where $\frac{nt}{no}$ = ratio of positive to neutral atoms produced

e = electron charge

w = work function of filament

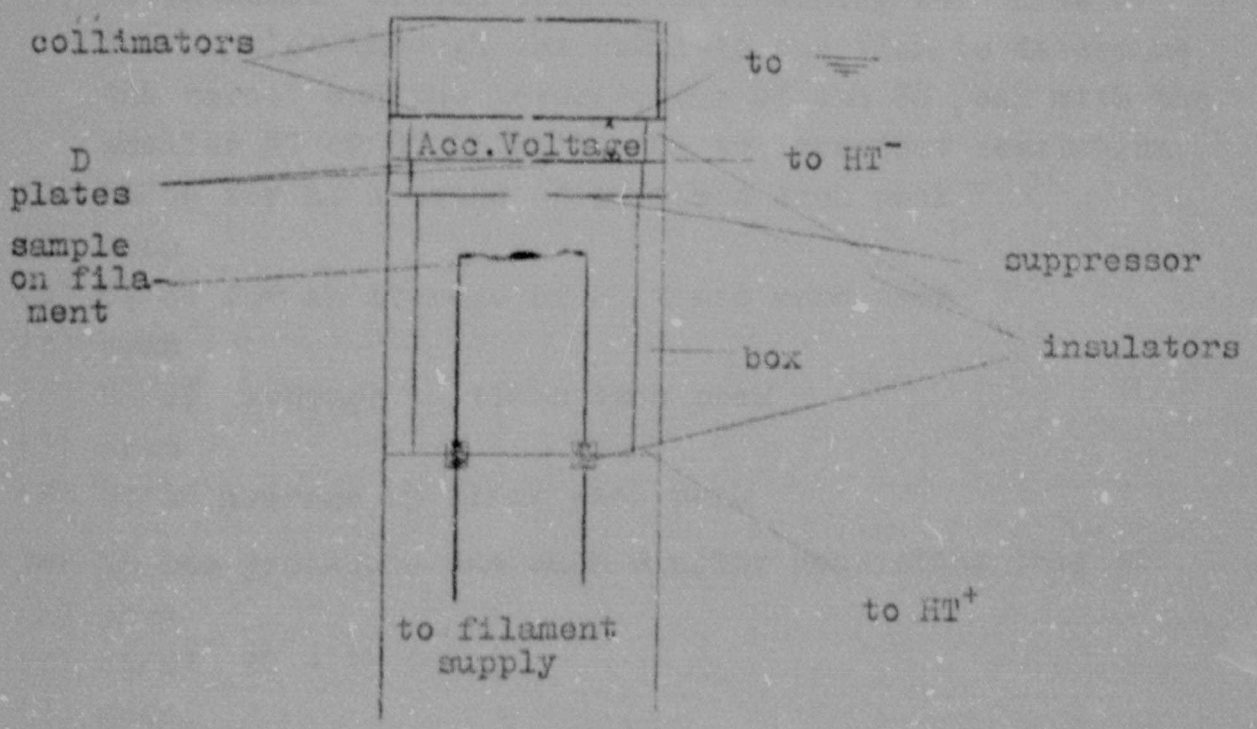
k = Boltzman's constant

t = temperature of filament

it is evident that a filament with higher work function will have at a given temperature higher efficiency of ionization. In the case of Rb, because of the low ionization potential, tantalum filaments with lower work function are satisfactory.

Fig. 11

Ion source



Once the source was in position it took from 1½ to 2 hours to reach a working vacuum for Rb runs, and four hours or more for Sr runs. The Sr samples were heated at 1.5 amps. for some hours before the measurements started to eliminate Rb that was possibly contained in the sample. At the beginning of the run, and until stable emission of good intensity was achieved, the filament temperature was

raised slowly for a period varying from a half to one hour or more for Sr, and less than half an hour for Rb.

