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An Rb/Sr and Pb/Pb Study of the Labrador Archean Complex

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Determination of the  $^{87}\text{Rb}$  decay constant

An Rb/Sr and Pb/Pb study of the Labrador Archean complex

by

Donald W. Davis



A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

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The undersigned certify that they have read, and  
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for acceptance, a thesis entitled .....  
..... DETERMINATION OF THE  $^{87}\text{Rb}$  DECAY CONSTANT  
.....  
AN Rb/Sr AND Pb/Pb STUDY OF THE LABRADOR ARCHEAN COMPLEX  
.....  
submitted by ..... DONALD W. DAVIS .....  
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### Abstract

The decay constant of  $^{87}\text{Rb}$  has been redetermined by measuring the amount of radiogenic  $^{87}\text{Sr}$  produced over a period of 19 yrs in 20 gram samples of purified  $\text{RbClO}_4$ , using isotope dilution techniques. The rubidium sample was spiked with  $^{84}\text{Sr}$  and the nanogram quantities of strontium separated by coprecipitation with  $\text{Ba}(\text{NO}_3)_2$ . Analyses were carried out on a 25 cm,  $90^\circ$  sector mass spectrometer equipped with a Spiraltron electron multiplier. Measurement of three independent ratios permitted continuous monitoring of the ion beam fractionation. The average of nine determinations gives a value for the decay constant of  $1.419(\pm 0.012) \times 10^{-11} \text{ yr}^{-1}$  ( $2\sigma$ ) ( $t(1/2) = 4.89(\pm 0.04) \times 10^{10} \text{ yr}$ ).

\* \* \*

Whole rock rubidium strontium analyses were done on samples from various early Archean assemblages in the Saglek Bay area of Labrador. These included the Uivak gneisses, the Nulliak assemblage, the Saglek dykes, two high iron intrusives, late syntectonic granites and two post-tectonic granites. None of the assemblages was found to define an isochron. This was interpreted as being due to limited migration of Rb and radiogenic Sr on the whole rock level. The scatter on an Rb-Sr diagram indicates maximum ages for whole rock closure of between 2900 and 2600 m.y..

Extrapolation of the Sr isotopic composition of the late granites back to the approximate time of their intrusion gives a variety of initial ratios scattering between mantle and crustal values.

Pb isotope ratios were determined on whole rock of the Uivak gneiss, the late granites and one Saglek dyke. The isotopic composition of the lead in the Uivak feldspar separates was also determined. The results again point toward open system behavior at about 2800 m.y.. An attempt is made to fit the distribution of these leads to a quasi-3 stage model involving evolution from leads of Amîtsoq feldspar composition at 3600 m.y. and refractionation at about 2850 m.y.. The late granites are quite non-radiogenic and tend to plot in the same region as the Uivak feldspars. It is suggested that they may be derived from partial melting of a lower crustal layer consisting of varying proportions of felsic and mafic material which had been subjected to granulite facies metamorphism shortly before intrusion of the granites.

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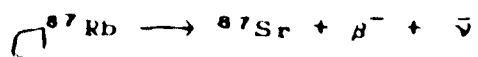
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## I Introduction

The rubidium 87 isotope decays into strontium 87 with the emission of a beta particle and an anti-neutrino as shown by the following equation:



The  ${}^{87}\text{Rb}$  nucleus decays from the spin 3/2 ground state to the spin 9/2 ground state of  ${}^{87}\text{Sr}$  (MacGregor & Wiedenbeck, 1954). This produces a change in angular momentum of 3 units, making it a third order forbidden beta transition, a highly improbable event, resulting in a half-life for the  ${}^{87}\text{Rb}$  isotope of about 50 billion years.

This decay process has proven to be an extremely useful geochronometer for several reasons. The half-life is of about the right order of magnitude for measuring geologic time intervals. Rubidium is a very widespread and dispersed element. The geochemical properties of rubidium are such that it tends to be concentrated in later forming phases during magmatic crystallization. Strontium, on the other hand, may be concentrated in the earlier phases so that the Rb/Sr ratio greatly increases in the later phases and it is possible to find a broad range of Rb/Sr values in common minerals.

The dating of a rock or mineral using this technique consists in doing a quantitative chemical analysis of the

amount of  $^{87}\text{Rb}$  in the rock or mineral and the amount of  $^{87}\text{Sr}$  daughter produced by the decay of the  $^{87}\text{Rb}$  since the formation of the specimen. This is usually accomplished by isotope dilution using a mass spectrometer. Obviously, knowledge of the age can at best be only as good as knowledge of the decay constant. The value of this constant has been in dispute for over 20 years. Table I lists most of the previous attempts at measuring it. The methods fall into three categories: radiometric, geological and chemical.

Radiometric methods are differential techniques. Since  $t = -(1/N)(dN/dt)$ , where  $N$  is the number of parent nuclei, one attempts to measure  $t$  directly by measuring the time rate of beta decay using any one of a number of different types of detectors. These experiments have usually produced widely disparate results. The principal reason for this is that the energy spectrum of the emitted beta particles has its maximum near zero and decreases rapidly to a cut-off point of about 275 kev. Therefore, although the average energy of the emitted particles is about 40 kev, many of them are emitted with very low energies, below the detection threshold of the detectors. In this situation, there are many possibilities for systematic error.

In contrast, the geological and chemical methods are integral techniques. They depend upon measuring the total amount of daughter accumulated over a known period of time. In the geological method, the age of a suitable rock is determined using another decay scheme such as uranium-lead

Table I

Previous measurements of the  $^{87}\text{Rb}$  decay constant

<u>Reference</u>	<u><math>t</math> (<math>\times 10^{-11}</math> yr<math>^{-1}</math>)</u>
<b>Gas Counters:</b>	
Haxel et al., 1948	1.15 $\pm$ .12
Kemmerich, 1948	1.15 $\pm$ .12
Curran et al., 1952	1.13
MacGregor and Wiedenbeck, 1952	1.11 $\pm$ .05
MacGregor and Wiedenbeck, 1954	1.12 $\pm$ .05
Flinta and Eklund, 1954	1.14 $\pm$ .04
Bahnisch et al., 1952	1.44
Geese-Bahnisch and Huster, 1954	1.61 $\pm$ .11
Libby, 1957	1.37 $\pm$ .04
McNair and Wilson, 1964	1.32 $\pm$ .03
Neumann and Huster, 1972	1.42 $\pm$ .03
<b>Solid Scintillators:</b>	
Lewis, 1952	1.17 $\pm$ .06
Egelkraut and Leutz, 1961	1.19 $\pm$ .02
Beard and Kelly, 1961	1.25 $\pm$ .02
Leutz et al., 1962	1.20 $\pm$ .02
<b>Liquid Scintillators:</b>	
Flynn and Glendenin, 1959	1.47 $\pm$ .03
Kovach, 1964	1.45 $\pm$ .03
Brinkman et al., 1965	1.33 $\pm$ .04
<b>Geological Comparison:</b>	
Aldrich et al., 1956	1.39 $\pm$ .06
Afanass'yev et al., 1974	1.42
<b>Chemical Analysis:</b>	
McMullen et al., 1966	1.47 $\pm$ .01

and the decay constant of  $^{87}\text{Rb}$  is adjusted so that the age given by the Rb-Sr technique will be the same. This involves the assumption that the rock formed in a very short time and remained undisturbed up to the present. Also, the value of the  $^{87}\text{Rb}$  decay constant as determined by this method will be affected by analytical uncertainties in the measurements using the alternate decay scheme as well as uncertainties in its decay constants.

The one technique which is capable in principle of supplying both good precision and good accuracy is to allow a sample of strontium-free rubidium to decay for a known time in the laboratory and to measure the amount of accumulated radiogenic  $^{87}\text{Sr}$  with a mass spectrometer using the isotope dilution method. For a relatively short decay time (c. 20 years) the decay constant may be written:

$$\lambda = \frac{^{87}\text{Sr}_0}{^{87}\text{Rb}} \times t^{-1}$$

where  $^{87}\text{Sr}_0$  is the amount of radiogenic strontium accumulated over time  $t$  by a known quantity of rubidium,  $^{87}\text{Rb}$ . This is the chemical method. The experimental problems are in the separation of the trace amounts of strontium from the rubidium to prevent isobaric interference in the mass spectrum and in measuring the strontium and rubidium quantitatively.

The two most often quoted measurements for the decay constant are those of Aldrich et al. (1956) and Flynn and

Glendenin (1959). Aldrich et al. found a value of  $1.395(\pm 0.056) \times 10^{-11} \text{ yr}^{-1}$  by adjusting the Rb-Sr ages in pegmatite minerals to agree with concordant U-Pb ages from the same rocks. Flynn and Glendenin found a value of  $1.475(\pm 0.031) \times 10^{-11} \text{ yr}^{-1}$  by measuring the beta decay rate of  $^{87}\text{Rb}$  with a liquid scintillator. The difference between these values is almost 6 per cent. The Aldrich value has been the most widely used although its precision is poor.

McMullen et al. (1966) attempted to measure the decay constant using the chemical method. In 1956 a purified  $\text{RbClO}_4$  sample was prepared, converting from about one kilogram of  $\text{RbCl}$  to the perchlorate by precipitation with perchloric acid. The product was then further purified by five successive recrystallizations in demineralized water to give batch A. Two months later a portion of this, batch B, was again recrystallized. Two more batches, C and D, were taken from A eleven months later and recrystallized slowly.

After seven years McMullen et al. measured the amount of radiogenic strontium produced over this period in portions of each batch. They found an average value for the decay constant of  $1.469(\pm 0.012) \times 10^{-11} \text{ yr}^{-1}$ . They did not monitor mass fractionation during the measurements, however, and this value may be subject to systematic error. The present experiment was performed on the same material 19 years after its purification. By this time a 20 g sample of  $\text{RbClO}_4$  would be expected to contain about 0.67 nanograms of  $^{87}\text{Sr}$ , assuming a decay constant of  $1.39 \times 10^{-11} \text{ yr}^{-1}$ . It is



quite feasible to measure such quantities using ion counting mass-spectrometric techniques. In the present investigation three independent mass ratios were measured during the course of each Sr analysis in order that individual corrections could be made for fractionation in the mass spectrometer.

## II Experimental Technique:

### Chemistry -

About 20 grams of  $\text{RbClO}_4$  was added to a weighed 250 ml Teflon beaker in a hood kept at an over pressure by filtered air. The beaker was then covered and reweighed.

After returning the beaker to the hood, a clean Teflon-coated magnetic stirring element was added and one of the spike vials was emptied into it and thoroughly rinsed with 1.5N HCl. Enough water was added to make about 200 ml of solution. The beaker was next covered with a quartz plate and the solution stirred magnetically and heated to just below the boiling point using a hot plate and a heat lamp until all of the  $\text{RbClO}_4$  dissolved. The heat was then reduced and the cover removed to allow the solution to partially evaporate. When approximately 50 ml remained, the solution was cooled with dry ice to precipitate as much of the perchlorate as possible. The solution was then decanted into a 100 ml Teflon beaker, evaporated under moderate heat to about 5 ml, cooled to  $0^\circ\text{C}$  and decanted into a 10 ml Teflon beaker. The solution, containing about 25 mg of  $\text{RbClO}_4$ , was evaporated to dryness to remove HCl. The residue was dissolved in about 1 ml of hot water, and the solution transferred to a small quartz centrifuge tube. The tube was cooled to  $0^\circ\text{C}$  and  $\text{RbClO}_4$  crystals were centrifuged out. The supernatant liquid was transferred to a 5 ml quartz centrifuge tube and about 2 mg of purified  $\text{Ba}(\text{NO}_3)_2$  added to

the tube which was then capped with Parafilm and inverted until the  $\text{Ba}(\text{NO}_3)_2$  dissolved. Vapour distilled 95%  $\text{HNO}_3$  was then added slowly until barium nitrate began to precipitate. More  $\text{HNO}_3$  was added to make about 5 ml of solution. The tube was capped, inverted several times and left to stand overnight. The barium nitrate crystals, containing the strontium, were centrifuged out and the acid decanted off. Residual acid in the tip of the tube was removed using a prewashed glass capillary. The tube was then refilled with acid, capped and inverted to rinse the crystals which were then centrifuged out and the acid removed as before. A minimum amount of water was added to redissolve the barium salt and the entire precipitation and rinsing procedure repeated. Subsequently, the barium and strontium were dissolved in 1 ml of 2.5N HCl and added to a Teflon column 5 mm in diameter and 55 mm long containing 1 ml Dowex 50W-X12 cation exchange resin. 2.5N HCl was passed through the column and the strontium was eluted in the fraction from 8 to 15 ml.

During the earlier analyses it was found that even after this procedure it was difficult to burn the remaining Rb off the filament in the mass spectrometer. From separation 13 onwards the following step was added. The solution was evaporated to dryness and dissolved in 1 drop of water. It was then loaded into a clean quartz micro-column containing a layer of Dowex 50W-X12 about 20 mm in length and 1 mm in diameter. 1.5N HCl was passed through the

column and the strontium was eluted in the fraction from 7 to 12 drops. The solution was then evaporated to a very small drop and loaded onto an oxidized tantalum filament using a quartz capillary. This additional step produced a substantial reduction in the amount of rubidium on the filament.

The filament load was treated with a small drop of phosphoric acid for runs 2 to 11 and with perchloric acid for runs 12 to 17. The temperature was slowly increased to fume off the excess acid and the filament finally heated to a dull glow for one second.

Analysis 1 was an unsuccessful attempt to separate the strontium and rubidium using cation exchange columns. Numbers 8 to 11 were loaded onto the filament using a larger amount of phosphoric acid than usual. This unfortunately had the effect of inhibiting the emission and sometimes caused it to be erratic. The only analysis of this group which produced reliable data was number 11. Analyses 7 and 12 did not succeed because of difficulties with the removal of rubidium.

The water used was distilled in a quartz fractionation column and had a strontium blank of 0.53 ng/100 ml. The acids were all distilled below the boiling point. The 6N HCl had a strontium blank of 1.94 ng/100 ml. The total blank of the separation procedure was determined by performing all the steps of a normal separation using only the spike. This was done twice during the course of the analyses. The first

measurement gave 1.10 ng and the second gave 1.05 ng. This is about the amount to be expected from the water and acids used. All equipment with which the solutions came into contact was cleaned with hot HCl for at least twelve hours and rinsed with pure water. Plastic gloves were worn during most of the operations, which were all carried out in a filtered-air hood.

#### Mass spectrometry -

Isotope ratio measurements were carried out with a 25 cm, 90° sector mass spectrometer equipped with oil diffusion pumps which maintained a pressure of about  $3 \times 10^{-8}$  torr during operation. Peak switching was accomplished by changing the magnetic field. Random fluctuations in the field were sensed by a set of Hall probes and compensated for by a feedback circuit controlling a Kepco operational power supply.

A 0.015 cm exit slit was used in conjunction with a 0.030 cm detector slit. This gave a resolution of more than 600, permitting the resolution of all hydrocarbon peaks in the strontium mass range. In the worst case, that of m/e 86, the hydrocarbon peak was less than 10% of the strontium peak and was fully resolved. Hydrocarbons with half integral mass-to-charge ratios were not observed.

Ion beams were detected with a Spiraltron electron multiplier operated typically at 3500 V. The output was fed into an Ortec 486 amplifier - pulse height analyser followed

by an Ortec 773 timer - counter. Each peak was counted for ten seconds. Peak switching and printout were controlled by a Texas Instruments 980A computer. The timing was carried out by a second Ortec timer. The strontium isotope ratios normally measured were 84/88, 87/88 and 86/88. Each peak was centered by incrementing the accelerating potential at the beginning of a run. Minor adjustments to the magnetic field could be made manually during a run, to correct for any drift.

The  $^{85}\text{Rb}$  peak was measured before and after each 87/88 run. Normally, about two hours were needed to burn off the rubidium sufficiently well to begin the analysis. Strontium measurements were started when the  $^{85}\text{Rb}$  peak was less than 2% of the  $^{87}\text{Sr}$  peak. The source was checked for contamination by periodically running a blank filament at high temperature. In no case was any strontium peak observed although occasionally a small amount of rubidium was detected at high temperatures (which required that the source assembly be cleaned). The background signal between peaks was measured at the end of each analysis.

#### Spikes -

The spike used in the measurements was NBS SkM-988 which contains 99.89%  $^{84}\text{Sr}$ . SRM-988 was diluted to a known concentration and stored in 1.5N HCl in a volumetric flask. After one further dilution with 1.5N HCl in a Teflon bottle, the spikes were aliquoted into quartz vials with a quartz

micro-pipette and individually weighed (nanogram set 5).

In order to test the procedures used in handling and measuring very small quantities of strontium, the known amount of  $^{84}\text{Sr}$  in a nanogram-sized spike was "determined" by comparison with NBS SRM-987 strontium.

Aliquots of normal strontium were made up using the NBS SRM-987 Sr standard in the following way. The carbonate was converted to the nitrate in a weighed platinum dish and dried overnight at  $250^{\circ}\text{C}$ . A stock solution was made up from this salt and the concentration determined by transferring a weighed portion into a platinum dish, drying and converting it to the sulfate by the addition of  $\text{H}_2\text{SO}_4$ . The sulfuric acid was then fumed off and the sample heated to a constant weight. The theoretical amount of strontium present as calculated from the NBS concentration and the dilution procedure was 0.11869 g. The amount measured was 0.11854 g. The discrepancy is 0.13%.

A known portion of the diluted SRM-987 stock solution was added to an aliquot of the  $^{84}\text{Sr}$  spike used for Rb-Sr analysis in this laboratory and the mixture analysed on the mass spectrometer. The known value of the  $^{84}\text{Sr}$  spike was  $2.4184 \pm 0.0005$  ug. The value calculated from the normal Sr concentration is  $2.4207 \pm 0.0032$  ug. A portion of the normal Sr was also mixed with an aliquot of the SRM-988 stock and analyzed. The calculated value of the  $^{84}\text{Sr}$  in the SRM-988 stock was  $1.1811 \pm 0.0005$  ug using the NBS value for the concentration. The measured value using the normal Sr stock

was  $1.1785 \pm 0.0036$  ug. The errors on the measurements are expressed as  $2\sigma$ . In both cases the measurements agree with the expected concentrations to within the error.

The dilute normal Sr stock was further diluted in a Teflon bottle and aliquoted into quartz vials in the same manner as the  $^{84}\text{Sr}$  spike. The contents of each of these vials could then be mixed with an aliquot of  $^{84}\text{Sr}$  spike and used to check the concentration of the spike by measuring the  $^{84}\text{Sr}/^{88}\text{Sr}$  and  $^{86}\text{Sr}/^{88}\text{Sr}$  ratios in the mixture. The  $^{84}\text{Sr}$  spikes were individually weighed out to a precision of  $\pm 0.01\%$ . The mean amount of the  $^{84}\text{Sr}$  spike in each vial was  $5.0814 \pm 0.0032$  ng total Sr, while that of the normal aliquots was  $19.858 \pm 0.018$  ng of normal Sr. Four of the nanogram-sized  $^{84}\text{Sr}$  spikes were mixed with normal Sr aliquots and the mixture analyzed. The results shown in Table II indicate that one could expect to be able to determine nanogram quantities of Sr to somewhat better than one per cent accuracy with these techniques. A small correction for a filament loading blank had to be made to these data. This was determined by measuring the 84/88 peaks during an analysis of the pure  $^{84}\text{Sr}$  spike. The mean of four analyses was  $60 \pm 11$  picograms normal Sr loading blank. This involves a correction factor of about 0.3%.

A second group of spikes (nanogram set 6) was prepared and used for analyses 16 and 17. Unfortunately the cross checks on set 6 indicated that the spike concentrations were about 1% lower than expected. These measurements were of



Table II

## Cross-checks of procedures and measurements

Nanogram set 5:

<u>Calculated value</u>	<u>Measured value</u>	<u>Diff</u>
5.0835 ng	5.0794 ng	(.08 ± .11)%
5.0822 ng	5.0648 ng	(.34 ± .59)%
5.0824 ng	5.0868 ng	(.09 ± .19)%
5.0813 ng	5.0845 ng	(.06 ± .11)%

good precision, and it is difficult to understand how such a large discrepancy could occur in one dilution. A possible explanation for the cross checks giving an inaccurate answer is that the loading blank was much greater than usual, although this is quite unlikely. The results of analyses 16 and 17 were not used in calculating the final value for the decay constant because of this uncertainty in the spike concentration. Inclusion of these data in the final calculation would not significantly alter the value obtained.

Rubidium 87 -

As mentioned previously, the four batches of rubidium perchlorate are designated A, B, C and D. The grain size of B is fine while that of C and D is quite coarse and A is intermediate. The amount of rubidium contained in the salt was determined by diluting a solution of known concentration

and adding a  $^{87}\text{Rb}$ -enriched spike. The isotopic composition was then measured using a triple filament ion source. Normal rubidium standards (NBS-984) were interspersed with the spiked runs to allow fractionation corrections to be made. These corrections were 0.34%. The isotopic composition of the unspiked salt was also measured and found to be the same as that of the standards.

The Cs and K concentrations in all four batches were measured by concentration-dilution flame photometry using Rb-enriched standards. The water content of A, B and D was measured by heating the samples for at least 12 hours at  $300^{\circ}\text{C}$  and reweighing. These three contaminants fail to account for the total contaminant measured by isotope dilution as seen in Table III. The sum of their weight percentages is less than the weight percentage of the total contaminant by about 1%. It was not possible to identify the additional contaminating material. It is believed that the isotope dilution measurements are accurate to within  $\pm 0.25\%$  and these were used to determine the correction factors. The amount of  $^{87}\text{Rb}$  contained in the samples is calculated from the amount of normal Rb assuming an isotopic abundance of 27.8346% (Catanzaro et al., 1969).

Ion counter dead time corrections -

The data were corrected for counter dead time using the formula:

Table III  
Measurement of Impurities in  $\text{KBClO}_4$

	$\text{KClO}_4$	$\text{CaClO}_4$	$\text{H}_2\text{O}$	Wt. % contaminant (Isotope dilution)
Batch A	2.2%	0.76%	0.30%	4.4%
				4.5%
				4.3%
				4.5%
				----- Mean: 4.4%
B	0.33%	0.16%	0.14%	1.5%
				2.0%
				1.9%
				----- Mean: 1.8%
				C
D	0.17%	0.13%	0.04%	1.5%

$$R = M(1 - M*t)^{-1}$$

where  $R$  is the true count rate,  $M$  is the measured count rate and  $t$  is the dead time of the detection system. Analyses 2, 3 and 13 to 17 were assumed to have a dead time of 1.01 usec. (see Table IV). The standard deviation in the dead time is about  $\pm 4\%$ . This amounts to less than  $\pm 0.2\%$  of any peak measured during the experiment and is usually much

Table IV

Dead times from Eimer &amp; Amend Sr analyses:

<u>EA-1</u>	<u>EA-2</u>
1.11 ± .11 usec	1.16 ± .10 usec
.90 ± .07	.70 ± .19
1.28 ± .11	.90 ± .19
.94 ± .08	
-----	-----
avg: 1.00 ± .04 usec	avg: 1.04 ± .09 usec

Overall average: 1.01 ± .04 usec

less.

Throughout analyses 4, 5, 6 and 11; a specially constructed fast discriminator was used (instead of the slower ORTEC amplifier) to reduce the dead time to an almost negligible value (0.13 usec). The schematic for this device is given in Fig. 1. The 0.13 usec is an estimate derived from twice the width of the output pulse. Use of the discriminator was discontinued after analysis 11 because it had a relatively high firing threshold. The voltage output spectrum of the Spiraltron decreases after long use and it was possible that some of the low energy pulses would not be counted.

