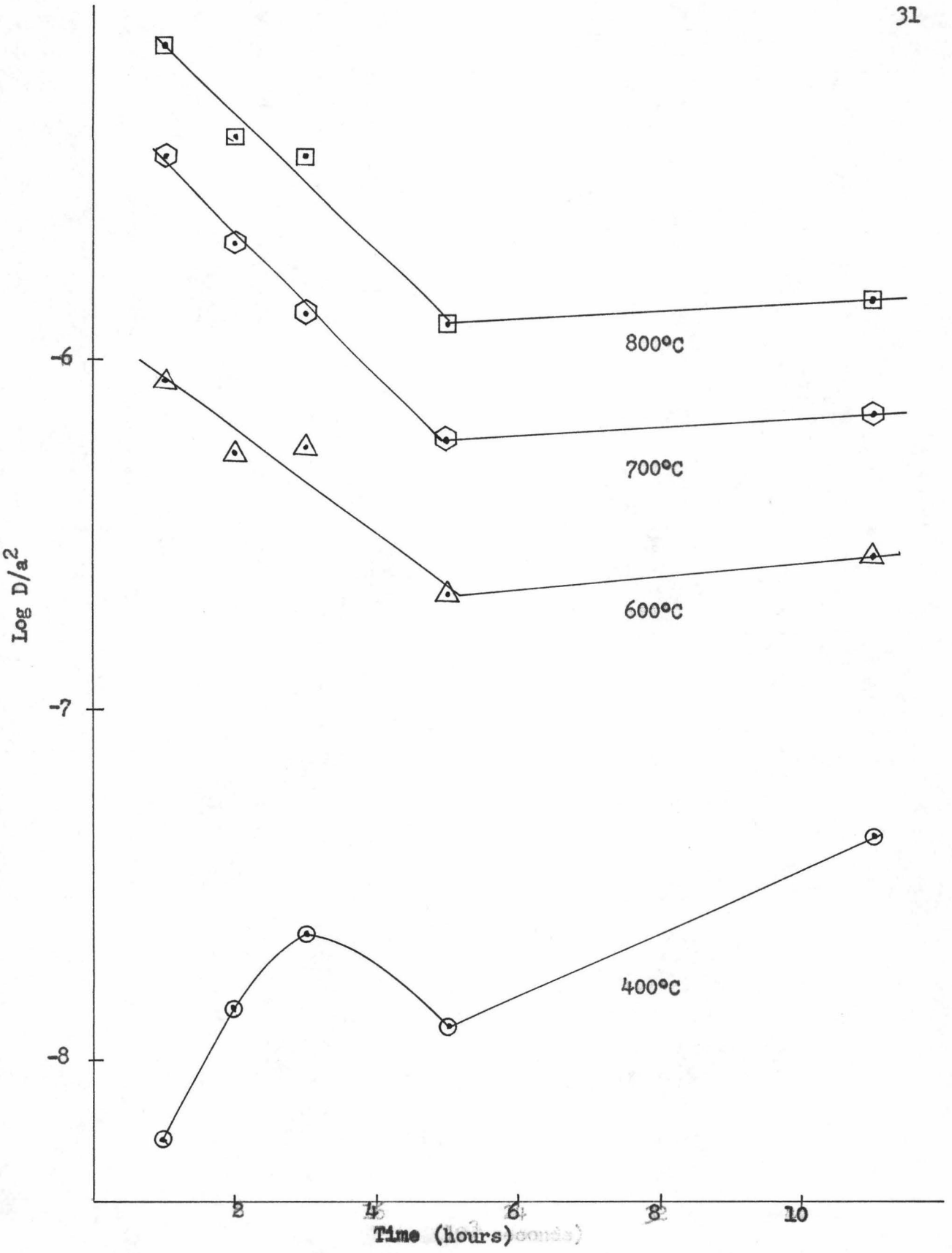


FIGURE 10 - Plot of Log D/a^2 vs Time for HK 121 at 400°, 600°, 700° and 800°C

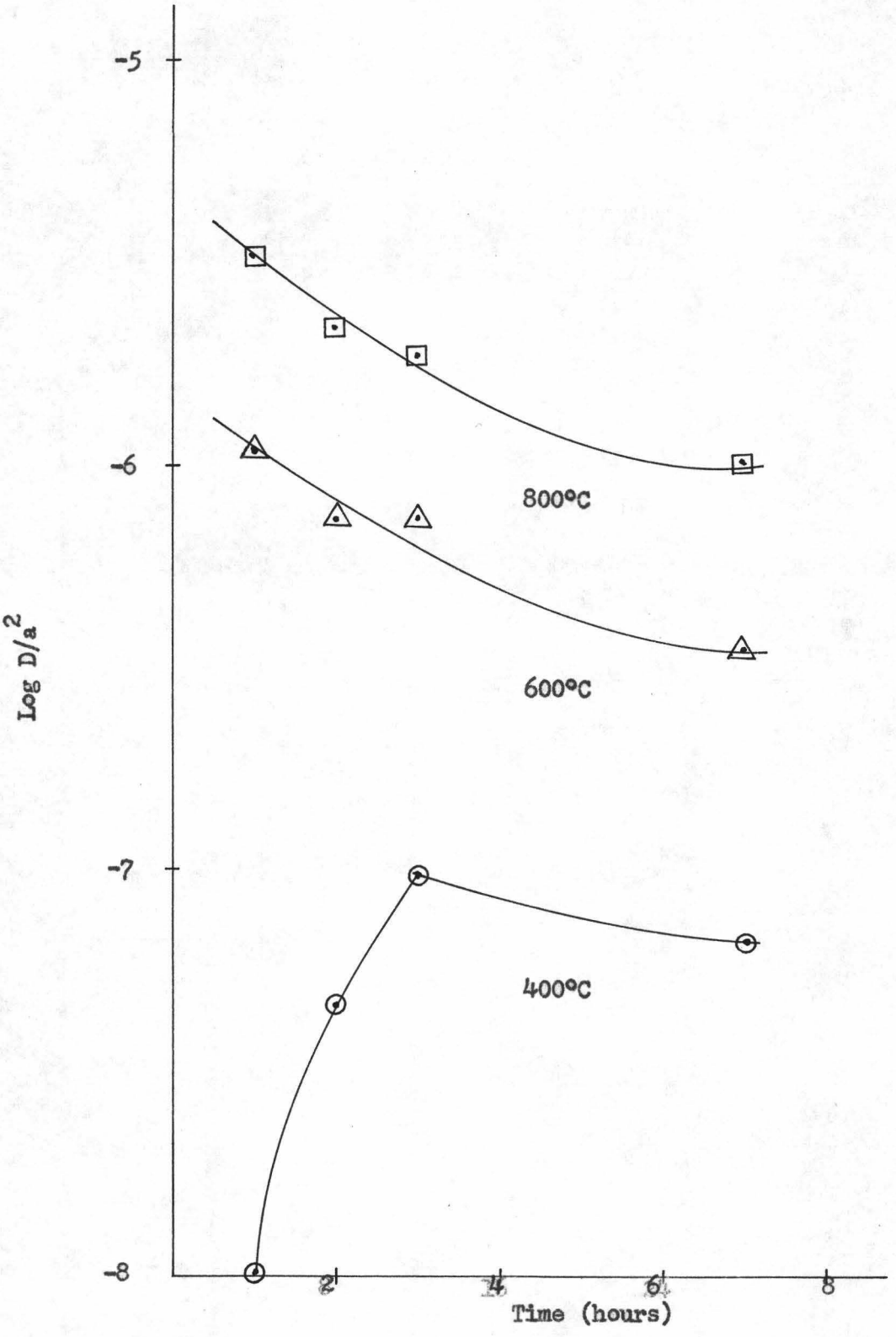


FIGURE 11 - Plot of Log D/a^2 vs Time for Palolo at 400°, 600° and 800°C

temperatures. Non-volume diffusion includes diffusion from areas in or at surfaces and surface irregularities. Now, diffusion from these cracks or surface irregularities requires that enough energy be available for the diffusion process as well as the desorption process from the surface. Since surface energies can be quite large, the low rates of diffusion which appear in the plots when the sample is first heated are not at all unusual[23]. After the Ar-40* trapped on the surfaces is released, the Ar-40* not bound by adsorption can escape with higher D/a^2 rates. Then, after this more rapid non-volume diffusion has taken place, the remaining Ar-40* can come only from volume sites, a process which proceeds at a slower D/a^2 rate. In support of this argument that surface-adsorbed material was being released, it should be noted that only the more rapid, characteristically high D/a^2 rates of non-volume diffusion appear during the first few hours of heating at subsequent temperature increments. Thus the curves for 400°C in Figures 10 and 11 are not as unusual as they might first appear.

Using the Arrhenius equation,

$$D = D_o \exp(-E/RT)$$

the activation energy, E, for volume diffusion of Ar-40* can be found from Log D/a^2 vs. 1000/T°K plots. Therefore the Log D/a^2 values for the volume diffusion segments of Figure 10 were plotted in Figure 12. The activation energy calculated for the volume diffusion from HK 121 was 15 kcal/mole.