Focussing was performed by varying the mean-potential on the D-plates (see fig. 11), and beam centering by varying the relative potential between the D-plates. The magnet current was varied to move from peak to peak by a system of switches with separate fine adjustments for each switch-position. Peak heights were compared by switching from peak to peak magnetically and remaining approximately half a minute in each peak position. In this time the position of the top of the peak was checked three or four times by scanning over a very short range by varying the accelerating voltage. The readings were taken as follows for Sr:

(1) mechanically driven continuous scanning for three or four cycles through the complete spectrum to determine the zeros and the interference of the 88 peak with the smaller 87 or 86 ("tail") due to imperfect resolution
(2) 88/86 for an average of 10 times each peak
(3) scan
(4) 87/86 for an average of 25 times each peak
(5) scan
(6) 88/86 average 10 times each peak
(7) scan
(8) 84/86 average 25 times each peak

For Rb the procedure was much simpler consisting only of:

(1) scan
(2) 85/87 20 - 25 times
(3) scan.

The records were read manually by drawing straight lines from peak to peak and taking contemporaneous readings of the two peaks at given intervals assuming uniform changes of intensity.

CHAPTER IV - THE EXPERIMENTAL RESULTS

1. PRECISION OF THE MEASUREMENTS

As previously described, the isotopic ratios were measured by means of a mass spectrometer by magnetic peak switching. Pairs of peaks were measured 20 or more times for each ratio required; the number of times each pair was measured depended on the stability of the emission, the peak shape and the spiking ratio. On occasion poor conditions in the mentioned factors tended to increase the error, but as far as possible an increase in the number of measurements for each pair of peaks was then made to reduce this effect. To determine the average scatter about the mean for the isotopic ratios, the mean deviation was calculated for about 30 samples chosen at random. The average mean deviation was approximately 0.15% and was in no instance greater than 0.45%. In order to gain a better idea of the scatter, the standard deviation was calculated in six cases, yielding values of 0.19, 0.21 and 0.21% for Rb^{85}/Rb^{87} ratios, and 0.16, 0.30 and 0.40% for Sr^{87}/Sr^{86} ratios.

The scatter about the mean of a set of measurements of an isotopic ratio depends on instrumental characteristics and is only a minor part of the possible error. This feature was demonstrated by duplicate measurements. In almost all cases measurements on each sample were duplicated and sometimes repeated three times. Duplicate and triplicate measurements were performed on different portions of the same sample weighed in different dishes and chemically treated independently. It was found that although the duplicate measurements frequently agreed to within one per cent of the previous ones, in other cases the difference was from 1.5 to 2.0%, and in a few instances more than 2%.

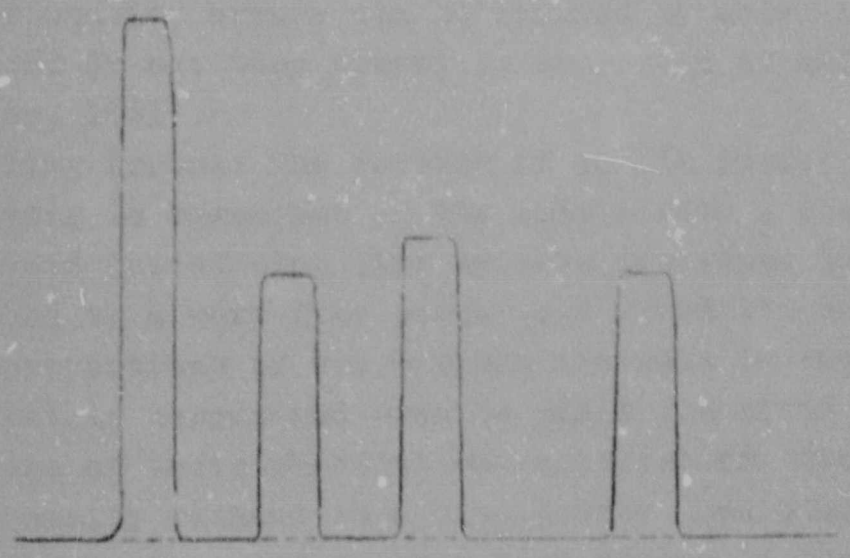
The reproducibility of a measurement from two different portions of the same sample can be influenced by various errors deriving from the chemistry, systematic instrumental error, the sampling and the weighing.