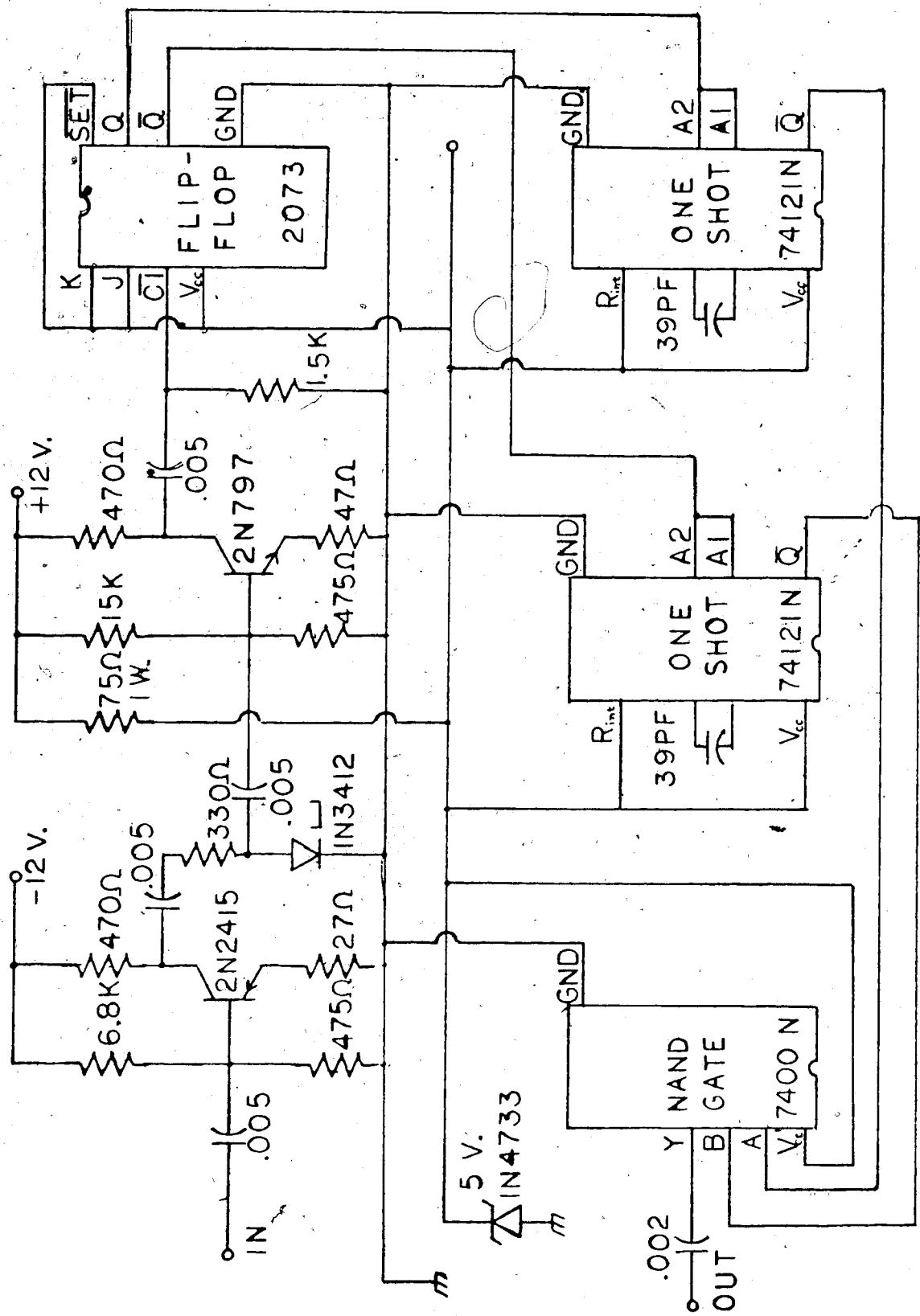


FIG. 1: FAST DISCRIMINATOR

### III Results and Discussion

Calculation of the decay constant from a single analysis requires an assumption about the fraction of  $^{87}\text{Sr}$  present in the blank. This will be a weighted average of the isotopic composition of the Sr blank added during the separation process and Sr which was already present in the salt. Unfortunately, the latter was not measured at the time the sample was purified. The total amount of strontium blank in each sample can be calculated from the  $^{84}\text{Sr}/^{88}\text{Sr}$  ratios listed in Table VI. This will be partly separation procedure blank and partly a blank originally present in the sample. Using a procedure blank of 1 ng as mentioned above, the maximum sample blank per gram of  $^{87}\text{Rb}$  may be calculated. This is listed in Table V. It is obvious from this table that the largest proportion of blank was contained originally in the sample. As has been mentioned, the procedure taken to purify the original sample involved conversion to the perchlorate by precipitation with perchloric acid followed by at least five successive recrystallizations in demineralized water. In view of this it seems exceedingly unlikely that much of the original strontium present in the  $\text{RbCl}$  would have remained, especially since the water used would probably have had a rather high strontium blank as evidenced by the results in Table V. It seems quite likely therefore that the remaining blank would have an isotopic composition characteristic of

Table V

Strontium blank originally present in  $\text{RbClO}_4$ , assuming a total separation blank of 1 nanogram

Sample	Maximum sample blank (ng/g $^{87}\text{Rb}$ )	% of total blank
4A	3.20	88%
5A	2.20	86%
14A	2.10	86%
2B	1.39	82%
3B	3.83	90%
11B	1.20	75%
13B	1.64	84%
15B	1.63	84%
6C	0.70	67%

that in the water used for the recrystallization.

If all the data are plotted on a graph of  $^{87}\text{Sr}/^{86}\text{Sr}$  vs  $^{87}\text{Rb}/^{86}\text{Sr}$  the best fit straight line is found to have an intercept of  $0.731 \pm 0.020$  ( $2\sigma$ ). This is quite high for a normal strontium blank and has a rather large uncertainty attached to it. It may also be affected by systematic errors since there is only a 20% probability that the  $\chi^2$  value of this data set would be exceeded by chance in a random distribution.

The errors on the individual analyses are calculated from the precision of the counting measurements on each

peak. Possible sources of systematic error which may contribute to a non-random distribution are error in the chemical contaminant, which is not likely to exceed 0.25%; error in the spike calibration, which is only significant for analyses 16 and 17 which were rejected on this account; error produced by the dead time, which is unlikely to exceed 0.1%; and an error for a non-linear fractionation trend.

The main instrumental difficulty encountered during the earlier analyses involved the field stabilizer. All runs within an analysis were selected on a basis of low  $\chi^2$  values and several runs were rejected in analyses 3, 5 and 6. Difficulties with the stabilizer had been resolved by the time number 13 was analyzed. The data from number 2 was rerun after this. The analyses which are considered most likely to be free of systematic error are 2, 13, 14 and 15. These all had steady emission, no instrumental difficulties, several replicate measurements on each ratio and they are all from batches A or B in which the contaminant is well known. Plotting these data on a graph of  $^{87}\text{Sr}/^{86}\text{Sr}$  versus  $^{87}\text{Rb}/^{86}\text{Sr}$  gives an intercept of  $0.683 \pm .032$  with a 60% probability of randomness.

Thus the direct determination of the initial blank composition is uncertain and we consider it better to choose the initial ratio from physical considerations, since the data are probably not free from systematic error. The initial value of  $^{87}\text{Sr}/^{86}\text{Sr}$  chosen was 0.709. This is the isotopic composition of the blank in the reagents used in



this laboratory. It is also the isotopic composition of seawater strontium. It therefore appears to be the most reasonable estimate for the original blank in the  $\text{RbClO}_4$ .

The decay constants for the individual analyses were derived from the data shown in Table VI and are listed in Table VII. A weighted mean was calculated. The weights are determined from the inverse square of the standard deviations which were determined according to the formula:

$$\% \sigma = (\% \sigma_7 - 0.5\% \sigma_6) / R + 2\% \sigma_6 + \% \sigma_4$$

where  $\% \sigma$  is the total percentage standard deviation;  $\% \sigma_7$ ,  $\% \sigma_4$ , and  $\% \sigma_6$  are the percentage standard deviations for the  $^{87}\text{Sr}/^{88}\text{Sr}$ ,  $^{84}\text{Sr}/^{88}\text{Sr}$  and  $^{86}\text{Sr}/^{88}\text{Sr}$  ratios, respectively and  $R$  is the fraction of the  $^{87}\text{Sr}$  that was radiogenic. A further percentage error of  $\pm 0.25\%$  was added to the mean decay constant from each batch to allow for an error in the  $\text{Rb}$  concentration. The value found for the decay constant is  $\lambda = 1.419 (\pm 0.012) \times 10^{-11} \text{ yr}^{-1}$ . The error quoted is a two sigma error. It does not include any error in the initial blank  $\text{Sr}$  composition.

The average of 2, 13, 14 and 15 (considered the most accurate analyses) is  $1.414 (\pm 0.015) \times 10^{-11} \text{ yr}^{-1} (2\sigma)$ . This is statistically indistinguishable from the overall mean. It is considered therefore that the overall mean  $\lambda = 1.419 (\pm 0.012) \times 10^{-11} \text{ yr}^{-1}$  represents the most reliable measurement of the decay constant of  $^{87}\text{Rb}$ . This value

Table VI

Results of all isotopic analyses and decay times

Sample	$^{84}\text{Sr}/^{88}\text{Sr}$	$^{87}\text{Sr}/^{88}\text{Sr}$	$^{86}\text{Sr}/^{88}\text{Sr}$	t(yr)
2B	1.04952 ±.00147	0.26701 ±.00051	0.11964 ±.00037	17.970
3B	0.66010 ±.00187	0.16258 ±.00056	0.11993 ±.00061	18.890
4A	0.75931 ±.00160	0.17780 ±.00047	0.11947 ±.00043	19.205
5A <sub>1</sub>	0.91286 ±.00213	0.21834 ±.00067	.12101 ±.00041	19.274
5A <sub>2</sub>	0.89050 ±.00173	0.21702 ±.00055	.11933 ±.00030	19.274
6C	2.12000 ±.00604	0.38474 ±.00093	0.12056 ±.00033	18.339
11B	1.57935 ±.00434	0.29589 ±.00120	0.12012 ±.00041	19.263
13B	1.06065 ±.00223	0.25509 ±.00068	0.12013 ±.00037	19.364
14A	0.92381 ±.00102	0.22332 ±.00030	0.12074 ±.00026	19.567
15B <sub>1</sub>	1.04616 ±.00246	0.26025 ±.00057	0.12115 ±.00048	19.383
15B <sub>2</sub>	1.04511 ±.00253	0.25912 ±.00068	0.12150 ±.00045	19.383
15B <sub>3</sub>	1.04479 ±.00226	0.25973 ±.00064	0.12074 ±.00046	19.383
15B <sub>4</sub>	1.03325 ±.00253	0.25973 ±.00064	0.12074 ±.00046	19.383

Table VI (cont'd)

<u>Sample</u>	<u><math>^{84}\text{Sr}/^{88}\text{Sr}</math></u>	<u><math>^{87}\text{Sr}/^{88}\text{Sr}</math></u>	<u><math>^{86}\text{Sr}/^{88}\text{Sr}</math></u>	<u>t(vr)</u>
16D <sub>1</sub>	1.09525 ±.00264	0.21565 ±.00073	0.12120 ±.00064	18.682
16D <sub>2</sub>	1.08537 ±.00182	0.21553 ±.00049	0.12063 ±.00032	18.682
17C <sub>1</sub>	1.65002 ±.00375	0.22634 ±.00065	0.12164 ±.00058	18.690
17C <sub>2</sub>	1.63732 ±.00285	0.22549 ±.00042	0.12071 ±.00021	18.690
17C <sub>3</sub>	1.62730 ±.00293	0.22549 ±.00042	0.12071 ±.00021	18.690
17C <sub>3</sub>	§ 1.60949 ±.00460	0.22549 ±.00042	0.12071 ±.00021	18.690

Table VII

Amount and fraction of radiogenic  $^{87}\text{Sr}$ , amount of  $^{87}\text{Rb}$   
and calculated decay constant for each sample

<u>Sample</u>	<u><math>^{87}\text{Sr}_\alpha</math></u>	<u>% rad.</u>	<u><math>^{87}\text{Rb}(\mu\text{g})</math></u>	<u><math>\lambda(\times 10^{-11}\text{yr}^{-1})</math></u>
2B	0.8227	68.34	3.2312	1.417 $\pm 0.011$
3B	0.6277	47.89	2.3130	1.437 $\pm 0.021$
4A	0.6483	52.45	2.3381	1.444 $\pm 0.016$
5A <sub>1</sub>	0.7843	61.04	2.8270	1.439 $\pm 0.016$
5A <sub>2</sub>	0.7830	61.08	2.8270	1.437 $\pm 0.013$
6C	0.7463	78.00	2.9178	1.395 $\pm 0.014$
11B	0.7044	71.41	2.5582	1.429 $\pm 0.018$
13B	0.8523	66.77	3.1324	1.405 $\pm 0.014$
14A	0.8012	61.96	2.9059	1.409 $\pm 0.008$
15B <sub>1</sub>	0.8988	67.31	3.2565	1.424 $\pm 0.015$
15B <sub>2</sub>	0.8972	67.12	3.2565	1.422 $\pm 0.016$
15B <sub>3</sub>	0.8934	67.30	3.2565	1.415 $\pm 0.016$
15B <sub>4</sub>	0.9035	67.30	3.2565	1.432 $\pm 0.016$

Table VII (cont'd)

<u>Sample</u>	<u><math>^{87}\text{Sr}</math></u>	<u>% rad.</u>	<u><math>^{87}\text{Rb}(\text{g})</math></u>	<u><math>t(\times 10^{-11}\text{yr}^{-1})</math></u>
16D <sub>1</sub>	0.6245	60.54	2.3757	1.407 ±.027
16D <sub>1</sub>	0.6262	60.62	2.3757	1.411 ±.019
17C <sub>1</sub>	0.4483	62.38	1.7247	1.391 ±.024
17C <sub>2</sub>	0.4449	62.39	1.7247	1.380 ±.016
17C <sub>3</sub>	0.4477	62.39	1.7247	1.389 ±.016
17C <sub>4</sub>	0.4527	62.39	1.7247	1.404 ±.018

compares favourably with the two most recent measurements of the decay constant which are that of Neumann and Huster (1974) who found  $1.42 (\pm 0.03) \times 10^{-11} \text{ yr}^{-1}$  by  $\beta$  counting experiments and Afanass'yev et al. (1974), who found  $1.42 \times 10^{-11} \text{ yr}^{-1}$  from comparisons between ages determined by U-Th-Pb, K-Ar and Rb-Sr methods on pegmatite materials.

## References

- Afanass'yev, G.D., Zykora, S.I., Gorokov, I.M. and Shainin, L.L. 1974: Correlativity of geochronometric ages yielded by coexisting minerals with different  $^{40}\text{K}$ ,  $^{87}\text{Rb}$  and some other radioactive element decay constants (Abstract). International Meeting for Geochronology, Cosmochronology and Isotope Geology, Paris.
- Aldrich, L.T., Wetherhill, G.W., Tilton, G.R. and Davis, G.L. 1956: The half-life of  $^{87}\text{Rb}$ . Phys. Rev. 104, 1045-1047.
- Bahnisch, I., Huster, E. and Walcher, W. 1952: Zu Halbwertszeit und Zerfallsschema des  $^{87}\text{Rb}$ . Naturwiss. 39, 379-380.
- Beard, G.B. and Kelly, W.H. 1961: "Self-Scintillation" study of the beta decay of  $^{87}\text{Rb}$ . Nucl. Phys. 28, 570-577.
- Brinkman, G.A., Aten, A.H.W. and Veenboer, J.Th. 1965: Natural radioactivity of  $^{40}\text{K}$ ,  $^{87}\text{Rb}$  and  $^{176}\text{Lu}$ . Physica, 31, 1305-1319.
- Catanzaro, E.J., Murphy, T.J., Garner, E.L. and Shields, W.R. 1969: Absolute isotopic abundance ratio and atomic weight of terrestrial rubidium, J. Res. Nat. Bur. Std. 73A, 511-516.
- Curran, S.C., Dixon, D. and Wilson, H.W. 1952: The natural radioactivity of rubidium. Phil. Mag. 43, 82-92.
- Egelkraut, K. and Leutz, H. 1961: Beta Spektrum und Halbwertszeit des  $^{87}\text{Rb}$ . Z. Physik 161, 13-19.
- Flinta, J. and Eklund, S. 1954: On the radioactivity of  $^{87}\text{Rb}$ . Ark. Fys. 7, 401-411.
- Geese-Bahnisch, I. and Huster, E. 1954: Neubestimmung der Halbwertszeit des  $^{87}\text{Rb}$ . Naturwiss. 41, 495-496.
- Haxel, O., Houtermans, F.G. and Kemmerich, M. 1948: On the half-life of  $^{87}\text{Rb}$ . Phys. Rev. 74, 1886-1887.
- Kemmerich, M. 1949: Die Halbwertszeit des Rubidiums 87. Z. Physik 126, 399-409.
- Kovach, A. 1964: A re-determination of the half-life of rubidium 87. Acta Phys. Hung. 17, 341-351.

- Leutz, H., Wenninger, H. and Ziegler, K. 1962: Die Halbwertszeit des  $^{87}\text{Rb}$ . Z. Physik 169, 409-416.
- Lewis, G.M. 1952: The natural radioactivity of rubidium. Phil. Mag. 43, 1070-1074.
- Libby, W.F. 1957: Simple absolute measurement technique for beta radioactivity. Analyt. Chem. 29, 1566-1570.
- MacGregor, M.H. and Wiedenbeck, M.L. 1952: The decay of rubidium-87, Phys. Rev. 86, 420-421.
- MacGregor, M.H. and Wiedenbeck, M.L. 1954: The third forbidden beta spectrum of rubidium-87. Phys. Rev. 94, 138-140.
- McMullen, C.C., Fritze, K. and Tomlinson, R.H. 1966: The half-life of rubidium-87. Can. J. Phys. 44, 3033-3038
- McNair, A. and Wilson, H.W. 1961: The half-life of rubidium-87. Phil. Mag. (8) 6, 563-572.
- Neumann, W. and Huster, E. 1974: The half-life of  $^{87}\text{Rb}$  measured as a difference between the isotopes  $^{87}\text{Rb}$  and  $^{85}\text{Rb}$ . Z. Physik 270, 121-127.



Appendix A

Purification of new  $\text{RbClO}_4$  stock for a future  
redetermination of the  $^{87}\text{Rb}$  decay constant

Two pounds of high purity rubidium perchlorate, lot 5080.11, were obtained from Terochem Laboratories Limited, Edmonton, Alberta. The following is the chemical analysis supplied by the company.

Chemical analysis, ppm:

Cs - 220	Al - 5	Mg - 1
K - 195	Ba - 10	Mn - 1
Na - 10	Ca - 1	Ni - 1
$\text{Li}^v$ - 10	Cr - 1	Pb - 1
Insol - 100	Cu - 1	Si - 1
	Fe - 1	Sr - 10

This material was purified as follows. The  $\text{RbClO}_4$  was weighed out into a Teflon beaker and then transferred into a 2 l Teflon bottle containing a magnetic stirring element. 1.6 - 1.7 Kg of water was added to the bottle. The liquid was stirred and heated with a hot plate and heat lamp in a pressurized hood until the  $\text{RbClO}_4$  dissolved completely. The bottle was then capped, covered with a plastic bag and transferred to a refrigerator where the solution was cooled to precipitate as much  $\text{RbClO}_4$  as possible. The liquid was then decanted, the bottle filled with fresh water and the dissolution and precipitation process begun again.

Since the solubility of  $\text{RbClO}_4$  is about 18 g per 100 g

of water at the boiling point and only about 0.5 g per 100 g of water near 0°C, this process results in only a minor loss of sample. The procedure was repeated to make 5 dissolutions and precipitations for batches A, B and D and 6 for batch C. During the first two, 1 S.D. ("sub-boiling distilled") water was used. This had been purified by being demineralized with an ion exchange column and then distilled beneath the boiling point using a glass cold finger. The final dissolutions used 2 S.D. water which had been purified by redistilling the 1 S.D. water beneath the boiling point using a quartz cold finger.

The following is a detailed description of the purification procedure for each batch:

Aug. 24, 1976; Batch A

About 300 g was added to the bottle along with 1.7 l of 1 S.D. water. It proved so difficult to dissolve the solid that about 150 ml of saturated fluid was poured off and water was added to make about 1.8 l of liquid.

Aug. 25 - 2nd precipitation, 1 S.D. water

Aug. 26 - 3rd precipitation, 2 S.D. water

Aug. 27 - 4th precipitation, 2 S.D. water

Aug. 27 - 5th precipitation, 2 S.D. water

The last precipitate came out at about 11 p.m., Aug. 27, 1976.

Batch B; 250 g  $\text{RbClO}_4$  in about 1.5 l of water

Aug. 30 - 1st precipitation, 1 S.D. water

Aug. 31 - 2nd precipitation, 1 S.D. water

Sept. 2 - 3rd precipitation, 2 S.D. water

Sept. 3 - 4th precipitation, 2 S.D. water

Sept. 4 - 5th precipitation, 2 S.D. water

The last precipitate came out at 12 noon, Sept. 4, 1976.

Batch C; 250 g  $\text{RbClO}_4$ .

Aug. 31 - 1st precipitation, 1 S.D. water

Sept. 1 - 2nd precipitation, 1 S.D. water

Sept. 2 - 3rd precipitation, 2 S.D. water

Sept. 3 - 4th precipitation, 2 S.D. water

Sept. 7 - 5th precipitation, 2 S.D. water

Sept. 9 - 6th precipitation, 2 S.D. water

The last precipitate came out at 3 p.m., Sept 9, 1976.

Batch D; 80 g  $\text{RbClO}_4$  in about 600 ml water

Sept. 6 - 1st precipitation, 1 S.D. water

Sept. 10 - 2nd precipitation, 1 S.D. water

Sept. 11 - 3rd precipitation, 2 S.D. water

Sept. 20 - 4th precipitation, 2 S.D. water

Sept. 21 - 5th precipitation, 2 S.D. water

The last precipitate came out at 4 p.m., Sept. 21, 1976.

The final precipitates were dried under a heat lamp in a pressurized hood and then transferred to plastic bottles where they were securely sealed and labeled. A portion of the original unpurified salt was also kept.

The supernatant liquid from the final precipitation was evaporated down and transferred to small plastic bottles, one for each batch. The content of each bottle was spiked and an attempt was made to measure the isotopic composition

of the strontium in the supernatant liquids. Also, a small portion of each purified salt except batch D was weighed out, spiked and the strontium blank separated and measured. Unfortunately extreme difficulty was encountered during these runs with the separation of rubidium so that the strontium signals were invariably quite weak. The following lists the results of each measurement.

Batch A:

Final supernatant -  $^{87}\text{Sr}/^{86}\text{Sr} = 0.7094 \pm .0049$

Total Sr blank in supernatant = 8.9 ng

Sr blank in 11.3 g of purified  $\text{RbClO}_4 = 2.31 \text{ ng}$

Batch B:

Final supernatant -  $^{87}\text{Sr}/^{86}\text{Sr} = 0.7173 \pm .0037$

Total Sr blank in supernatant = 6.3 ng

Sr blank in 9.09 g of purified  $\text{RbClO}_4 = 1.39 \text{ ng}$

Batch C:

Final supernatant -  $^{87}\text{Sr}/^{86}\text{Sr} = 0.7112 \pm .0067$

Total Sr blank in supernatant = 2.9 ng

Sr blank in 11.15 g of purified  $\text{RbClO}_4 = 1.89 \text{ ng}$

Batch D:

Sr blank in 600 ml of supernatant = 2.3 ng

The isotopic composition of the Sr blank in Batch D could not be measured because of difficulties with Rb on the filament. All the above blanks include the procedure blank, added during the separation process, which is likely to be 1-2 ng. Assuming a separation procedure blank of 1 ng, the original blank in the batches will be 0.9 ng/g of  $^{87}\text{Rb}$ ,

0.33 ng/g and 0.6 ng/g for batches A, B and C respectively. In most cases, this appears to be considerably less than in the McMullen et al. samples.

Three portions of the original, unpurified  $\text{RbClO}_4$  were also taken and the isotopic composition of the strontium was measured in three different ways. First, a weighed portion of the salt was taken, the Sr separated and the isotopic composition measured on the 25 cm instrument using the Spiraltron detector. A second weighed portion was taken and the isotopic composition of the Sr measured on the same instrument using a Faraday cup collector. Finally, a third portion was weighed out, spiked and both the isotopic composition and amount of Sr measured on a Micromass-30 mass spectrometer equipped with a Faraday cup. The results are as follows:

25 cm instrument, Spiraltron detector:

0.345 g  $\text{RbClO}_4$  -  $^{87}\text{Sr}/^{86}\text{Sr} = 0.7077 \pm .0032$

25 cm instrument, Faraday cup:

2.14 g  $\text{RbClO}_4$  -  $^{87}\text{Sr}/^{86}\text{Sr} = 0.7094 \pm .0004$

Micromass-30, Faraday cup:

0.878 g  $\text{RbClO}_4$  -  $^{87}\text{Sr}/^{86}\text{Sr} = 0.7084 \pm .0010$

Total Sr = 0.266 ug/gm  $\text{RbClO}_4$

The amount of Sr impurity in the  $\text{RbClO}_4$  is much less than that quoted in the original analysis and its  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is certainly quite close to 0.709. Since the only other component in the blank for the purified salt is the reagent blank, which is also .709, this must be the isotopic

composition of the original Sr. This lends further support to the choice of .709 as the isotopic composition of the blank in the McMullen et al. samples.

It is suggested that during the future decay constant determination, every effort be made to eliminate the hydrocarbon peaks. Perhaps conducting the measurements on a mass spectrometer with a vacuum system not employing oil diffusion pumps would help in this regard. If the hydrocarbon peaks can be made negligible, wider slits can be used, leading to a much higher beam intensity. It is also suggested that the micro-column not be used during the chemical procedure, but instead the sample should be passed twice through the Teflon column. The author has found during later Rb-Sr work on whole rocks that this results in negligible Rb on the filament, whereas the micro-column may give a less efficient separation.

#### IV Introduction and Geologic Background

The purpose of this study is to investigate the chronology and evolution of the Laborador Archean complex by examining the response of rubidium-strontium and lead isotope systems in samples from various assemblages, to the metamorphic events which have affected the complex. The samples were collected from the Saglek Bay area and include whole rocks from the Nulliak assemblage, the Uivak gneisses, the Saglek dykes, the late syntectonic granites, two post tectonic granites and two samples of high iron intrusives.

