The Application of Neutron Activation to the
determination of ages of young terrestrial rocks

by

Charles James Yonge

Submitted in fulfilment of the requirements
for the degree of Master of Philosophy

Department of Physics,
University of Surrey.

December, 1976.
ABSTRACT

The $^{39}\text{Ar} - ^{40}\text{Ar}$ dating method has been developed over the past decade and applied with great success to Lunar samples and meteorites. The potential of the method as applied to terrestrial samples has still to be fully realized because of the greater complexity of terrestrial rocks. One promising area of research is the application to dating very young rocks where the $^{39}\text{Ar} - ^{40}\text{Ar}$ method should be more sensitive than the conventional K-Ar dating.

The work described in this thesis was an attempt to investigate the area of young rock dating and involved both the development of the necessary techniques and the application to a specific geological problem.

On the technical side, a static mass spectrometer and associated argon extraction and purification system was constructed capable of detecting $5 \times 10^{-13}$ ccSTP of argon. In parallel with this, the appropriate techniques for fast neutron irradiation of large (20g) samples with low fluences, were developed.

The application of the technique involved the investigation of suitable young rock neutron monitors. Two geological samples of known age were studied for this purpose; Bishop Tuff sanidine ($0.7 \times 10^6$ years) and Bern muscovite ($18.7 \times 10^6$ years).

Finally, the methods developed were successfully applied to a suite of East African volcanic rocks with ages in the range ($0.1-2.3) \times 10^6$ years. The significance of this study is twofold in that the ages relate to; (a) the elucidation of the pluvial (glacial) cycles in East Africa and (b) the rate of petrogenesis of lavas from a single magma body.
To Odile
ACKNOWLEDGEMENTS

The author would like to express his gratitude to the following:

Dr. G. Turner for suggesting this research topic and guiding the work at Sheffield.

Mr. N.M. Spyrou for being willing to supervise the project and his encouragement thereafter.

Mr. P. Wilkinson for providing the samples from Mount Kilimanjaro and his comments on the geology.

Professor T. Kaiser for the use of the facilities of the physics department at the University of Sheffield.

Drs. P.H. Cadogan and M.F.C. Lynch for their many invigorating discussions and helpful suggestions during my research period.

The technical staff of the physics department at Sheffield; in particular Mr. A. Row and Mr. I. Murr for making the component parts of the UHV system and Mrs. A. Johnson for assisting with the diagrams.

All my friends for their encouragement throughout my time at Sheffield.
# CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER 1</th>
<th>Introduction</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHAPTER 2</td>
<td>$^{40}\text{Ar}/^{39}\text{Ar}$ Dating</td>
<td>5</td>
</tr>
<tr>
<td>2.1</td>
<td>Age Equation</td>
<td>5</td>
</tr>
<tr>
<td>2.2</td>
<td>Nuclear Reactions</td>
<td>7</td>
</tr>
<tr>
<td>2.3</td>
<td>$^{39}\text{Ar}$ Recoil</td>
<td>15</td>
</tr>
<tr>
<td>2.4</td>
<td>Effect of Extraneous Argon on the Dating of Young Rocks</td>
<td>16</td>
</tr>
<tr>
<td>2.5</td>
<td>Argon Release Patterns and Isochron Plots</td>
<td>19</td>
</tr>
<tr>
<td>2.6</td>
<td>Analytical Precision</td>
<td>26</td>
</tr>
<tr>
<td>CHAPTER 3</td>
<td>Experimental Methods</td>
<td>28</td>
</tr>
<tr>
<td>3.1</td>
<td>Mass Spectrometry</td>
<td>28</td>
</tr>
<tr>
<td>3.1.1</td>
<td>Introduction</td>
<td>28</td>
</tr>
<tr>
<td>3.1.2</td>
<td>Electronics and Data Handling</td>
<td>29</td>
</tr>
<tr>
<td>3.2</td>
<td>Argon Extraction and Purification</td>
<td>34</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Components, Pumping and Bakeout</td>
<td>34</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Furnace Design And Loading Assembly</td>
<td>39</td>
</tr>
<tr>
<td>3.2.3</td>
<td>Argon Purification</td>
<td>43</td>
</tr>
<tr>
<td>3.3</td>
<td>Mineral Separation</td>
<td>46</td>
</tr>
<tr>
<td>3.4</td>
<td>Sample Irradiation</td>
<td>48</td>
</tr>
<tr>
<td>CHAPTER 4</td>
<td>Limits to K-Ar Dating</td>
<td>50</td>
</tr>
<tr>
<td>4.1</td>
<td>Introduction</td>
<td>50</td>
</tr>
<tr>
<td>4.2</td>
<td>Justification for the New System</td>
<td>51</td>
</tr>
<tr>
<td>4.3</td>
<td>Performance of the New System</td>
<td>53</td>
</tr>
</tbody>
</table>
CHAPTER 5 Discussion of Results

5.1 Introduction 59
5.2 Bishop Tuff 60
5.3 Mount Kilimanjaro 63
5.4 Future Work 71

BIBLIOGRAPHY 72

APPENDIX Tables of Results

FIGURE Between Pages
1 Interference effects from neutrons 4–5
2 Choice of sample size for various ages 4–5
3 Schematic layout of mass spectrometer 28–29
4 Ion source 30–31
5 Typical mass spectrometric scan 31–32
6 & 7 Gas extraction system (plan & elevation) 33–34
8 Metal valve assembly 34–35
9 Furnace 38–39
10 Furnace calibration curve 39–40
11 Arrangement of samples during irradiation 47–48
13 to 18 Isochrons & release patterns (Bishop Tuff) 60–61
20 to 29 " & " (Kilimanjaro) 70–71

PLATE
1 Mass Spectrometer 33–34
2 Furnace components 39–40
3 Loading assembly 40–41

TABLE
1 Argon isotopes in neutron-irradiated rocks 4–5
2 Age data of samples analysed in this work 58–59
CHAPTER 1

Introduction

The idea of K-Ar dating was initially suggested in 1940 by the M.I.T. physicist Robley D. Evans even before it was proved that $^{40}$Ar was a decay product of $^{40}$K, (Goodman and Evans, 1941). However, he felt that because of the abundance of atmospheric argon and the difficulty of making non-radiometric corrections, the method would never be capable of extensive application.

Aldrich and Nier (1948) demonstrated that the correction could be made by careful determination of isotopic composition. Early determinations were made by Smits and Gentner (1950) and Gerling et al. (1952).

The potassium-argon radiometric age calculation for the ideal clock is based on the ratio of radiogenic $^{40}$Ar to $^{40}$K, aftercsubtracting the atmospheric component, according to the following expression:

$$
\frac{^{40}\text{Ar}}{^{40}\text{K}} = e^{\lambda t} - 1
$$

from which,

$$
t = \frac{1}{\lambda} \ln \left( \frac{^{40}\text{Ar}}{^{40}\text{K}} + 1 \right)
$$

where,

$^{40}$Ar = argon-40 produced by the decay of $^{40}$K (potassium-40) in the rock,

t = the time (radiometric age) required to generate the measured amount of Ar from the measured amount of K, and

$$
\lambda = \lambda_e + \lambda_\beta ,
$$

the sum of partial decay constants of $^{40}$K due to electron capture and beta decay respectively.

For valid age determinations (Holmes, 1962), it is necessary
that at time $t_0$, when the radioactive clock was set, the system contained no extraneous argon-40 and subsequently remained a closed system accumulating radiogenic $^{40}$Ar. That is to say that the system neither gained nor lost either $^{40}$Ar or $^{40}$K. If later metamorphic or hydrothermal events occur which do not completely outgas the previous radiogenic Ar accumulated from the time of formation of the rock then intermediate ages can result, (see for example Fitch et al., 1969).

The $^{39}$Ar-$^{40}$Ar dating technique involves the conversion by fast neutrons of $^{39}$K to $^{39}$Ar from which $^{39}$Ar can be analysed simultaneously with $^{40}$Ar in a mass spectrometer. If all the $^{40}$Ar is radiogenic then the ratio of these two isotopes is proportional to the parent/daughter ratio ($^{40}$K/$^{40}$Ar) and an age can be calculated. The method has the advantages of; (a) overcoming the difficulties of sample inhomogeneity (in the conventional K-Ar method whole-rock samples are split and the K and Ar measured separately) and, (b) improves precision by measuring the isotopic ratio rather than the elemental $^{40}$Ar/$^{40}$K ratio although ultimately the precision rests on the accuracy of the monitor sample age.

The implementation of a step-wise degassing experiment allows a number of analyses to be made on the same sample; effectively measuring the $^{40}$Ar/$^{39}$Ar ratio in different minerals or different sites within a given mineral. If the ratio does not vary throughout the run then an unambiguous age may be attributed to the sample. If variations in the ratio are obtained then it suggests that the retention history is complicated and open to interpretation (Turner, 1972).
A K-Ar analysis of such a sample would yield a meaningless age. See for examples figs 13-28.

The first suggestion of the $^{39}\text{Ar} - {^{40}\text{Ar}}$ method came from Sigurgeirsson (1962), who considered theoretically two major aspects of the method, namely; the interference of neutron reactions (and their correction) and the potential of the step-wise degassing experiment. He published this brilliant paper in Icelandic resulting unfortunately, in it's translation only recently. It was Merrihue (1965) who independantly put forward the idea that the $^{40}\text{Ar} /^{39}\text{Ar}$ ratio could be used to calculate K-Ar ages and Merrihue and Turner (1966) who then suggested releasing the argon in a step-wise degassing experiment from which a spectrum of apparent ages could be obtained. They further suggested that the data could be presented on an isotope correlation diagram where the $^{40}\text{Ar} /^{36}\text{Ar}$ (ordinate) is plotted against the $^{39}\text{Ar} /^{36}\text{Ar}$ ratio (abscissa). The assumption was that if two types of gas of distinct composition are present; $^{40}\text{Ar}$ and $^{39}\text{Ar}$ derived from K, and $^{40}\text{Ar}$ and $^{36}\text{Ar}$ present as extraneous, then a plot of all the heating steps should give a straight line; the slope yielding the age and the intercept (ordinate) revealing the extraneous $^{40}\text{Ar} /^{36}\text{Ar}$ composition. (e.g. fig 13) The major problem associated with the analysis of young rocks is the presence of atmospheric argon incorporated in the sample. The atmospheric argon-40 may be subtracted from the total argon-40 by the assumption that argon-36 is derived only from the atmosphere and that the atmospheric $^{40}\text{Ar} /^{36}\text{Ar}$ ratio of 295.5 (Nier et al., 1950) is the present day value. A mass spectrometric scan allows the argon 40, 39 and 36 to be measured for each extraction, and it may be seen that the
precise measurement of the small $^{36}$Ar fraction is of prime importance. The stepwise degassing experiment does to some extent allow the partial separation of the atmospheric from the radiogenic and occasionally another component known as excess. These components can be identified from the isotope correlation diagram; the 'atmospheric' correction being made from the intercept thus removing the need to make an assumption for the initial $^{40}\text{Ar}/^{36}\text{Ar}$ ratio (as in the case of ages obtained from apparent age spectra).

It is important at this juncture to mention the effect of interfering neutron reactions to the dating of young rocks, particularly the K-derived $^{40}\text{Ar}$ and Ca-derived $^{36}\text{Ar}$ which affect the measurement of radiogenic $^{40}\text{Ar}$ and atmospheric $^{36}\text{Ar}$ respectively (see Table 1). Despite pessimistic speculations by other workers, Turner (1971a) demonstrates that regardless of the age of the sample, it was possible to choose conditions in the reactor such that interference corrections were kept to a minimum. See for example chapter 2 and fig. 1.

The purpose of this work was to apply the $^{39}\text{Ar}-^{40}\text{Ar}$ method to the dating of young rocks (less than $10^6$ years) and to overcome the associated problems by the techniques mentioned above.
## TABLE 1  Argon Isotopes Present in Neutron-irradiated Rocks

after Turner (1976)

<table>
<thead>
<tr>
<th>Source</th>
<th>$^{36}\text{Ar}$</th>
<th>$^{37}\text{Ar}$</th>
<th>$^{38}\text{Ar}$</th>
<th>$^{39}\text{Ar}$</th>
<th>$^{40}\text{Ar}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric argon</td>
<td>$\approx 1.00$</td>
<td>$&lt;10^{-4}$</td>
<td>$&lt;10^{-4}$</td>
<td>$0.190$</td>
<td>$295.5$</td>
</tr>
<tr>
<td>Neutron interactions on $^{41}\text{K}$, $^{43}\text{Ca}$</td>
<td>$(1-3)\times10^{-4}$</td>
<td>1.0</td>
<td>$(1.0-1.3)\times10^{-2}$</td>
<td>1.00</td>
<td>$(1-6)\times10^{-2}$</td>
</tr>
<tr>
<td>Neutron interactions on $^{35}\text{Cl}$</td>
<td></td>
<td></td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Major reactions responsible with Q-values(MeV) and target isotope abundance (%): $^{39}\text{K}(n,d)^{38}\text{Ar}(-4.1,93.1)$, $^{41}\text{K}(n,\alpha,\beta^{-})^{38}\text{Ar}(-0.1,6.9)$, $^{39}\text{K}(n,p)^{39}\text{Ar}(+0.22,93.1)$, $^{40}\text{K}(n,p)^{40}\text{Ar}(+2.29,0.0119)$, $^{41}\text{K}(-5.58,6.9)$.

Major reactions: $^{40}\text{Ca}(n,\alpha)^{36}\text{Ar}(-7.04,97.0)$, $^{40}\text{Ca}(n,\alpha)^{37}\text{Ar}(+1.75,97.0)$, $^{42}\text{Ca}(n,\alpha)^{38}\text{Ar}(-6.25,0.64)$, $^{42}\text{Ca}(n,\alpha)^{39}\text{Ar}(+0.35,0.64)$, $^{43}\text{Ca}(n,\alpha)^{40}\text{Ar}(+2.29,0.14)$, $^{44}\text{Ca}(n,\alpha)^{40}\text{Ar}(-8.85,2.06)$.

Major reaction: $^{37}\text{Cl}(n,\gamma,\beta^{-})^{38}\text{Ar}$.