The Chemistry Error: It is impossible to reproduce exactly the same conditions for each sample - errors are caused by

contamination which can derive from the beakers and the ion exchange columns, or from small impurities in the acids and in the water used. In the latter cases the contaminating agent is presumaoly natural Sr and would decrease the Sr^{87}/Sr^{86} ratio. If the contamination derives from the columns the Sr can have high Sr^{87} content and therefore increase the Sr^{87}/Sr^{86} ratio. This type of contamination is the most dangerous because, contrary to the natural Sr contamination, it can effect the Sr^{87}/Sr^{86} and Rb^{87}/Sr^{86} ratios in opposite directions.

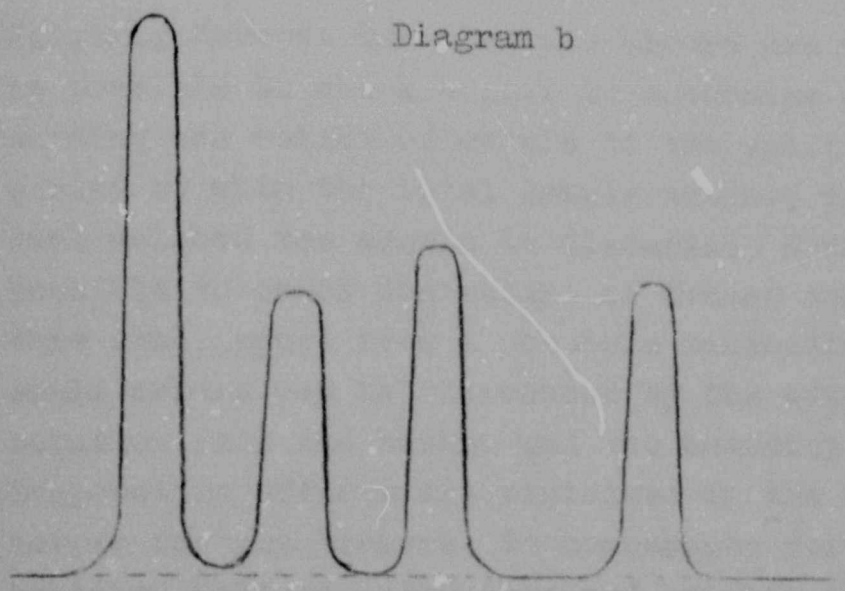
Instrumental Error: The greatest uncertainty in measurements of Sr ratios derives from the peak shape or "tail". The ideal peak shape is shown in diagram a.

Diagram a



The ideal peak is unattainable and in practice peaks resembling diagram b were used. In this case the separation of ions of different masses is not perfect and the Sr^{87} beam for instance contains a certain number of Sr^{88} ions. It is commonly said that in such cases the Sr^{87} is on the "tail" of the Sr^{88} peak. "Tail" corrections can be made by estimating the shape of the base of the major peak but errors are inevitably introduced.

Diagram b



"Tail" problems rarely arise with Rb but there is the problem of fractionation errors. As previously discussed, fractionation errors can be reduced by normalizing in the case of Sr but they cannot be corrected at all for Rb (Jäger, 1963).

Sampling Errors: The portion of sample powder needed for analysis is taken out of the bottle with a clean spatula. To avoid introducing bias by this procedure the rock is crushed to a very fine powder and mixed thoroughly so that the proportions of the various minerals in the sample are accurately reproduced even in small fractions of the powder. Because of their physical characteristics, mica flakes are less easily reduced to a fine powder than other minerals, and the presence of coarser mica flakes in the sample powder can introduce error since two sample fractions can contain different proportions of mica. If a large fraction of the Rb contained in the rock derives from the mica, this effect becomes worse.