Archean high grade gneiss terrain exists in the Nain province along the coast of Labrador, along part of the western and eastern coasts of Greenland and in the Lewisian complex of north-west Scotland. All of these areas are considered to have once formed a continuous complex known as the North Atlantic Craton which was fragmented and dispersed by the opening of the Atlantic Ocean and the Labrador Sea. They are surrounded for the most part by Proterozoic mobile belts apparently consisting of reworked Archean gneiss, which suggests that the craton may have once extended over a wider area than at present.

##### Greenland:

The best preserved and most intensely studied areas of this craton are on the west coast of Greenland (Fig. 2).

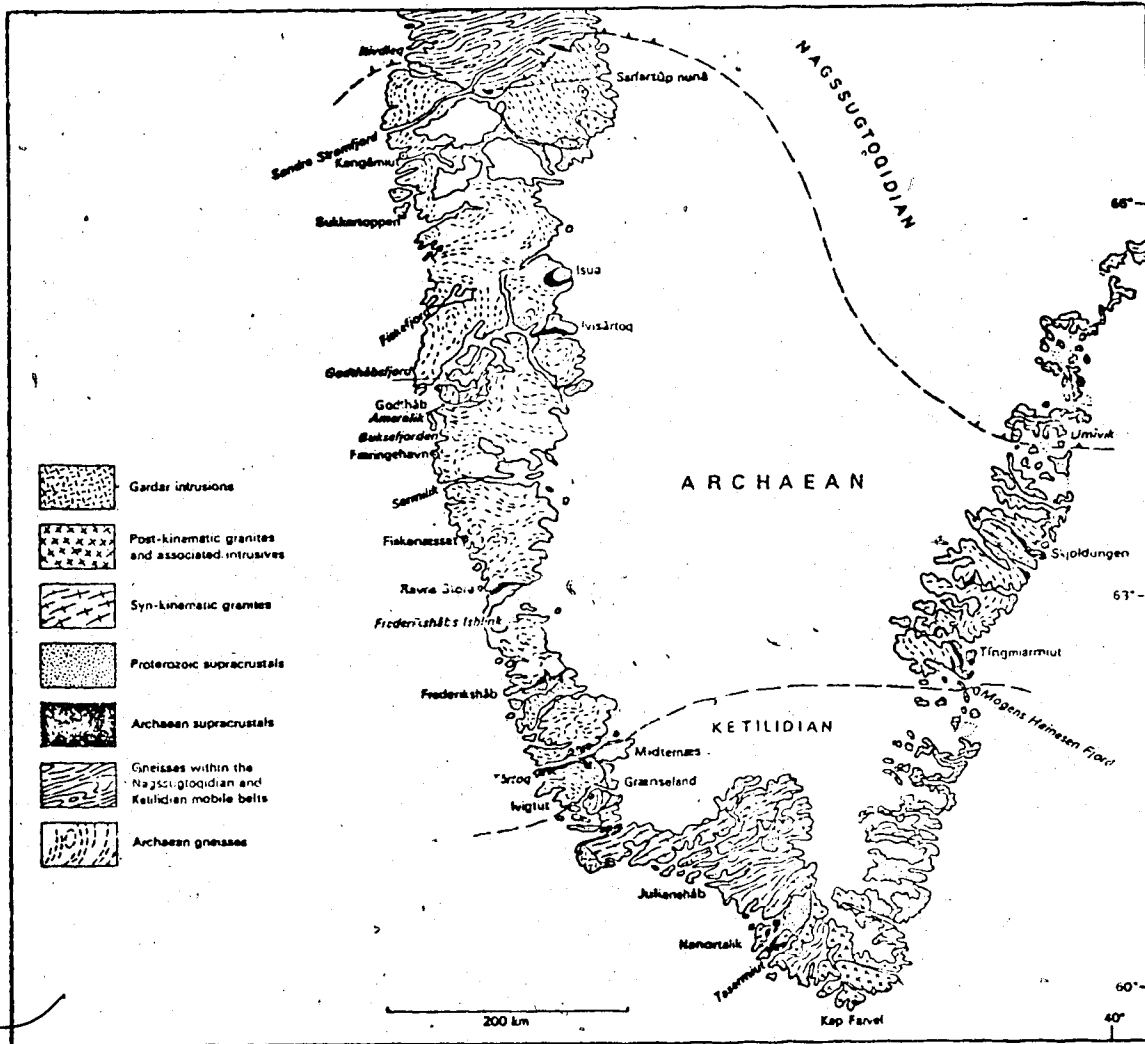


FIG 2: MAP OF THE GREENLAND ARCHEAN COMPLEX



This region will be described in some detail since it is important to establish the relationship between it and the complex which exists on the Labrador coast. The most important source of reference is Bridgewater et al. (1976). All Rb-Sr dates mentioned are corrected to a decay constant of  $1.42 \times 10^{-11} \text{ yr}^{-1}$  (Davis et al., 1977).

The terrain is observed to consist of 80-90% quartzofeldspathic orthogneisses derived largely from tonalitic to granitic igneous rocks. These are intercalated with units of metavolcanic amphibolite, minor amounts of paragneiss and concordant units of meta-anorthosite and associated metabasic igneous rocks. The mineral assemblages are chiefly in the high amphibolite and hornblende granulite facies with the principle assemblages having been formed after the main tectonic events which produced layering and complex folds. The most common assemblages were formed under high temperature, medium pressure conditions. High pressure assemblages are rare.

Studies chiefly around the Godthaab and Isua areas have determined the main lithostratigraphic units of the complex. The oldest rocks discovered to date are the Isua supracrustals which consist of basic and ultrabasic greenschists, metasediments and quartzofeldspathic rocks arranged in a semi-circular arc 10-20 km in diameter around a gneiss dome near Isua. The gneisses along the contact of the belt have given an Rb-Sr whole rock age of  $3622 \pm 140 \text{ m.y.}$  (Moorbath et al., 1972). The ironstones from the

supracrustals give a Pb-Pb whole rock isochron age of  $3760 \pm 70$  m.y. (Moorbath et al., 1973) most probably representing an event involving uranium depletion. The belt is cut by meta-dolerite dykes resembling the Ameralik dykes observed in the Godthaab area. It contains mostly amphibolite facies minerals which have been partly retrogressed to greenschist facies.

The area between Isua and Sermilik consists of 20 to 40% intensely deformed quartzo-feldspathic gneiss known as the Amîtsoq gneiss. This can be distinguished from younger gneisses by the presence of abundant deformed amphibolite bodies derived from basic dykes known as the Ameralik dykes. The gneisses have been most intensely studied in the Godthaab area where they contain isolated inclusions of supracrustal rocks generally similar to those of the Isua succession. The following Rb-Sr whole rock isochrons have been determined for groups of Amîtsoq gneisses from various localities (Moorbath et al., 1972):

Area	Date	$(^{87}\text{Sr}/^{86}\text{Sr})_0$
Narssaq	$3,671 \pm 90$ m.y.	$.7015 \pm .0008$
Qilangarssuit	$3,661 \pm 100$ m.y.	$.7009 \pm .0011$
Praestefjord	$3,612 \pm 230$ m.y.	$.7001 \pm .0017$
Isua	$3,622 \pm 140$ m.y.	$.7011 \pm .0020$

Zircon discordia and Pb-Pb whole rock isochron dates give values of about 3650 m.y. (Baadsgaard, 1973; Black et al., 1971).

The Amîtsoq gneisses are very inhomogeneous with a thin

pegmatite layering. They have been largely reworked to the point of destruction of the primary features. The only area where they preserve primary features is around Isua. Here they are seen to consist of monotonous grey granodioritic gneisses with biotite as the main mafic mineral. In places they are seen to be polyphase with paler phases intruding the darker, elsewhere they are monotonous grey gneisses with pegmatite layering. These structures are considered to be primary features reflecting movement during crystallization.

Major element and rare earth abundances of the Amîtsoq gneisses suggest they are polygenetic and derived from 2 or 3 suites:

(a) Grey, layered to homogeneous gneisses, mainly granodioritic, tonalitic or trondjemitic in composition, interpreted at Isua as a syntectonic calc-alkaline suite similar to the later Nûk gneiss.

(b) Augen and doric gneisses having high potassium contents and high Fe/Mg ratios. These may possibly represent later post-orogenic rapakivi-like granite suites.

(c) Leucocratic sheets cutting augen gneisses. These in some cases show a highly fractionated rare earth distribution, being very depleted in heavy rare earths (O'Nions and Pankhurst, 1974). These patterns show that the gneisses could not have been derived from a single cogenetic suite. The fractionated rare earth distributions could only have been produced by fractionation of garnet either from a basaltic melt at pressures in excess of 25 kbar or by

partial melting of garnet-rich granulite or amphibolite. The Isua gneisses have been found to possess K/Rb ratios of 250 or less, whereas the augen gneisses have higher ratios, averaging around 600.

Although minor in volume the Ameralik dykes provide the most useful stratigraphic marker in the complex. They consist of metadolerite and amphibolites occurring as dykes or concordant layers and lenses in the Amîtsoq gneisses and have been recognized only between Isua and Sermilik. A small proportion contain sericitized megacrysts and recrystallized aggregates of plagioclase commonly concentrated close to one margin.

Conformable bodies of amphibolitic rocks associated with small amounts of pelite, semi-pelite and quartz-cordierite schists make up 10 to 20% of the gneiss complex and are known as the Malene supracrustals. These supracrustals are very widespread, occurring in Greenland, Labrador and Scotland. They are derived from basic and ultrabasic volcanics, intrusives and metasediments of submarine origin. The volcanics are more abundant than the non-volcanics and vary from tholeiitic pillow lavas and breccias to rocks derived from andesitic or dacitic pyroclastics. Layered basic and ultrabasic intrusives are abundant. The metasediments consist mostly of chemical or clay-rich sediments with small amounts of clastics. Mg and Mg-Fe rich sediments with low alkali contents form distinct units. The Malene supracrustals are intruded by the Nûk

gneisses but apparently not by the Ameralik dykes. No primary sedimentary contacts have been observed between the supracrustals and the Amîtsoq gneiss. Some contacts transgress along the supracrustal sequence suggesting that the Amîtsoq units may have been emplaced as thrust slices.

Anorthosites and associated leucogabbroic and gabbroic rocks occur as concordant layers and trains of inclusions throughout the complex. The primary features are best preserved in the Fiskenaasset complex. The anorthosites were emplaced as sub-horizontal sheets into meta-volcanics probably equivalent to the Malene supracrustals. They are intruded by the Nûk gneiss.

The Nûk gneisses refer to a group of quartzo-feldspathic gneisses that do not contain Ameralik dykes and are intruded into older formations such as the Malene supracrustals and anorthosites. They occur as deformed sheets intruded syntectonically into the layered complex and make up over 50% of the area around Godthaabsfjord. The most abundant type is a biotite-bearing tonalite or granodiorite with less than 5% K-feldspar. They form a typical sêdic calc-alkaline suite similar to more recent calc-alkaline suites except for higher Na/K, low U and high Th/U. K/Rb averages about 330. It is not known to what extent they form a cogenetic suite. There is no evidence that they were derived from older sialic material. Samples taken from a number of areas down the coast give ages from 2720 to 2868 m.y. with initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of .7015 to .7031.

The different suites of samples scatter coherently together on an Rb-Sr diagram in a fashion similar to the Amîtsoq gneiss (Moorbath and Pankhurst, 1976). Possibly 70 to 80% of the gneiss complex was formed or remobilized at the same time as emplacement of the Nûk gneisses and they may record a time of substantial crustal thickening of the craton.

A period of intense deformation followed the intrusion of the Nûk gneisses producing major nappes, upright folds and widespread dome and basin interference patterns and imposing a regional foliation upon the complex. This was followed by the intrusion of a series of syntectonic to late tectonic granites contemporaneous with or just preceding a period of regional granulite metamorphism. The granites include intrusive bodies of porphyritic granite, diffuse bodies formed by in situ recrystallization of earlier gneisses and intrusive bodies of charnockitic granites and associated norites.

The granulite facies event has been dated using a series of metamorphosed anorthosites and gneisses which give a Pb-Pb whole rock isochron age of  $2,850 \pm 100$  m.y. (Black et al., 1973). Activity continued for at least 300 m.y. after the granulite event with the intrusion of a series of high K post-tectonic granites. The Qôrquut granite is one of the largest of these bodies. An Rb-Sr isochron date for a suite of samples from this body gives  $2467 \pm 90$  m.y. with an initial Sr ratio of  $0.709 \pm .007$  (Moorbath and Pankhurst, 1976).

Labrador:

Within the ~~last~~ few years field work in the Nain province of Labrador has revealed areas with a history as complex and ancient as that of the Greenland province (Collerson et al., 1976; Bridgewater and Collerson, 1975). The block of Archean rocks is bounded by the Churchill province to the north and west and the Makkovik sub-province to the south (Fig. 3). Both of these are Proterozoic mobile zones active during the Hudsonian orogeny and are considered to be equivalent to the Greenland Naassugtoqidian and Ketilidian mobile belts, respectively. The Archean block itself is disrupted by the Proterozoic Nain anorthosite-adamellite complex so that the best exposures are to the north roughly between Saglek Bay and ~~the~~ and to the south in the area around Hopedale.

The most extensive field work and sampling has been carried out in the Saglek area (Fig. 4) where a lithostratigraphic complex very similar to that in the Godthaabsfjord area has been found to exist. East of the Handy fault rocks have been affected by several phases of amphibolite facies metamorphism. Younger granites have brought up inclusions of high grade gneiss suggesting that the area may be underlain by granulite facies rocks. To the west of the fault most of the gneisses are either granulite facies or retrogressed from granulite facies. In the transitional zone, textural and mineralogical evidence indicates that a late static granulite facies event,

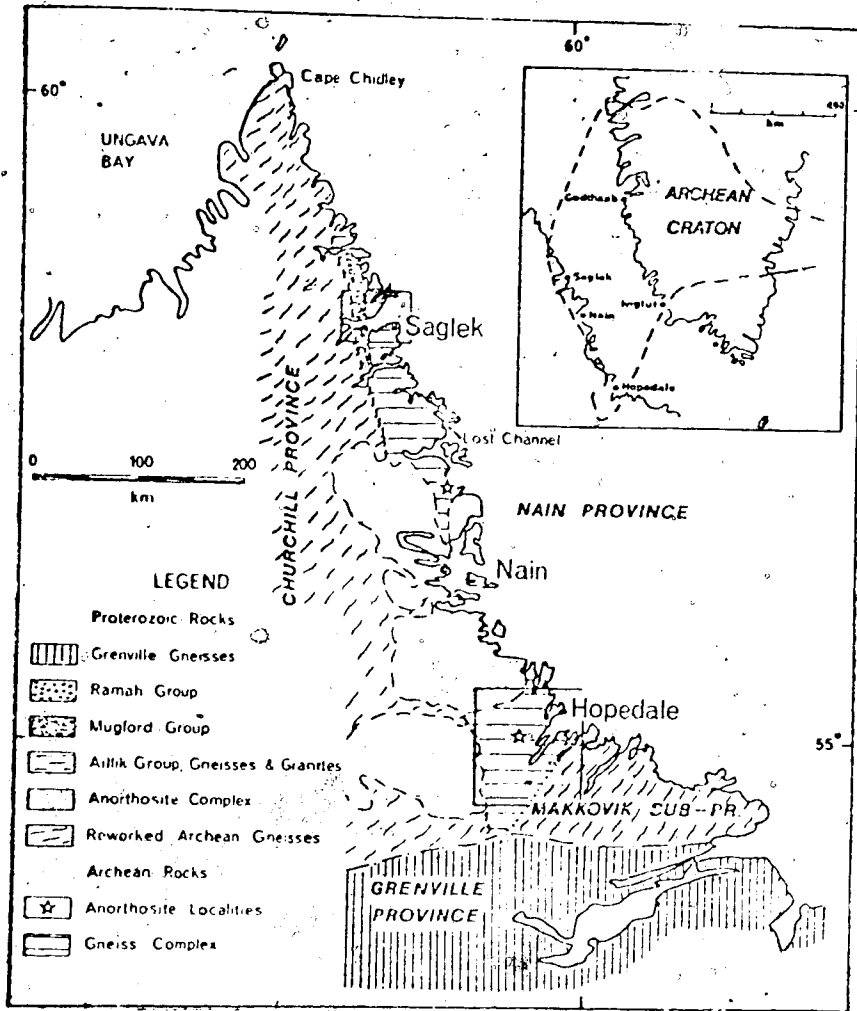


FIG 3: MAP OF THE LABRADOR ARCHEAN COMPLEX



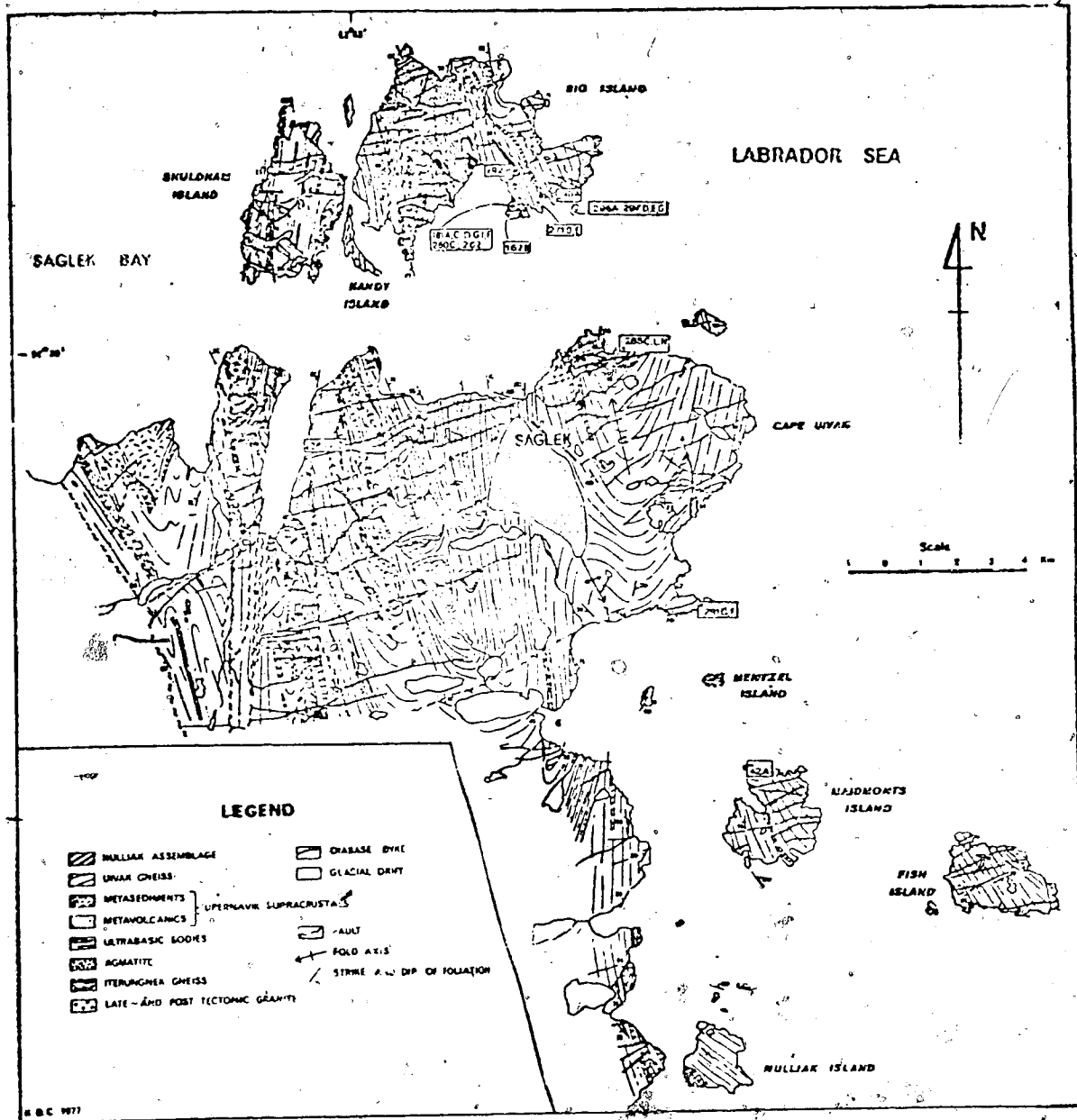


FIG 4: MAP OF THE SAGLEK BAY AREA, LABRADOR

possibly equivalent to the 2800 m.y. Greenland event, recrystallized earlier amphibolite facies rocks to the granulite grade. Within the granulite area to the west, this event appears to have been impressed on earlier granulite facies rocks. The two sides of the fault may represent different crustal levels of the same assemblages.

All the rocks before the late granites are very strongly deformed with extensions of 2:1 or more. The majority of discordant structures were rotated parallel to the regional strike. Only occasional outcrops of gneiss show preservation of primary features.

The most abundant rock type in the area is a group of polyphase quartzo-feldspathic rocks known as the Uivak gneisses. As in the Amitsoq gneisses in Greenland they can be distinguished in the field by the presence of abundant, deformed discordant bodies and disrupted pods of metamorphosed dykes known as the Saglek dykes. Discordant relations are preserved locally. The groundmass of these dykes is usually fine grained and granoblastic and contains dispersed plagioclase megacrysts or aggregates of megacrysts and anorthositic xenoliths. As with some of the Ameralik dykes, the distribution of the plagioclase megacrysts commonly occurs along one margin of the dyke or concentrated in pockets which may contain 60% megacrysts and xenoliths.

The oldest granitic rocks in the complex are a suite of layered grey gneisses making up over 50% of the total complex. These are known as the Uivak I gneisses. They are

leucocratic biotite-bearing rocks with a distinct schistosity and layering defined by K-feldspar rich pegmatitic veins and lenses. They form a monotonous suite composed mostly of quartz (15-30%), sodic oligoclase (55-60%), K-feldspar (5-15%) and green biotite (5-15%). Chemically they range between tonalites and quartz monzonites and they all plot on a calc-alkaline differentiation trend near the alkali corner of an AFM plot (Bridgewater and Collerson, 1975). The rocks appear to represent tectonically reworked and metamorphosed equivalents of tonalitic and granodioritic plutons. The Rb content is rather high for rocks of granodioritic composition and averages 110 ppm. The K/Rb ratios are low having an average of 195 and a general correlation is evident between K and Rb. The Ba contents are low with an average of 232 ppm.

The migmatitic nature of the rocks combined with their unusual concentrations of K, Rb and Ba and the absence of much hornblende suggests that the rocks may have suffered alkali metasomatism with the introduction of alkali-rich, Ba-poor magmas or fluids along shear plains and grain boundaries during an early phase of metamorphism, perhaps leaving a depleted granulite residue similar to the Scourian of Scotland at a deeper crustal level (Bridgewater and Collerson, 1975).

The grey Uivak I gneisses had already acquired a strong schistosity before the emplacement of another suite, the

Uivak II gneisses. These comprise less than 5% of the complex and are made up of iron-rich porphyritic granodioritic and dioritic gneisses also cut by Saglek dykes. They outcrop as a series of discontinuous bodies surrounded by the Uivak I gneiss. There are four main rock types recognized. The major part of the suite consists of coarse-grained granitic gneiss with large streaked out feldspar augen. Hornblende-rich ferrodiorites are found as smaller lenses. Hornblende-rich dykes are seen to have intruded the Uivak I gneiss. They are largely broken up and deformed. Finally, a biotite-rich inhomogeneous quartz monzonite sheet is also intruded into the Uivak I gneiss.

The porphyritic gneisses are rich in oligoclase with K-feldspar present only as interstitial material. The augen are composed of oligoclase aggregates, individual crystals enclose rounded quartz grains. Iron-rich biotite is the dominant mafic mineral accompanied by subordinate hornblende.

The Uivak II suite shows much more chemical variation than the Uivak I gneisses, sharing in common only its iron-rich nature. The suite lies toward the more mafic end of the differentiation trend (Bridgewater and Collerson, 1975). The division between these gneisses tends to mirror that between the different suites of Amîtsoq gneisses (Bridgewater et al., 1976). Again the Uivak II suite resembles more recent late to post tectonic iron-rich granites such as the rapakivi suite.

An Rb-Sr whole rock isochron age of  $3545 \pm 72$  m.y. with an initial Sr ratio of  $0.7014 \pm .0008$  has been determined on a set of 5 Uivak I gneisses and two Uivak II samples from the Saglek area (Hurst et al., 1975). All samples plot on the isochron and the date is considered to have resulted from metamorphic homogenization rather than magmatic intrusion. An age of  $3542 \pm 106$  m.y. but with an initial ratio of  $0.7044 \pm .0010$  has been obtained on a set of samples from the Hebron area which are geologically and geochemically similar to the Uivak gneiss (Barton, 1975).