### DECAY CONSTANTS OF $^{40}\text{K}$

<table>
<thead>
<tr>
<th>Decay Constant</th>
<th>Decay Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda = 5.305\times10^{-10}/ yr$</td>
<td>$\lambda_c = 0.585\times10^{-10}/ yr$</td>
</tr>
<tr>
<td>$\lambda_p = 4.72 \times 10^{-10}/ yr$</td>
<td></td>
</tr>
</tbody>
</table>

### COMPOSITION OF POTASSIUM

<table>
<thead>
<tr>
<th>$^{41}\text{K}$</th>
<th>$^{40}\text{K}$</th>
<th>$^{39}\text{K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.9%</td>
<td>0.0119%</td>
<td>93.1%</td>
</tr>
</tbody>
</table>

### ATMOSPHERIC ARGON RATIO

<table>
<thead>
<tr>
<th>$^{40}\text{Ar}/^{36}\text{Ar}$</th>
<th>$^{40}\text{Ar}/^{38}\text{Ar}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>295.5</td>
<td>1.581</td>
</tr>
<tr>
<td>5.35</td>
<td>5.35</td>
</tr>
</tbody>
</table>
SAMPLE WEIGHT (GRAMS)

SAMPLE AGE (YEARS)

Figure 2

10^{-4} 10^{-3} 10^{-2} 10^{-1} 10 10^2

10^{-4} 10^{-5} 10^{-6} 10^{-7} 10^{-8} 10^{-9} 10^{-10}

% 1.0% 0.3% 0.1% 0.05% 0.02% 0.01% 0.001%
2.1 Age Equation

The age equation derived below assumes that only $^{39}$Ar is produced in the reactor and that no other interferences are present.

The $^{40}$Ar is present in the sample due to the decay of $^{40}K$ by K-capture ($\beta$-emission leads to calcium-40) giving the K-Ar equation:

$$^{40}Ar = ^{40}K \cdot \frac{\lambda_K}{\lambda}(e^{t/T}-1)$$

(1)

where $T$ is the mean life of $^{40}K$ and the other symbols retain their former meaning.

The amount $^{39}$Ar produced in the $^{39}K(n,p)^{39}$Ar reaction is given by:

$$^{39}Ar = ^{39}Kt_i \int \sigma(E)\phi(E)dE$$

(2)

where

- $^{39}K$ = number of potassium-39 atoms present in the sample,
- $t_i$ = duration of irradiation,
- $\phi(E)dE$ = neutron flux between energy $E$ and $E+dE$,
- $\sigma(E)$ = cross-section for the $^{39}K(n,p)^{39}$Ar reaction at energy $E$.

Dividing equation (2) into (1) gives:

$$\frac{^{40}Ar}{^{39}Ar} = \frac{1}{J}(e^{t/T}-1)$$
or
\[ t = T \ln(1 + J(\frac{^{40}Ar}{^{39}Ar})) \] (3)

which is the age equation and \( J \) is defined as:

\[ J = \frac{^{40}K_i}{^{39}K_r} \frac{\lambda}{\lambda_e} \int \varphi(E) \sigma(E) dE \] (4)

From which it may be seen that provided the potassium isotopes occur within the sample with natural abundances or that the \( ^{39}K/^{40}K \) ratio is constant then \( J \) is proportional to the integrated neutron flux and for a given location is independent of the sample. For the Herald Reactor at A.W.R.E. which was used in the present work the appropriate relationship between \( J \) and integrated fast neutron flux \( F \) (\( E \) greater than 0.18 MeV) is;

\[ J = 0.6 \times 10^{-20} F. \] (4a)

* provided that the value for the effective cross-section is used.*
2.2 Nuclear Reactions

Mitchell (1968) foresaw limitations to the $^{39}\text{Ar} - ^{40}\text{Ar}$ method as applied to very young rocks in terms of interfering isotopes, that is to say, isotopes of argon, other than $^{39}\text{Ar}$, produced by neutron induced reactions. He concluded; "On both theoretical and experimental grounds, it would appear that, in the form described, the $^{39}\text{Ar} - ^{40}\text{Ar}$ method for determining K-Ar ages is suitable for minerals of ages as small as $10^6$ years, if their K/Ca content is greater than unity."

Brereton (1970) was more pessimistic and suggested that in extreme cases (such as young minerals), the correction placed very serious limits on the precision of the method particularly with samples of a high Ca or very high K content. He advocated (Brereton, 1971 and 1972) that only samples of more than ten million years should be dated and that for younger samples the McDougall et al. (1969) K-Ar approach be used in preference.

The findings of Dalrymple and Lanphere (1971) were more optimistic and they concluded that for a neutron fluence, $4 \times 10^{18}$ n.cm$^{-2}$, the precision was not lost for samples of K/Ca greater than unity as young as $0.5 \times 10^6$ years and for K/Ca less than unity, of $10 \times 10^6$ years. They suggested that for younger the combination of large air, Ca and K derived argon corrections made the precision of the $^{40}\text{Ar}/^{39}\text{Ar}$ method less than that of the conventional technique unless the irradiation parameters were suitably adjusted, going on to point out the seriousness of the Ca-derived $^{36}\text{Ar}$ and the need of a uniform neutron flux for large samples.

Turner (1971a) has demonstrated that regardless of the age of a rock, it is possible to choose conditions, in part-
icular sample size and integrated neutron flux, such that the interference corrections are small.

In the case of samples used in this work all interferences were kept to less than 1%. The derivation of the conditions which made this possible is dealt with below in detail.

Interfering isotopes produced in the reactor during irradiations come from three principle sources; firstly, alpha particles and secondary protons, secondly, photonuclear reactions from gamma rays and thirdly, the neutrons themselves.

Mitchell (1968) demonstrated that the fluence of protons and alpha particles was so small compared with the neutron flux that these effects could be ignored. He suggested that the second source involving photonuclear reactions might likewise be ignored since in the Herald reactor the maximum energies achieved by gamma photons is around 6.5 MeV, whereas 8.5 MeV is required to remove a nucleon in the region of mass 40.

The third source involving the neutrons themselves does potentially impose limitations on the method. Principal target elements need to be considered; calcium, potassium, argon and chlorine. Table I lists the relevant reactions for argon isotopes in neutron irradiated minerals. Each argon isotope is considered in turn.

(i) Argon-40:

Brereton (1970) found that two components of $^40\text{Ar}$ were produced in the reactor, namely from Ca and K. A third possible effect arises from the removal of argon by neutron interactions. Mitchell (1968) showed that to a first approximation the $^40\text{Ar}$ from Ca is negligibly small due to the low abundance of $^{43}\text{Ca}$ from which it is produced. $^40\text{Ar}$ from K is however, more serious.
The production ratio for $^{40}\text{Ar}/^{39}\text{Ar}$ from neutrons has been calculated by three workers; Brereton (1970), Mitchell (1968) and Berger and York (1970). The highest value of $(3.14\pm 0.7) \times 10^{-2}$ obtained by the latter workers was used in the calculations below. In fact the results differed by a factor of 2.5 which may be due to the large positive Q-value of the reaction coupled with a softer neutron spectrum. Turner (1971a) shows that this contribution can be kept small relative to the radiometric $^{40}\text{Ar}$ by a suitable choice of irradiation parameters as can be seen in fig. 1. The condition for K-derived $^{40}\text{Ar}$ to be less than 1% of the radiogenic $^{40}\text{Ar}$ is:

$$^{40}\text{Ar}/^{39}\text{Ar} \geq 100 \cdot (3.14\pm 0.7) \times 10^{-2} \geq 3$$

(5)

correspondingly, from equation (6);

$$\frac{e^{t/T-1}}{J} \geq 3 \quad \text{or,}$$

$$J \leq \frac{e^{t/T-1}}{3}$$

(6)

and from (4a),

$$F \leq 5.5 \times 10^{19} (e^{t/T-1}) \ n \cdot cm^{-2}$$

(7)

(ii) Argon-$^{39}$:

The interference of K-derived $^{39}\text{Ar}$ comes from calcium. The amount of Ca-derived $^{39}\text{Ar}$ may be compared with that produced from potassium (on which the dating method depends) as follows:

$$^{39}\text{Ar}_k = 39\sigma_k \cdot K \cdot F$$

(8)
where; $39\sigma_k$ = effective cross-section for the $^{39}K(n, p)^{39}Ar$ reaction for neutrons with a $^{235}U$ fission spectrum, and

$k = subscript relating to potassium.$

Similarly, one may write:

$$39Ar_{Ca} = 39\sigma_{Ca}\cdot Ca\cdot F \quad (9)$$

$39\sigma_k$ has been estimated from monitor measurements (Turner, 1970a) as $71^{±4}$ mb. $39\sigma_{Ca}$ has been calculated from the ratio $39\sigma_{Ca}/37\sigma_{Ca}$ (Brereton, 1970 and Berger et al., 1970) and the value $37\sigma_{Ca}$ (Turner, 1970a and 1970b) was given as $(2.2±0.5)x10^{-2}$ mb.

Thus dividing equation (9) into (8) and substituting values yields:

$$\frac{39Ar_k}{39Ar_{Ca}} = (3.2±0.7) x 10^{-3} \cdot \frac{K}{Ca} \quad (10)$$

This ratio is independent of the integrated neutron flux and depends solely on the $K/Ca$ ratio. To express this in another way; for the $39Ar_{Ca}$ to be less than, say, 1% of the $39Ar_k$ then:

$$\frac{K}{Ca} = 0.032^{±0.007}$$

This condition was easily satisfied for the young, highly potassic rocks analysed in the present work.

The condition that sufficient $39Ar$ be produced during
the irradiation is relevant to the discussion of interference and is considered here. Sufficient $^{39}$Ar can only be gauged against other peaks, particularly the adjacent mass 40 peak where attenuation of the ion beam produces a wing effect spreading over adjacent mass numbers. Turner (1971) considers that in practice a $^{40}$Ar/$^{39}$Ar ratio greater than 300 is undesirable and he derives a condition in which the $^{40}$Ar/$^{39}$Ar ratio is set arbitrarily at this value. From equation (1) sufficient $^{39}$Ar production can be expressed as:

$$\frac{^{40}\text{Ar}}{^{39}\text{Ar}} = \frac{e^{t/T-1}}{J} \leq 300$$

from which

$$J \geq \frac{e^{t/T-1}}{300}$$

for the Herald core

$$F \geq 5.5 \times 10^{17} (e^{t/T-1}) \text{ n.cm}^{-2}$$

(iii) Argon-38:

$^{38}$Ar is produced from Ca, K and Cl as well as being naturally present as an atmospheric component (the atmospheric $^{40}$Ar/$^{38}$Ar is 1581). Brereton (1970) suggested that it would be useful to employ a $^{40}$Ar/$^{38}$Ar dating technique ($^{39}$K(n,d)$^{38}$Ar reaction) as a semi-quantitative check on the $^{40}$Ar/$^{39}$Ar method. However, very small quantities of Cl present would make this unreliable by the $^{37}$Cl(n,$\gamma$,$^{38}$Ar) reaction. Just how much Cl in relation to K is derived below. By analogy to equation (8)
\[ 3^{\text{Ar}} = 38\sigma_k \cdot K \cdot F \]  \hspace{1cm} (13)

and \[ 3^{\text{Ar}} = 38\sigma_{\text{Cl}} \cdot (37\text{Cl}/\text{Cl}) \cdot F_{\text{th}} \]  \hspace{1cm} (14)

where \[ 38\sigma_k = \text{cross-section (effective) for } 39\text{K}(n,d)^{38}\text{Ar} \text{ reaction} \]

\[ 38\sigma_{\text{Cl}} = \text{cross-section for the } 37\text{Cl}(n,\gamma,p)^{38}\text{Ar} \text{ reaction} \]

\[ F_{\text{th}} = \text{thermal neutron flux} \]

Combining equations (13) and (14) such that \[ 3^{\text{Ar}} = 38^{\text{Ar}}_{\text{Cl}} \] and rearranging yields:

\[ \frac{K}{\text{Cl}} = \frac{38\sigma_{\text{Cl}} \cdot 37\text{Cl} \cdot F_{\text{th}}}{38\sigma_k \cdot \text{Cl} \cdot F} \]  \hspace{1cm} (15)

when assigned the appropriate values namely; \[ 38\sigma_{\text{Cl}} = 430 \text{ mb}, \]

\[ 38\sigma_k = 0.71 \text{ mb}, \]

\[ 37\text{Cl}/\text{Cl} = 0.24 \text{ and } F_{\text{th}}/F = 1.7 \text{ then:} \]

\[ \frac{K}{\text{Cl}} = 242 \]

or 0.41% Cl will produce the same amount of \( 3^{\text{Ar}} \) as compared to 100% K. The value \[ F_{\text{th}}/F \] is given for the Herald reactor.

Because of the interference from small amounts of \( 37\text{Cl} \) a check on the atmospheric correction likewise cannot be made.

(iv) Argon-37:

\( ^{37}\text{Ar} \) is almost entirely produced from the \( ^{40}\text{Ca}(n,\alpha)^{37}\text{Ar} \) reaction (Brereton, 1970 has shown the \( ^{39}\text{K}(n,\alpha)^{37}\text{Ar} \) reaction to be negligible). This being the case, the \( ^{37}\text{Ar} \) can be used to measure the Ca content of the sample. The reactions producing interference from Ca are \( ^{42}\text{Ca}(n,\alpha)^{39}\text{Ar} \) and \( ^{40}\text{Ca}(n,\alpha)^{36}\text{Ar} \) (see table 1 and below).
Corrections for the Ca-derived $^{36}\text{Ar}$ and $^{39}\text{Ar}$ can be made on the basis of $^{36}\text{Ar}/^{37}\text{Ar}$ and $^{39}\text{Ar}/^{37}\text{Ar}$ ratios either from the inclusion of a calcium monitor during the irradiation (Turner, 1971b) or from the samples themselves (Turner, 1970a).

(v) Argon-$^{36}$:

Although Mitchell (1968) cites four reactions in which $^{36}\text{Ar}$ is produced, it is only the $^{40}\text{Ca}(n,n\alpha)^{36}\text{Ar}$ reaction which is significant. The importance of $^{36}\text{Ar}$ interference is related to the use of $^{36}\text{Ar}$ in the correction procedure for atmospheric $^{40}\text{Ar}$ (atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ ratio = 295$^{\pm}$5). The effect of this interference on the correction for atmospheric $^{40}\text{Ar}$ may be kept to 1% or less of the $^{40}\text{Ar}/^{39}\text{Ar}$ ratio (Turner, 1971a). The condition requires that 295$^{\pm}$5 times the $^{36}\text{Ar}$ from calcium be less than 1% of the $^{40}\text{Ar}$ in the sample or that:

$$\frac{^{40}\text{Ar}}{^{36}\text{Ar}}_{\text{Ca}} \geq 29550$$  \hspace{1cm} (16)

Rewriting equation (2)

$$^{40}\text{Ar} = K \cdot \frac{^{40}\text{K}}{K} \cdot \frac{\lambda_{s}(e^{t/T}-1)}{\lambda}$$

and by analogy to equation (8)

$$^{36}\text{Ar}_{\text{Ca}} = ^{36}\text{Ar} \cdot \frac{\text{Ca}}{\text{F}}$$  \hspace{1cm} (17)

Combining equations (2), (16) and (17)

$$\frac{^{40}\text{Ar}}{^{36}\text{Ar}}_{\text{Ca}} = \frac{1}{^{36}\text{Ar} \cdot \frac{\text{Ca}}{\text{F}}} \cdot K \cdot \frac{^{40}\text{K}}{K} \cdot \frac{\lambda_{s}(e^{t/T}-1)}{\lambda} \geq 29550$$
and rearranging

$$F = \frac{1}{\beta \delta \sigma_{\text{Ca}}} \cdot \frac{\lambda_{\text{Ca}}}{\lambda_{\text{K}}} \cdot 40 \lambda_{\text{K}} \cdot \frac{e^{(t/T-1)}}{0.2955}.$$  \hspace{1cm} (18)

$\delta \sigma_{\text{Ca}}$ is obtained from the relative production rates of $^{36}\text{Ar}$ and $^{37}\text{Ar}$ (Brereton, 1970) and the effective cross-section for $^{37}\text{Ar}$ from calcium (2875 mb), giving the value $7 \times 10^{-3}$ mb.