All the sample portions analysed in this investigation were isolated from the powders with a spatula; it would be more accurate however, to split the initial powder into successively smaller statistically representative fractions by means of a splitting machine until the desired amount of powder is obtained.

Weighing Errors: The absolute errors are very small and it is possible to check errors in recording of the weights by summing the weight of sample in the split solutions and comparing it with the total sample weight; in cases of discordant weights the sample is discarded. However, it is not possible to check the weight of tracer solution added. In this case, apart from a possible subjective error, other small errors can be introduced by the evaporation of the solution from the beaker and the humidity of the room. Evaporation effects are minimized by the use of "parafilm" covers for the beakers. To compensate for difference in humidity between laboratory and balance room the beakers are allowed to stand for some minutes before the weighing and spiking is peformed.

As divergence among duplicated measurements, for reasons discussed above, is often far greater than the uncertainty in each particular measurement, this divergence is assumed to be representative of the possible error in the final data.

Ability to reproduce a given result does not necessarily prove that the results are accurate. Systematic bias can be introduced at any stage in the treatment of samples, for example: constant contamination level from water and acids, or recorder faults.

In order to check for a systematic bias deriving from the instrument measurements, the interlaboratory standard Eimer and Amend $SrCO_3$ was run at intervals of time by Dr. H.L. Allsopp, R. Davies and the author. The results are listed in table no. 2 together with means of values obtained in other laboratories and on different types of instruments. The B.P.I. mean falls within these results and is approximately 0.004% higher than the mean of these. It can therefore be assumed that systematic instrumental error is small.

To check on systematic errors introduced in spiking (e.g. error in the spike isotopic ratios or in the spike concentration), spiked samples of the Bern 4B international biotite standard (Jäger et al., 1963) were measured. The Rb results (Allsopp - personal communication, 1967) of 168, 170,

168, 171 ppm. are in good agreement with the data published by Jäger et al. The Sr results - 280 and 247 ppm. - are also within the limits of the published data, but in this case the scatter of the values obtained by different laboratories is very large, probably because of the heterogeneity of the Bern 43 Sr composition, and cannot be used to indentify possible systematic bias in the Sr results. For this purpose there exists a need for a Sr international standard having very homogeneous composition, for example a finely powdered felspar or total rock.

Finally the contamination level, as discussed in Chapter III, was checked by blank runs.

2. THE ISOCHRON PLOT

Ages and initial ratios were calculated by the isochron plot previously described.

The regression line (isochron) for a given set of samples was calculated and plotted on a diagram together with the sample points. The 95% confidence limits for the intercept on the y-axis and for the slope of the isochron were calculated assuming no error in x (Acton, 1959 - Chap.2 pp. 19-26). This method, although giving an idea of the order of magnitude of the errors, is not exact since errors are also present in the x-axis. The abscissa represents in fact the ratio Rb^{87}/Sr^{86} in which appear the combined errors of the Sr and Rb measurements. The calculation of the confidence limits for slope and intercept assuming errors in x as well as in y (York, 1966; McIntyre et al, 1966) is a complicated procedure and practical only if performed by means of a computer; it is felt that use of the exact procedure is unjustified with the relatively unprecise data now available. In the near future Sr^{87}/Sr^{86} ratios will be measured again with a more precise mass spectrometer to prepare the present data for publication, and only after this will the York calculation be carried out.

3. THE NELSPRUIT MIGMATITE

The origin of the Nelspruit migmatite has been discussed in Chapter II. All the authors quoted there have ascribed the migmatite to the autochthonous granite of Read's granite series; Visser et al (op.cit.) and Van Eeden & Marshall (op. cit.) suggest that the rocks of the Swaziland System participated to form the migmatite; Ramsay, Viljoen and Anhaeusser (op.cit.) on the other hand, propose that the migmatite derived only from rocks of the basement assemblage, and that the Nelspruit migmatite was intruded by a younger granite. Viljoen (1964) suggests that the granitic magma was generated by the orogenic stresses connected with the updoming of the remobilized and migmatized basement. This magma intruded along the contact between the stratified rocks and the migmatite and caused the metamorphism of the surrounding Swaziland System rocks.