A still older sequence of supracrustal rocks, the Nulliak assemblage, occurs interlayered in the Uivak I gneiss and as xenoliths in the Uivak II suite. These consist in aluminous garnet-sillimanite with minor calc-silicate layers and some graphite. They range from continuous units up to two kilometers along strike and 50-100 m wide to small, fragmented, inclusions within the Uivak gneiss.

On Mentzel Island the Uivak II gneisses are observed to contain mega-xenoliths which are remnants of a layered diorite gabbro-anorthosite body. This plutonic suite, known as the Mentzel plutonic association, is also intruded by Saglek dykes and may be considered an early phase of the Uivak II protoliths.

Tectonically interleaved with the Uivak gneiss is an abundant and variable suite of metavolcanic and metasedimentary rocks known as the Upernavik supracrustals. They are not seen to be cut by Saglek dykes. The

metasediments range from pelites to quartzites and marbles. The metavolcanics are generally fine grained schistose amphibolites. Some units show small scale layering with alternating dark amphibole-rich units grading into more felsic rocks, perhaps representing graded volcanic ash units or intensely deformed pillows. Layered igneous bodies ranging from a few meters to 50 m in width locally cut across earlier layering in the metasediments. Ultramafic masses (meta-peridotites) occur as pods and layers in the gneiss complex ranging up to several hundred meters in width and traceable along strike for up to 1 km. No primary sedimentary contacts are observed between the Upernavik supracrustals and the Uivak gneisses. The Upernavik supracrustals appear to be analogous to the Malene supracrustals in Greenland.

A younger group of quartzo-feldspathic gneisses, the Iterungnek gneisses, occurs as deformed sheets intrusive into the Uivak gneisses and the Upernavik supracrustals and as migmatitic lenses and stringers breaking up the earlier gneisses and supracrustals. They are not cut by Saglek dykes. An Rb-Sr whole rock isochron from a set of these samples has been found to give an age of  $3067 \pm 156$  m.y. and an initial ratio of  $0.7063 \pm .0012$  (Hurst et al., 1975). Isotopic and field evidence indicates that they have been largely derived by remobilization of earlier gneiss.

There exist several generations of granitic gneisses intrusive into the Iterungnek gneisses. Some were derived

by remobilization of the Iterungnek while other syntectonic sheets clearly transgress the refoliated gneisses and are emplaced along the axial planes of the main folds of the area. These syntectonic granites are younger than the phase of deformation which lead to the interlayering of old gneisses and supracrustal rocks and younger than the remobilization phase dated for the Iterungnek. They contain local granulite facies assemblages however, and are thus older than or contemporaneous with the regional metamorphic event which reached granulite facies to the west. The period of major crustal thickening recorded on the Greenland coast by the intrusion of the Nûk gneisses appears not to have occurred here. The syntectonic granites are much less abundant in area than the Nûk.

A younger group of late syntectonic granite gneiss sheets was emplaced along discordant shear zones and transgresses all earlier structures. They possess a relatively simple fabric showing evidence of only one main phase of deformation and where they intrude granulite facies assemblages there is often a retrogressed zone in the surrounding country rocks. The later granites are generally markedly richer in potassium than their remobilized equivalents. The last major phase of granitic activity was a pervasive intrusion of medium to coarse grained K-rich post-tectonic granites and pegmatites.

In summary, both the Greenland and Labrador complexes, where they are well preserved, appear to have been dominated

by sub-horizontal tectonic processes which resulted in the interleaving and thrusting of one formation into another. This contrasts with the dominantly vertical tectonic regimes witnessed in the Archean granite-greenstone terrains of South Africa, Western Australia and most of the Canadian Shield. These regions are characterized by low-grade greenstone belts engulfed in a sea of high grade granite-gneiss which was evidently emplaced by diapiric processes.

The presence of these horizontal movements renders precarious relative age determinations based on stratigraphy. As an example, the absence of dykes in the Upernavik and Malene supracrustals does not definitely imply that they are younger than the Uivak and Amitsoq gneisses. It is conceivable that these formations were deposited elsewhere, perhaps at the same time as the Isua supracrustals and then tectonically transported and thrust into the gneiss complex after intrusion of the Saglek and Ameralik dykes (Bridgewater et al., 1974). Such a possibility cannot be discounted until isotopic methods succeed in determining an absolute age of deposition.



## V Theory of Rb-Sr and Pb-Pb Systematics

### Rb-Sr systematics

The Rb-Sr dating technique is based on the decay of the  $^{87}\text{Rb}$  isotope to  $^{87}\text{Sr}$ . The molar concentration of  $^{87}\text{Sr}$  measured in the sample at present ( $t = 0$ ) is given by the equation:

$$^{87}\text{Sr} = ^{87}\text{Rb}[\exp(\lambda t) - 1] + ^{87}\text{Sr}_0$$

where  $^{87}\text{Rb}$  is the molar concentration of the  $^{87}\text{Rb}$  isotope presently measured in the sample,  $\lambda$  is the  $^{87}\text{Rb}$  decay constant,  $t$  is the age of initial isotopic homogenization measured positively into the past and  $^{87}\text{Sr}_0$  is the amount of  $^{87}\text{Sr}$  present at time  $t$ .

Since it is more convenient and revealing to deal with isotopic ratios, this equation is usually divided by the concentration of  $^{86}\text{Sr}$  isotope, which is invariant with time, to give the working equation:

$$^{87}\text{Sr}/^{86}\text{Sr} = ^{87}\text{Rb}/^{86}\text{Sr}[\exp(\lambda t) - 1] + (^{87}\text{Sr}/^{86}\text{Sr})_0$$

This equation contains two parameters so that the determination of an age  $t$  from a single rock or mineral specimen requires an assumption about the initial Sr isotopic composition,  $(^{87}\text{Sr}/^{86}\text{Sr})_0$ . An age determined in this way is known as a model age. If measurements are made

on two or more samples with differing values of  $^{87}\text{Rb}/^{86}\text{Sr}$  but which have been isotopically homogenized at time  $t$ , it is possible to determine both the age  $t$  and the initial isotopic composition. The data from such a suite of samples may be plotted in one of two ways. The most popular is to treat  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{87}\text{Rb}/^{86}\text{Sr}$  as the dependent and independent variables, respectively. On such a graph, a cogenetic suite of samples should form a straight line known as an isochron. The slope will be equal to  $\exp(\lambda t) - 1$  and the ordinate will be intersected at  $(^{87}\text{Sr}/^{86}\text{Sr})_0$  as shown in Fig. 5.

A second way of representing the data is to treat  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $t$  as the dependent and independent variables respectively as shown in Fig. 6. To obtain a linear equation the abscissa should be proportional to  $\exp(\lambda t) - 1$ . Since  $t$  is very small,  $\exp(\lambda t) - 1 \cong \lambda t$ . In practice, computing the value of  $^{87}\text{Sr}/^{86}\text{Sr}$  at a time approximately equal to the time of formation and joining this point to the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio at  $t = 0$  provides a very good approximation. The slopes of the lines will be nearly proportional to the mean  $^{87}\text{Rb}/^{86}\text{Sr}$  of each sample since its formation. The lines should all intersect at a time equal to the age of isotopic homogenization and at the initial isotopic composition  $(^{87}\text{Sr}/^{86}\text{Sr})_0$ . This diagram contains the same information as the isochron one but it is sometimes more useful in cases where the isotopic systems have been disturbed since it gives a clearer view of the isotopic evolution of the

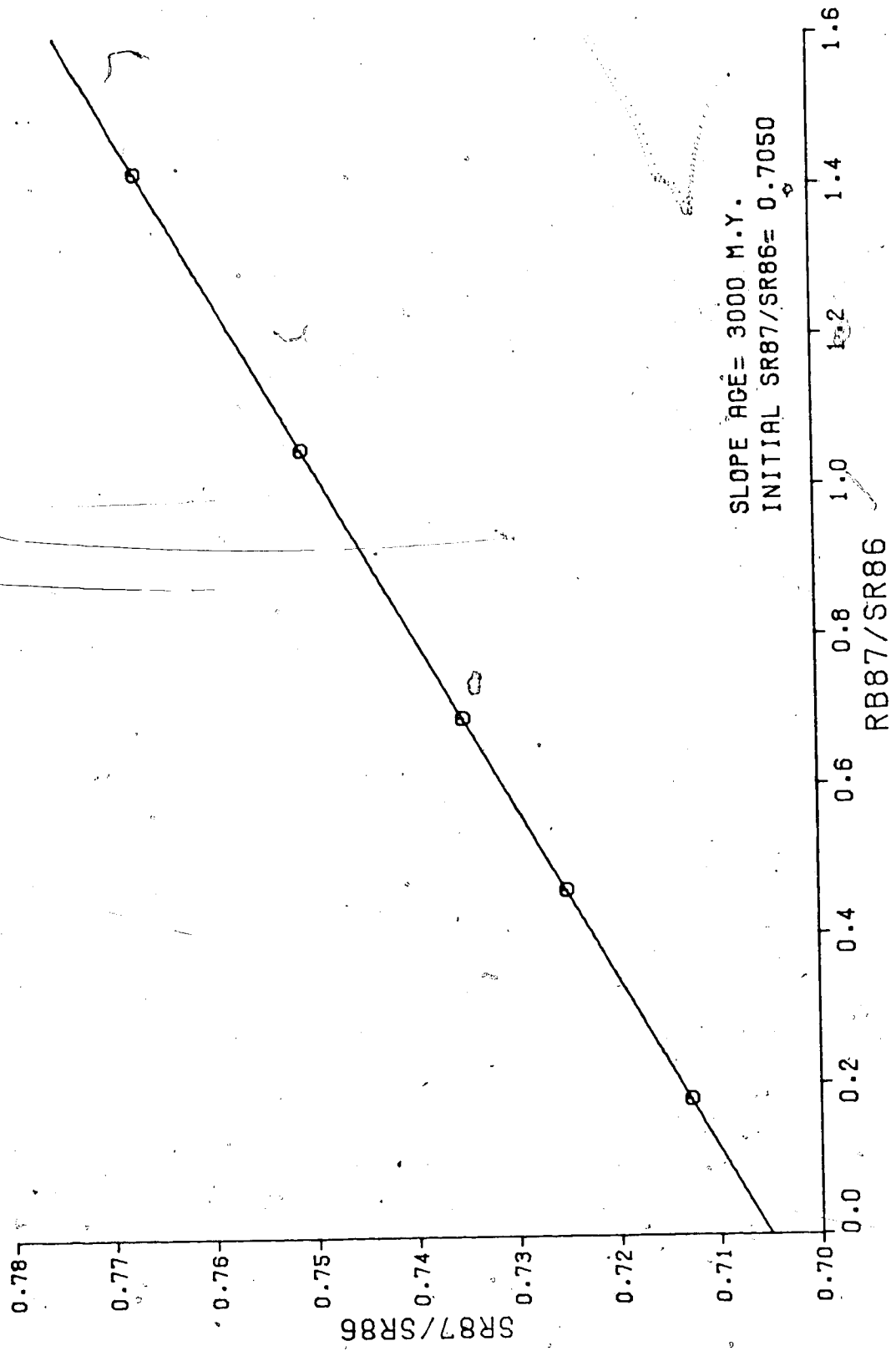


FIG 5: RB-SR ISOCHRON PLOT

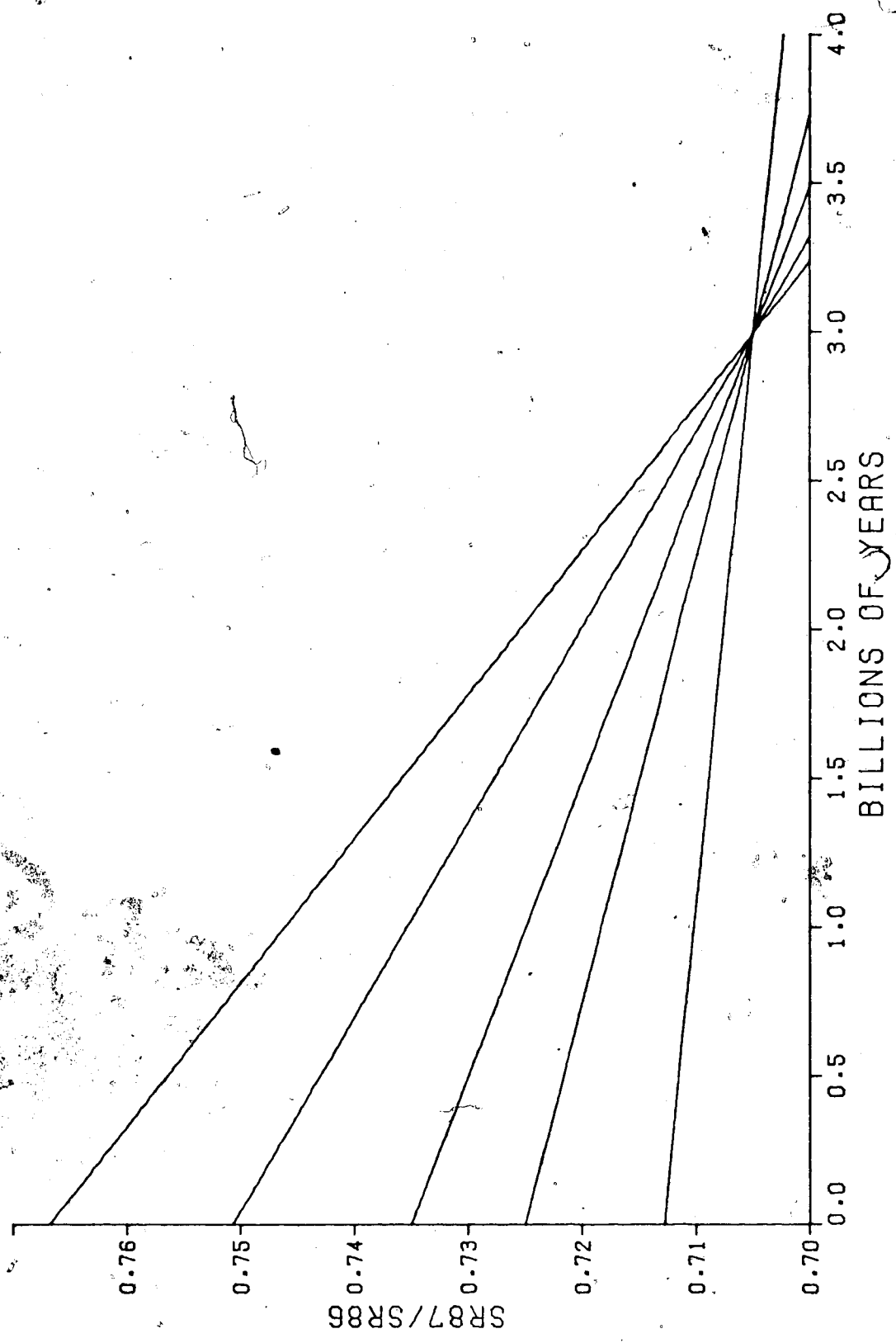


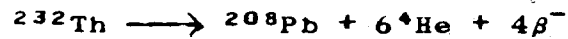
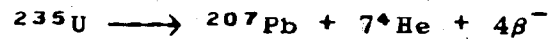
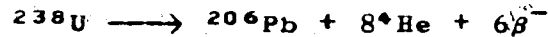
FIG 6: SR GROWTH CURVES FOR A SUITE OF COGENETIC SAMPLES

samples.

The samples selected for dating may be mineral separates from a single rock specimen such as high Rb/Sr micas combined with medium-to-low Rb/Sr K-feldspar and apatite, or they may be a set of whole rocks selected from a single formation to give a broad range of Rb/Sr values. The usefulness of the technique depends upon the complete homogenization of Sr isotopes at some time in the past and upon the minerals or rocks having remained closed systems with respect to the movement of Rb and Sr from that time to the present. Initial homogenization is very likely to occur in the case of crystallization from a magma. If there have been no subsequent thermal events, the mineral ages should give the true ages of the rock. Many samples of interest, however, may have been subjected to one or more episodes of metamorphism of sufficient grade to recrystallize some of the minerals or render them open to diffusion of parent and daughter elements. In this case, provided the range of diffusion has been limited to substantially less than the size of the whole rock, the whole rock technique should still produce isochrons giving the initial age. A thorough review of Rb-Sr systematics may be found in Faure and Powell, 1972.

#### Pb-Pb systematics-

The Pb-Pb technique uses lead isotopes resulting from two of the following decay systems:



Of these, the most useful are the two uranium series since uranium isotopes are not significantly separated during normal geochemical reactions whereas U and Th may be.

The most popular method of presenting the data is on a  $^{207}\text{Pb}/^{204}\text{Pb}$  versus  $^{206}\text{Pb}/^{204}\text{Pb}$  diagram,  $^{204}\text{Pb}$  is a non-radiogenic isotope. The problem of interpreting the Pb isotope distribution in a suite of rocks consists in fitting it to a model which will normally be described by a set of episodic variations in the U/Pb ratio of the sample at discrete times.

If the U/Pb ratio should remain constant, the evolution of the lead isotopes over geologic time would be described by the following equations:

$$x_1 = a_0 + u[\exp(\lambda t_0) - \exp(\lambda t_1)]$$

$$y_1 = b_0 + (u/137.88)[\exp(\lambda' t_0) - \exp(\lambda' t_1)]$$

where  $x_1 = ^{206}\text{Pb}/^{204}\text{Pb}$  and  $y_1 = ^{207}\text{Pb}/^{204}\text{Pb}$ , both at time  $t_1$ ;  $a_0 = ^{206}\text{Pb}/^{204}\text{Pb}$  and  $b_0 = ^{207}\text{Pb}/^{204}\text{Pb}$ , both at time  $t_0$ ;  $u = ^{238}\text{U}/^{204}\text{Pb}$  at the present time  $t = 0$ ;  $\lambda = 0.155125 \times 10^{-9} \text{ yr}^{-1}$ , the decay constant of  $^{238}\text{U}$ ; and  $\lambda' = 0.98485 \times 10^{-9} \text{ yr}^{-1}$ , the decay constant of  $^{235}\text{U}$  (Jaffey et al., 1971). The time  $t$  is measured positively into the past. When plotted on a diagram, these two parametric equations

describe a growth curve as shown in Fig. 7. The values of  $a_0$  and  $b_0$  were determined by measurements of the lead isotopic composition in the troilite phase of the Canyon Diablo meteorite,  $a_0 = 9.307$  and  $b_0 = 10.294$  (Tatsumoto et al., 1973). The isotopic composition of Pb in the earth is assumed to have had the values  $a_0$  and  $b_0$  at time  $t_0$ , which is referred to as the age of the earth. This may be determined most accurately in the following way. There exists a group of lead ores which appear to a good approximation to fall on a single growth curve. Their ages, as determined by their position on the lead growth curve are somewhat younger than their geologic ages as determined by other methods, however. The difference between the lead age and the true age becomes more pronounced as the samples get younger, indicating that the fit to a single stage model is only an approximation. The samples may be fitted to a more sophisticated model for  $u$  variation in the crust-mantle system over geologic time. The model is solved for an optimum value of  $t_0$  which produces lead ages for the ores most closely matching their geologic ages. The value used here is  $t_0 = 4509$  m.y. which was determined by Cumming and Richards (1975) for a model involving continuous  $u$ -variation.

Since the previous equations are linear in  $u$ , a suite of leads which all began with an initial isotopic composition  $x(i)$ ,  $y(i)$  at time  $t_1$  and then evolved in environments of different  $u$  until time  $t_2$  when all the

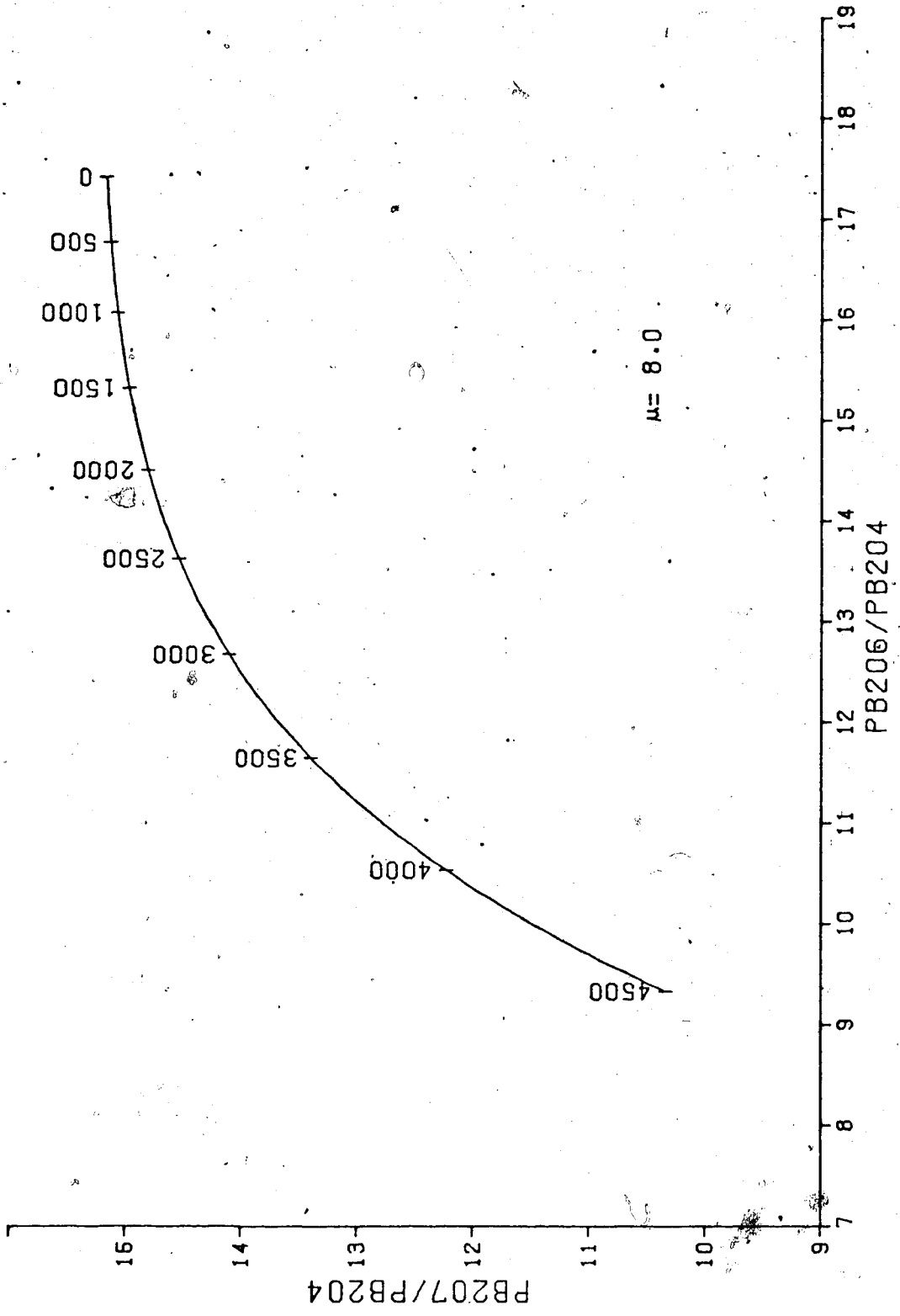


FIG 7: PB GROWTH CURVE



uranium was removed from the system will distribute themselves along a straight line of slope:

$$\frac{y - y(i)}{x - x(i)} = \frac{1}{137.88} \frac{\exp(\lambda t_1) - \exp(\lambda t_2)}{\exp(\lambda t_1) - \exp(\lambda t_2)}$$

If they continue to evolve until the present then  $t_2 = 0$  and this equation can be solved for  $t_1$  (Fig. 8). This is a two stage model. The line passes through the primary growth curve at  $t = 0$  and  $t = t_1$ .

The general three stage model involves evolution in a constant  $u$  environment from the formation of the earth until a certain time  $t_1$ , then fractionation of the global system into various subsystems having  $u_1(i)$  until a second time  $t_2$  when the subsystems are again fractionated into subsystems characterized by values  $u_2(ij)$ .