Substituting the appropriate values into equation (17) yields:

$$F = 6.3 \times 10^{19} \cdot \frac{\lambda_{\text{K}}}{\lambda_{\text{Ca}}} \cdot \frac{e^{(t/T-1)}}{n \cdot cm^{-2}}.$$ \hspace{1cm} (19)

This condition was met by all of the samples analysed; for example see fig. 1 and appendix.

(vi) Argon Removal:

The removal of argon isotopes through neutron interactions is usually assumed to be minimal, Turner (1971a), Brereton (1970) and Mitchell (1968). For example, given a cross-section of 100 b and a fluence of $10^{20}$ n.cm$^{-2}$, only 1% of the isotope would be removed. The thermal cross-sections for $^{36}\text{Ar}$, $^{38}\text{Ar}$ and $^{40}\text{Ar}$ are 6, 0.8 and 0.53 b respectively and with a typical thermal flux of $10^{16}$ n.cm$^{-2}$ this interference may be ignored.

(vii) Contamination from cosmic rays:

This source of interference might arise from the cosmic ray production of $^{36}\text{Cl}$ (half-life = $3.08 \times 10^5$ years, decays to $^{36}\text{Ar}$) in samples by the following reactions $^{39}\text{K}(n,\alpha)^{36}\text{Cl}$, $^{35}\text{Cl}(n,\gamma)^{36}\text{Cl}$ and $^{33}\text{S}(\alpha,\gamma)^{36}\text{Cl}$ (Lambert et al., 1966). However the production rate of $^{36}\text{Cl}$ by cosmic ray neutrons is too low to account for any significant amount of $^{36}\text{Ar}$ (Davis Jr. et al., 1955).
2.3 $^{39}\text{Ar}$ recoil

This effect has been considered by Mitchell (Ph. D. thesis), Turner and Cadogan (1974) and Huneke and Smith (1976). The recoil following the $^{39}\text{K}(n,p)^{39}\text{Ar}$ reaction is capable of producing spatial translations of around 0.1 $\mu$m which has been thought to account for anomalies in the age spectra of Lunar samples and meteorites. Specifically, a sharp decrease at high temperature in the $^{40}\text{Ar}/^{39}\text{Ar}$ ratio or a monotonic decrease over the whole for fine-grained samples (Turner et al., 1971). The total gas $^{40}\text{Ar}/^{39}\text{Ar}$ ratio in the latter case usually leads to a meaningful age which suggests a redistribution of the $^{40}\text{Ar}$ or $^{39}\text{Ar}$ or both.

$^{40}\text{Ar}$ has an energy of around 23 eV after electron capture by the $^{40}\text{K}$ atom. This may lead to a displacement of a few inter-atomic distances which is sharp contrast to 0.08 $\mu$m (300keV), the $^{39}\text{Ar}$ displacement. From this the $^{40}\text{Ar}/^{39}\text{Ar}$ ratio can be expected to vary if the K-concentration is discontinuous in the order of 0.08 $\mu$m. Thus if the K-phases in the samples are coarse-grained then most of the $^{39}\text{Ar}$ will recoil into sites equivalent to those containing $^{39}\text{K}$. 
2.4 The effect of Extraneous Argon on the dating of young rocks

Damon (1968) and Dalrymple and Lanphere (1969b) divide extraneous argon into two components; excess and inherited. The latter authors define excess as $^{40}$Ar that is somehow incorporated into rocks and minerals by processes (for example, diffusion) other than in situ radioactive decay of $^{40}$K. Any $^{40}$Ar that is produced within mineral grains by the decay of $^{40}$K before the event being dated or inadvertently introduced in the laboratory is termed as inherited.

(i) Excess:

Dalrymple and Lanphere (1969a) have concluded that; "The occurrence of excess $^{40}$Ar is too rare to provide a satisfactory explanation for very many K-Ar ages that appear anomalous."

The case is examined here for young volcanic rocks where it is assumed that no subsequent metamorphic events have taken place. Evernden and Curtis (1965) report on three historic lavas from Alaska, Italy and New Guinea on which determinations of feldspars led to 'zero' ages. Unfortunately, the analytical data is absent from this paper and does not allow upper limits for the amount of excess argon to be determined. Dalrymple (1967) calculated upper limits for excess $^{40}$Ar on sanidine samples from California by assuming that the apparent ages were all due to excess $^{40}$Ar (ages ranged between 6,000 and 12,000 years). His conclusions were that for older samples, these amounts were purely routine and would not affect the K-Ar measurements, further emphasising that the study provided no evidence for the presence of excess $^{40}$Ar. Later work by Dalrymple (1969b) revealed excess $^{40}$Ar in five, and excess $^{36}$Ar in three, of twenty-six historic subaerial lava flows studied. The samples
had ratios either higher or lower than the atmospheric value at the 95% confidence level. He suggests that the origin of the excess $^{36}\text{Ar}$ may be due either to the incorporation of primitive argon that had been stored in the mantle in very low K environments or the enrichment in $^{36}\text{Ar}$ as atmospheric argon diffused into the rocks as they cooled. Cherdynsev and Shitov (1967) have found that active volcanic gases have atmospheric argon ratios 1 to 7% lower. Damon et al. (1967) have reported concentrations of excess $^{40}\text{Ar}$ in plagioclase phenocrystals from a late Pliocene basalt. Krummenacher (1970), in attempting to ascertain the causes of anomalous ratios by using $^{36}\text{Ar}/^{38}\text{Ar}$ in addition to $^{40}\text{Ar}/^{36}\text{Ar}$, concluded that of twenty-seven samples, nine contained excess in either $^{36}\text{Ar}$ or $^{40}\text{Ar}$. McDougall et al. (1969) and McDougall (1970) found excess radiogenic argon in subaerial basalts from the Auckland volcanic field and on the young volcanic island of Réunion respectively. The values obtained for the excess $^{40}\text{Ar}$ were between $2 \times 10^{-9}$ and $10^{-8}$ ccSTP/g in the former and $2 \times 10^{-9}$ rising to $7 \times 10^{-9}$ ccSTP/g in younger samples in the latter. The earlier gave rise to the development of a technique described later, namely the isochron correlation plot, to examine the K-Ar data in more detail. It is because of the findings of these workers that the isochron plot was regarded as a more reliable age indicator. The argument for this is discussed in the proceeding two sections.

(ii) Inherited Argon:

Inherited can come from two principal sources; the laboratory during handling and foreign material incorporated during implantation. Xenolithic or xenocrystic material is

* $^{40}\text{Ar}/^{36}\text{Ar}$.
particularly a problem when handling young samples and is discussed in connection with sample 191 in Chapter 5.
The stepwise degassing experiment is performed by taking the sample under analysis through a series of heating steps in a furnace. The gas is analysed successively in a mass spectrometer where the isotopes $^{40}\text{Ar}$, $^{39}\text{Ar}$ and $^{36}\text{Ar}$ are measured. After various corrections which are described in detail later, the data is plotted in the manner shown in fig 15, the $^{40}\text{Ar}/^{39}\text{Ar}$ ratio plotted against the percentage of $^{39}\text{Ar}$ released.
2.5 Argon Release Patterns and Isochron Plots

Data from the stepwise degassing experiment may be plotted as an argon release pattern in which the fraction of $^{39}\text{Ar}$ released (abscissa) is plotted against the $^{40}\text{Ar} / ^{39}\text{Ar}$ ratio (ordinate) for each temperature step (see for example fig. 14). This type of plot has been used extensively by workers such as Turner et al. (1966), Turner (1968 and 1970a) and Lanphere and Dalrymple (1971). It is preferred to the non-quantitative type of plot used by Fitch et al. (1969) and Brereton (1972) in which each step is plotted with equal value and the relative size of gas fractions are not readily apparent.

The effect of a stepwise heating experiment is to release argon differentially from different sites within the sample. Chronological information can be extracted from the release pattern if it is assumed that the $^{39}\text{Ar}$ is located essentially in the same crystal lattice sites as the K from which it was produced and that variations in $^{40}\text{Ar} / ^{39}\text{Ar}$ be taken to reflect real variations in the $^{40}\text{Ar}/K$ throughout the sample. For example, variations can commonly arise from argon loss. If the ratio is found not to vary, it may be used as a criterion to identify undisturbed samples but does not necessarily lead to a correct age (Lanphere and Dalrymple, 1971).

Turner (1968) calculated theoretical $^{40}\text{Ar} / ^{39}\text{Ar}$ release curves for diffusive argon loss from samples of various grain geometries but points out that the potential usefulness of the method does not depend on any detailed theoretical model although the analysis is useful for interpreting experimental data. In a recent paper, Turner (1976) summarises and discusses
four commonly observed types of release pattern and reviews
the method which has been applied with great success to many
meteorites and Lunar samples. See for example: Turner (1970a
and b), Turner (1971a and b), Turner et al. (1971), Hussain et
al. (1971), Davis et al. (1971), Turner (1972), Turner et al.
(1972), Podosek et al. (1972), York et al. (1972), Kirsten et
al. (1972), Stettler et al. (1972), Huneke et al. (1973),
Podosek and Huneke (1973a and b), Turner and Cadogan (1973),
Stettler et al. (1973), Turner et al. (1973a and b), Jessberger

Although some Lunar samples have spectra that differ
significantly from the model release patterns and their inter-
pretation is uncertain, crystallization ages and thermal
histories have been derived from the spectra and for the Lunar
samples the inferred K-Ar ages are consistent with the available
Rb-Sr data.

Fitch et al. (1969) developed a quantitative model for the
interpretation of $^{40}\text{Ar}/^{39}\text{Ar}$ of rocks and minerals from complex
terrains but unfortunately did not report on samples of known
geology and age to test this model. Lanphere and Dalrymple (1971)
studied ten terrestrial samples whose geologic history was known
but whose conventional ages were incorrect because of extraneous
argon and argon loss. They obtained age spectra that generally
did not fit the models of Turner and Fitch et al. and in no
case recovered the known crystallization ages. Apart from the
work of Fitch et al. (1969) and Turner (1971), both of whom
cite examples of undisturbed terrestrial samples, Dalrymple
and Lanphere (1973) have also made an important study of eleven
such samples. Their findings suggest that the age spectra of
all the samples agreed reasonably consistently with the models of Turner and Fitch et al. Small departures were felt to be either due to the sample not being totally undisturbed or to gas fractions being too small (less than 2%). On the latter point they recommend that 4 to 5% would be a safer limit and go on to indicate that most anomalous increments occur before reaching the 'plateau' and may be consistent with argon loss from the sample. Their final conclusions were that the age spectra of their samples differed significantly from those found for disturbed terrestrial samples of Fitch et al. (1969) and Lanphere and Dalrymple (1971) and that the study could distinguish undisturbed from disturbed rocks and/or detect argon loss or extraneous argon present. It appears then, that although the technique is a valuable tool for complex areas, the interpretation of complex spectra is still uncertain.

The greatest potential for the method as applied to young rocks relates to the ability to separate and identify excess and air argon. How the excess may be identified varies according to how it is located in the sample. If it is loosely bound then the spectra may be exemplified by high $^{40}\text{Ar}/^{39}\text{Ar}$ ratios at low temperatures but if it is located in highly retentive sites then high ratios will occur in the high temperature steps. If, however, it is homogeneous throughout the sample then the excess component will increase all ratios equally and thus be unidentifiable unless, of course, reference can be made to other samples.

Merrihue and Turner (1966) suggested the possibility of separating the atmospheric and radiogenic components by the stepwise degassing technique. The results of Fitch et al. (1969) and Mitchell et al. (1968) suggest that the bulk of atmospheric
contamination is released during the low temperature steps. If the standard air correction is applied then the associated error is reduced at high temperatures. Unfortunately, the recovery of ages depends on the standard air correction which assumes that the present day $^{40}\text{Ar}/^{36}\text{Ar}$ value of 295.5 was the same at the time of crystallization of the rock as it is now. In addition, comments made by Dodson et al. (in answer to Fitch et al. (1969) pointed out the consistent inverse relationship between the apparent ages and the atmospheric contamination for a number of samples. The extent of the correlation possibly reflecting the degree to which the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio differs from that of the atmospheric. They also pointed out a further uncertainty as to whether or not the $^{40}\text{Ar}/^{36}\text{Ar}$ in the 'atmospheric' argon was in fact a constant at all heating steps. On the basis of this it was decided that the isotope correlation method, described in the latter part of this section, which does not make an assumption for the atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ ratio should be used as an age indicator.

The $^{40}\text{Ar}/^{36}\text{Ar}$ versus $^{39}\text{Ar}/^{36}\text{Ar}$ isotope correlation diagram developed by Merrihue and Turner (1966) is equivalent to the plot developed by McDougall et al. (1969) ($^{39}\text{Ar}$ is replaced by $^{40}\text{K}$) with the essential difference being that the points were obtained from the stepwise degassing of a single specimen and not from a number of geologically equivalent samples. The method for presenting K-Ar data is described first.

Thus the plot of McDougall et al. (1969) for the treatment of conventional data represented $^{40}\text{Ar}/^{36}\text{Ar}$ (ordinate) against $^{40}\text{K}/^{36}\text{Ar}$ (abscissa) where the slope formed by the K-Ar data points was proportional to the sample's age. The method assumed
that the atmospheric component could be added to the samples either in situ or in the laboratory after the 'clock' was set. Mussett and Dalrymple (1968) showed that the latter source of contamination did not arise to any significant extent whilst handling the samples. The interpretation of Hayatsu and Carmichael (1970), who incorporated the findings of Mussett and Dalrymple (1968), was analogous to that of the Rb-Sr isochron method; the $^{36}\text{Ar}$ was assumed to be in the sample from the beginning and all the argon was equilibrated to yield an homogeneous $^{40}\text{Ar}/^{36}\text{Ar}$ ratio throughout the samples when the clock was set. Using this method, their isochrons yielded initial ratios of 380, 488 and 275. Roddick and Farrar (1971) obtained initial ratios of 1200, 200 and a negative value. These types of plot have been summarised by Shafiqullah and Damon (1974).