A similar scheme was followed for the Palolo sample. Figure 11, which corresponds to Figure 10 for HK 121, shows similar results. The curve for 400°C has been explained above. The curves for 600°

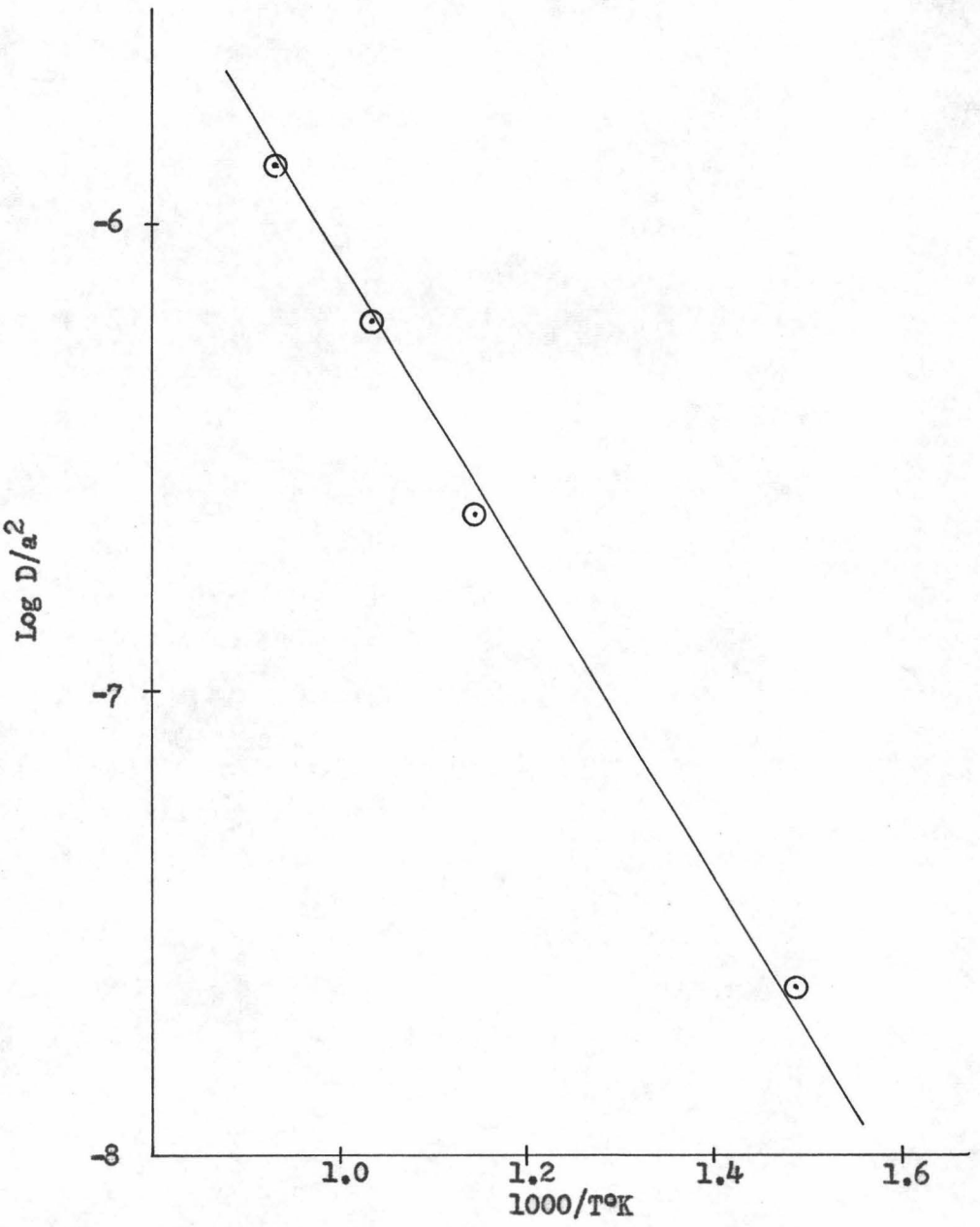


FIGURE 12 - Plot of Log D/a^2 vs 1000/T°K for HK 121

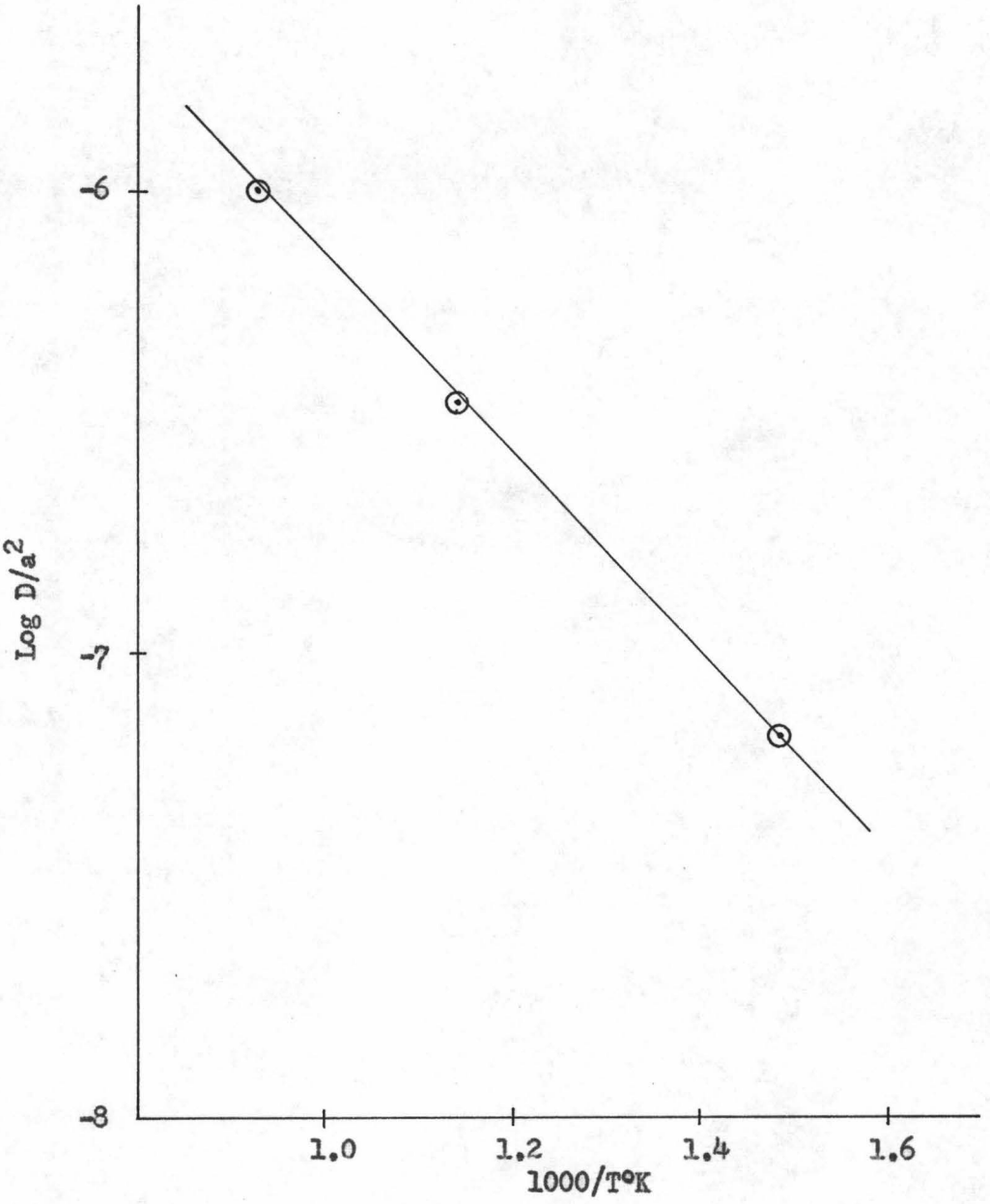


FIGURE 13 - Plot of Log D/a^2 vs 1000/T°K for Palolo

and 800°C are similar to the higher temperature curves for HK 121 in Figure 10, in that they show a high loss of Ar-40* during initial heating, with volume diffusion setting in with lower D/a^2 rates as heating was continued. A Log D/a^2 vs. 1000/T°K plots was made for the Palolo sample (Figure 13) and the resulting single line indicated that there was only one type of volume diffusion taking place, with an activation energy of 9.8 kcal/mole.

The data for the potassium-aluminum-silicate (KAS) in Barnes' work[2] was treated in a similar manner. Table 5 for KAS is comparable to Tables 3 and 4 for HK 121 and Palolo, respectively. Figure 14 was drawn from this data. As can be seen, the curves are similar in shape to those of HK 121 and Palolo (Figures 10 and 11, respectively). There is no curve which is comparable in shape to that of the 400°C curves in Figures 10 and 11 because the KAS was not heated for several time periods at the initial temperature. Such curves, as pointed out above, would appear only with the very first heating periods. The curves which are plotted show the decrease in the D/a^2 values with a tendency to level off as volume diffusion begins. As can be seen, the curve for 600°C reaches a plateau at about $4\frac{1}{2}$ hours. Thus, although the sample was not heated for longer periods of time at 700° and 800°C, it can probably be assumed that the D/a^2 value would become constant with time after approximately four hours. The general shapes of the curves indicate that this probably is a valid assumption.