The resulting general distribution of points will be fan-shaped with its apex at the lead composition which the systems possessed at  $t_1$ . The lower boundary of the distribution will have a slope age equal to  $t_2$  while the upper boundary will intersect the primary growth curve at  $t_1$  and  $t_2$ . This behavior can be most easily understood by considering Fig. 9. The lead of the system evolves in a constant  $u$  environment until  $t_1$ . It is then fractionated into a number of subsystems with varying  $u$  which all evolve along different growth curves until  $t_2$ . Since they all began with the same initial lead, the endpoints of these growth curves must all lie along a straight line, which will

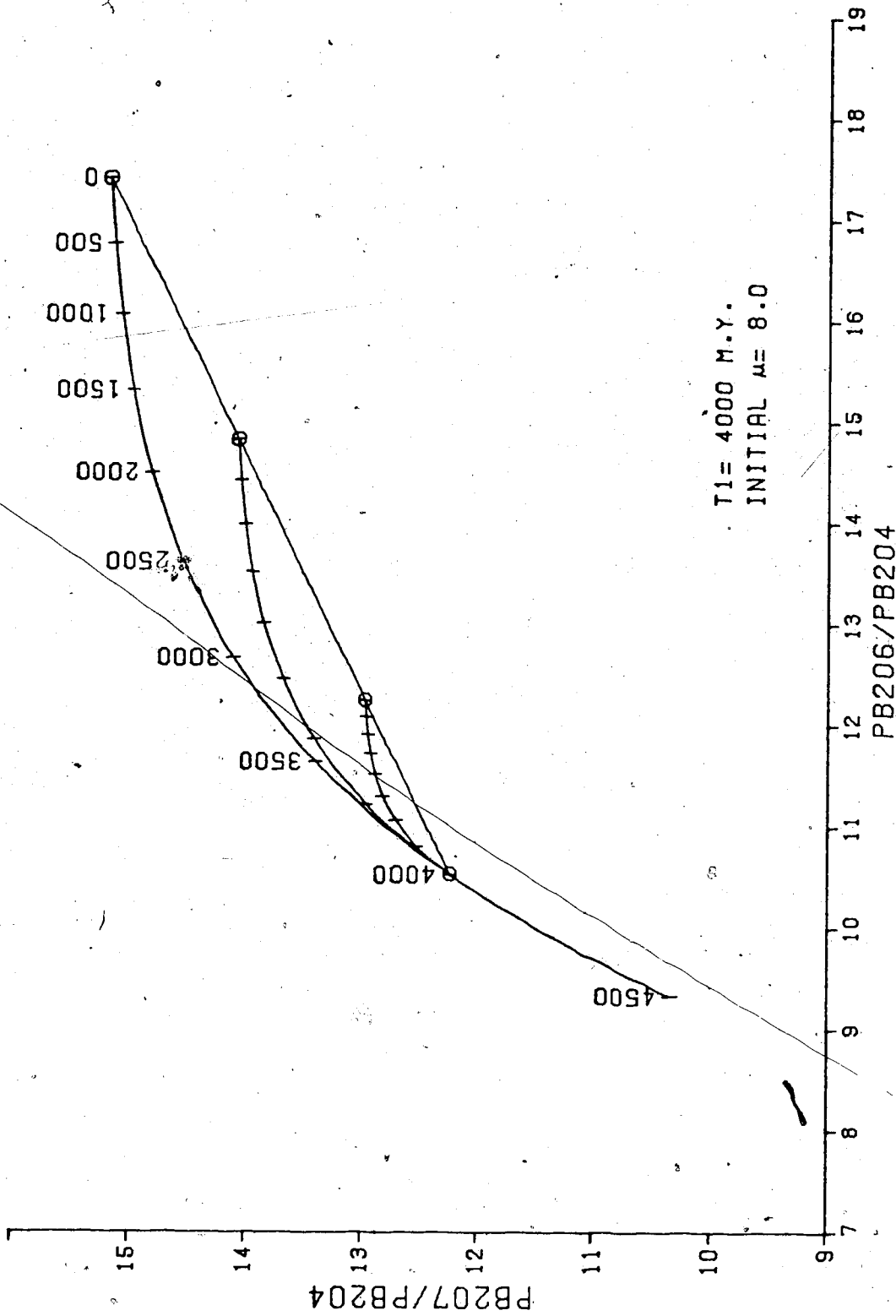


FIG 8 : PB ISOTOPIC EVOLUTION OF SAMPLES WHICH UNDERWENT A 2 STAGE HISTORY

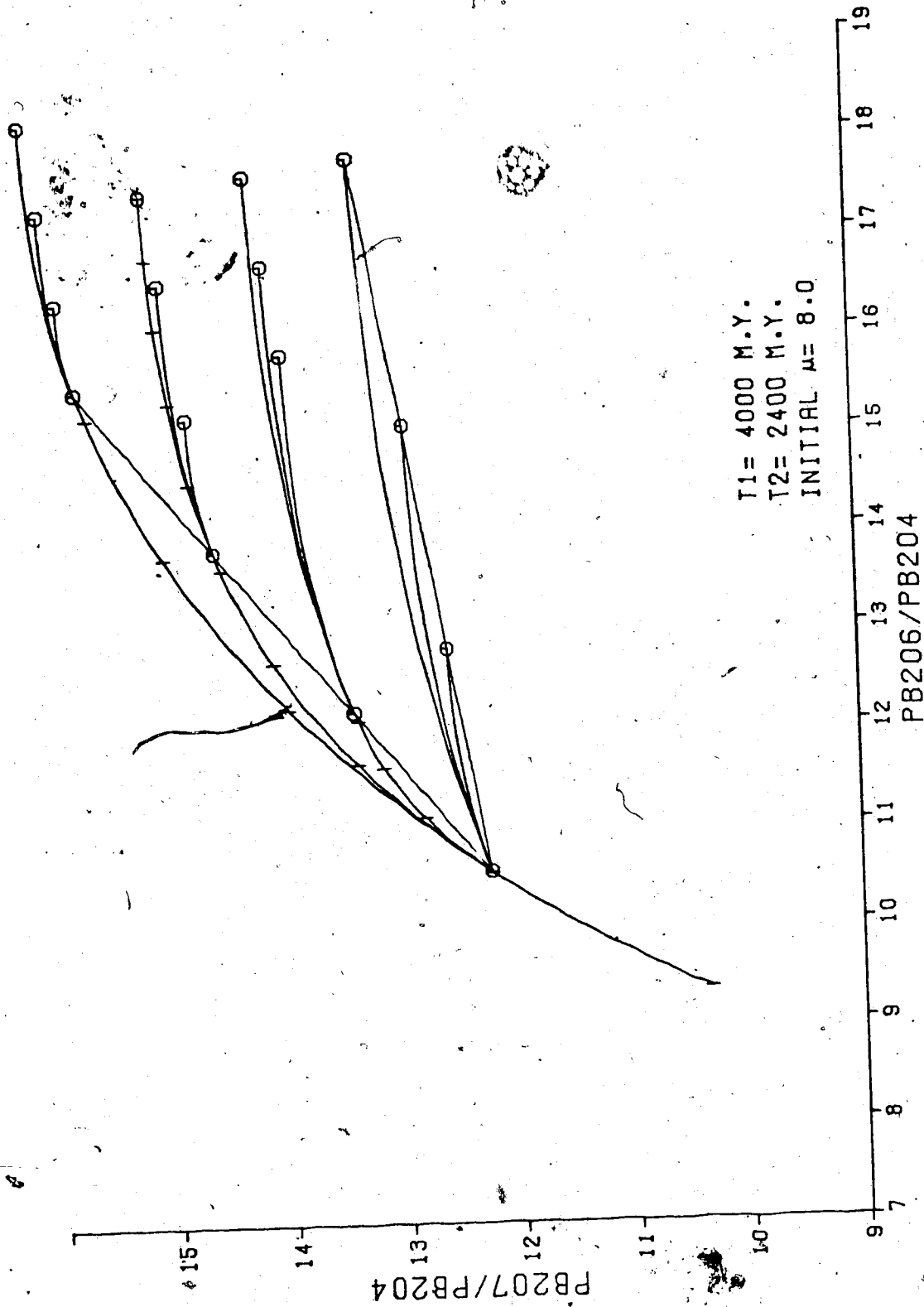


FIG 9: PB ISOTOPIC EVOLUTION OF SAMPLES WHICH UNDERWENT A 3 STAGE HISTORY

intersect the primary growth curve at  $t_1$  and a  $t_2$  for the time when they are refractionated, just as in the two stage model. The subsystems are refractionated into sub-subsystems at time  $t_2$  and since each group of sub-subsystems shares a common initial lead, the ends of their resulting growth curves must again lie along a straight line. The lines will all be parallel and if the systems continue to evolve to the present, they will have a slope age equal to  $t_2$ . It can be seen therefore that the upper boundary of the distribution is defined by the line joining  $t_1$  and  $t_2$  on the primary growth curve, since this represents the systems which had all their uranium removed during the second stage and were "frozen-in". The lower boundary will be defined by that isochron which has as its initial lead the system which was stripped of uranium during the first event at  $t_1$ . The parallelism of the distribution will be more evident if the range of  $u$  values produced by the first event is limited so that a skewed rectangular distribution results. It is also possible that the systems may gain lead during the fractionating events. This will not change the overall distribution however, provided the total system remains closed.

If the fractionating events are not episodic but instead the systems remain open to diffusion and re-equilibration of U and Pb for a finite time, the above distribution would be smeared to an extent dependent on the time interval in which the systems were open. A model

consisting of more than 3 episodic stages would produce a similar overall distribution as the 3 stage model, provided a sufficient range of samples were available to cover the complete distribution. The bounding lines of the distribution would have the same significance, only the slope age of the lower bound would represent the age of the last metamorphic event. The presence of the intermediate events may not be evident in the general distribution. A full treatment of episodic lead models may be found in Gale and Mussett, 1973.

## VI Results and Discussion

The results of all Rb-Sr analyses are listed in Table VIII. The data for the Uivak I and Saglek dyke samples are plotted on an  $^{87}\text{Sr}/^{86}\text{Sr}$  vs.  $^{87}\text{Rb}/^{86}\text{Sr}$  diagram in Fig. 10 and those for the Uivak II and high iron intrusives are plotted in Fig. 11. Previous work on a set of Uivak gneiss samples indicated that they had been isotopically reset at 3545 m.y. (Hurst et al., 1975). It was therefore expected that these samples would plot on a similar isochron. It is obvious, however that most of the samples, if not all, have not behaved as closed systems with respect to subsequent metamorphic events. They all scatter about a 3600 m.y. reference isochron. The Uivak I suite is fairly monotonous with respect to its Rb/Sr ratio, possessing a limited range as one might expect from its mineralogy. The Uivak II suite has a much wider range but there is at least as much scatter with low Rb/Sr samples tending to be too radiogenic and the higher samples tending to be the opposite. The Saglek dykes have been just as affected as their host rocks, exhibiting the entire range of scatter of the gneisses.

Various studies have demonstrated the susceptibility of mineral systems such as micas to remobilization of rubidium and strontium under metamorphic conditions (Hart, 1964; Kesmarky, 1977; Baadsgaard and van Breemen, 1970). Whether or not the whole rocks are disturbed will depend upon the range of migration of these elements. The lack of

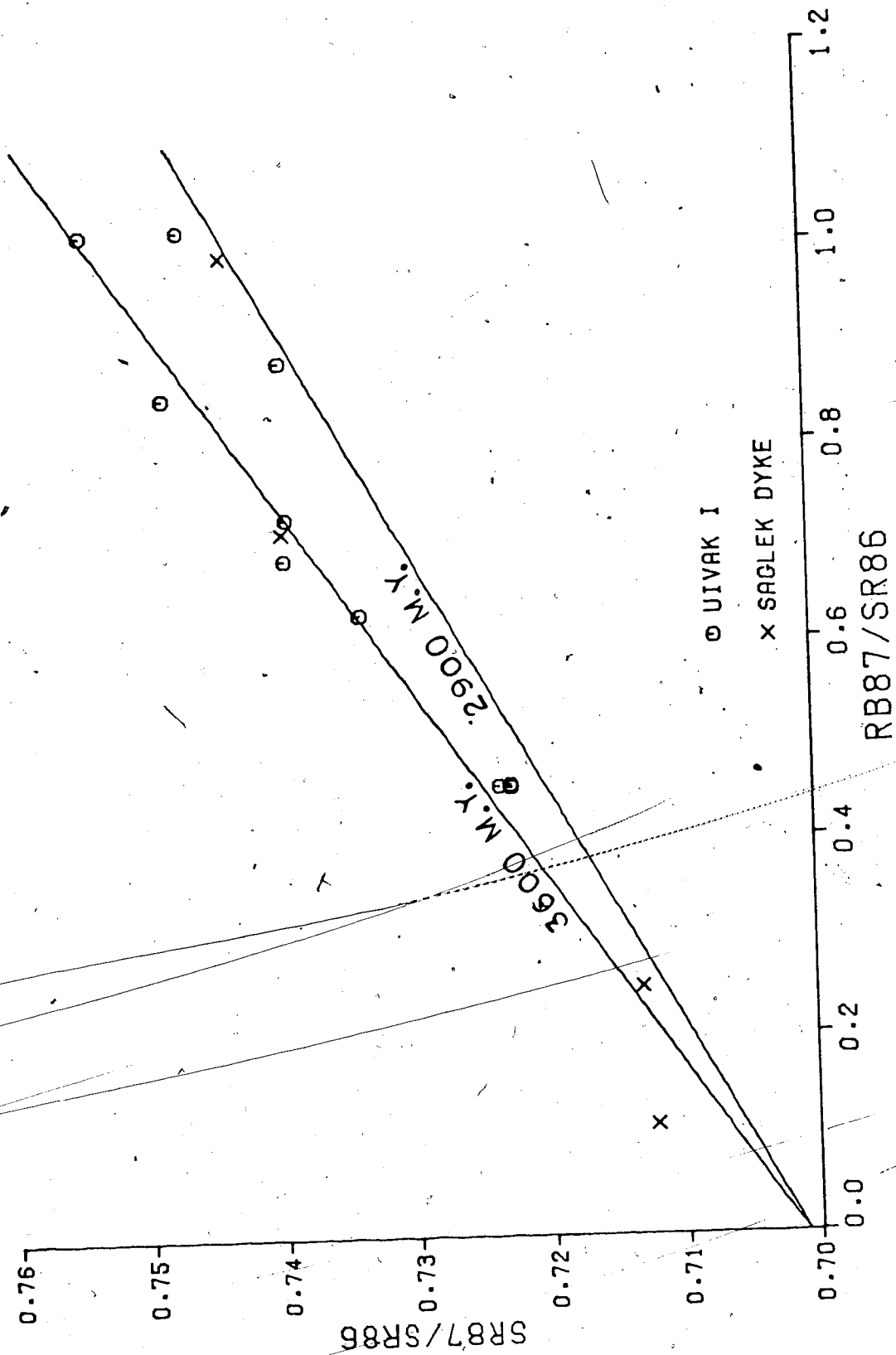


FIG 10: RB-SR RESULTS FOR UIVAK I AND SAGLEK DYKE SAMPLES

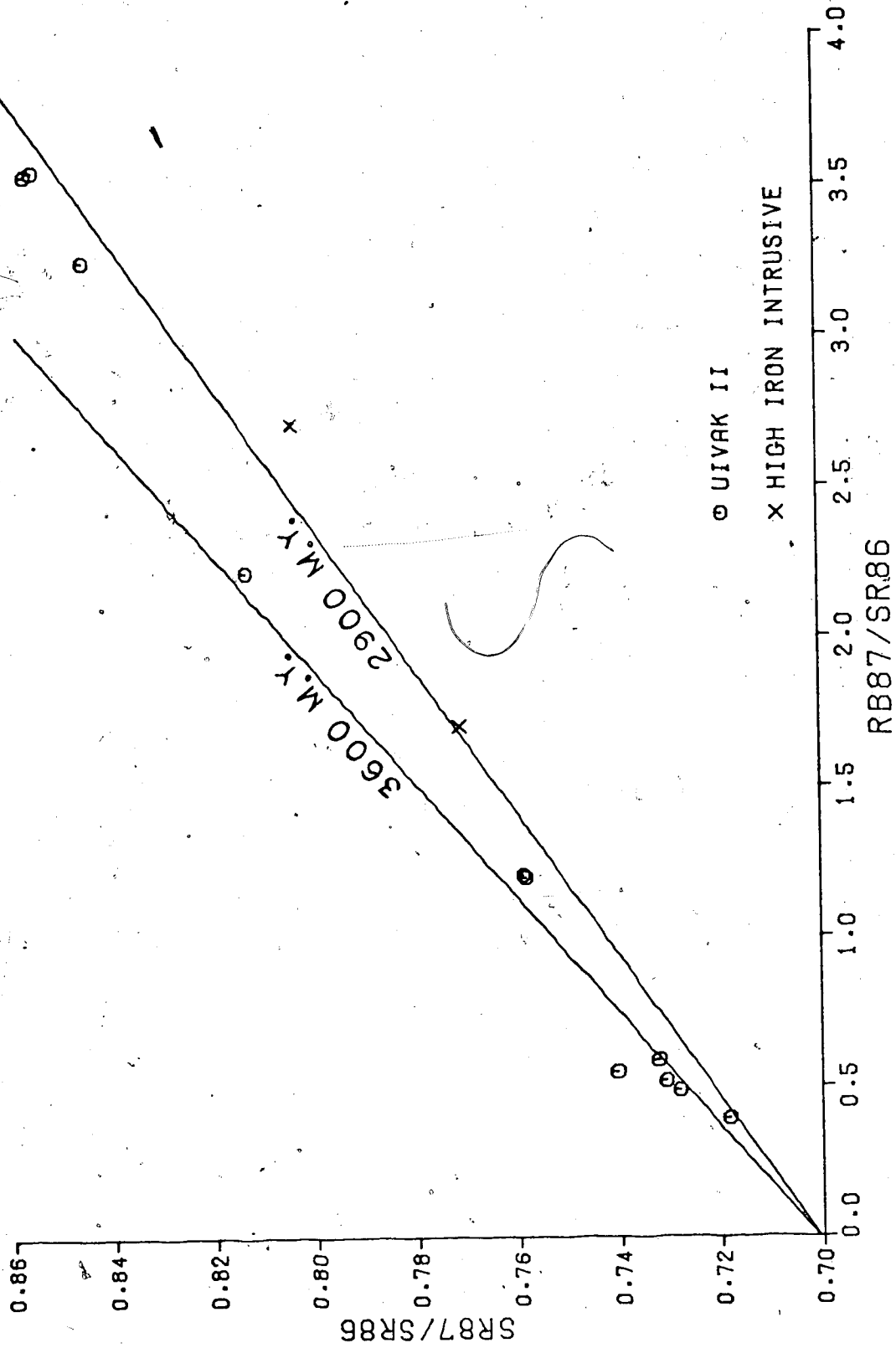


FIG 11: RB-SR RESULTS FOR UIVAK II SAMPLES AND HIGH IRON INTRUSIVES



Table VIII  
Rb-Sr Analytical Data

No.	Sample	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Rb}/^{86}\text{Sr}$	Rb ppm	Sr ppm
<u>Set 1</u>					
1	75-291D Uivak II	0.8547 ±.0006	3.543	201	167
2	74-162C Uivak II	0.8450 ±.0007	3.244	192	173
3	74-161I H. I. I.	0.8037 ±.0001	2.706	253	273
4	74-161G H. I. I.	0.7713 ±.0001	1.700	108	185
5	75-287 Uivak II	0.7584 ±.0001	1.193	128	312
6	75-282 Uivak II	0.7184 ±.0001	0.3935	136	999
<u>Set 2</u>					
1	75-248B Sag Dyke	0.7131 ±.0001	0.2495	9.2	107
2	75-160Z Sag Dyke	0.7434 ±.0001	0.9901	46	134
3	74-161E Sag Dyke	0.7393 ±.0001	0.7110	54	222
4	75-7B Sag Dyke	0.7122 ±.0001	0.1100	7.1	187
5	75-271E L. S. G.	0.7093 ±.0001	0.1492	8.9	173
<u>Set 3</u>					
1	75-285L P. T. G.	0.7878 ±.0001	2.096	174	243
2	74-39 L. S. G.	0.7571 ±.0001	1.352	139	299
3	74-47A L. S. G.	0.7552 ±.0001	1.016	82	234
4	75-28W L. S. G.	0.7357 ±.0001	0.8741	136	452
5	75-262 P. T. G.	0.7215 ±.0001	0.5187	243	1355

Table VIII (cont'd)

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No.	Sample	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Rb}/^{86}\text{Sr}$	Rb ppm	Sr ppm
<u>Set 4</u>					
1	75-252H Null. A.	0.7754 ±.0008	1.600	80	145
2	75-285C Null. A.	0.7833 ±.0002	1.756	29	49
3	75-289B Null. A.	0.7419 ±.0002	1.020	98	280
4	74-92B Null. A.	0.7401 ±.0004	0.8668	93	313
<u>Set 5</u>					
1	75-285N Null. A.	0.7956 ±.0001	0.7181	14	56
2	75-285B Null. A.	0.7188 ±.0001	0.3214	3.5	32
3	75-271D Null. A.	0.7137 ±.0001	0.2688	15	157
<u>Set 6</u>					
1	75-281D Uivak II	0.8561 ±.0001	3.530	201	167
2	75-287 Uivak II	0.7590 ±.0003	1.202	129	310
3	74-42A Uivak II	0.8132 ±.0001	2.213	107	141
4	74-47A L. S. G.	0.7555 ±.0001	0.9866	80	234
5	75-271F L. S. G.	0.7381 ±.0001	0.9402	128	396
6	75-285C Null. A.	0.7837 ±.0001	1.744	29	49
<u>Set 7</u>					
1	74-47B L. S. G.	0.7322 ±.0001	0.5292	53	292
2	75-7C L. S. G.	0.7518 ±.0001	1.201	149	359
3	74-298 Uivak I	0.7538 ±.0001	1.014	128	366

Table VIII (cont'd)

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No.	Sample	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Rb}/^{86}\text{Sr}$	Rb ppm	Sr ppm
<u>Set 7</u>					
4	75-291F Uivak I	0.7392 ±.0001	0.8828	106	349
5	74-40A Uivak I	0.7392 ±.0001	0.6830	83	354
6	75-260C Uivak I	0.7226 ±.0001	0.4518	135	864
<u>Set 8</u>					
1	74-161A Uivak I	0.7235 ±.0001	0.4538	117	744
2	74-161B Uivak I	0.7227 ±.0001	0.4545	132	842
3	74-161C Uivak I	0.7390 ±.0001	0.7246	95	380
4	75-260B Uivak I	0.7336 ±.0001	0.6269	92	425
5	75-320 Uivak I	0.7465 ±.0001	1.016	149	424
6	75-296A Uivak I	0.7480 ±.0001	0.8487	121	414
<u>Set 9</u>					
1	74-161D Uivak II	0.7407 ±.0001	0.5464	25	132
2	74-162A Uivak II	0.7325 ±.0001	0.5858	24	118
3	75-297L Uivak II	0.7312 ±.0001	0.5147	74	416
4	75-297F Uivak II	0.7283 ±.0001	0.4840	73	433

H. I. I. - High Iron Intrusive

L. S. G. - Late Syntectonic Granite

P. T. G. - Post Tectonic Granite

susceptibility of Rb/Sr systems in whole rocks indicates that under many circumstances the Rb and Sr will become rapidly trapped in minerals having a low chemical potential for these elements (such as K-feldspar) before they have a chance to migrate far. Many studies have shown, however, that whole rocks can become partially open systems during thermal events (Wasserburg, et al., 1964; Heier and Compston, 1969; Cumming and Scott, 1976; Krogh and Davis, 1973; Hofmann, 1971) or even completely reset by them (Taylor, 1975).

It is clear that if the scale of strontium isotope re-equilibration and Rb migration is much less than the size of the specimen, the whole rocks should fall on an isochron recording the initial age of the sample. Following the argument of Roddick and Compston (1977), the formation may be visualized as consisting of a set of subsystems each of which is just large enough to have an Rb/Sr ratio equal to that of the formation as a whole. If the range of migration is larger than the scale of one such subsystem, then the whole rocks should fall on an isochron recording the age of the metamorphic event. If it is less than this volume but larger than that of the sample then a scatter will be observed.

There are a number of arguments which suggest that the events affecting the Uivak gneisses involved only limited migration of Rb and Sr within the formation, without any large scale introduction of material from outside. The

Uivak I grey gneisses exhibit a fairly narrow range in Rb concentration. The Rb concentration of 10 grey gneiss samples as reported by Bridgewater and Collerson (1975) varies between 70 ppm and 145 ppm with a mean of 111 ppm. The Rb contents of five grey gneiss samples which fall on an isochron form an even narrower distribution with a mean of 122 ppm and a range of 109-137 ppm. The present ten grey gneisses have a mean of 116 ppm and a range of 83 ppm to 149 ppm. Only one sample falls slightly outside the range exhibited by the previous ten samples. There is therefore no overt evidence of Rb metasomatism in the group as a whole, although limited Rb migration between the rocks may have occurred. In view of the rather monotonous mineralogy and limited range in Rb/Sr values for the suite it also seems likely that the smallest volume having a Rb/Sr ratio characteristic of the formation as a whole would not be very large. This assumes that there is no secular variation in Rb and Sr concentration within the formation. This suggests that the range of migration may not have been very great, perhaps comparable in scale to the size of the whole rock specimen.

In the case where the mobility of the elements has been limited to an exchange between the various subsystems within the formation, a lower limit can be established for the value of the  $^{87}\text{Sr}/^{86}\text{Sr}$  at the end of the last metamorphic event. This cannot be lower than the ratio that the formation began with at the time it was first completely

homogenized. In view of the work of Hurst et al. (1975), it seems reasonable to assume that a pervasive homogenization of the Uivak gneisses occurred at about 3545 m.y. and left the formation with an initial ratio of about 0.701. It is therefore possible to establish an upper limit to the age of the last metamorphic event which disturbed the Rb-Sr systems in the rocks by drawing a reference isochron which just bounds the lower scatter of the samples and passes through the initial ratio of 0.701. This is done in Figures 11 and 12 and shows that the last metamorphic event could not have occurred much before 2900 m.y.. The scatter is much too great to have been produced at 3545 m.y. since this would have required ratios below 0.699, the primordial value for the earth at the time of its formation (Papanastasslou and Wasserburg, 1969). Generally the samples might be expected to scatter between the isochron representing initial homogenization and the isochron for the last metamorphic event. There would probably be some tendency for the rocks to scatter above the initial isochron for low values of Rb/Sr (giving very high model ages) because of  $^{87}\text{Sr}$  gain, whereas they will tend to scatter on or below the isochron for higher Rb/Sr values because of  $^{87}\text{Sr}$  loss.