The treatment of $^{39}\text{Ar}-^{40}\text{Ar}$ data involves plotting the measured ratios, $^{40}\text{Ar}/^{36}\text{Ar}$ (ordinate) and $^{39}\text{Ar}/^{36}\text{Ar}$ (abscissa) for each gas increment. Interfering isotopes generated from nuclear reactions are assumed to be absent (or are corrected for). The slope of the isochron is determined by a least squares fit to the data and several two-error equations have been developed for this purpose; the York (1969) equation, allowing for correlated errors, makes the method more suitable for the $^{40}\text{Ar}/^{39}\text{Ar}$ isochron analysis. The reason for this being that the $^{36}\text{Ar}$ measured in the gas fraction is often small and subject to large errors. The dominating uncertainties in the $^{36}\text{Ar}$ give rise to highly and positively correlated errors. $^{36}\text{Ar}$ error lines can be defined which run subparallel to the isochron plot (providing the intercept is relatively close to zero) passing,
in each case, through individual data points and the origin. An error in $^{36}\text{Ar}$ will tend to shift data points along such lines and is similar in all respects to the $^{20}\text{Pb}$ error line employed in Pb-Pb analyses. Thus a large error in $^{36}\text{Ar}$ will tend to shift points along the isochron and have a minimal effect on its slope. Brooks et al. (1972) have pointed out that any least squares regression must have a normal distribution of errors which, in the case of $^{40}\text{Ar}/^{39}\text{Ar}$ analyses whose results are not exactly reproducible, has to be an assumption. That is, it ignores real variations in $^{40}\text{Ar}/K$. Dalrymple et al. (1973) agree that a test of normality is required but feel that because of the time consuming nature of the experiments it is more profitable to work on a greater variety of samples and accept the assumption without verification. It is therefore not possible to apply the usual tests for goodness of fit (Crow et al., 1960 and York, 1969) and distinguish between isochrons (resulting from random error) and 'errorchrons' which have additional scatter resulting from geological error (Brooks et al., 1972) or experimental artifacts (Huneke, 1975).

The method of York (1969), used in this work, weights each data point inversely to the square of its standard deviation involving the calculation of a correlation coefficient for each point. That is:

$$r = \frac{(1-S_{^{40}\text{Ar}/^{36}\text{Ar}})+(1-S_{^{39}\text{Ar}/^{36}\text{Ar}})}{2}$$

(20)

where the standard deviations ($S$) are in percent. The $^{40}\text{Ar}$ peak was used as a reference and was assumed to have zero error and thus (20) becomes:

- 24 -
\[
 r = 1 + \frac{(1 - S_{39}/S_{36})}{2} \tag{21}
\]

for this work.
2.6 **Analytical Precision:**

Estimates on the analytical precision to assess the quality of individual results are necessary if inter-comparisons with age data, obtained by other methods, are to be made. Berger and York (1970) and Dalrymple and Lanphere (1971) have introduced methods of estimating analytical errors in the $^{39}$Ar-$^{40}$Ar technique. The errors quoted in this work, based on these methods, have been calculated by the equations derived below.

Analytical errors arise in the following ways:
(i) From measured isotopic ratios particularly involving $^{36}$Ar.
(ii) From uncertainty in the monitor age and variations in neutron fluence between monitor and sample.

Taking the age equation:

$$ t = T \ln \left( 1 + \frac{^{40}Ar}{^{39}Ar} J \right) $$

let $ R = \frac{^{40}Ar}{^{39}Ar} $ and $ y = R \cdot J $  

then $ \frac{\sigma^2(y)}{y^2} = \frac{\sigma^2(R)}{R^2} + \frac{\sigma^2(J)}{J^2} $  

and if $ x = \ln(1+y) $, the absolute error in $x$ is:

$$ \sigma^2(x) = \frac{(1/1+y)^2 \cdot \sigma^2(y)}{} $$(23)

combining the last two equations gives:

$$ \sigma^2(x) = \frac{R^2 \cdot J^2 \left( \frac{\sigma^2(R)}{R^2} + \frac{\sigma^2(J)}{J^2} \right)}{(1+R \cdot J)^2} $$

(24)
Therefore the fractional error in $t$ is:

$$\frac{\sigma^2(t)}{t^2} = \frac{T^2 R^2 J^2 \left( \left( \frac{\sigma^2(R)}{R^2} \right) + \left( \frac{\sigma^2(J)}{J^2} \right) \right)}{t^2 (1 + R \cdot J)^2}$$ (25)

This equation is equivalent to that quoted by Dalrymple and Lanphere (1969).

In this work errors are quoted at one standard deviation and have been assigned considering only the errors in isotopic ratios.

Further errors occur from: the monitor age ($18.6^{+0.7}_{-0.3} \times 10^6$ years), the flux factors (varying from 0.980 to 0.993 over the phial; see fig 11), and the decay constants (see table 1).
CHAPTER 3

Experimental

3.1 Mass Spectrometry

3.1.1 Introduction

The Mass Spectrometer used in this work is a 90° sector focussing instrument of 6 cm radius (V.G. Micromass 6). Power supply systems, ion source, magnet and detectors are described in the proceeding sections.

The instrument is capable of detecting masses from 2 upwards and has an upper sensitivity of 100 amps/torr. The upper limit of resolving power is 400 and is adjustable. Two ion sources were available, the open type allowing direct insertion of the sample into the ionization chamber being used for the present work. Both a Faraday Collector and electron multiplier were attached to the instrument; for maximum sensitivity the Faraday plate was withdrawn from the ion beam and the electron multiplier used throughout. Peak scanning was done magnetically, the field being varied continuously to 'sweep' the peaks. A peak switching facility was not available. A potentiometric chart recorder was used to record the mass spectra which were subsequently analysed using a 'pencil follower' digitizer.
3.1.2 **Electronics and Data Handling**

Figure 3 represents a schematic layout of the mass spectrometer in which the following instruments occur.

(i) **Chopper Amplifier**:

This is a solid-state amplifier designed for full scale (F.S.) measurements of $3 \times 10^{-14}$ to $10^{-6}$. The peak-to-peak noise corresponds to around $3 \times 10^{-16}$ amps (0.4 s time constant) with a drift of less than $10^{-15}$ amps/hr and a linearity of less than 0.4%. This is close to the limiting Johnson noise for the 10¹¹ ohm input resistor.

The remote head is connected directly to the current source (Faraday plate) and a multicore cable from the main amplifier enables the gain and the response of the system to be selected. The chart recorder, used to record the scans, makes use of the 0-100mV output into a load of 10kohms.

(ii) **Amplifier (FA2)**:

The FA2 is principally used in conjunction with the electron multiplier from which it converts the output current into a suitable voltage for driving the chart recorder. It's conversion range being $10^{-4}$ to $10^{-9}$ amps yielding a F.S. of 10V or 100mV at the recorder socket. With a gain of around $10^3$, a 10⁸ ohm input resistor and a 0.3s time constant, the noise level is around $10^{-16}$ amps.

(iii) **Emission Control**:

This samples the trap current in the ion source and a feedback circuit regulates the filament current to preset trap values of 4, 20, 100 and 200 μamps. The latter value was employed in this work to obtain maximum sensitivity. A protection circuit prevents the filament current from rising.
above 4.2A in case of an emission regulation failure. In addition to this the unit was linked to a trip on the ion pump power supply which cuts off power to the emission regulator in the event of rising pressure.

(iv) **Multiplier Supply:**

An output range of 0-5kV was provided but in practice 3kV was normally used corresponding to a gain in the electron multiplier of around $10^3$. A useful gain in sensitivity could be got at 3.5kV, problems were encountered at these higher settings as the gain stability was found to degrade with increasing output voltage.

(v) **Voltage Scan Unit:**

This unit provides a means of controlling either the magnet current or the ion accelerating voltage. An output voltage, variable in the range of 0-10V or 0 to -10V, was used for scanning the accelerating voltage or electromagnet current. Possible scan times range from $10^3$ to 0.1s; in practice, a typical scan for argon took 100s. The mass region of the scan and the width of the scan were also adjustable.

(vi) **Programme Power Supply:**

This supplies EHT for the ion acceleration voltage and may be preset or controlled by the scan control unit. The drive of 0-10V programmes the ion acceleration voltage over the range 20V to 5kV. In practice it was preset at 1kV.

(vii) **Electromagnet Supply:**

This supplies the magnet with a variable current of 0 to 5A which allows scanning to be made automatically, single or repetitive.

(viii) **Analyser Section:**
FIG 4 — ION SOURCE

end view with magnets removed
As has been stated earlier the spectrometer analyser consists of a 90° sector of 6cm radius and 114(4½") diameter Fc64 copper gasket flanges are welded to either end. The ion source flange has eight ceramic feedthrough connections.

(ix) Ion Source:

This has an open construction for so called, residual gas analysis. The construction materials are primarily alumina and stainless steel with the electrodes aligned on precision ground ceramic rods. This assembly is mounted on the source flange with two 10BA screws (fig.4). The electrode leads run through to the ceramic feedthroughs by means of connecting blocks and the complete assembly may be removed from the flange by withdrawing the mounting screws and slackening the 12BA clamping screws in the connecting blocks. The two small permanent magnets mounted on the filament mounting plate are for focussing the electron beam to maximize ionization. The source slit widths are 0.25mm.

The following adjustments are available for setting the source up; the half-plate voltage for beam centring, the ion repellor voltage and magnetic compensation. The half-plate voltage is applied to the pair of electrodes and is used to align the ion beam with the apertures in the ion beam path. The ion repellor voltage is applied to an electrode close to the electron beam and is adjusted to optimise the focussing of the ions as they are impelled from the ion source chamber. These two adjustments are proportional to the EHT output; the half-plate being between 0 and 8% positive and the ion repellor between 92 to 100% positive.

(x) Resolving Section:
Fig 5: Typical example of a single mass spectrometric scan (from A to B) of mass peaks 40 to 36. One division of the mass 40 peak corresponds to $8 \times 10^{-10}$ ccSTP $^{40}$Ar, one division of the other peaks corresponds to $8 \times 10^{-11}$ ccSTP $^{40}$Ar. The scan time is 100s.
The construction is similar to that of the ion source consisting of an externally adjustable resolving slit and an electron suppressor, the latter being earthed when the electron multiplier is in use. The resolving slit width used throughout was found to be optimum at 1.0mm giving a reduced resolution (60 approximately) but yielding a flat-topped peak and a spectrum in which roughly equal times were donated to peak tops and zeros. Greater resolution for the same sensitivity could be obtained with the width at 0.25mm and still more at 0.05mm but the latter gave a x3 loss in sensitivity.

(xi) **Electron Multiplier Detector:**

The E.M. is a 17-stage venetian blind type with beryllium oxide/copper dynodes glazed to an Fc64 flange for attachment to the analyser. A magnetic shield is fitted and a resistor chain built into the socket (contained inside the end of the shield) to give the voltages required by the dynode chain. Two BNC sockets are mounted in the end of the shield; one being the collector output and the other, the HT input.

(xii) **Kipp and Zonen (BD8) Potentiometric Chart Recorder:**

This is of the flat-bed variety based on automatic potentiometric compensation. The instrument has an f.s.d. of 20cm with a response time of 0.6s, the accuracy is given at 0.3% f.s.d. and linearity at less than 0.3% f.s.d. The stability is 0.1μV/°C zero drift and the input impedance is 1Mohm.

The way in which the recorder was used was to set the scan% control so that repetitive scans could be made between masses 35 and 40. This mode was employed when the sample was present in the spectrometer. After pumping, one scan was made to measure possible background interference. Peaks were analysed using a DMAC pen follower with a teletype. A programme was then used to
convert this data to peak heights versus time and editing could be carried out at this stage. A peak interpolation programme calculated peak heights at zero time (i.e. the time at which the sample was admitted to the spectrometer) and subsequently stored the information on a disc file. Further editing could intervene before a final programme calculated the ages, including corrections for interfering isotopes, radioactive decay, blanks and air corrections if so desired.
FIG 7
GAS EXTRATION SYSTEM

PLAN

MS.6

V5
V4
V3
V1
V2
V10
NP10

Diff. Pump (C) = (A)

Lunar Spectrometer

V6

V8

V7

GP50 Furnace

to IP1 (B)

FURNACE

ELEVATION

Pirani gauge
3.2 Argon Extraction and Purification System

A complete layout of the system may be seen in figs. 6 and 7 and plate 1.

3.2.1 Components, Pumping and Bakeout

A system was required that would not only operate at UHV but also that could be effectively baked out. Thus its construction was predominantly of stainless steel; the sole glass components being the sample loading 'tree', charcoal 'finger' and litre calibration bottle. In each case, the glass-ware was attached to the stainless steel joints by means of a kovar seal.

The stainless steel joints fell into two categories; those of the 45° knife edge type clamping a high purity copper gasket and those which clamped a gold (99%) O-ring between two flat-machined surfaces. Three sizes of the former were used in construction; (large) P64 for the spectrometer flanges, standard 2½" for GP50 getter attachment and finally, very useful Mini-conflat seals were incorporated almost exclusively throughout the system. Gold O-rings were employed where continual demounting of the loading assembly was required or where a non-standard size of component presented itself.

Metal valves, whether used singly or in a back-to-back configuration, were developed and constructed in the department for the system and followed a general design indicated in fig. 8. The principle and mode of operation are described briefly: The volume A is sealed by the gold O-ring 5 and the HCCF copper valve seat (whose position is maintained by the valve closing screw 2 at 15 ft-lbs). When the closing screw is withdrawn the bellows assembly 7 contracts, allowing A to connect with volume B. The gasket pressure plate protects the delicate corrugations...
1 — position of fixing bolts
2 — valve closing screw
3 — valve cap
4 — gasket pressure plate
5 — gold wire seal
6 — HCCF copper valve seat
7 — bellows assembly
8 — keyway
9 — bellows
by keying-in the bellows' shaft, preventing torsional strain and limiting the contraction to 0.60". The lubricating bush ensures free operation of the valve.

Electrical connections were made by means of copper electrodes fed through ceramic seals. These were either of a multiple (source flange of the MS6) or single heavy-duty type capable of withstanding currents of up to 100A during furnace operation, earthing in the latter case being made to the frame.

Pumping of the system to attain UHV can be best explained with reference to fig. 7. The arrangement is such that both the apparatus comprising the 'Lunar' spectrometer and gas extraction systems (1) and (2) and the system under discussion can be pumped to HV by the common use of line AB. Thus a Metrovac (A033C) diffusion pump with liquid nitrogen cold trap, was backed by a Metrovac rotary pump, the arrangement achieving pressures of around $2\times10^{-6}$ torr (monitored by a Pirani gauge) which were amply low enough to introduce one of the ion pumps. In this case the ion pump IP 1 was switched in and as soon as it could sustain and start to reduce the pressure (about 10 mins.) valve V9 was closed. In normal use the ion pump IP 2 maintained the gas extraction system at UHV except when pumping out the furnace between extractions, although initially the system had to be pumped out via the furnace before being isolated by valve V4.