What appears to be unusual about the plots in Figure 14 is that the 700° and 800°C curves appear to have the same D/a^2 for volume diffusion. Thus, when Log D/a^2 vs. 1000/T°K is plotted for

Table 5

Data for Diffusion Curves for KAS

Temperature (°C)	Cumulative time (hours)	D/a^2	Log D/a^2
600	1	2.45×10^{-7}	-6.61
	2	1.60×10^{-7}	-6.79
	3	1.47×10^{-7}	-6.83
	$4\frac{1}{2}$	1.26×10^{-7}	-6.90
	$5\frac{1}{2}$	1.26×10^{-7}	-6.90
700	1	8.08×10^{-7}	-6.09
	2	4.38×10^{-7}	-6.36
	3	3.05×10^{-7}	-6.52
	4	2.34×10^{-7}	-6.63
800	1	9.51×10^{-7}	-6.02
	2	4.77×10^{-7}	-6.32
	3	3.20×10^{-7}	-6.49
	4	2.34×10^{-7}	-6.63

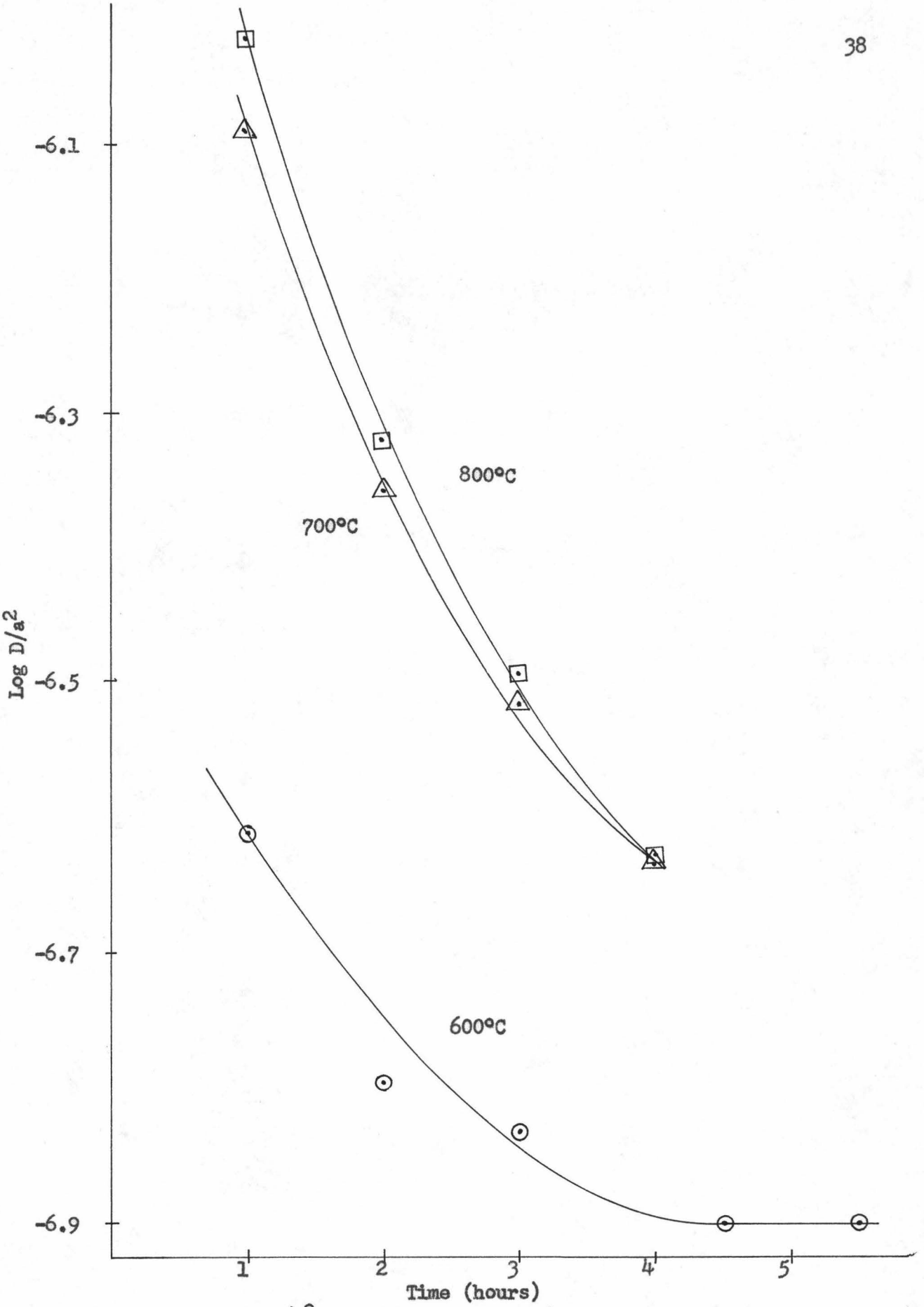


FIGURE 14 - Plot of Log D/a^2 vs Time for KAS at 600°, 700° and 800°C

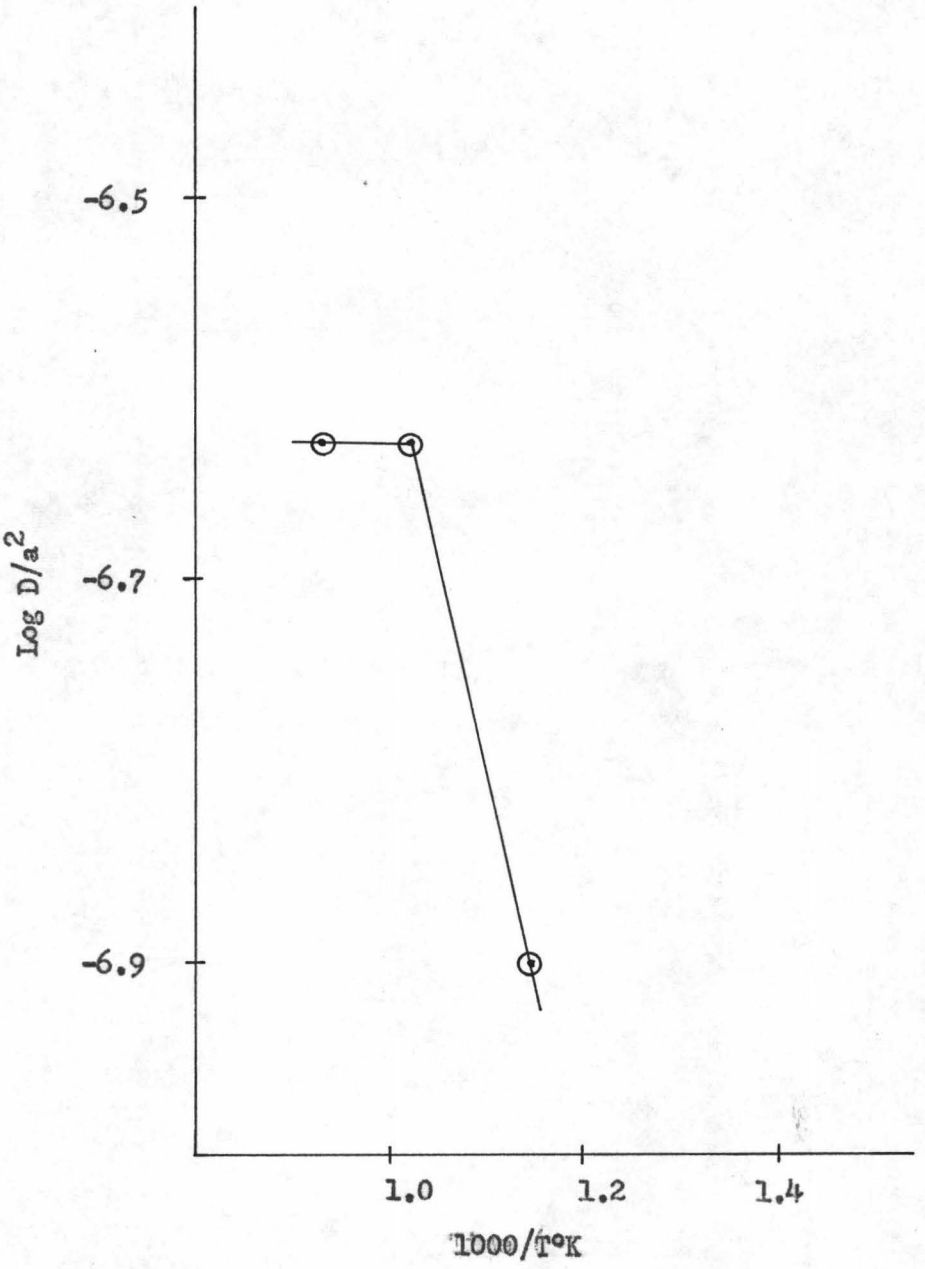


FIGURE 15 - Plot of Log D/a^2 vs 1000/T°K for KAS

KAS, there are two activation energies for volume diffusion. (See Figure 15) The activation energy of 0.04 kcal/mole is very small and probably results during a change of phase or other internal transitions within the glass between 700° and 800°C, as suggested by Barnes[2]. X-ray diffraction powder photographs of the KAS were made before and after the heating process. The photograph of the material before heating showed no diffraction lines at all, indicating a completely amorphous structure. The photograph taken after the heating had a definite diffraction pattern corresponding to that of crystalline leucite.

Assuming that the activation energies for volume diffusion also apply at lower temperatures, then F, the fraction of argon lost at temperatures usually used for bakeout can be calculated. The data are summarized in Table 6 and plotted as Figure 16. As can be seen from the plot, the fraction of argon lost increases rapidly with increase in bakeout temperatures. If KAS were baked out at 400°C for 12 hours, it would lose about 23% of its total Ar-39 content, while a Palolo sample would lose about 17% of its total Ar-40* content and HK 121 about 10%.