Although it has been demonstrated that common Sr can become mobile under metamorphic conditions (Krogh and Davis, 1973; Baadsgaard and van Breemen, 1970), it seems reasonable that under most conditions its mobility on the whole rock scale would be much less than that of Rb and the radiogenic

component of strontium. The bulk of the normal Sr component is usually dispersed within the feldspars where it is securely held within the host lattice. The results of Hart (1964) suggest that the feldspar lattice strongly retains Sr under elevated thermal conditions. The radiogenic component is usually present in a foreign lattice from which it will have a greater tendency to diffuse.

The strontium isotope development of the Uivak I samples, extrapolated back into the past, is plotted in figures 12, 13 and 14. For the reasons outlined above, the assumption will be made that the range of Rb concentrations observed in the grey gneiss suite by Bridgewater and Collerson is representative of those rocks at 3545 m.y. and that the Sr concentration of each rock has remained constant since that time. It is then possible to accompany each rock by an envelope computed from the normal Sr concentration of the rock and the range of Rb concentrations observed in the formation as a whole. This sets probable limits on the isotopic development of Sr in the rock before the last metamorphic event. The lower scatter of the samples indicates that they must have been affected at or after 2900 m.y.. U-Pb data on zircons from these rocks and others in the complex (Baadsgaard et al., 1977) indicate that these systems became closed to uranium and lead at about 2500 m.y.. The envelopes are therefore terminated at 2500 m.y.. Assuming for simplicity that only one episodic event disturbed the whole rocks, then this event most

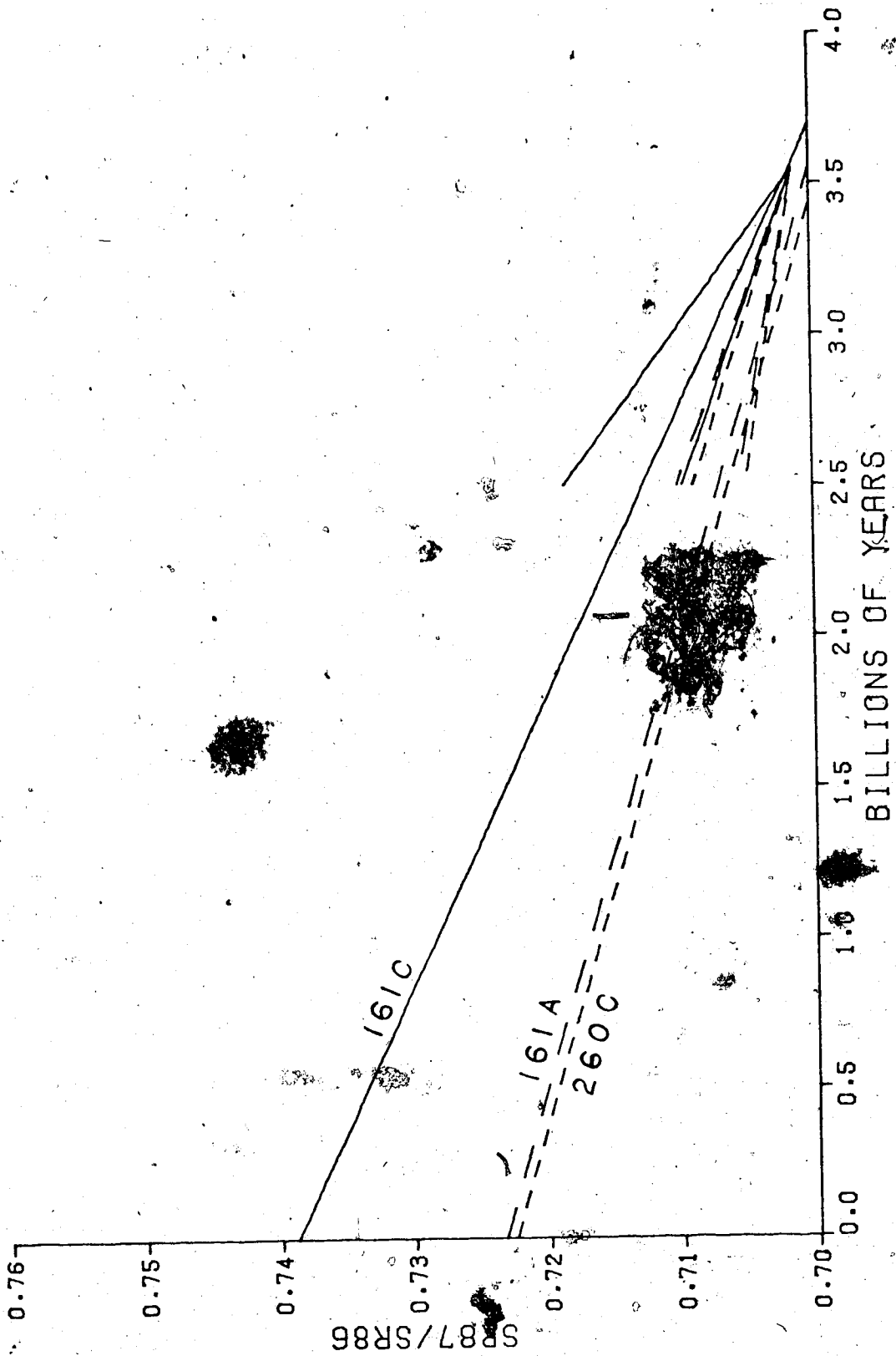


FIG 12: SR GROWTH CURVES FOR UIVAK I SAMPLES



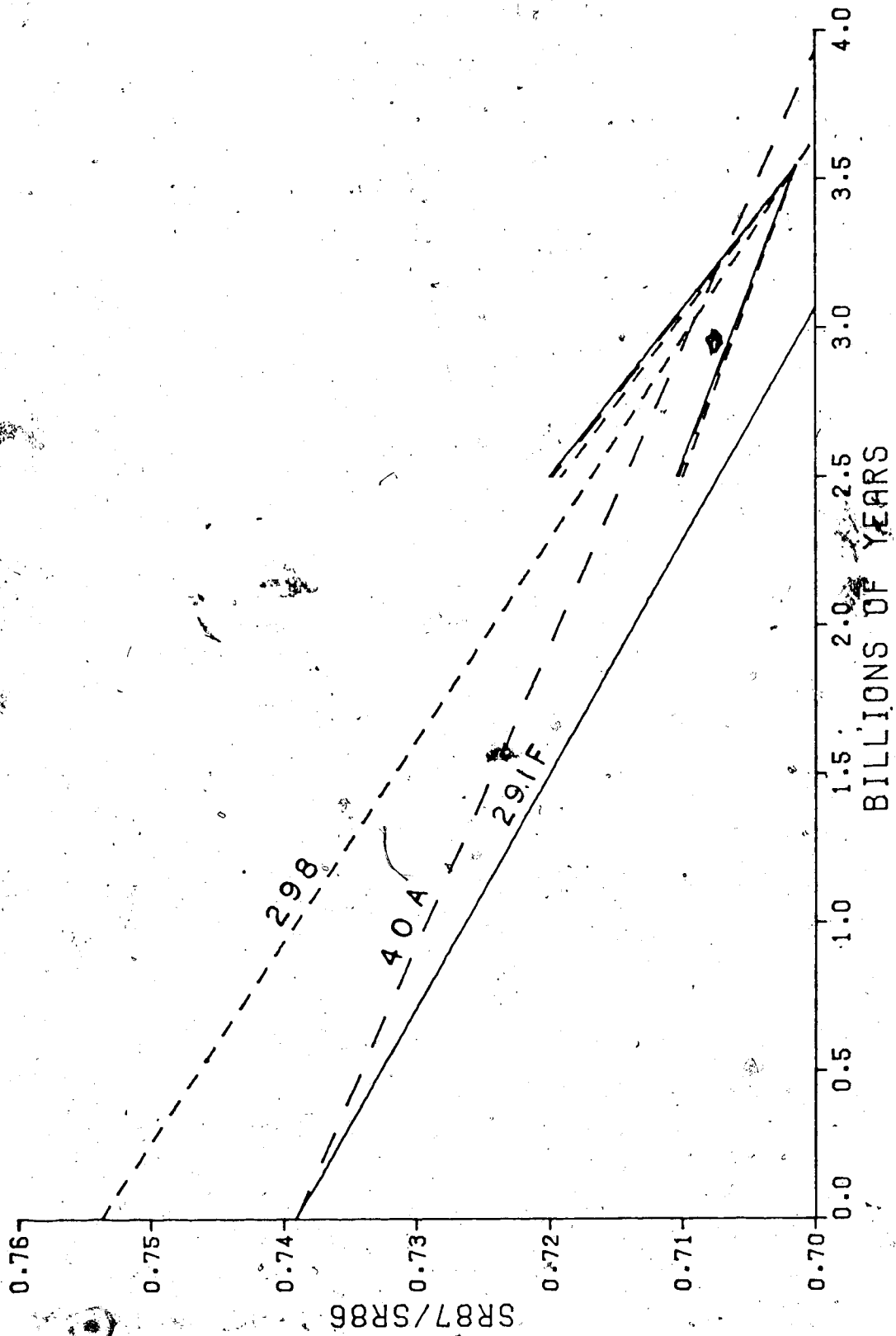


FIG 13: SR GROWTH CURVES FOR UIVAK I SAMPLES

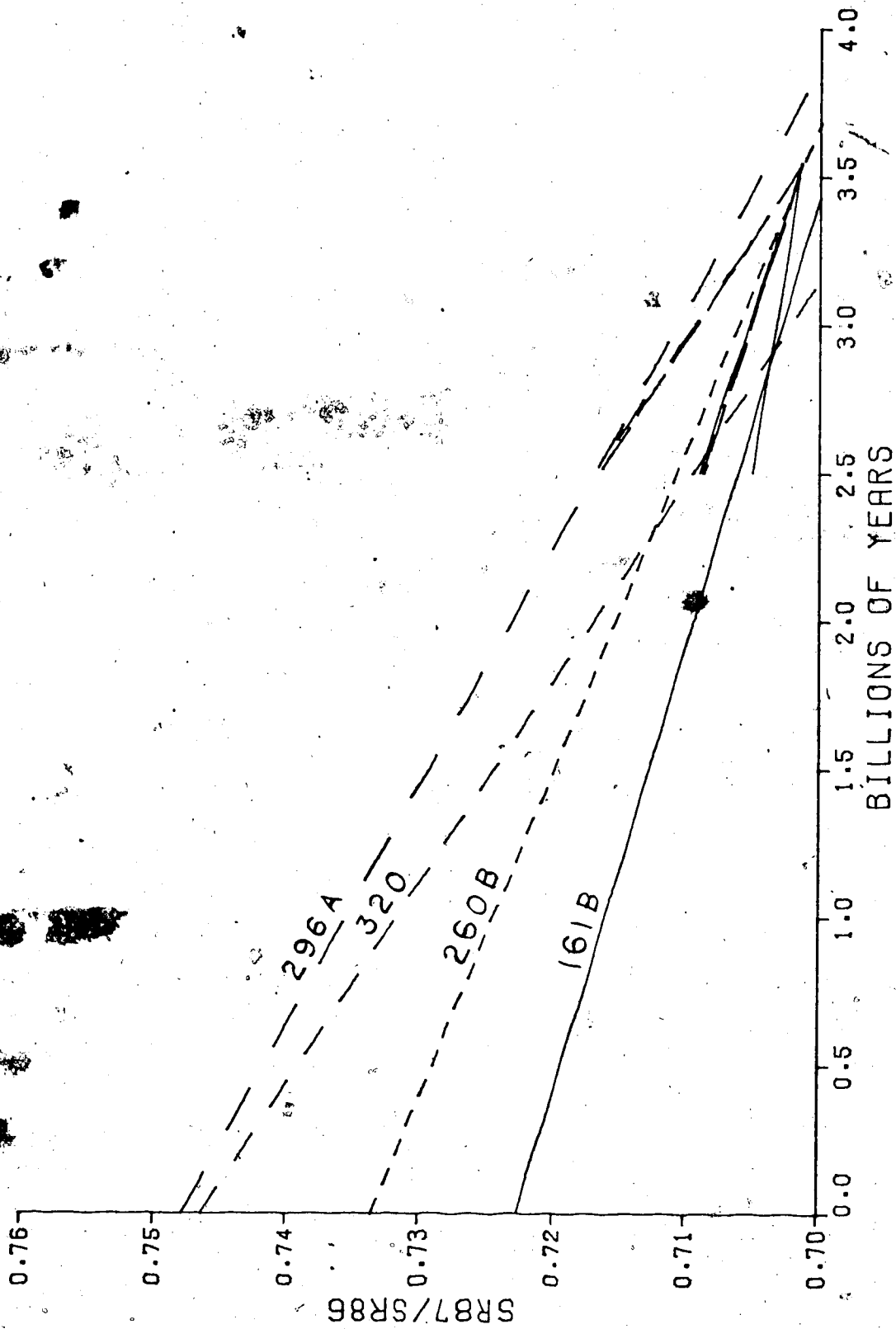


FIG 14: SR GROWTH CURVES FOR UIVAK I SAMPLES

probably occurred between 2900 m.y. and 2500 m.y.. In this case, the isotopic evolution of the rocks can be described by two straight lines of different slope. One line begins at 3545 m.y. and proceeds within the envelope to some time between 2900 m.y. and 2500 m.y.. The path of the Sr isotopic evolution then changes to the other line, the one extrapolated backward from the present. If there is no movement of radiogenic  $^{87}\text{Sr}$ , the slope but not the position of the line will be discontinuous at the time of disruption. If there is movement of both Rb and  $^{87}\text{Sr}$ , then both the slope and the position of the path will be discontinuous at this point. From this argument it is possible to see that sample 291F has almost certainly lost  $^{87}\text{Sr}$  during a thermal event. Sample 320 may have lost  $^{87}\text{Sr}$  while 296A may have gained. A combination of gain and loss of Rb and  $^{87}\text{Sr}$  can explain the histories of the others. Samples 161A, 161B and 260C which plot almost together on the isochron diagram all appear to have lost  $^{87}\text{Sr}$  and/or gained Rb whereas 40A may have gained  $^{87}\text{Sr}$  or perhaps lost Rb. Samples 161C, 260B and 298 appear to have been little altered.

The Uivak II samples have less well constrained Rb values. Their Rb concentrations are spread over a very wide range from 24 ppm to 210 ppm. The mean of all the samples however is roughly that of the grey gneisses. Their Sr evolutionary paths extrapolated backward from the present are plotted in Fig. 15. If an exceptionally low Rb sample such as 162A lost its Rb through a metamorphic event, then

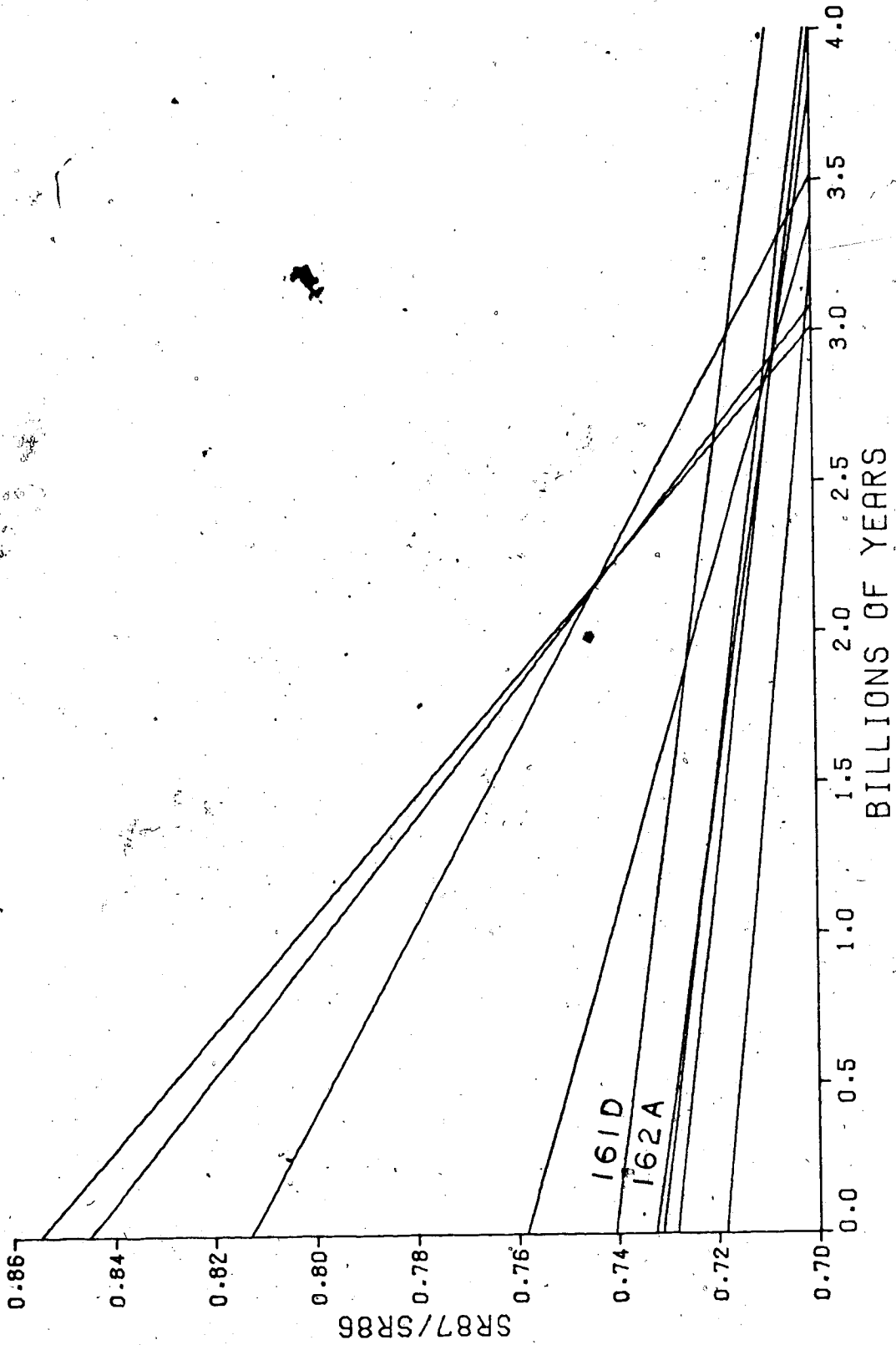


FIG 15: SR GROWTH CURVES FOR UIVAK II SAMPLES

it must also have lost considerable amounts of  $^{87}\text{Sr}$ . If, on the other hand, one such as 161D had about the same Rb content from its initial resetting at 3545 m.y. then it must have gained a great deal of  $^{87}\text{Sr}$ .

The high  $\text{Fe}_2\text{O}_3$  plutonic suite, which intrudes the Uivak gneisses is of uncertain stratigraphic age. Zircons from both 161I and 161G have given ages of 2600-2700 m.y. (Baadsgaard et al., 1977). They fall distinctly below the scatter of the Uivak samples. An upper bound to the time when they became closed can be established by finding the isochron which encompasses them from below and passes through the smallest possible initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio, about 0.701. This is found to be 2600 m.y.. In view of the zircon data, this is probably not the age of intrusion, but an age of closure to migration of Rb and Sr. Again, the whole rocks have probably not been completely reset since an isochron drawn between the two points would give an age of 2200 m.y. which is improbably low.

The samples from the Nulliak assemblage supracrustals behaved similarly to the Uivak gneisses. As shown in Fig. 16 they have a somewhat lower scatter and are bounded by a 2700 m.y. isochron passing through 0.701. U-Pb measurements on zircons from 92B and 285N showed them to be almost concordant at about 2500 m.y. (Baadsgaard et al., 1977). 285N has obviously had its  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio increased enormously at some point in its history (Fig. 17).

One might expect that under metamorphic conditions in

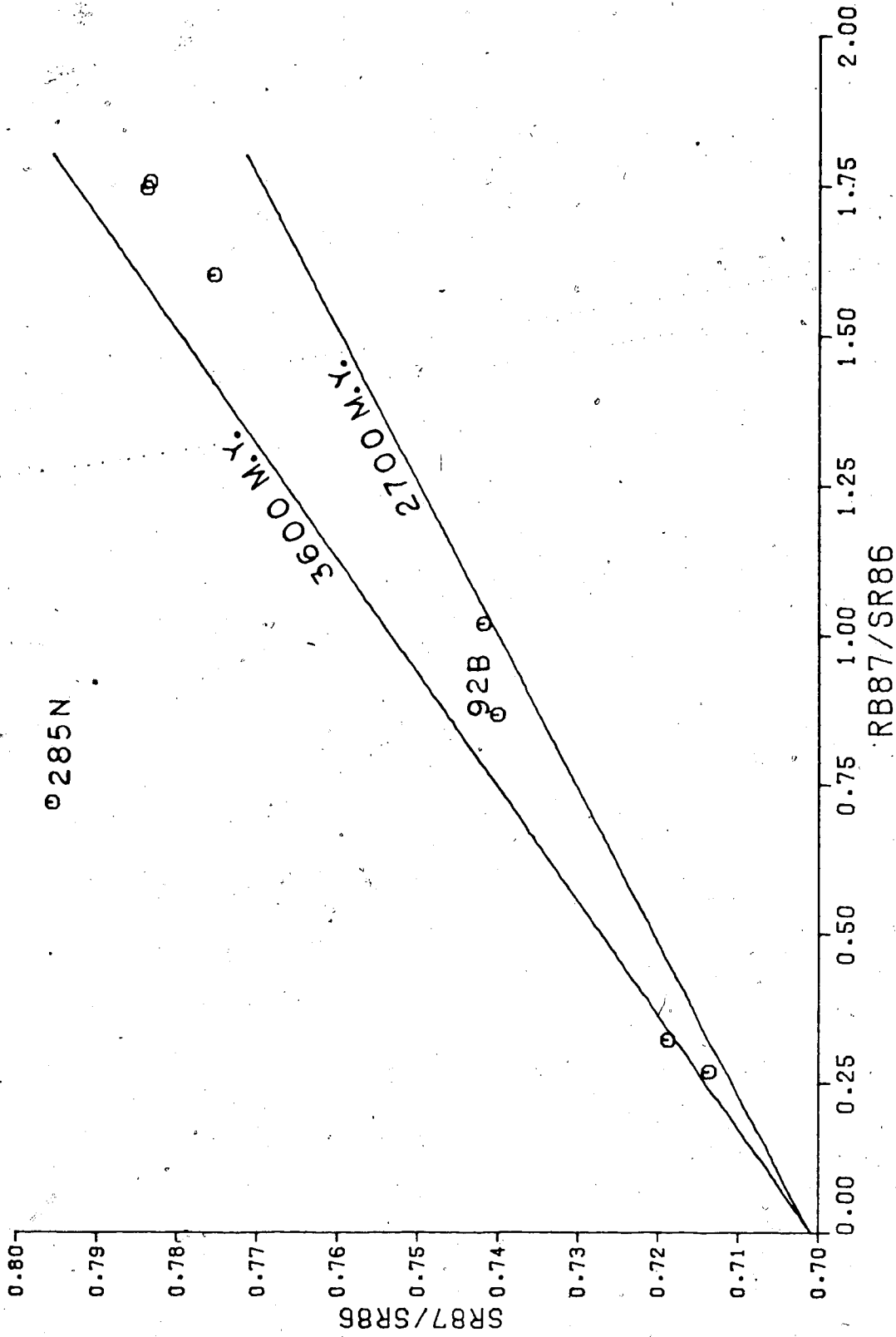


FIG 16: RB-SR RESULTS FOR THE NULLIAK ASSEMBLAGE

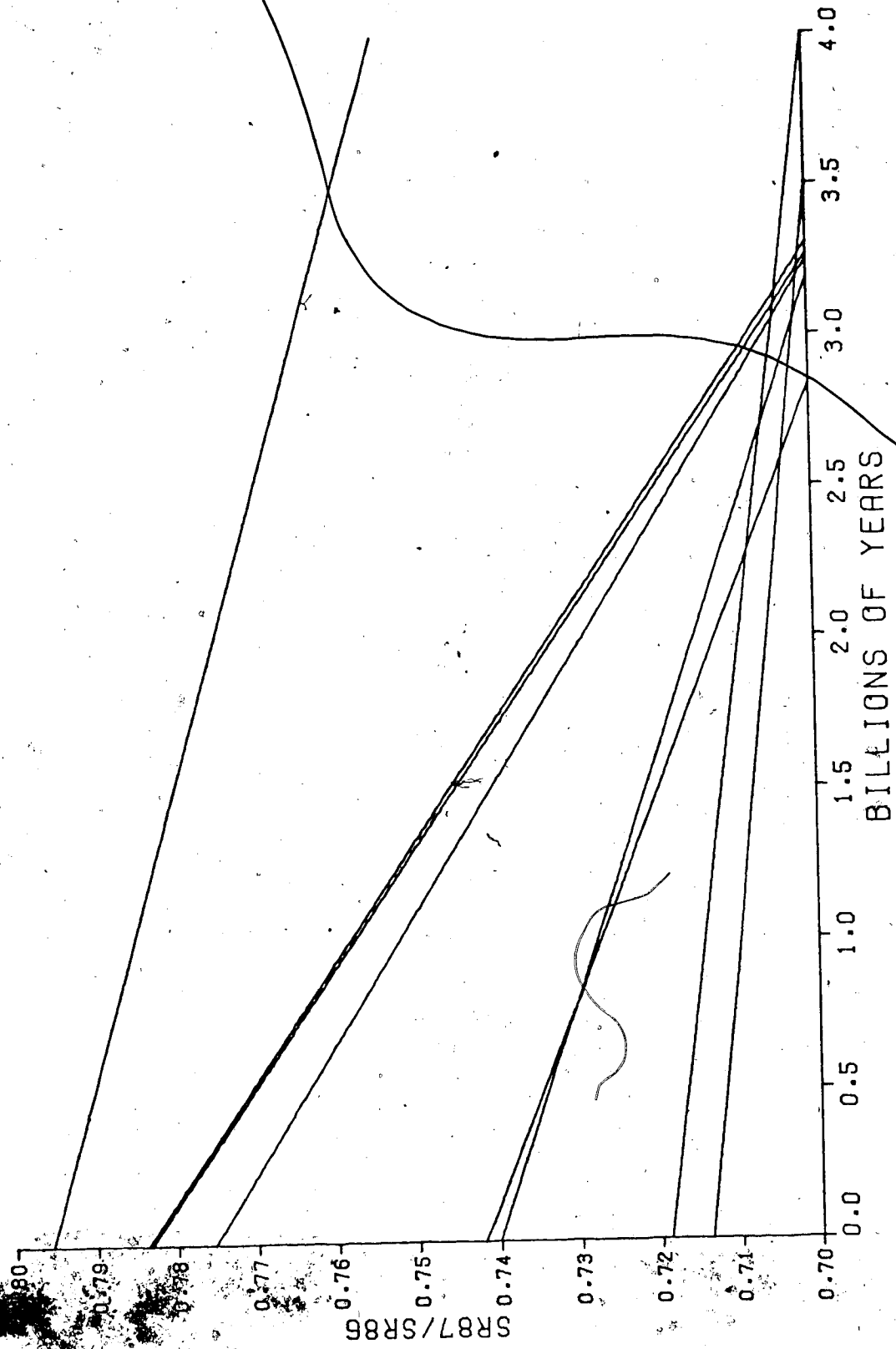


FIG 17: SR GROWTH CURVES FOR THE NULLIAK ASSEMBLAGE

which  $^{87}\text{Sr}$  is mobile but not common Sr, rocks having a high concentration of Sr would be affected less than those having a smaller concentration. This effect appears to be evident with the supracrustals since the rocks which give high model ages such as 285N and 285B contain relatively small amounts of common Sr. The effect may be masked somewhat by the diffusion and redistribution of Rb. One problem concerning the behavior of whole rocks with respect to strontium under metamorphic conditions is that even if conditions are severe enough to cause complete remobilization of Rb and  $^{87}\text{Sr}$  within the formation, the rocks will never appear as closed systems unless the common Sr is remobilized as well to produce a uniform initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio. This may require extreme conditions, perhaps involving partial or even complete remelting.