The Getter Ion pumps (IP 1 and 2) were of the Ferranti type FJD 15 with unslotted cathodes. In use these were found to be less efficient than the smaller capacity PJAD 8 l/s pump connected to the 'Lunar' spectrometer. However, both pumps could be run from the same power supply, requiring 7kV for
their operation. A meter measured the sum of the currents taken by the two pumps.

The getter ion pumps use a Penning discharge in a magnetic field. The ionisation causes a sputtering of the material (Ti) by ion bombardment, the deposited film then sorbs the active gases onto its surfaces and the rare gases are buried by continuous deposition. The pump may be started from around $10^{-5}\text{torr}$ but at this pressure the pump dissipates its maximum power and the discharge does not remain between cathode and anode. The discharge exerts an effect on the walls of the pump causing desorption which results in an initial rise in pressure particularly as the pumping speed is very low in this range. The resultant heating of the pump causes a further degassing, increasing the starting time and drastically shortening the life of the electrodes. It was for these reasons that the diffusion pump was applied until a pressure of around $2\times10^{-6}\text{torr}$ was achieved.

Occasionally small leaks occurred particularly following bakeout and in each case were traceable to joints.Leaks in glassware could, in principle, be traced with a Tesla coil but leaks from this source never arose. Since the system was mainly made up of stainless steel, leaks fell into the category of 'small' and 'very small'. The former being traced by squirting acetone onto the joints and looking at the meter on the ion pump supply. The response (noticeable at pressures less than $10^{-6}\text{torr}$) gave rise to an initial drop followed by a sharp rise. Very small leaks were diagnosed by using argon or helium in conjunction with the mass spectrometer. Fortunately both types of leak were nearly always cured by tightening up
the joints. During the construction of the system, each successively built up part was tested for leaks by a separate mass spectrometer leak detector. With this approach, the usual harrowing problem of leaks was reduced to some degree, although not eliminated completely.

To facilitate the baking out procedure, the complete system was set out on two movable tables constructed of a dural frame with asbestos tiles forming the top, allowing the placement of an oven. Fig 6 and Plate 1 shows the table which contains the MS 6 and purification system. The ion pump IP 2 and power supply were mounted, partly for safety, under the table. The calibration flask was positioned here likewise, for convenience.

The oven was constructed of aluminium with walls containing asbestos bricks and incorporating thermostatically controlled heating elements. Parts of the apparatus which could not be reached by the oven were wrapped in heating tape (ISOS 2 métre 220W tape was found to be the most convenient).

In the initial stages it was necessary to bake out the MS 6 and associated purification system. Care had to be taken not to exceed the manufacturer's recommendations of 250°C since higher temperatures would have oxidised the dynode plates in the electron multiplier and subsequently reduced its sensitivity. During bakeout the magnet was removed and once the Ti getter (NP 10) had been outgassed, the spectrometer filament was taken to its highest emission setting of 200 μA but only when the pressure had fallen below 10⁻⁶ torr (the facility for running the filament during bakeout was not provided and appropriate modifications had to be made).
Baking of the furnace and CP 50 Ti getter was achieved using heating tape only attaining temperatures of around 300°C. When the pressure fell below $2 \times 10^{-6}$ torr, both getter and furnace (without water cooling) were gradually taken up to maximum temperature.

Throughout the baking procedure valves were either open or closed off to 'finger' tightness.
3.2.2 Furnace Design and Loading Assembly

The problems of design stemmed from the need to provide a furnace and loading facility to take large samples of up to 30g. The immediate problems of furnace construction were two-fold; firstly, the need for a filament of suitable size and power to contain and heat a crucible, and secondly, to provide a crucible large enough to take a number of sizeable samples.

A furnace barrel with water jacket (fig 7) was available and a somewhat arbitrary decision was taken to attempt to fit the designed contents into this arrangement. The added advantage of this was that a similar furnace had been used successfully in this laboratory (Lynch 1976). Faced with this size of structure (see fig 9 which has a 1:1 scale), the problem was whether or not the volume could cope with the number of heat shields required (five were used) and if the kovar seal, rated at 500°C, could accommodate the heat flow being in close proximity to the heater. The other problem was that the restricted volume could only house an internal type of heating element and since one of such a size had not been tested at the time, the possibility of high blank levels had to be considered.

However, the final arrangement (fig 9) was found to be satisfactory and the blank levels are discussed in chapter 4. In a simpler design, where a guide tube led from the tree directly to the crucible, the kovar seal cracked when the furnace was being run at maximum temperature during a bakeout. A modified arrangement involving a freely hinged heat shield and funnel was implemented and no further trouble was encountered. The advantage of such a device, apart from the
Furnace Calibration

FIG10
diversion of radiant and conductive energy away from the seal, was that sputtered material from the samples was prevented from moving upwards into the arms of the loading tree.

The furnace used in the laboratory for Lunar work incorporated an internal filament which had been constructed from four strips of tantalum (1mm by 0.075mm cross-section) spot-welded to form a cylinder whose walls were of a criss-cross pattern. The numerous spot-welds tended to make the material brittle causing failure around the welds. Furthermore, the design led to a sagging of the structure lowering the electrical resistance, resulting in a fall in the temperature characteristic. A new design was sought and this (plate 2) was made from a sheet of 0.005" thick tantalum and has an alternately slotted form welded along one seam only. The machining of the slots was accomplished by placing the sheet on a cylindrical former and setting this in araldite. The filament, then in a cylindrical slotted form, could be reclaimed by dissolving the glue in concentrated HNO₃. Once in use, after an initial change in characteristics (fig 10), the filament was found to work successfully and was readily capable of carrying current densities of up to 2x10⁴ A/cm².

Previously, small crucibles had been machined from 3/8" or 1/2" tantalum rod. However, the size of rod required for crucibles of volumes around 30cm³ involved an unreasonable cost as did ready-made crucibles from manufacturers. To produce a sufficiently large crucible at a modest cost sheets of 0.005" tantalum were cut out, by means of a fly-press,
to the shape of a disc. The crimped sectors were spot-welded to give the crucible rigidity and, finally, three arms were attached symmetrically to position it centrally within the heating element. This type of crucible was only partly successful and required changing after the passage of three to four samples. If this were not done then the crucible material tended to react with the sample causing perforations.

Heat shields were made from 0.003" tantalum sheet, their separation, to avoid thermal conduction, being achieved by patterned indentations between adjacent shields along the surface of the metal.

The furnace barrel was fitted at either end with 5" diameter flanges to take; at the bottom end, a base plate and the top, the loading assembly. The base plate was machined to take a mini-conflat seal which connected the furnace to the system and allowed an electrical feedthrough to supply power to the filament, fig(10). The loading assembly flange, as with the base plate, used gold O-ring seals and since this part of the system was subject to continual demounting the arrangement was found to be convenient. Furthermore, the filament could easily be removed by disconnecting it from the support uprights and electrical feedthrough. Subsequent removal of the furnace assembly required only that the three holding screws be withdrawn from the base plate.

The loading assembly has a tree-like structure (plate 3) since it has been shown to be the simplest and most effective way of multiple sample loading. Arriving at the end of a long line of ingenious and more complicated devices it gets around
the difficulties of operating a mechanism housed inside a UHV cavity from without. The present form of the tree is little modified from that of the Lunar loading assembly with the only differences being in the diameter of the lower tier of arms (1"O.D.) to take the larger samples, and the replacement of magnetic cylindrical lugs by mild steel sheet formed into boatlike structures. The latter permitted a greater manipulation of the samples. The tree is capped by a single limb which contains a ball-bearing. The ball-bearing was drawn aside during furnace calibration but otherwise it protected the optical window from fogging so that the temperature could be measured with an optical pyrometer.
3.2.3 Argon Purification

The basis for cleaning up the gas sample after it had left the furnace lay in the operation of two getter pumps, a CP 50 and NP 10. The non-evaporable getter cartridges used therein had been developed by SAES and are described at length in their technical reports 12, 14, 20 and 21. However, the construction of the getter pump consisted of a cartridge of getter material (St 101 alloy; 84% Zr, 16% Al) placed around an axial heater. The large surface area for the gas-solid interaction being provided by pressing the powdered active material onto a metal strip and pleating this in concertina fashion. The advantage of the getter action (preliminary physical adsorption followed by surface chemisorption and diffusion) meant that the Noble gases were not affected and furthermore, Pisani and Della Porta (TR 12 and 14) demonstrated its applicability in the removal of hydrogen, nitrogen, carbon monoxide and particularly water vapour. It should also be emphasized that getter devices do not require magnets, high voltages and complicated control systems.

Both getters were run during normal operation at the same temperature, 400°C, and when the surfaces became saturated, a clean surface was obtained by thermal treatment (activation) at 800°C. The larger CP 50 getter, used in conjunction with the furnace, was operational at 2.3A and activated for 15 minutes at 4.7A (in practice, after the extraction system had been exposed to atmospheric pressure, it took a great deal longer than 15 minutes to bring about an operational state. This was due to the pump being unable to cope with the quantities of gas coming from the large surface area of the cartridge.
In future applications it would be desirable to separate the furnace from the getter so that the latter could be closed during sample loading. The NP 10 was run intermittently and unlike the CP 50 did not require water cooling. However, a housing had to be designed for it and it was felt necessary to introduce heat shields to reduce thermal conduction to other parts of the system. The NP 10 was operational at 0.8A and could be activated at 1.2A.

The procedure for preparation of the gas for analysis was as follows (see fig 7). The gases, diffused from the sample by the furnace, were firstly cleaned by the concurrent running of the CP 50 getter. After heating for half an hour at a particular temperature and following a period of five minutes cooling, the gas was condensed onto the evacuated 'finger', containing activated charcoal, for 10 minutes and using a liquid nitrogen cold trap. Valve V10 was then closed and NP 10 activated, open to IP 2. Valve V3 was closed once the getter had been set to operational, the gas admitted to the getter volume and the finger isolated. After 5 minutes at operation followed by 10 minutes cooling the gas was ready for analysis and (remembering to close off the ion pump at V1) it was expanded into the mass spectrometer and isolated at V2. Unfortunately, it was not possible to tell if dangerous pressure levels of gas were likely to be admitted to the mass spectrometer. As a rough check, the meter on the ion pump power supply was observed, after condensation, whilst pumping out the furnace.

The above procedure allowed an experimental cycle to be
established, the furnace being restarted whilst the previous sample was analysed.
3.3 Mineral Separation

The separation of minerals for analysis from the samples presented no great problem. The principal reasons for this being that they were accessible in large quantities and the minerals were generally in the form of large phenocrysts incorporated in a fine glassy matrix suitable for hand-picking after crushing. The yield was usually around 1% of the starting material except where the matrix glass was required. On no occasion was it necessary to use more sophisticated methods of separation although the removal of material using simple magnetic or electrostatic devices greatly facilitated hand-picking. A rudimentary piston-and-cylinder arrangement was developed in order that the samples could be crushed within the department avoiding any cross-contamination which could have arisen from the use of commercial rock crushing equipment available in the Geology department. The crusher was operated by means of a 5 ton/sq ins hydraulic press. After each crushing, the piston and cylinder were cleaned by re-machining the appropriate surfaces.

Sieving was carried out using Endercott stainless steel test sieves. All separated samples were cleaned by sonication in iso-propyl alcohol to remove adhering grains and washed in high purity acetone and distilled water three times.

Standard Bern Muscovite (4M): Prepared by the University of Bern (Dalrymple and Lanphere, 1971 and Private communication). Bishop Tuff 191,192 and 193: Crushed and sieved, hand-picked grains were taken from two fractions; greater than 20 BS and 710-180 Mic meshes. The majority of the matrix glass was removed electrostatically leaving a small amount of pyrite to be extracted and discarded. 2.32g of sanidine mineral were
ARRANGEMENT OF SAMPLES DURING IRRADIATION

SH 33 WITH VARIATIONS IN NEUTRON FLUENCE

Diagram showing the arrangement of samples with variations in neutron fluence. The distance along the phial from the base in cm is indicated, with layers labeled from Ni7 to Ni 1, each with different materials such as Al foil, KF, Ni6, Ni5, Ni4, Ni3, Ni2, Ni1, CaF2, and layers marked with fast fluence (x10^16 n.cm^-2).
obtained for splitting.

**Kilimanjaro Samples:**

(i) K138 Nepheline Phonolite: After crushing, a fraction was removed for hand-picking from mesh sizes of between 11 and 20 BS. The phonolitic matrix was extracted by means of a strong permanent magnet. 4.0g of glass and 4.7g of nepheline were obtained.

(ii) K2053 Glassy Phonolite: The separation process was carried out as in (i) except that anorthoclase phenocrysts were also obtained. The fractions were; nepheline (2.8g), anorthoclase (2.2g) and glass (2.6g).

(iii) K764 Obsidian: The rock was crushed and fragments were hand-picked. 2.4g were removed.

(iv) K2491 (CD391) Rhomb Porphry Feldspar: These occurred in the form of large phenocrysts (1-2cm) from which the matrix had been weathered away. The faces of the crystals were cut away using a diamond saw to remove any further weathering and 2.1g of the material were used.

(v) K2465 Rectangle Porphry Feldspar: These being much the same were treated in a similar way to (iv) and 3.1g were used.

(vi) K814 Nepheline Group: After crushing, nepheline was hand-picked from mesh sizes of between 11 and 20 BS, the matrix being largely removed by magnet. 1.2g of the material were used.
3.4 Sample Irradiation

Since the samples were of low ages, they needed to be large and irradiated in a low fluence (about $10^{16}\text{n}\cdot\text{cm}^{-2}\text{fast}$). This presented two problems; firstly, flux variation across samples of large dimensions and secondly, the difficulty of obtaining a low flux in the Herald Reactor. The Herald is a light-water-moderated, highly enriched uranium fuelled reactor with a fast/thermal ratio of 0.6 in the centre of the core and 0.3 in the beryllium reflector row at the outside edge of the core. The neutron energy spectrum consists of a moderated fission spectrum, with energies ranging from 0.1 MeV to an upper limit of 10 MeV and peaking at 0.7 MeV.

Originally it was thought that samples would need to be irradiated outside the core in order to attain low fluxes. However, the variations were large; for a cylindrical container of 1.25" diameter by 9" long, vertical variation was 25% and lateral variation was around 20%. Rotation of the cannister could have reduced the latter to 5%. Unfortunately, the VT 6 shuttle facility had a 'dog-leg' involving two 45° bends making this very difficult to do. For simplicity and greater precision the samples were loaded into G 9 where the variations were of the order of 1% horizontally and a profile of those vertically may be seen in fig(11), for a cannister of 1" (diameter) by 9".