The migmatite is a very heterogeneous rock. It includes a number of phases varying in texture and composition. At first it was suspected that the chemical heterogeneity of the rock would be reflected in local variations in the initial isotopic composition of the Sr. Therefore, to study expected differences and possibly differentiate original phases of the migmatite, sampling was directed at collecting as many different rock phases as possible. The samples, selected from a large collection, comprised fifteen of representative phases of the migmatite, three of the contact phase, four of the pegmatites and one containing a felsic vein with "basic behind".

The total rock results from the migmatite samples:
Contrary to expectations, the sample points lie on an isochron with deviations within the limits of experimental error as can be seen from table 4, where the deviation of the measured from the theoretical values of the Sr^{87}/Sr^{86} ratios are represented. The slope and intercept of the isochron plot were calculated at the 95% confidence limits. They yield an age of 2.992 b.y. $\pm$ 0.070 and an initial Sr^{87}/Sr^{86} ratio of 0.7052 $\pm$ 0.0019 The total rock results are shown in table 3, and the isochron plot is shown in figure 12.

Discussion: It is commonly accepted (Turner & Verhoogen, 1960 - pp.185-388; Von Platen, 1963; Winkler, 1965; etc.) that during the process of migmatite formation the rock never reaches complete fusion, therefore isotopic homogenization must at least in part be due to diffusion through solid phases and is thus a slower process than in magmatic melts. Pidgeon (1964) found that the Sr in the migmatite associated with the Cooma granite was not completely isotopically homogenized and that two sets of samples, some three miles apart, seem to lie on two parallel isochrons with significantly different initial Sr^{87}/Sr^{86} ratios. He suggests that this was caused by initial differences in the Sr isotopic composition of the original rocks that formed the migmatite.

Thus heterogeneity in isotopic composition of the Sr contained in the various phases of the Nelspruit migmatite could be expected except if the Sr^{87}/Sr^{86} ratio in the primordial earth crust at the time of migmatization was rather uniform, and this seems unlikely according to the following: the Nelspruit migmatite had an initial ratio close to 0.705; values of 0.706 and 0.707 approximately have been found for slightly older granitic rocks which occur on the Swaziland side of the Barberton Mountain Land (Davies, personal communication, 1967). The Fig Tree shales (Allsopp et al., 1967) yield an initial ratio of approximately 0.715. These values are higher than the average present day Sr^{87}/Sr^{86} ratio of 0.704 for rocks believed to be of mantle origin (Heier et al, 1965); and early procambrian rocks of this source must have had an even lower Sr^{87}/Sr^{86} ratio as suggested by Hedge & Walthall (1963) and supported by initial ratios close to 0.701 found by Allsopp (1965) and McElhinny (1966) for ancient mafic rocks.

The above confirms that the earth's crust at the time of formation of the migmatite was already well differentiated from the mantle and that probably its Sr isotopic composition was heterogeneous. However, the initial isotopic composition of the Sr in the different phases of the Nelspruit migmatite over a distance of some 15 miles is homogeneous; it is there-

fore proposed that the homogenization of the Sr isotopes was attained over a long period of time during which the rock was under uniform conditions at relatively high temperatures, and that this was a regional phenomenon. These conditions suggest deep burial, although at the time of formation of the Nelspruit migmatite. due to the steep thermal gradient and the lesser thickness of the earth crust (Engel , 1966), these conditions might have obtained at a depth of only a few miles.

The homogeneity of the initial isotopic composition of the Sr suggests that the age obtained for the Nelspruit migmatite marks the end of a granitization process which involved all the rock phases studied, including the homogeneous granite bodies (see Chapter II). Had the homogeneous phases intruded after migmatization and been derived from a different source, they would probably have had a different initial isotopic composition.