The late granites might have been expected to have behaved as closed systems. Including 47A and 47B however, they exhibit the entire range of scatter of all the samples considered so far. They are just bounded by the 2700 m.y. mantle-derived reference isochron as shown in Fig. 18. Even the two post tectonic granites, which exhibit no evidence of deformation, cannot form an isochron since the age of about 2900 m.y. would be too high. U-Pb analysis of zircons from these rocks shows them to be about 2500 m.y. old (Baadsgaard et al., 1977). Also the initial Sr isotopic composition would be too low for the mantle at this time. It must be concluded that the post-tectonic granites inherited variable



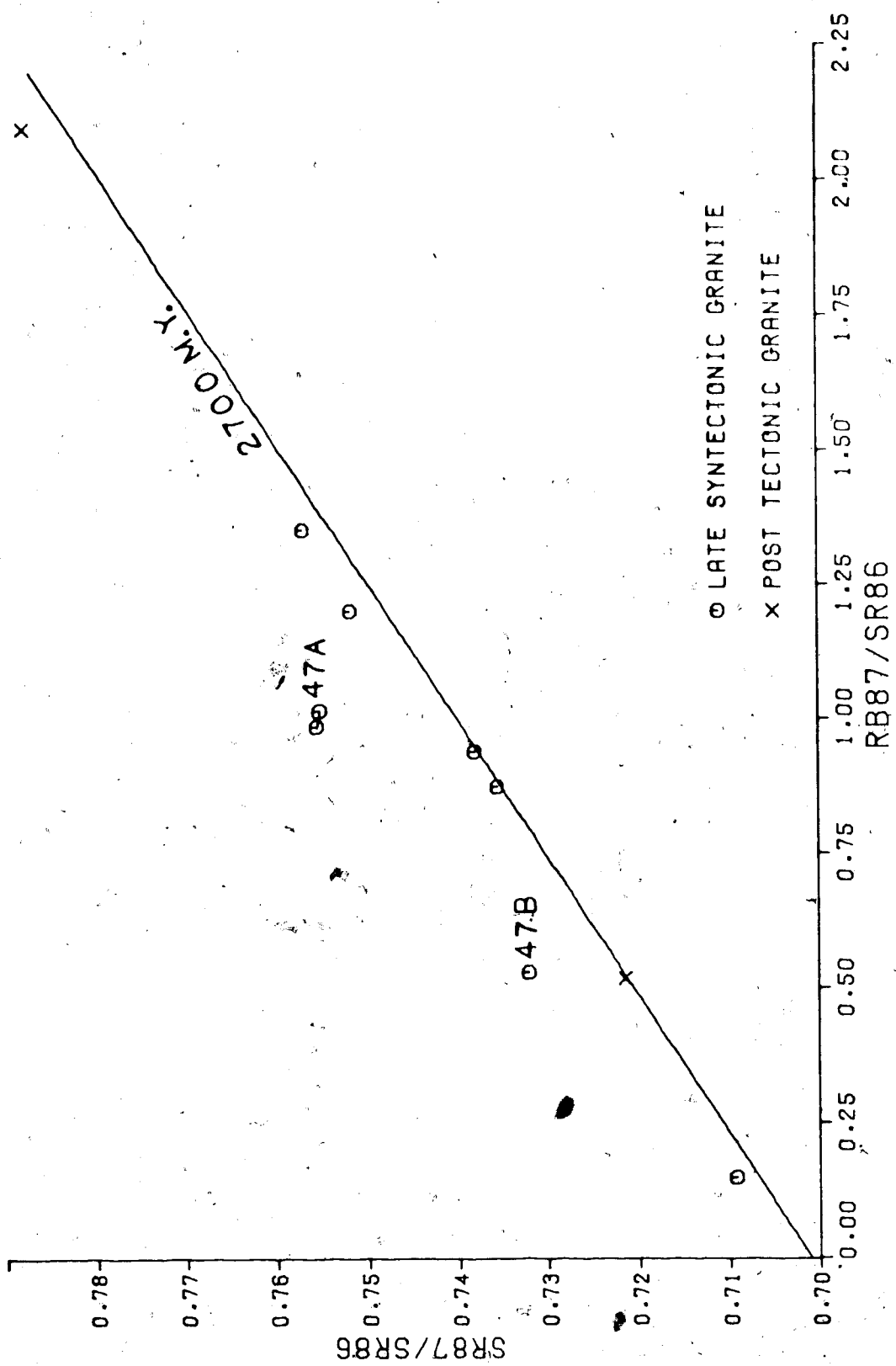


FIG 18: RB-SR RESULTS FOR THE LATE SYNTECTONIC AND POST TECTONIC GRANITES

amounts of radiogenic crustal Sr. As shown in Fig. 19, a sample such as 262 could not have inherited very much since its initial ratio at 2500 m.y. is only slightly above the mantle value. On the other hand 285L may have been formed by remelting of Uivak gneiss material since its initial ratio at 2500 m.y. is about equal to that which the Uivak gneiss would have had.

Similarly for the late syntectonic granites, 47A and 47B appear to have incorporated large amounts of crustal strontium. The others scatter about mantle-derived isochrons of about 2700-2900 m.y.. There is no evidence in any case that the late syntectonic granites form a cogenetic suite. All that can be said is that their initial strontium appears to be governed by an admixture of a crustal component and a mantle component.

The Pb-Pb results are listed in Table IX and plotted on a  $^{207}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$  diagram in Fig. 20. As with Rb-Sr they exhibit a broad scatter and in fact the different suites are virtually indistinguishable from each other within the scatter.

The Uivak II suite, plotted in Fig. 21, is the most radiogenic. There are only four samples but they form a fairly good line with a slope age of about 2900 m.y.. The Uivak I suite, also, plotted in Fig. 21, has much more scatter. Some of the samples were done twice, once by the author and independently in different laboratories and on different mass spectrometers. These replicate measurements

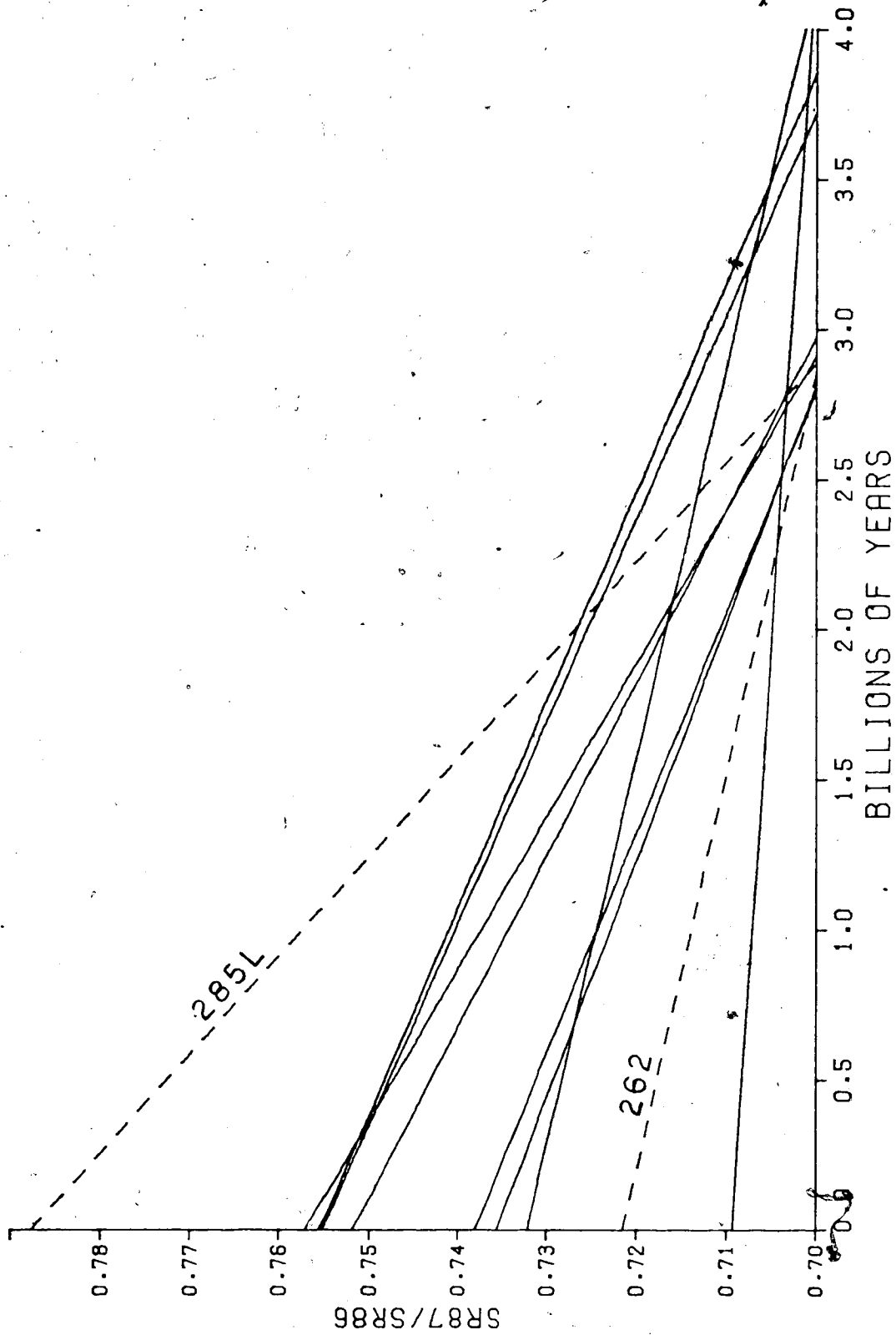


FIG 19: SR GROWTH CURVES FOR THE LATE SYNTECTONIC AND POST TECTONIC GRANITES

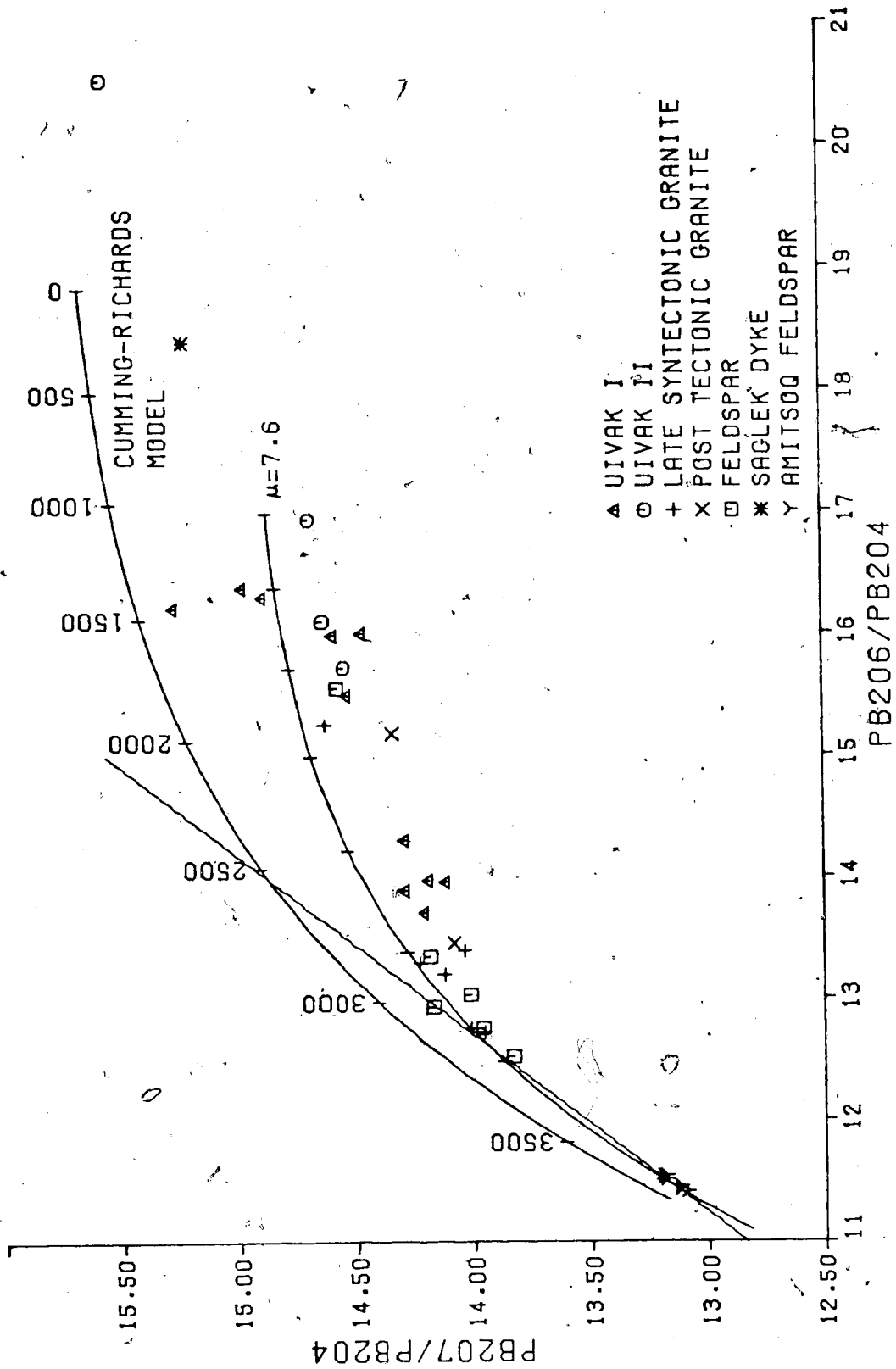


FIG 20: PB-PB RESULTS ON ALL SAMPLES

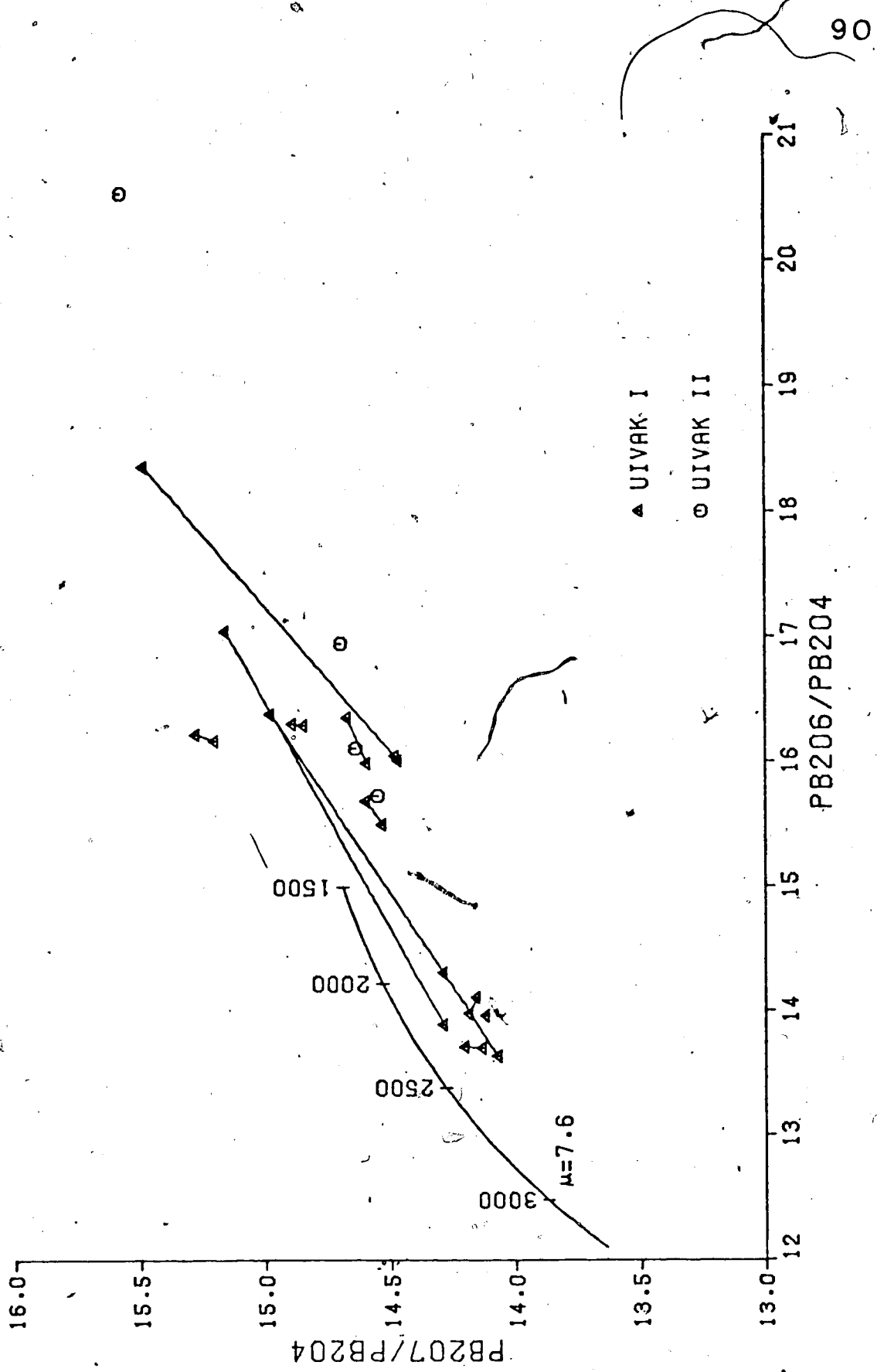


FIG 21: PB-PB RESULTS ON UIVAK GNEISSES

Table IX  
Pb-Pb Analytical Data

No.	Sample	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
<u>Set 7</u>				
1	74-47B L. S. G.	12.727 ±.001	13.956 ±.001	34.622 ±.006
2	75-7C L. S. G.	13.402 ±.003	14.036 ±.004	43.619 ±.014
3	74-298 Uivak I	16.216 ±.016	15.272 ±.015	37.268 ±.037
4	75-291F Uivak I	16.379 ±.008	14.976 ±.008	37.154 ±.021
5	74-40A Uivak I	17.041 ±.004	15.154 ±.004	38.133 ±.013
6	75-260C Uivak I	18.353 ±.007	15.482 ±.007	38.690 ±.018
<u>Set 8</u>				
1	74-161A Uivak I	15.680 ±.010	14.595 ±.008	34.795 ±.017
2	74-161B Uivak I	14.307 ±.011	14.290 ±.010	34.267 ±.005
3	74-161C Uivak I	13.700 ±.009	14.133 ±.003	35.346 ±.004
4	75-260B Uivak I	13.979 ±.010	14.188 ±.010	38.688 ±.020
5	75-320 Uivak I	15.986 ±.034	14.593 ±.032	35.984 ±.058
6	75-296A Uivak I	16.300 ±.019	14.890 ±.019	35.874 ±.038
<u>Set 9</u>				
1	74-161D Uivak II	20.529 ±.030	15.566 ±.020	36.825 ±.035
2	74-162A Uivak II	16.943 ±.002	14.693 ±.002	34.696 ±.004
3	75-297L Uivak II	16.104 ±.005	14.635 ±.004	40.643 ±.020
4	75-297F Uivak II	15.721 ±.011	14.548 ±.010	40.382 ±.031

Table IX (cont'd)

No.	Sample	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
<u>Set 10</u>				
1	74-47A L. S. G.	13.202 ±.004	14.126 ±.004	32.778 ±.010
2	75-271E L. S. G.	12.758 ±.001	14.011 ±.003	32.325 ±.006
3	75-271F L. S. G.	15.255 ±.002	14.628 ±.002	35.538 ±.005
4	75-28W L. S. G.	13.297 ±.007	14.230 ±.008	43.000 ±.028
5	75-285L P. T. G.	13.463 ±.002	14.084 ±.004	40.200 ±.014
6	75-262 P. T. G.	15.183 ±.025	14.338 ±.034	43.275 ±.081
<u>Set 11</u>				
1	74-161A Uivak I	15.495 ±.001	14.532 ±.002	34.634 ±.005
2	74-161C Uivak I	13.711 ±.002	14.205 ±.003	35.622 ±.009
3	74-161F Uivak I	13.962 ±.002	14.117 ±.003	34.533 ±.009
4	74-40A Uivak I	13.891 ±.001	14.290 ±.002	37.322 ±.008
5	75-260C Uivak I	16.005 ±.006	14.469 ±.005	39.525 ±.018
6	74-161E Sag Dyke	18.391 ±.004	15.226 ±.005	37.413 ±.013
	74-161A Plag.	13.350 ±.002	14.184 ±.004	32.920 ±.012
	74-161C K-feld.	12.756 ±.005	13.960 ±.005	32.818 ±.020
	74-161F Plag.	12.525 ±.006	13.832 ±.004	33.135 ±.026
	74-40A Feldspar	13.036 ±.007	14.013 ±.008	33.896 ±.026
	75-260C Plag.	12.935 ±.020	14.170 ±.020	33.188 ±.068
	75-260C K-feld.	15.554 ±.011	14.577 ±.028	35.394 ±.068

are joined by tie lines. Most of the discrepancy can probably be accounted for by inhomogeneity in sampling, since some of the samples from which Pb was extracted during the Rb-Sr separation process were very small, down to 50 mg.

It can be seen from the scatter that the leads have undergone a complex history. Leads in feldspar mineral separates from some of the samples were analysed and compared with those from the corresponding whole rocks to determine whether this would reveal a possible 3 stage history. The whole rock analyses had been redone by the standard Pb extraction procedure using samples of about 1 g. However, the tie lines between the minerals and their whole rocks, plotted in Fig. 22, are not parallel and have slope ages from 3600 m.y. to 2500 m.y.. The Uivak feldspars are also distinctly different from the Amîtsoq feldspars (Baadsgaard et al., 1976).