Cadmium shielding, it was thought, might be necessary to remove thermal neutrons giving rise to reactions which are described later. However, Miller et al. (1971b) have demonstrated that their earlier fears of detrimental effects from these reactions (Miller et al. (1971a)) were unfounded.

*see fig 1.
The irradiation, designated SH 33 was carried out with the reactor being run at low power for a period of 22.5 hrs, culminating in an integrated fast dose of approximately $1.3 \times 10^{16} \text{n.cm}^{-2}$. The samples were packed in high purity Al foil (99.99% Al), each forming a disc such that they could be loaded column-wise into a quartz phial, fig(11). Nickel flux monitoring wires (weighed to 10/ug) were arranged at intervals down the column. After loading, the phial had a 6mm quartz tube attached to it so that it could be evacuated and sealed conveniently. AT A.W.R.E. Aldermaston further flux wires were arranged around the phial before it was dropped into a 12" Al cannister and prior to it's entry into the reactor.

Analysis of the samples was not initiated until a month after the irradiation to remove any harmful, short-lived decay products (after a week 0.2 mSv was recorded at 1 metre). When the samples were subsequently taken from the phial, great care was exercised in their handling. In addition to the normal procedures of safety; air samplers, respirators and so on, it found very convenient to use a self-adhering plastic wrapping material known as Caterwrap.
CHAPTER 4
Limits to K-Ar Dating

4.1 Introduction

Conventional K-Ar techniques are readily applied to samples with ages of a few tens of million years and above. It may be seen that a number of difficulties arise in attempting to apply the method to younger samples. Some of the limitations imposed by argon interferences coming from the sample itself have already been discussed in chapter 2. In this section two further important factors are considered with particular reference to the present work. These are; firstly, the detectable limits (and sensitivity) of the mass spectrometer and secondly, argon background interferences occurring through gases being absorbed and subsequently outgassed from the system, particularly the furnace and spectrometer (the latter referred to as memory), inspite of careful cleaning procedures.
Justification for the New System

With typical high resolution systems, the 'detectable limit' (here defined as the amplitude of the noise level from the detector amplifier) may correspond to sample sizes of the order of $5 \times 10^{-11}$ ccSTP of argon-40. The 'Lunar' spectrometer achieves these sort of limits in this laboratory. The justification for a more sensitive system may be seen from the following argument. One gramme of potassium produces $4 \times 10^{-12}$ ccSTP $^{40}$Ar/year, requiring, with present limits of detection, highly potassic samples of large size in the range of $10^6$ years or less. Furthermore, this is limited to some extent by contamination from air argon and although the incorporation of a stepwise degassing experiment may partially separate the atmospheric component, the $^{36}$Ar has to be multiplied by 295.5 to make the atmospheric argon correction. Thus $5 \times 10^{-11}$ ccSTP $^{36}$Ar is equivalent to around $1.5 \times 10^{-8}$ ccSTP $^{40}$Ar. This last figure corresponds to an age of about $2 \times 10^5$ years for a sample of one gramme in weight and 10% K-content taken through five heating steps. If this sample is typical, then further problems arise in that typical $^{39}$Ar-$^{40}$Ar extraction systems can rarely cope with samples that exceed one gramme in weight (a new system developed by Costa et al. (in press) for the analysis of young rocks is suitable for samples up to 3g in weight).

To extend the range of analysis to young thus necessitates two major developments; those of a more capacious gas extraction system with the associated purification techniques for large samples and the implementation of a more sensitive mass spectrometer.

*This figure is given at the 'limit of detection'; see page 55.*
Another important advantage for the use of a new spectrometer stems from the problem of 'memory'. The memory effect occurs when gas from an earlier sample is released from the walls of the mass spectrometer by ion bombardment during the running of a new sample. If the concurrent samples are of very different ages then this source of contamination can become serious. The mass spectrometer employed in the Lunar science programme habitually handled rocks of around $10^9$ years in age making it highly unsuitable for the young rock programme.
4.3 Performance of the New System

(i) Background Data:

The blank levels described here have been achieved by rigorous baking schedules which are dealt with in chapter 3. The 'hot' blank levels (around 1200°C), measured after each sample analysis, from the furnace were between 0.56 and 0.96 \(x10^{-9}\) ccSTP\(^{40}\)Ar (average value 0.74\(x10^{-9}\) ccSTP\(^{40}\)Ar) for sample weights between 100mg and 5g with no detectable correlation between the size of blank and sample weight. These extremely favourable results suggest that providing the samples are of a reasonable size (the crucible can cope with 30g) and that the GP 50 getter pump can deal with the undesired volatiles, then an appropriately sized sample can be used for analysis and this does not itself impose a limit on the sensitivity requirements of the spectrometer. The hot blank levels compare well with those of Costa et al. (in press), who report average levels of 5.7\(x10^{-9}\) ccSTP\(^{40}\)Ar in a young K-Ar system. The hot blanks for the system were found to be acceptable as they were of two to three orders of magnitude less than the atmospheric component measured from the samples analysed. A problem that is envisaged, however, is that during runs particularly with large samples (greater than 1g), a major proportion of the material is transported out of the crucible ultimately forming a crust on the walls of the furnace and just how this effects blank levels is not yet known. A simple remedy would be to fit a replaceable liner, easily removable after the running of a batch of samples.

The contaminative source from argon background arises from \(^{40}\)Ar memory in the mass spectrometer and this could be
greatly reduced, although not eradicated completely, by baking for the duration of a day. This could be improved perhaps if the analyser tube was to be taken to higher than 250°C (limit for the electron-multiplier dynodes). The presence of some memory was not found to be serious since all argon peaks were extrapolated back to zero time and, in addition the spectrometer was restricted to the analysis of young samples.

The appearance of spurious peaks (around $10^{-11}$ to $10^{-12}$ ccSTP$^{40}$Ar) in the mass range of 36 to 40 occurred when the NP 10 getter pump was running operationally at 400°C. In the normal running situation it was switched off and cooled for 5 minutes in the presence of the sample gas. This procedure removed these peaks beyond the limits of detection. It was also necessary to bake the ion pump IP 2 several times to reduce the $^{40}$Ar background emanating from it. Subsequently this procedure lowered the background to $4\times10^{-11}$ ccSTP $^{40}$Ar. No other peaks in the mass range 36 to 40 were detected from the pump at any time.

The background levels in the spectrometer and cold extraction were undetectable implying that interferences, particularly from hydrocarbons such as $^{36}$HCl, are at levels below detectable limits ($4\times10^{-13}$ ccSTP argon).
(ii) Spectrometer Characteristics:

The sensitivity was limited by the electron-multiplier noise and suffered an initial loss in gain of an order of magnitude but reaching a steady-state value thereafter. The noise level which was set to an amplitude of one division and (time constant 0.3 s on the potentiometric recorder) corresponded to a current of $4 \times 10^{-16} \text{A}$ (equivalent to $4 \times 10^{-13} \text{ccSTP}^{40}\text{Ar}$ or a partial pressure of $3 \times 10^{-13} \text{torr}$) the previously defined 'detection limit', the measured sensitivity being $6.1 \times 10^{-3} \text{A/torr}$.

The minimum detectable current can be calculated from the Nyquist equation for Johnson noise and is attributed to thermal oscillations in the input resistor. The R.M.S. fluctuations in the current are given by:

$$\Delta i = \frac{1}{G}(4kT\Delta f/R)^{\frac{1}{2}}$$

where

- $G = \text{electron-multiplier gain (} \times 10^3)$
- $k = \text{Boltzmann's constant}$
- $T = \text{absolute temperature}$
- $\Delta f = \text{band width (3.3)}$
- $R = \text{value of the input resistor (} 10^{11} \text{ohms)}$

The value of $4 \times 10^{-16} \text{A}$ obtained in this way corresponds to an ion beam of $2.5 \times 10^3$ ions/sec. This value is a reasonable one since any greater sensitivity is accompanied by comparatively larger statistical fluctuations.

The results indicate that the $^{36}\text{Ar}$ (discrimination 1.004) measurements were made with errors of a few percent for values of $4 \times 10^{-12} \text{ccSTP}^{40}\text{Ar}$ or ten times the detection limit. In practice signals can be measured to a greater accuracy than
the amplitude of the noise level. This is possible because a response time is chosen such that the noise is averaged across the top of the peak which gives rise to several oscillations on top of the peak (and at the zero between the peaks) and a favourable signal/noise ratio can readily be detected. Extrapolations to zero time involves the measurement of six peaks resulting ultimately in errors in peak heights of a few percent. See fig 5.

The normal running characteristics of the mass spectrometer were as follows; ionizing potential 60V, emission current 200\(\mu\)A and accelerating potential 1kV. The electron-multiplier supply gain was normally set to 3.0kV although to enhance the noise level to one division, a calibrated value of between 3.5 and 4.0kV was incorporated. This represented a gain of twenty. In practice, gain changes were made using the FA 2 amplifier control only.

When setting up the mass spectrometer, the following points regarding sensitivity were considered with respect to the source efficiency and where possible improvements have been made.

The accelerating potential was set at 1kV and although by increasing this the sensitivity was enhanced it also did tend to increase the effect of memory by absorbing ions of increased velocity. In this case the memory was felt to be the more important consideration. The ionization potential was maintained at 60V, the optimum setting for argon. Other values were tried but led to a reduction in peak height corresponding to multiple charged ions at higher potentials and an insufficient ion production at low potentials. The
emission current was run at the maximum setting of 200\(\mu\)A; an enhancement of this value to increase ion efficiency (calculated at \(10^{-3}\) ions/s/sample atom) brings about a conflicting space charge effect. The maximum effective current is given by the solution to Poisson's equation for charge distribution in a box of side 1 (in practice, about 1cm) and is calculated thus:

\[
\Delta \phi = \frac{\rho l^2}{8\varepsilon_0}
\]  

(27)

for electrons moving at velocity \(v\) in a box of side 1 the charge distribution \(\rho\) is:

\[
\rho = \frac{i_e}{l^2v}
\]  

(28)

giving the maximum effective emission current \(i_e\) as:

\[
i_e = 8\varepsilon_0 \Delta \phi v
\]  

(29)

where the undefined quantities are:

- \(\varepsilon_0\) = permittivity of free space
- \(\Delta \phi\) = maximum drop in potential due to space charge at the centre of the box
- \(v\) = velocity of electrons at 60eV ionization potential

If \(\Delta \phi = 1\)V, then the emission current maximum comes out to be 700\(\mu\)A but the source magnets of 100gauss which spiral the electrons, effectively increasing their path reduces the possible emission current. It appears that unless the interior
of the ion source can be redesigned then the higher values of emission current will spread the energy of the ions and degrade the ion beam.

Other initial adjustments were made on the source slit (see chapter 3), half-plate (for beam centring), ion repellor voltage and electromagnet. The half-plate was optimised at the limit of adjustment and was used in this position throughout. The ion repellor voltage was tuned over the mass range required but the sensitivity was not fully optimised as, if the adjustment was taken beyond the maximum, the sensitivity fell off rapidly. Once set up, it was not altered again as the discrimination is affected by the adjustment. The electromagnet had to be removed during bakeout but could be replaced afterwards without further movement. It's position was checked from time to time.
<table>
<thead>
<tr>
<th>Sample</th>
<th>AGE (x10^6) years</th>
<th>Intercept (40Ar/36Ar)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Isochron Plot</td>
<td>Total Fusion</td>
</tr>
<tr>
<td>Bishop Tuff</td>
<td></td>
<td></td>
</tr>
<tr>
<td>191</td>
<td>0.73 ± 0.07</td>
<td>0.79 ± 0.07</td>
</tr>
<tr>
<td>192</td>
<td>0.74 ± 0.01</td>
<td>0.82 ± 0.04</td>
</tr>
<tr>
<td>193</td>
<td>0.96 ± 0.01</td>
<td>1.02 ± 0.03</td>
</tr>
<tr>
<td>Kilimanjaro</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K138</td>
<td>0.10 ± 0.01</td>
<td>0.09 ± 0.01</td>
</tr>
<tr>
<td>K764</td>
<td>one release 0.45 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>K2491</td>
<td>0.35 ± 0.01</td>
<td>0.35 ± 0.04</td>
</tr>
<tr>
<td>K2465</td>
<td>0.67 ± 0.05</td>
<td>0.47 ± 0.03</td>
</tr>
<tr>
<td>K314</td>
<td>2.29 ± 0.03</td>
<td>2.26 ± 0.04</td>
</tr>
</tbody>
</table>

See page 27 for an explanation of the errors.
CHAPTER 5
Discussion of Results

5.1 Introduction

The samples analysed were chosen for the following reasons. Initially, verification of the $^{39}\text{Ar}^{40}\text{Ar}$ technique was required for young rocks and for this a well documented young sample, the Bishop Tuff (Dalrymple et al., 1965), was taken for analysis. It was hoped too, that this rock of $0.7 \times 10^6$ years would ultimately be a suitable monitor for the application of the method to a specific geological problem, that of dating lavas from Mount Kilimanjaro.

The monitor sample used in the Bishop Tuff analysis was the interlaboratory standard 4M Bern Muscovite (Dalrymple and Lanphere, 1971) whose age is $18.7 \times 10^6$ years. The Bern Muscovite was also carried over to the final part of the work, that of resolving ages from Mount Kilimanjaro, as the reactor conditions could be chosen such that it was suitable for monitoring these rocks down to ages of $10^5$ years.

All the data from samples described in this chapter is tabulated in the appendix, table 2 and figures 13 to 28.
5.2 The Bishop Tuff

Sanidine phenocrysts were obtained from the welded tuff which also contained inclusion of pyrite (Sheridan and Michael, 1972). The age of the Bishop Tuff is $0.7 \times 10^6$ years made from several determinations. The phenocrysts were found to be suitable for the $^{39}$Ar-$^{40}$Ar method because of the undisturbed nature of the rock and high potassium content (see Dalrymple et al., 1965). The earliest age determinations by Evernden et al. (1957) were affected by the inherited argon-40 problem which became apparent later. The dates from the Bishop Tuff are also important because it overlies glacial till and outwash from one of the early glaciations in the Sierra Nevada, California.

Sample 191 was not analysed by the MS 6 system. The analysis, at an early stage in the programme, using the 'Lunar' spectrometer resulted in large $^{35}$Ar errors. All subsequent samples were run on the new system.

The age spectrum of 191 seen in fig 14, yields a downward, monotonically stepped plot corresponding partly with the drop in atmospheric contamination with temperature. As such, little information can be gleaned from it. The correlation diagram, fig 13, gives an age of $0.73 \times 10^6$ years with an intercept of 351 which is consistent with the results of Dalrymple et al. (1965).