The volume diffusion proceeds more rapidly in Palolo than in HK 121. This is not unusual because the rocks are composed of different minerals probably with different grain sizes. The Palolo rock is made up of about 29% albite, 20% anorthite, 16% hypersthene and 15% diopside, while HK 121 has about 38% albite, 26% orthoclase and 16% quartz[15].

If a natural sample were mixed with the KAS and baked out at a temperature above 150°C, then it would lose more of its contaminating

Table 6

Fraction of Argon Released by Volume Diffusion
at Different Temperatures During a 12-Hour Heating Period

Sample	Temperature (°C)	F, Fraction Released (10^{-2})
KAS	400	23.3
	300	5.13
	200	1.97
	150	1.03
	100	0.449
HK 121	400	10.4
	300	3.98
	200	0.996
	150	0.389
	100	0.117
Palolo	400	17.3
	300	9.31
	200	3.79
	150	2.05
	100	0.940

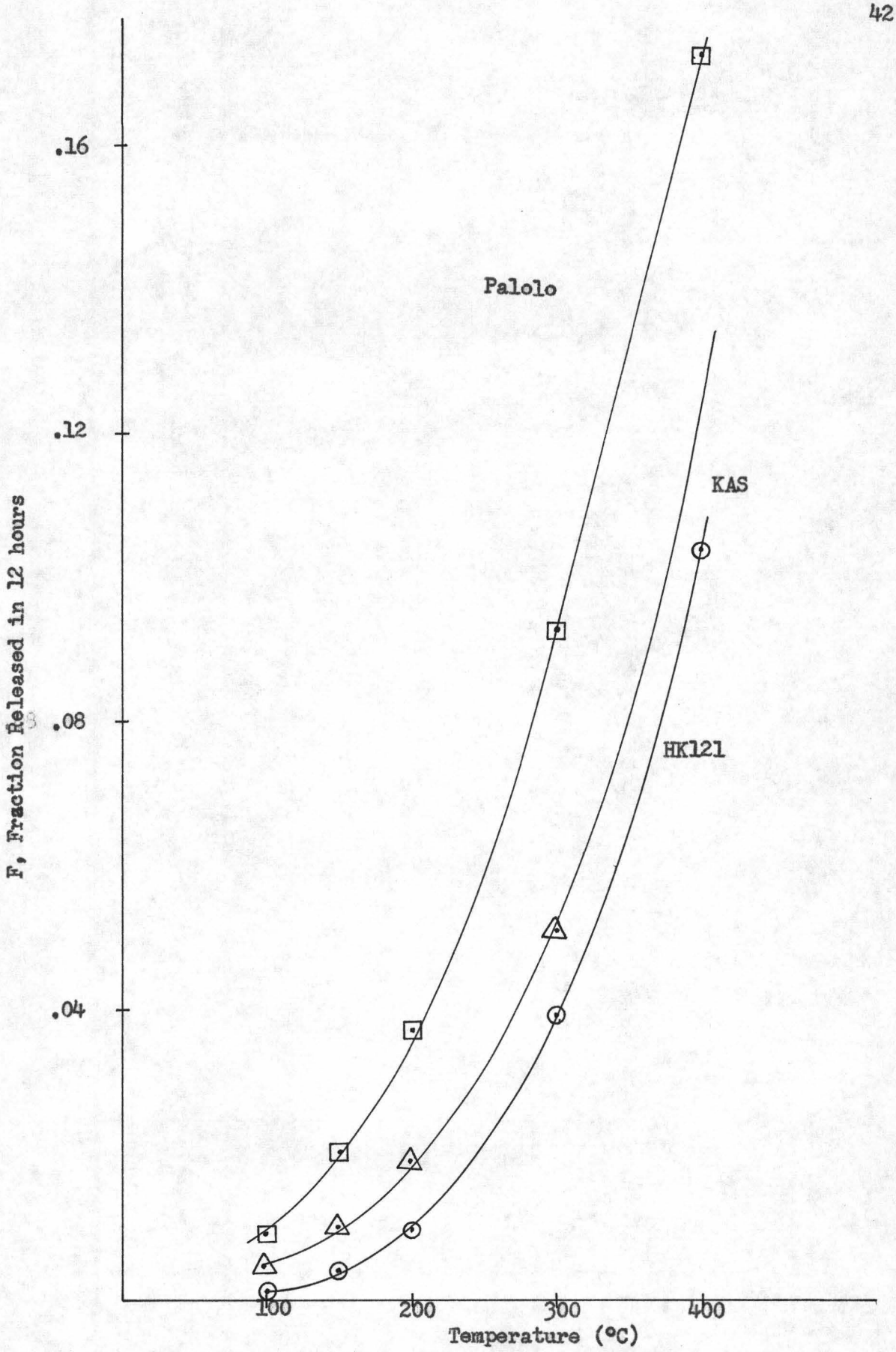


FIGURE 16 - Plot of Fraction Released in 12 hours by Volume Diffusion vs Temperature for KAS, HK 121 and Palolo

air Ar-40 and the amount of Ar-40* can be found from a plot like Figure 16. The average amount of Ar-40* lost by non-volume diffusion at each temperature during the first five hours of heating was about 10% for HK 121 and 14% for the Palolo sample. Non-volume diffusion can be expected to vary from sample to sample of even the same rock because it is diffusion from surface and surface irregularities which naturally would differ from sample to sample. Therefore with additional diffusion studies, perhaps an average value to be used in calculating the amount of Ar-40* lost due to non-volume diffusion can be found.