The migmatization probably postdates the deposition of the Swaziland System as shown by lead ratio ages from zircon (Van Niekerk et al., 1967), and lead ages from galenas and a jamesonite (Ulrych et al., 1967) from these rocks indicating an event at approximately 3.4 b.y.

Fig Tree shales deriving from the metamorphic aureole of the migmatite have been dated at 3.0 b.y. (Allsopp et al., 1967). The cooling time of the migmatite possibly was sufficiently long for homogenization to take place in the adjacent shales. However, since the metamorphism that affected them was very mild (Viljoen, 1964; Anhaeusser, 1964; Viljoen & Anhaeusser, 1965) homogenization of the Sr isotopic composition due to solid diffusion was a very slow process, and it is therefore possible that the shales were regionally homogenized by burial in the same way as the migmatite but at lower temperatures.

The separated minerals apparent ages and discussion:

The significance of separated mineral ages has been discussed in Chapter I. As this investigation is not concerned with metamorphic events postdating migmatization, only a few

mineral phases - chloritised biotite and K-felspar - were investigated to check whether they would yield ages concordant with the total rock age. The mica fractions were 90 - 95% pure; the felspar fractions of the first separation (alpha) were only 80 - 85% pure; the fractions of the second separation (beta) were more purified, approximately 90 - 95%.

A list of these results is given in table 6 where 0.705 was used as initial Sr^{87}/Sr^{86} ratio in the age calculations. It was found that almost all the points representing each mineral were situated below the total rock isochron, indicating radiogenic Sr loss (see figure 13). Some of the mineral ages obtained could be interpreted as being due to the metamorphism of the Mpageni granite, but others, considering that the samples lie a few miles from the intrusive, are rather low indicating either an event younger than the Mpageni or that the Mpageni intrusion was effective regionally.

Lanphere et al. (1963) attempted to establish the time of metamorphism from biotite-total rock joins. These can yield ages close to that of the metamorphism provided that the Sr^{87}/Sr^{86} ratio in the biotite approximates that of the total rock during metamorphic homogenization.

Two biotite-total rock joins were calculated for the Nelspruit migmatite yielding an apparent age of 2.55 b.y. and 2.58 b.y. which is close to that found for the Mpageni granite. Initial ratios of 0.713 and 0.709 which are close to the Sr^{87}/Sr^{86} ratios for the total rocks at the time of metamorphism, were found for the biotite-total rock joins. This probably confirms that the migmatite was subjected to only one metamorphic episode at the time of emplacement of the Mpageni granite and which was regionally effective.

The "contact phase":

Three samples were collected from the contact phase by M.J. Viljoen and the author for a preliminary investigation. Two

of the samples show gneissic fabric and the third has been mylonitized due to the updoming of the migmatite after crystallization of the contact phase (Viljoen, personal communication, 1967). The results of the isotopic work are shown in table 5. The apparent ages, calculated arbitrarily using 0.705 as initial Sr^{87}/Sr^{86} ratio, are close to that of the migmatite. the maximum deviation (sample AA12) being 4.1%.

The reproducibility of the contact phase results is not as good as that obtained for the Nelspruit migmatite, possibly because of sampling errors arising from the presence of uncrushed mica flakes.

The slope of a join AA10, AA11 and AA12 was calculated and yields an age of approximately 2.92 b.y. and an initial ratio of 0.718. These results however are of dubious significance because of the small number of samples used and the uncertain origin of sample AA10 which has high Rb/Sr ratio characteristic of pegmatitic rocks, while its relationship to the contact phase could not be established because of mylonitization.

Although difference in age between the contact phase and the migmatite could not be ascertained, the results so far obtained show a marked difference in the Rb/Sr ratios between the migmatite and the contact phase. Even if sample AA10 is not taken into account because of its uncertain origin, the two remaining samples have Rb/Sr ratios twice as large as the highest ratio recorded for the migmatite and more than four times the average Rb/Sr ratio. The Rb content in the contact phase is comparable to that of some of the migmatite samples but the Sr content is lower. The reason for this might be related to a compositional variation noted by Anhaeusser (1966) who found an increase in the ratio of potash to sodium felspar in the contact zone and proposed that the contact phase represents the late phase of the granitization cycle. In this case the migmatite and contact phase would probably have the same absolute age and similar initial ratio.