Sample 192 yielded a more interpretable release pattern (fig 15) but corresponds to a rather high age of $0.82 \times 10^6$ years. The partial removal of atmospheric contamination in the early stages suggests that a lower age might be assigned to the sample. The correlation plot (fig 16) which is felt to be more
SLOPE = 7.86 ± 0.09
INTERCEPT = 311.5 ± 12.2

AGE = 0.96 ± 0.01 MY
ATMOSPHERIC CONTAMINATION

% ATMOSPHERIC CONTAMINATION

1% —

CD

CO

% 39Ar RELEASED

BISHOP TUFF SANIDINE 193

APPARENT K-Ar AGE (MY)

830°C

1000°C

1040°C

840°C

1110°C

1170°C

1200°C

% 39Ar RELEASED
reliable (see chapter 2) gave an age of $0.74 \times 10^6$ years with an intercept of 317, which is consistent with the work of Dalrymple et al. (1965).

Sample 193 gave the best isochron plot, fig 17, but indicates an age of $0.96 \times 10^6$ years. The total age, corresponding to the plateau in fig 18, is also high at $1.02 \times 10^6$ years. The ages are difficult to evaluate but three logical explanations are possible: one, that it is correct, two, that the sample is contaminated from xenolithic material in the original rock or three, that contamination has occurred during analysis from a previous sample.

Possibility one seems unlikely in the face of the two results presented here and by Dalrymple et al. (1965). Possibility two also seems unlikely since all the samples analysed were taken from splits of the same sample and have undergone the same preparatory treatment. However, it is as well to bear in mind that Gilbert (1938), Dalrymple et al. (1965) and Evernden et al. (1964 and 1965) suggest that previously published ages of around one million years have been affected by the presence of inherited argon-40. Possibility three appears to be the most likely since the monitor (4M) Bern Muscovite was run immediately prior to 193 and may not have been completely outgassed in spite of the satisfactory high temperature blank levels recorded. This final point stresses the need for samples of very different ages to be outgassed in separate crucibles. Where the ages are close together the least potassic should be run first. This procedure was adopted for the Kibo succession samples from Mount Kilimanjaro.

The above results indicate that more samples of the
Bishop Tuff should be analysed to gain greater consistency of results before it can be considered as a useful laboratory standard.
5.3 Mount Kilimanjaro

(i) The Geological Setting:

The simplified relationships of Mount Kilimanjaro rocks are summarized in figs 19 and 29. In broad terms, the lavas of Mawenzi to the east and Shira to the West are overlain by the younger Kibo succession. Unfortunately, the younger rocks mask completely the underlying lavas making the relationship between the Mawenzi and Shira successions unclear.

Lithologically, Shira is very similar to Mawenzi but the depth of weathering is greater on the former and, although there is presently higher rainfall on this side, it may indicate that Shira represents the earliest eruptions of the three. Infact, the material removed by denudation suggest that it's height may well have been in excess of 18,000' rather than it's present level of 13,000'. Later effusions of Shira may have paralleled the lower Mawenzi; namely, Ol Molog and Neumann Tower lavas and later Mawenzi activity seems to have been contemporaneous with the lower Kibo lavas.

(ii) Time Relationships:

On the basis of geochemical correlations, Downie and Wilkinson (1972) suggest that the three successions of vulcanism are derived from a single parent magma and it's differentiates. The average rate of effusion of magma during the pre-Kibo history was about three times that of the Kibo stage (fig 19 shows the relative thicknesses of Kibo lavas at a scale of 1mm/1000'). In view of the close correlation of geochemical evolutionary stage with stratigraphy in Kibo, a time scale is of great importance in estimating the rate of petrogenic processes.

A further use for the time scale arises since Kilimanjaro
<table>
<thead>
<tr>
<th>Geological Succession</th>
<th>Ages ($x10^6$ years) measured by various workers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recent glaciation</td>
<td>Evernden &amp; Curtis 1965</td>
</tr>
<tr>
<td></td>
<td>Mitchell (priv.com)</td>
</tr>
<tr>
<td></td>
<td>Curtis &amp; Williams</td>
</tr>
<tr>
<td></td>
<td>Logatchev &amp; Williams</td>
</tr>
<tr>
<td></td>
<td>Yonge *</td>
</tr>
<tr>
<td>Inner Crater</td>
<td>3rd Glaciation 0.19</td>
</tr>
<tr>
<td>Caldera Rim</td>
<td>0.19</td>
</tr>
<tr>
<td>Small Rectangle</td>
<td>0.35</td>
</tr>
<tr>
<td>Porphyry</td>
<td>0.35</td>
</tr>
<tr>
<td>Lent</td>
<td>2nd Glaciation 0.25</td>
</tr>
<tr>
<td>Rhomb Porphyry</td>
<td>0.25</td>
</tr>
<tr>
<td>Penck</td>
<td>0.36</td>
</tr>
<tr>
<td>Upper Rect. Porphyry</td>
<td>0.36</td>
</tr>
<tr>
<td>Upper Trachy andesite</td>
<td>0.463</td>
</tr>
<tr>
<td>Lower rectangle</td>
<td>1st Glaciation 0.463</td>
</tr>
<tr>
<td>Porphyry</td>
<td>0.67</td>
</tr>
<tr>
<td>Lava Tower</td>
<td>0.514</td>
</tr>
<tr>
<td>Lower Trachyandesite</td>
<td>0.514</td>
</tr>
<tr>
<td>Mawenzi</td>
<td>0.514</td>
</tr>
<tr>
<td>Neumann Tower</td>
<td>0.95</td>
</tr>
<tr>
<td>Ol Molog</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>0.850</td>
</tr>
<tr>
<td></td>
<td>1.100</td>
</tr>
<tr>
<td>Shira</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>2.29</td>
</tr>
</tbody>
</table>

* This work * Baker et al. (1971)
represents a rare instance of the occurrence of glaciers in equatorial regions and like the glaciers of Ruwenzori and Mount Kenya these are a relic of colder, wetter climatic conditions of the region during the Pleistocene. At the present time on Kilimanjaro, permanent ice is present only on Kibo but the distribution of moraines and other deposits of glacial origin suggest that formerly a much greater area of the mountain was covered by ice. Recession of the ice is now so rapid that it seems likely that within a few decades the shining cap of Kibo will have ceased to exist.

Unlike the glaciers of Ruwenzori and Mount Kenya, the numbers of observations of glacial deposits interbedded with lavas has established a fuller understanding of the succession of glacial and interglacial episodes (fig 19). Accurate dating of the lavas would enable the correlation of glacial periods with other areas. The correlation suggested between the African 'Pluvials' still seems, in part, to be largely tentative.

A fuller understanding of ages on Kilimanjaro would also have an important bearing on the relationship of fossil man to Pleistocene chronology.

The results obtained in this work are discussed in the following section; starting from the oldest and going to the youngest sample in a stratigraphic sense (see also fig 19), and errors are quoted in table 2.
(iii) Samples from Mount Kilimanjaro:

**K814 Shira Group:**

As pointed out earlier, the Shira succession was thought to be the oldest. The ages obtained from the sample gave $2.29 \times 10^6 \text{ years (isochron)}$ and $2.26 \times 10^6 \text{ (age spectrum)}$ and although these values are greater than previously thought, there seems no immediate grounds on which to suspect the data. Indeed, the age of $2.2 \times 10^6 \text{ years}$ for the Ol Molog (Logatchev et al., 1972) seems to endorse it. The ages for the Ol Molog obtained by Curtis and Williams (see Baker et al., 1971) appear to be too spread out to add usefully to the present information. The $0.95 \times 10^6 \text{ year date of Logatchev et al. (1972)}$ came from a sample collected some 15km east of the summit of Kibo and suggests a tentative age for the Neumann Tower being consistent with ages of $0.514 \times 10^6 \text{ years}$ for the (upper) Mawenzi and $2.29 \times 10^6 \text{ years}$ for the Shira.

**K2465 Lower Rectangle Porphyry:**

The sequence suggests that the age should be bracketed by the Lava Tower ($0.46 \times 10^6$) and the Rhomb Porphyry ($0.35 \times 10^6$). The release pattern, fig 25, presents clear evidence for disturbed systematics of which one of two causes is likely; firstly, gas loss seen in the earlier temperatures or, secondly, excess $^{40}\text{Ar}$ appearing in the high temperature steps. Without further analysis it is impossible to say which cause, if not both, is present. The isochron plot data is too spread to contribute any further information (fig 26). If excess $^{40}\text{Ar}$ is the cause then an age of around $0.45 \times 10^6 \text{ years}$ could be assigned making it consistent with published data. If however, argon loss occurred, perhaps due to subsequent reheating or weathering, and an age of $0.73 \times 10^6 \text{ years}$ assigned then two
possibilities arise. Firstly, that the disturbed systematics are more complicated and the age is incorrect or secondly, that the published K-Ar ages are suspect. If the latter were the case, then the suggestion is that the sequence and hence the first glaciation occurred earlier than previously thought. Whatever the possibilities are, it is important to point out that a K-Ar age for this sample would have been misleading and that the information at best indicates that the age lies between 0.39 and 0.78 $\times 10^6$ years.

**K2491 Rhomb Porphyry:**

The structure of the release pattern, fig 23, suggest slightly disturbed systematics to a considerably lesser degree than K2465. The correlation plot yields a good isochron (fig 24) and with the total age both give dates of $0.35 \times 10^6$ years. These results are consistent with the age of $0.36 \times 10^6$ years published by Evernden and Curtis (1965).

**K764 Lent Group:**

With 87% of the gas released in one extraction, the date of $0.4 \times 10^6$ years was essentially a total fusion or K-Ar age. The sample consisted of matrix glass which may account for this behaviour. The 'age' is consistent with an age of $0.4 \times 10^6$ years measured by Evernden and Curtis (1965) and totally inconsistent with both an average of three ages of $0.25 \times 10^6$ years measured by Mitchell (Downie and Wilkinson, 1972) and the age of the Rhomb Porphyry underlying it. The lateral extent of the Lent lavas of around 80km, fig 29, and the wide distribution of collection may account for the
discrepancy in the ages measured. A release pattern may reveal the presence of a disturbed system but a heating schedule will have to be carefully chosen. Further work involving the analyses of mineral assemblages from this sample may resolve the problems associated with using obsidian as a dating material.

**K138 Inner Crater Group:**

This sample had a comparatively low atmospheric component; falling to 18% in the fourth extraction (fig 27) which has contributed to the quality of the data. The isochron plot, fig 28, yields a date of $0.10 \times 10^6$ years, a value consistent with the Kibo succession and bracketing the fourth glaciation; placing it between $0.19$ and $0.1 \times 10^6$ years. In addition, this date places at least a lower limit on the the age of $0.1 \times 10^6$ years or less inferred from stratigraphy (Downie and Wilkinson, 1972).
(iv) General Discussion:

Fig 19 shows schematically the geological sequence on Mount Kilimanjaro with ages obtained both by other researchers and this work.

Three of the ages measured are unambiguous and fit in with the stratigraphic relationships within the geological succession and are, in general, consistent with the dates determined by other workers.

The first of these ages; from the Inner Crater Group (sample K138), extend the chronology of the Kibo succession by presently providing the only date (0.1x10^6 years) for this stage. This fits with a K-Ar age measured by Mitchell of 0.19 x10^6 years for the Caldera Rim Group which lies below it and confirms predictions made by Downie and Wilkinson (1972) of this youngest lava being around 0.1x10^6 years old.

The second age, obtained from sample K2491 (Rhombo Porphyry) of 0.35x10^6 years, fits closely with a K-Ar age for the Rhomb Porphyry determined by Evernden and Curtis (1965) and is consistent with three K-Ar ages by Mitchell (average 0.25x10^6 years) for the Lent Group which overlies it. The correlation plot (fig 24) yields a good isochron whose ^40Ar/^36Ar intercept at 295.6 is very close to the present day atmospheric ratio. Thus it is worth noting that a very similar age would have been returned from a conventional K-Ar determination (see also the 'total fusion age' in Table 2).

The third age of 2.29x10^6 years for the Shira group is at present the only available date for this lowest succession and is in accord with a date of 2.2x10^6 years published by Logatchev et al. (1972) for the stratigraphically younger Ol Molog succession. The date of Curtis and Williams (Baker
et al., 1971) for the Ol Molog succession are widely spread out and only the $1.1 \times 10^6$ years date appears to be consistent with the dates of $0.95 \times 10^6$ years for the Neumann Tower (Logatchev et al., 1972) and $0.514 \times 10^6$ years for the Mawenzi (Evernden and Curtis, 1965).

Two of the ages obtained by this study do not present clear ages and their interpretation is in some doubt. However, the $^{39}\text{Ar}-^{40}\text{Ar}$ approach revealed disturbed systematics in sample K2465 (Lower Rectangle Porphyry), see the release pattern in fig 25. Two interpretations may be advanced. The first is that the sample contained excess argon-40 which is released preferentially at high temperatures. On this interpretation, the minimum age recorded ($0.39 \times 10^6$ years) would be regarded as an upper limit to the crystallisation age. This would be consistent with the Evernden and Curtis (1965) ages of $0.463 \times 10^6$ years for the Lava Tower and $0.514 \times 10^6$ years for the Mawenzi, both of which underlie it and their date of $0.36 \times 10^6$ years and of this work of $0.35 \times 10^6$ years for the Rhomb Porphyry which lies above it.

The alternative interpretation for sample K2465 is that it has suffered argon-40 loss and that a crystallisation age of $0.78 \times 10^6$ years should be inferred from the high temperature steps. This interpretation would imply that other ages obtained by the $\text{K-Ar}$ method; namely, Lava Tower and Mawenzi, have similarly suffered argon-40 loss and are yielding low ages. Without further confirmatory evidence these interpretations are put forward to point out the possible short-comings of the $\text{K-Ar}$ method in its inability to identify disturbed systems. This example also serves to underline the importance of the $^{39}\text{Ar}-^{40}\text{Ar}$ approach. The conclusion which makes the fewest assumptions is that the age of the Rhomb Porphyry K2465 is $\leq 0.39$ or $\geq 0.78$ ($\times 10^6$ years).
of evidence for argon loss in the release pattern from sample K2491 which is stratigraphically younger than K2465 and yielded an age of \(0.35 \times 10^6\) years suggests that the excess argon interpretation is most feasible. It also leads to fewer conflicts with the published K-Ar data.

Further anomalous ages are obtained for the Lent group both by this work (sample K764; fig 22) and Evernden and Curtis (1965) of \(0.45\) and \(0.4 \times 10^6\) years respectively. These conflict with three Mitchell K-Ar ages \(0.25 \times 10^6\) years average) for the Lent Group and the Rhomb Porphyry ages which underlie it. The anomalous ages may be due excess argon-40 in the matrix material (from which the sample was taken) and the sample was problematic in that \(87\%\) of the gas was released at \(970^\circ\)C and no interpretation of the age spectrum could be made. The vast lateral extent of the lavas over the area from which the sample locations were widely dispersed may account for these discrepant ages.