Although the volume diffusion loss of Ar-39 from KAS and the Ar-40* loss from HK 121 and Palolo are not the same, Naughton's proposal[10] of using Ar-39 as the diluting isotope could still be used successfully. If additional diffusion studies were made on other Hawaiian rocks more generally representative of the types used for K-Ar dating (e.g., tholeite basalts) then perhaps general trends could be found and diffusion studies, an extrememly time-consuming procedure, as shown in II.C., would not have to be carried out for each rock to be dated. This study is a first step in that direction.

Some suggestions for future work.

As stated above, additional diffusion studies should be done in order to be able to routinely apply Naughton's proposed method of using Ar-39 as a tracer isotope. If such studies are carried out, the following suggestions might be useful.

First, a larger sample should be used for diffusion studies. The samples used in this research weighed about one-half gram.

Because the amount of Ar-40* which diffuses out at one time-temperature setting is usually about 1 or 2% of the total Ar-40* present in the sample, the quantities measured were in the range of 3×10^{-9} cc. If however, a rock contained about 3×10^{-7} cc/gm of Ar-40* and a two-gram sample were used for diffusion studies then the amounts measured would be about 1×10^{-8} cc, a more reasonable quantity.

The following suggestions for improvement in procedures may seem trivial to a casual reader. But a person engaged in scientific research knows that the many little problems which arise in active research can add up to big problems. With this in mind, the following suggestions are made.

Improvements should be made on the gas extraction and purification system. First, more automatic timing devices should be considered for use. A step in this direction was made by attaching a timer to the Ti getter so that it could be turned on and off automatically. Second, the time involved in each run could perhaps be shortened if a better oven were constructed for the Ti getter so that it could be brought up to operating temperature more rapidly.

Another improvement in the system would be to place a charcoal finger between valve 2 and the pumping section. For these studies, liquid nitrogen was placed around the U-tube in Section IA in order to make certain the system was as clear as possible of contaminating gases from the previous run. However, it was noted that the pressure before and after liquid nitrogen was placed around the U-tube was not very different. But when liquid nitrogen was placed on a

charcoal finger, the pressure in the system improved greatly. This is due to the well-known fact that charcoal is an excellent adsorbent. Thus, if a charcoal finger were placed between valve 2 and the pumps, then with liquid nitrogen on the finger, the other charcoal fingers and molecular sieve traps in IA and IB could be flamed out. Then with valve 2 closed and liquid nitrogen removed, the finger could be gently flamed in order to release the contaminants which would be quickly removed by the pumps. Another advantage of placing the finger between valve 2 and the pumps is that it would be within the bake-out area.

Finally, for fusion runs the sample in the sidearm had to be made to fall into the molybdenum crucible in the quartz chamber. Much trouble was encountered on occasion when the bulky sample packets became lodged sideways in the chamber and did not fall into the crucible. Therefore it is suggested that future workers wrap the samples in the shape of a small pyramid or cube. The pyramidal or cube shape would make it possible to manipulate the samples in the sidearms without fear that all might accidently roll into the furnace (as might happen if the packets were in the shape of a sphere), and yet be compact enough to fall into the crucible without becoming lodged in the chamber.

IV. Summary

This study has shown that Naughton's proposal[10] for using Ar-39 in an irradiated artificial glass sample as the tracer isotope for potassium-argon dating in order to reduce air contamination and improve quantitative determinations of Ar-40* is promising. Two Hawaiian rocks, HK 121 and Palolo, were studied and their diffusion parameters found.

Non-volume diffusion was apparent during the first few hours of bakeout with volume diffusion gradually becoming the mode of mass transport. Low D/a^2 rates during the first heating periods were believed to be due to the fact that energy was needed initially for both desorption and diffusion. From the information gathered, the Ar-40* loss of HK 121 and Palolo and the Ar-39 loss of KAS for a given time with respect to temperature were plotted. Such plots could be used by future workers to determine the amounts of Ar-40* lost during the bakeout.

Additional diffusion studies on rocks more representative of those used for potassium-argon dating might indicate general trends in diffusion losses at higher bake-out temperatures. If this were so, then Naughton's proposal[10] for using Ar-39 in artificial silicate glasses for the tracer isotope could be used routinely in future geochronological studies.

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