These preliminary results, although insufficient to delineate possible difference in age between the migmatite and

the contact phase, are encouraging for future investigation.

The pegmatites:

Four samples from two pegmatites intruding the migmatite were analyzed and approximate ages were calculated arbitrarily using 0.705 as the initial Sr^{87}/Sr^{86} ratio (see table 7). Three of the samples derive from the same pegmatite and the fourth, AA13P, derives from another pegmatite closer to the contact migmatite-Swaziland System rocks.

AA13P, plotted on a Sr evolution diagram (see figure 15), lies below the Nelspruit migmatite isochron. Consequently this pegmatite has either not remained a closed chemical system or it is younger than the migmatite since, if the closed chemical system requirements had obtained, it would be contemperaneous with the Nelspruit migmatite only if its initial Sr^{87}/Sr^{86} ratio was close to 0.667 which is impossibly low.

OG38F and OG38G yield apparent ages approximating that of the migmatite and lie close to the 2.99 b.y. isochron on a Sr evolution diagram. The third sample, OG38B, however lies below this line and yields an age significantly lower than the other two. Probably this portion of the pegmatite did not remain a closed chemical system and lost part of its radiogenic Sr. If this was due to metamorphism the proximity of the sample to the boundary of the pegmatite might account for the loss of radiogenic Sr, but since this aspect of the location was not recorded this could not be verified. The loss of radiogenic Sr may also be due to localized leaching caused by either hydrothermal solutions or weathering.

This problem can only be solved by more adequate sampling comprising various portions of the pegmatite at different distances from the pegmatite boundaries and of the adjacent migmatite.

Since the pegmatites are intrusive in the migmatite it is possible that they are younger. In figure 15 a tentative line of best fit was traced for the points available. The slope of this line yields an approximate age of 2.88 b.y. and an initial ratio close to 0.715. The number of samples however is too small to draw any conclusions.

The "basic behinds":

Felsic material in the migmatite is frequently bordered by basic selvages (Chapter II). Two samples containing "basic behinds" were collected (see photographs 9 & 10). The one with the more marked rim and more favourable Rb/Sr ratio, AA9, was chosen for isotopic work.

A slice of this sample 2 inches thick, containing the "basic behind", was sawn off and broken into fragments 1 - 2 inches in diameter. From these, sawing as close to the respective boundaries as possible with a diamond saw, approximately 50 gm. of the 2 mm. thick "basic behind" (AA9BB), and 100 - 200 gm. of the felsic portion (AA9F) and of the mafic portion (AA9M) were isolated. The results of isotopic measurements on these portions are shown in table 8 and are plotted on a Sr evolution diagram in figure 16, and ages were calculated using 0.705 as initial Sr^{87}/Sr^{86} ratio.

While the felsic portion yields an age close to that of the migmatite, the other two portions are noticeably different: AA9BB yields a lower and AA9M a higher age.

If the felsic band was formed during migmatization, the three different portions were isotopically homogenized and later, probably due to metamorphism or a prolonged cooling period of the rock, the basic rim being thin and rich in biotite, might have behaved as a single mineral losing some of its radiogenic Sr to the mafic portion of the sample. This movement of radiogenic Sr from the "basic behind" could be checked by analyzing samples at successively larger distances from it

4. THE MPAGENI GRANITE

Total rock results and discussion:

Five total rock samples of the Mpageni granite were analysed. The results are listed in table 9 and an isochron plot is shown in figure 17. Two of the five samples, AA4A and AA43, derive from a syenitic body (Chapter II) and were found to lie on the isochron with very small deviations (table 10). The syenitic body is thus considered to have the same age and initial Sr^{87}/Sr^{86} ratio as the Mpageni granite. A sixth