At the present time, including this work, the radiogenic ages for Kilimanjaro are few and there is some conflict in the evidence. The present work indicates that some of this conflict may arise as a result of excess \(^{40}\)Ar, however, the latest facts that emerge are these: Eruptions from a Kilimanjaro centre first commenced about \(2.3 \times 10^6\) years ago. Later Mawenzi lavas are around \(0.5 \times 10^6\) years indicating that about \(90\%\) of the mountain had erupted by this time, an average rate of \(3 \times 10^6\, \text{m}^3/\text{yr}\). Kibo began to erupt about the same time, continuing until \(0.1 \times 10^6\) years ago. Thus nearly all the \(450\, \text{km}^3\) of Kibo lavas erupted during \(0.4 \times 10^6\) years, a rate of \(10^6\, \text{m}^3/\text{yr}\). The ages obtained for the Inner Crater Group now bracket the 4\(^{th}\) glaciation on Kibo, placing it between \(0.1\) and \(0.19 \times 10^6\) years. Similarly, the age for the 3\(^{rd}\) glaciation, bracketed between the the Caldera Rim Group and the Rhomb Porphyry, is now endorsed by a further age of \(0.35 \times 10^6\) years (sample K2491).
In addition to providing information about a specific geological problem, the above work has demonstrated at least two valuable aspects of the \(^{39}\text{Ar} - ^{40}\text{Ar}\) technique as applied to young volcanics. These are that the method can yield ages for samples as young as 100,000 years and that disturbed systematics can be readily detected in contrast to the conventional K-Ar method.

5.4 Future Work

The prime aim of the work was in the technical development to provide a system for dating young rocks. From this point of view, the technique should be tested on younger, possibly even historical samples, initially between the ages of \(10^3\) to \(10^5\) years.

For the Kilimanjaro chronology there is clearly a need to measure more ages; in particular, the Small Rhomb Porphyry, the Upper Rectangle Porphyry and Upper Kibo Trachyandesite. In addition, to measure ages of different minerals from the same sample and widely dispersed samples of the same lithology. The former may provide an area in which to study the excess argon problem and the latter to obtain reproducible ages. For the immediate future it would seem provident to confine the study to the Kibo Succession.

Ultimately, future work will require the introduction of a young monitor sample and appropriate nuclear reactor conditions to irradiate the samples. For the former, it is suggested that further analyses are carried out on the Bishop Tuff and for the latter, the University of London Reactor Centre can supply the required fluences.
SLOPE = 18.73 ± 0.28
INTERCEPT = 304.6 ± 3.0
AGE = 2.29 ± 0.03 MY

(39Ar/36Ar)
LENT GROUP K 764

AGE (MAJOR RELEASE) = 0.45 ± 0.02 MY
RHOMB PORPHYRY K2491

% ATMOSPHERIC CONTAMINATION

(40Ar/39Ar) (°C)

% 39Ar RELEASED

APPARENT K-Ar AGE (MY)

740°C

970°C

1070°C

1170°C

1210°C
RHOMB PORPHYRY K 2491

SLOPE = 2.86 ± 0.05
INTERCEPT = 295.6 ± 0.4

AGE = 0.350 ± 0.01 M.Y.
ATMOSPHERIC CONTAMINATION

LOWER RECTANGLE PORPHYRY (K 2465)

% ATMOSPHERIC CONTAMINATION

740°C

970°C

1070°C

1107°C

1210°C

% 39Ar RELEASED

APPROXIMATE K-Ar AGE (M.Y.)
Lower Rectangle Porphyry (K2465)

Slope = 5.5 ± 0.4
Intercept = 279.1 ± 2.2

Age = 0.67 ± 0.05 MY

(39Ar/36Ar)
Fig. 29

MOUNT KILIMANJARO (central peak)

**Kibo Succession**

- **I C**: Inner Crater Group
- **C R G**: Caldera Rim Group
- **S R P**: Small Rhomb Porphyry Group
- **R P**: Rhomb Porphyry Group
- **P**: Pench Rhomb Porphyry Group
- **U R**: Upper Rectangle Porphyry Group
- **U K T**: Upper Trachyandesite Group
- **L**: Lower Rectangle Porphyry, Lava Tower
  - Trachytes and Lower Trachyandesite Groups

**Mawenzi Succession**

- **N T**: Neumann Tower Group
- **O M**: Ol Molog Group

**Miscellaneous**

- **P**: Parasitic
- **G**: Glacier
5.4 Future Work

The prime aim of the work was the technical development to provide a system for dating young rocks. From this point of view, the technique should be tested on younger, possibly even historical samples initially between the ages of $10^3$ and $10^5$ years.

For the Kilimanjaro chronology there is clearly a need to measure more ages, in particular, the Small Rhomb Porphyry, The Upper Rectangle Porphyry and Upper Kibo Trachyandesite. In addition, to measure ages of different minerals from the same sample and widely dispersed samples of the same lithology. The former may provide an area in which to study the excess argon problem and the latter to obtain reproducible ages. For the immediate future it would seem provident to confine the study to the Kibo succession.

Ultimately, future work will require the introduction of a young monitor sample and appropriate nuclear reactor conditions to irradiate the samples. For the former, it is suggested that further analyses are carried out on the Bishop Tuff and for the latter, the University of London Reactor Centre can provide the required fluences.
BIBLIOGRAPHY


TURNER, G. and CADOGAN, P.H. (1973). \(^{40}\text{Ar}/^{39}\text{Ar}\) chronology of chondrites. Meteoritics, 8.


YORK, D., KENYON, J.W. and DOYLE, R.J. (1972). $^{39}\text{Ar}-^{40}\text{Ar}$ ages of Apollo 14 and Apollo 15 samples. Proc Third Lunar Sci.
APPENDIX
### TABLE I: 191 Bishop Tuff Sanidine 0.729g  K/Ca = 6.7

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>$^{39}{\text{Ar}}/^{36}{\text{Ar}}$</th>
<th>$^{40}{\text{Ar}}/^{36}{\text{Ar}}$</th>
<th>% atmos.</th>
<th>$^{40}{\text{Ar}}/^{39}{\text{Ar}}$</th>
<th>Apparent Age x10^6 years</th>
</tr>
</thead>
<tbody>
<tr>
<td>770</td>
<td>11.4 ± 1.9</td>
<td>432 ± 53</td>
<td>68.4</td>
<td>11.9 ± 4.2</td>
<td>1.46 ± 0.52</td>
</tr>
<tr>
<td>870</td>
<td>37.10</td>
<td>612.113</td>
<td>48.2</td>
<td>8.1 ± 1.9</td>
<td>1.00 ± 0.24</td>
</tr>
<tr>
<td>1060</td>
<td>94.30</td>
<td>820.196</td>
<td>36.1</td>
<td>5.5 ± 1.0</td>
<td>0.68 ± 0.12</td>
</tr>
<tr>
<td>1100</td>
<td>163.61</td>
<td>1513.471</td>
<td>19.6</td>
<td>7.4 ± 0.6</td>
<td>0.91 ± 0.08</td>
</tr>
<tr>
<td>1130</td>
<td>83.28</td>
<td>687.164</td>
<td>43.7</td>
<td>4.6 ± 1.1</td>
<td>0.57 ± 0.14</td>
</tr>
<tr>
<td>1180</td>
<td>72.20</td>
<td>596.120</td>
<td>49.6</td>
<td>4.1 ± 1.1</td>
<td>0.50 ± 0.14</td>
</tr>
</tbody>
</table>

### TABLE II: 192 Bishop Tuff Sanidine 1.094g  K/Ca = 6.7

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>$^{39}{\text{Ar}}/^{36}{\text{Ar}}$</th>
<th>$^{40}{\text{Ar}}/^{36}{\text{Ar}}$</th>
<th>% atmos.</th>
<th>$^{40}{\text{Ar}}/^{39}{\text{Ar}}$</th>
<th>Apparent Age x10^6 years</th>
</tr>
</thead>
<tbody>
<tr>
<td>740</td>
<td>2.39 ± 0.18</td>
<td>349 ± 3</td>
<td>84.6</td>
<td>19.6 ± 1.6</td>
<td>2.40 ± 0.23</td>
</tr>
<tr>
<td>870</td>
<td>2.36 ± 0.18</td>
<td>311.4</td>
<td>94.8</td>
<td>4.3 ± 1.9</td>
<td>0.53 ± 0.24</td>
</tr>
<tr>
<td>1000</td>
<td>6.83 ± 0.25</td>
<td>354 ± 10</td>
<td>83.5</td>
<td>7.5 ± 1.2</td>
<td>0.92 ± 0.15</td>
</tr>
<tr>
<td>1040</td>
<td>24.2 ± 2.7</td>
<td>433 ± 39</td>
<td>68.2</td>
<td>5.3 ± 1.5</td>
<td>0.83 ± 0.19</td>
</tr>
<tr>
<td>1070</td>
<td>28.4 ± 3.5</td>
<td>537 ± 64</td>
<td>54.9</td>
<td>8.1 ± 2.0</td>
<td>1.13 ± 0.24</td>
</tr>
<tr>
<td>1110</td>
<td>57.5 ± 4.4</td>
<td>638 ± 40</td>
<td>46.3</td>
<td>5.7 ± 0.4</td>
<td>0.76 ± 0.05</td>
</tr>
<tr>
<td>1140</td>
<td>52.4 ± 2.6</td>
<td>598 ± 23</td>
<td>49.3</td>
<td>5.5 ± 0.3</td>
<td>0.73 ± 0.04</td>
</tr>
<tr>
<td>1170</td>
<td>44.1 ± 4.4</td>
<td>624.17</td>
<td>47.3</td>
<td>7.1 ± 0.4</td>
<td>0.97 ± 0.03</td>
</tr>
<tr>
<td>1200</td>
<td>16.6 ± 0.9</td>
<td>448.11</td>
<td>65.8</td>
<td>8.6 ± 0.6</td>
<td>0.11 ± 0.03</td>
</tr>
<tr>
<td>1210</td>
<td>0.19 ± 0.18</td>
<td>298 ± 1</td>
<td>98.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE III: 193 Bishop Tuff Sanidine 0.982g K/Ca = 6.7
J-value \((0.6450 \pm 0.0086)\times 10^{-4}\) Flux Factor 0.993

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>(^{39}\text{Ar}/^{36}\text{Ar})</th>
<th>(^{40}\text{Ar}/^{36}\text{Ar})</th>
<th>% atmos</th>
<th>(^{40}\text{Ar}/^{39}\text{Ar})</th>
<th>Apparent Age x10(^6) years</th>
</tr>
</thead>
<tbody>
<tr>
<td>740</td>
<td>11.3</td>
<td>265</td>
<td>100.0</td>
<td>0.386</td>
<td>0.047</td>
</tr>
<tr>
<td>970</td>
<td>165.1</td>
<td>359</td>
<td>82.3</td>
<td>0.386</td>
<td>0.005</td>
</tr>
<tr>
<td>1070</td>
<td>691</td>
<td>789</td>
<td>37.4</td>
<td>0.714</td>
<td>0.018</td>
</tr>
<tr>
<td>1170</td>
<td>1555</td>
<td>1564</td>
<td>18.9</td>
<td>0.816</td>
<td>0.017</td>
</tr>
<tr>
<td>1210</td>
<td>288</td>
<td>520</td>
<td>56.8</td>
<td>0.779</td>
<td>0.021</td>
</tr>
</tbody>
</table>

* Based on Ni flux wire measurements made by P. Roscoe of A.W.R.E. Aldermaston (see also fig. 11.)
<table>
<thead>
<tr>
<th>TABLE V: K764 Lent Group 2.41g K₂O/CaO = 1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>J-value (0.6450 ± 0.0086)x10⁻⁴ Flux factor 0.974</td>
</tr>
<tr>
<td>Temp °C</td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>740</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>970</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>1170</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>1210</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TABLE VI: K2491 Rhomb Porphyry 2.14g K₂O/CaO = 0.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>J-value (0.6450 ± 0.0086)x10⁻⁴ Flux Factor 0.978</td>
</tr>
<tr>
<td>Temp °C</td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>740</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>970</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>1070</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>1170</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>1210</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
**TABLE VII: K2465 Rectangle Porphyry**

K$_2$O/CaO = 0.7  
J-value (0.6450 ± 0.0086)x10$^{-4}$  
Flux Factor 0.980

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>39Ar/36Ar</th>
<th>40Ar/36Ar</th>
<th>% atmos</th>
<th>40Ar/39Ar</th>
<th>Apparent Age x10$^6$ years</th>
</tr>
</thead>
<tbody>
<tr>
<td>740</td>
<td>1.2 ± 0.01</td>
<td>284.6</td>
<td>100.0</td>
<td>3.30</td>
<td>0.40</td>
</tr>
<tr>
<td>970</td>
<td>40.8 ± 1.6</td>
<td>430.4</td>
<td>68.7</td>
<td>3.17</td>
<td>0.09</td>
</tr>
<tr>
<td>1070</td>
<td>31.6 ± 1.0</td>
<td>427.6</td>
<td>69.2</td>
<td>4.17</td>
<td>0.51</td>
</tr>
<tr>
<td>1170</td>
<td>30.9 ± 0.7</td>
<td>483.1</td>
<td>61.2</td>
<td>6.06</td>
<td>0.74</td>
</tr>
<tr>
<td>1210</td>
<td>21.1 ± 0.5</td>
<td>422.3</td>
<td>70.2</td>
<td>5.99</td>
<td>0.73</td>
</tr>
</tbody>
</table>

**TABLE VIII: K814**

K$_2$O/CaO = 0.1  
J-value (0.6450 ± 0.0086)x10$^{-4}$  
Flux Factor 0.986

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>39Ar/36Ar</th>
<th>40Ar/36Ar</th>
<th>% atmos</th>
<th>40Ar/39Ar</th>
<th>Apparent Age x10$^6$ years</th>
</tr>
</thead>
<tbody>
<tr>
<td>830</td>
<td>7.5 ± 0.2</td>
<td>448.9</td>
<td>65.9</td>
<td>19.1</td>
<td>2.34</td>
</tr>
<tr>
<td>970</td>
<td>15.2 ± 0.6</td>
<td>574.12</td>
<td>51.5</td>
<td>17.50</td>
<td>2.14</td>
</tr>
<tr>
<td>1000</td>
<td>17.4 ± 1.2</td>
<td>604.40</td>
<td>48.9</td>
<td>17.01</td>
<td>2.08</td>
</tr>
<tr>
<td>1110</td>
<td>11.2 ± 0.3</td>
<td>508.4</td>
<td>58.2</td>
<td>18.10</td>
<td>2.21</td>
</tr>
<tr>
<td>1170</td>
<td>21.2 ± 1.0</td>
<td>693.28</td>
<td>42.6</td>
<td>18.10</td>
<td>2.21</td>
</tr>
<tr>
<td>1210</td>
<td>16.0 ± 0.7</td>
<td>655.13</td>
<td>45.1</td>
<td>21.50</td>
<td>2.64</td>
</tr>
</tbody>
</table>