It seems highly unlikely that the Uivak feldspar leads are inherited from a c. 3600 m.y. event. Not only do they show a rather broad scatter, but they plot well to the right of the 3600 m.y. isochron passing through primordial troilite lead. The striking similarity in structure and stratigraphy of the Uivak and Amîtsoq suites makes it reasonable to hypothesize that they form part of the same complex. The Uivak gneisses should therefore have possessed leads of similar isotopic composition to the Amîtsoq feldspars at about 3600 m.y.. Under this assumption, it is possible to develop a quasi-3 stage model to explain the



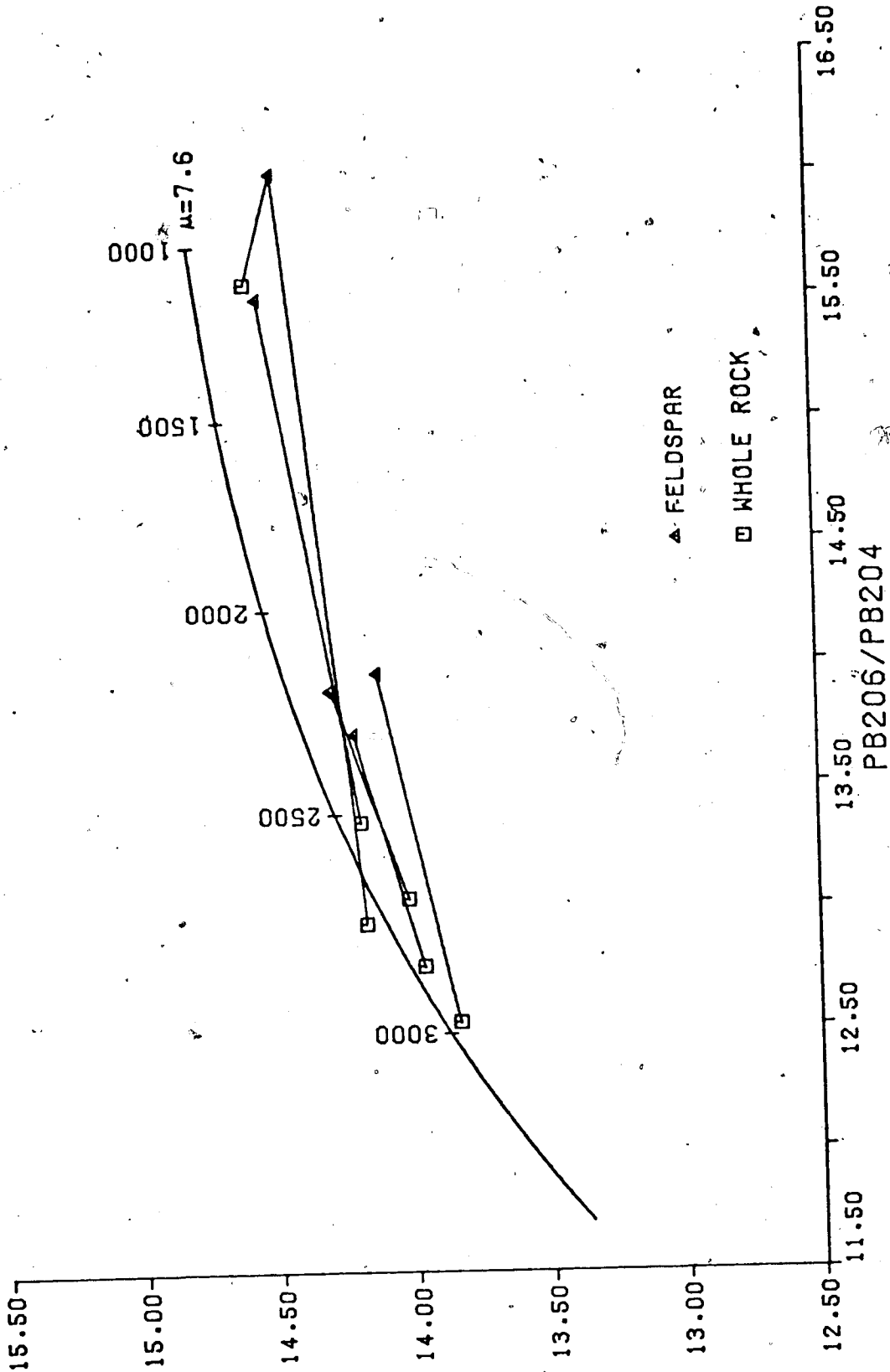


FIG 22: PB-PB RESULTS ON UIVAK WHOLE ROCKS AND FELDSPAR SEPARATES.

present day distribution of feldspar and whole rock leads. This will only be a rough approximation to the true situation since the Uivak gneisses appear to have been fractionated by metamorphic processes about 100 m.y. after the Amîtsoq gneisses, so that we are dealing with at least a 4 stage model in the strict sense. However, scatter and uncertainties in the data do not justify a more detailed model.

Ideally, if the system had been fractionated at 3600 m.y. and then during some later episodic event the feldspars had been equilibrated with the whole rock, the whole rocks remaining closed systems, one would expect to see the Uivak feldspars aligned with the Amîtsoq feldspars and the line should intersect the primary growth curve at 3600 m.y. and the date of the second event. The whole rocks should also be aligned with each other and with the Amîtsoq feldspars and have a slope age of 3600 m.y.. This in fact would reduce to a two stage model since the whole rocks would not see the second event and the feldspars would serve to record it. Individual whole rocks should be joined to their corresponding feldspars by parallel lines having slope ages equal to the age of the second event. As we have seen, this is not the case, although with the exception of 298 the whole rocks do form a broadly rectangular distribution with the feldspars having an average slope age of about 2800 m.y.. The feldspars also have a fairly broad scatter in the direction of the 2800 m.y. isochron. This behavior is

most likely due to two reasons. First, the second metamorphic event was probably not episodic. As has been seen, the Rb-Sr distribution indicates that the Uivak whole rocks could not have become closed to diffusion of Rb and radiogenic Sr at a date earlier than 2900 m.y. and the more susceptible Nulliak assemblage samples could not have been closed much earlier than 2700 m.y.. Zircon, sphene and apatite data on the same rocks give ages much younger than this (Baadsgaard et al., 1977). The Uivak zircons have evidently been partially reset by an "event" at roughly 2500 m.y.. The sphenes are highly colinear, giving a slope age of 2530 m.y.. The same is true of the apatites which give a slope age of 2435 m.y.. It seems likely therefore that high grade conditions, allowing limited diffusion of lead, persisted for several hundred million years after the onset of the granulite event. This would account for most of the lateral scatter in the feldspars. Second, not only were the whole rocks open to diffusion of U and Pb but this diffusion and re-equilibration was most likely incomplete, leading to a variable mixing of lead between the samples and a fractionation of the  $\mu$  values. These processes should lead to a broad rectangular distribution of points which is what is observed. As mentioned, the only salient exception to this pattern is sample 298 which is enriched in  $^{207}\text{Pb}$ . Interestingly, this sample also happens to lie almost on the 3545 m.y. Rb-Sr isochron. The rock cannot have remained a closed system with respect to both U and Pb however, since a

line of slope age equal to 3545 m.y. running through it does not meet the Amîtsoq feldspars but strikes the top of the distribution of Uivak feldspars. This could be explained if the sample had had an unusually high  $u$  value between 3600 m.y. and about 2900 m.y. and had then lost uranium. Similarly, the other two samples which appear to have preserved their Rb-Sr systematics relatively well, 161C and 26B, both lie to the left of a 3545 m.y. isochron passing through the Amîtsoq feldspars. The only one that has a feldspar separate is 161C. The slope age between the feldspar and the whole rock is about 3200 m.y. which may indicate incomplete equilibration of lead in the feldspar.

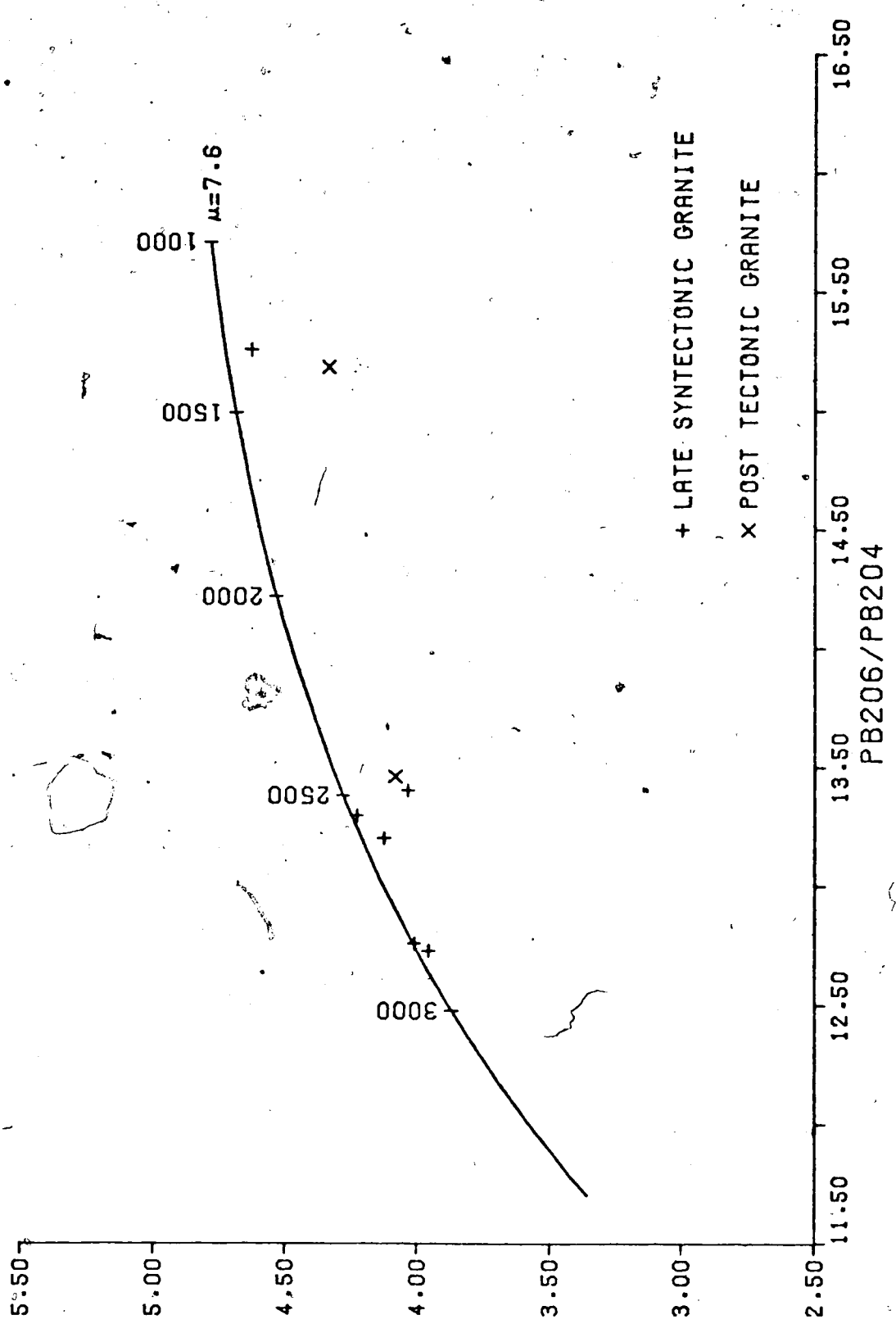
It is possible to test this model for consistency by looking at the relationship between the leads in the Amîtsoq and Uivak feldspars. Drawing a line which passes through the Amîtsoq feldspars and the left edge of the scatter in the Uivak feldspars, the  $u$  value for the growth curve which is intersected by this line at 3600 m.y. is calculated to be 7.60. The second intercept age will then be 2840 m.y.. This should represent the latest age for the onset of the second metamorphic event, possibly the granulite facies event. Considering the uncertainties, it is consistent with the slope age of the distribution, seen to be about 2800 m.y., and with the Rb-Sr closure age of the Uivak gneisses. It also closely approximates the age of the granulite facies metamorphism in Greenland which was measured to be  $2850 \pm 100$  m.y. (Black et al., 1973).

Pb-Pb measurements on Amittuq whole rocks (Baadsgaard et al., 1976) have indicated that these rocks were severely depleted in uranium at about 3600 m.y.. They are in many cases only slightly more radiogenic than their feldspars. It would appear from the data however that the Uivak whole rocks were not similarly depleted but continued to evolve with a higher  $\mu$  until they had the present composition of their feldspars at about 2840 m.y.. At this time an event occurred which refractionated the U/Pb ratios. The Uivak I rocks appear to have all lost uranium whereas the Uivak II samples were less affected and in at least one case, gained uranium. The changes in  $\mu$  may also be due to gain and loss of lead but this is geochemically less likely to have occurred. These changes in  $\mu$  are not surprising in view of the episodes of pervasive granulite facies metamorphism which appear to have affected the area. It is known that rocks which have been subjected to intermediate pressure granulite facies metamorphism and higher grades are often severely depleted in U, Th and Rb (Lambert and Heier, 1967, 1968; Heier and Thorenson, 1971). Th is not as consistently depleted as U, while Rb is depleted more than K, leading to high K/Rb ratios. In amphibolite facies gneisses the Th and U should be present mainly in the epidote minerals and zircons while the Rb will be concentrated in the micas and K-feldspar. Epidote is not stable under granulite facies conditions. The micas also break down to form K-feldspar plus other reaction products with no affinity for Rb. The Rb

does not appear to enter the K-feldspar but is evidently lost along with U and Th (Heler, 1973). The fact that medium to high pressure granulite facies gneisses are somewhat depleted in silicon with respect to equivalent rocks of lower metamorphic grade suggests that the U, Th and Rb may enter a melt phase and migrate to higher crustal levels. Later retrogression from granulite to amphibolite grade does not appear to affect the trace element concentrations.

The low  $\mu$  values and Pb isotopic composition of the AmItsoq feldspars around Godthaab suggest that they may have been subjected to granulite facies metamorphism at some time shortly before 3600 m.y.. The Uivak gneisses may not have been similarly affected because they were at a shallower crustal level. On the other hand, if Bridgewater and Collerson are correct in assuming that the event dated at 3545 m.y. represents metasomatic addition of Rb to the crust, then these fluids would have also probably contained uranium, perhaps enriching the presently exposed level of Labrador crust in the trace elements it had lost through a previous granulite facies metamorphism.

There are two interesting features about the leads extracted from the late and post-tectonic granites (Fig. 23). One is that most of them are as non-radiogenic as the Uivak feldspars, which implies that these samples contain almost no uranium. The other feature is that they plot in the same position as the Uivak samples and exhibit the same scatter. The lead isotopic data by itself could most easily



be interpreted by saying that the granites resulted entirely from the fusion of crustal material. This seems unlikely in view of the Rb-Sr data, however, because many of the samples preserve evidence of an initial Sr isotopic composition well below that of the average for the Uivak gneisses. It is conceivable that the rocks could have been derived from a mixture of crustal and differentiated mantle material if the mantle tapped by the intrusions had a lead isotopic composition very close to that of the Uivak feldspars at the time of granitic intrusion. This would mean that this section of the mantle was distinctly less radiogenic than predicted by the Cumming and Richards model. There is evidence that this may indeed have been the case since the isotopic ratios of the leads from the Nûk feldspars plot well within the range of the Uivak feldspars and late granites (Baadsgaard, pers. comm.). As has been mentioned, the Nûk gneisses display uniformly low initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and are considered to have been derived from the mantle. The very low  $u$  values of the granites are in conflict with this model however. Uranium should be concentrated very strongly in a partial melt, at least as much as lead, so that if the late granites were derived by partial fusion of either mantle material or the Uivak gneisses as we now see them, they should possess reasonably high  $u$  values. Most of the late granites however are distinctly less radiogenic than the least radiogenic of the Uivak samples.



It has already been mentioned that one way of severely depleting rocks in uranium is to subject them to medium or high pressure granulite facies metamorphism. Field and petrographic evidence indicates that these rocks were never subjected to granulite facies metamorphism, moreover the average Rb concentration of the late syntectonic granite samples is only slightly below that of the Uivak gneisses although some individual samples such as 271E do appear to be quite depleted in Rb. The two post-tectonic granites have considerably higher Rb concentrations than the Uivak I gneisses.

The lead evidence suggests that the source of these rocks must have been severely depleted in uranium and it would therefore have most likely been a deeper crustal layer which had been subjected to at least pyroxene granulite facies metamorphism. Furthermore, the isotopic composition of the leads indicates that the granulite event affecting the source rocks must have occurred very shortly before the intrusion of the granites. This would presumably have been a result of the c. 2850 m.y. granulite event. The metamorphism would first have removed almost all the uranium from the source rocks. Partial fusion of the residuum would have later formed the granites which were intruded into fissures opened along the axial planes of folds resulting from late stage deformation of the complex. Rubidium would have been depleted in the residuum also but not to the same degree as uranium. Partial fusion would have tended to concentrate the

available rubidium in the granitic melt so that the resulting Rb concentrations in the granites may not appear severely depleted. The depletion in thorium appears to have been quite unpredictable. Although many of the late syntectonic granites have low  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios, two of them, 28W and 7C, have extremely high ratios despite the fact that both these samples have very low  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios. Also, both post-tectonic granites exhibit very high  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios. This lack of coherence between U and Th is evident in the Uivak gneisses as well and appears to be a common effect of high grade metamorphism.

The apparent non-radiogenic nature of the initial strontium in many of the samples still remains to be explained. There is no definite correlation between the initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the granites and their  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios. The three samples which should have the highest initial ratio all have non-radiogenic lead whereas the two samples with relatively radiogenic lead evidently both had low initial Sr ratios. Since the metamorphic event must have occurred immediately before formation of the granites, the Sr in the source rocks would not have remained long in an Rb depleted environment.

The easiest way to explain the observations would be to assume that the late granites were not derived from Uivak gneiss alone but from a mixture of metamorphosed Uivak gneiss and more mafic material having lower  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. Such material could be derived from partial melting

of the Upernavik supracrustals which are known to have been tectonically interleaved with the Uivak gneisses before the occurrence of the latest granulite facies event. The non-uniform nature of the initial Sr isotopic composition could be explained by different proportions of amphibolitic and gneissic material.

There are several other interesting although more remote possibilities for explaining the Sr data from the late granites. It has already been emphasized that radiogenic Sr and common Sr can behave differently under metamorphic conditions because of their locations in the rock. Much of the radiogenic component of the strontium would have been concentrated in the micas and would have been liberated from them when they decomposed under granulite facies metamorphism. It is conceivable that a great deal of this unsupported  $^{87}\text{Sr}$  could have escaped from the system in a fluid phase along with U, Th and Rb. Whether or not this will happen depends upon the tendency of the feldspars to trap the strontium before it can escape. Evidently this mechanism is not effective in keeping the Rb within the system although the smaller, more highly charged Sr ion may be trapped more easily. This probably happens in many cases. The results of Baadsgaard et al. (1976) showed a great deal of unsupported  $^{87}\text{Sr}$  in the plagioclase as well as in epidote and apatite minerals separated from the Amîtsoq gneiss.

Some paragneisses from the Grenville province of

Ontario have been observed to possess oxygen isotopic ratios which are lower than the sedimentary sources of these rocks (Shieh and Schwarcz, 1974). It was suggested that the oxygen isotopes had equilibrated with a reservoir from the mantle and that this mechanism might also be effective in lowering strontium isotopic ratios on a regional scale. Such a phenomenon was suggested by Pidgeon and Hopgood (1975) to explain their Rb-Sr and U-Pb results on gneisses from the Frederikshaab area of Greenland.

Large scale movement of strontium is a radical model and is probably unnecessary for explaining the present data. It is important nevertheless to establish whether or not it can occur. If it can, it opens up new possibilities for the origin of formations such as the Nûk. Such models, if they have any validity, suggest that the major part of the continental crust may have been formed very early in the earth's history and that the rate of addition of new crust may have been very much less over the course of geologic time than has been indicated by more conventional Rb-Sr models (Hurley et al., 1962).

## VII. Conclusions

Movement of Rb and  $^{87}\text{Sr}$  has taken place in the Uivak gneisses on a limited scale. About the only information which can be derived regarding the chronology of the rocks from their scatter on an Rb-Sr diagram is an estimate of the earliest date at which they could have become closed systems. For the Uivak gneisses this date is about 2900 m.y.. The Pb-Pb results on the Uivak whole rocks and feldspars extracted from these rocks exhibit a distribution which can be explained by evolution from lead of Amîtsoq feldspar composition at about 3600 m.y. and refractionation at about 2850 m.y.. If this model is correct, it implies that the Uivak gneiss did not have its U/Pb ratio as severely fractionated at about 3600 m.y. as the Amîtsoq gneiss. Pb-Pb data on these rocks have indicated that they acquired extremely low u values at this time (Baadsgaard, et al., 1976).

The Nulliak assemblage supracrustals appear to have become closed systems at 2700 m.y. or later. Similarly, the earliest date for closure of the high iron intrusives is 2600 m.y..

The earliest reasonable date at which the late granites could have become closed systems is about 2700 m.y.. Many of the samples preserve evidence of an initial Sr isotopic composition well below that of the average for the Uivak gneiss. Others however could have been derived entirely by

fusion of crustal material. This appears to be true for both the late syntectonic granites and the post-tectonic granites. Many of the granites are quite non-radiogenic (depleted in uranium) and their distribution on a Pb-Pb diagram is indistinguishable from that of the Uivak gneisses. Their Pb isotopic ratios appear to be well below the mantle average at this time.

The unradiogenic nature of the leads suggests that these rocks were derived by partial fusion of a deeper crustal layer which had been subjected to at least pyroxene granulite facies metamorphism leading to severe uranium depletion at some time shortly before the intrusion of the granites. The variable nature of the initial strontium isotopic composition implies that this layer must have consisted originally of variable amounts of high Rb/Sr felsic material such as the Uivak gneiss and low Rb/Sr mafic material possibly derived from the Upernavik supracrustals.

In conclusion, the present data along with field evidence and other isotopic and chemical data from the North Atlantic Craton are compatible with a model involving crustal thickening by dominantly horizontal tectonic processes in a region of high, possibly unstable geothermal gradient. This leads to very high grade metamorphism of material in the lower crust involving partial melting and subsequent vertical migration of large ion lithophile elements upwards, leading to enrichment of the upper crust in these elements.

The horizontal mobility of the crust at this time combined with continuous vertical crustal differentiation may conceivably produce rocks which have been both depleted and enriched in U, Th and Rb at different times by metamorphic activity. This may make precarious the interpretation of Rb-Sr dates and assumptions about previous history from initial Sr ratios. Whenever possible, Rb-Sr whole rock analyses should be combined with Pb-Pb isotopic determinations of whole rocks and separated feldspars. Cesium determinations might also be carried out since there is evidence that the K/Cs ratio may be a sensitive indicator of metamorphic grade (Heier and Brunfelt, 1970).

## References

- Baadsgaard, H. and van Breemen, O. 1970: Thermally induced migration of Rb and Sr in an adamellite. *Eclogae Geol. Helv.* **63**, 31-44.
- Baadsgaard, H. 1973: U-Th-Pb dates on zircons from the early Precambrian Amîtsoq gneisses, Godthaab District, West Greenland. *Earth planet. Sci. Lett.* **19**, 22-28.
- Baadsgaard, H., Lambert, R.St.J. and Krupička, J. 1976: Mineral isotopic age relationships in the poly-metamorphic Amîtsoq gneisses, Godthaab District, West Greenland. *Geochim. et Cosmochim. Acta* **40**, 513-527.
- Baadsgaard, H., Collerson, K.D. and Bridgewater, D. 1977: The Archean gneiss complex of Labrador: I. Preliminary U-Th-Pb geochronology. Unpublished.
- Barton, J.M. 1975: Rb-Sr isotopic characteristics and chemistry of the 3.6 b.y. Hebron gneiss, Labrador. *Earth planet. Sci. Lett.* **27**, 427-435.
- Black, L.P., Gale, N.H., Moorbath, S., Pankhurst, R.J. and McGregor, V.R. 1971: Isotopic dating of very early Precambrian amphibolite facies gneisses from the Godthaab District, West Greenland. *Earth planet. Sci. Lett.* **12**, 245-259.
- Black, L.P., Moorbath S., Pankhurst, R.J. and Windley, B.F. 1973:  $^{207}\text{Pb}/^{206}\text{Pb}$  whole rock age of the Archean granulite facies metamorphic event in West Greenland. *Nature Phys. Sci.* **244**, 50-53.
- Bridgewater, D., McGregor, V.R. and Myers, J.S. 1974: A horizontal tectonic regime in the Archean of Greenland and its implications for early crustal thickening. *Precamb. Res.* **1**, 179-197.
- Bridgewater, D. and Collerson, K.D. 1975: The major petrological and geochemical characters of the 3600 m.y. Uivak gneisses from Labrador. *Contr. Mineral. Petrol.* **54**, 43-59.
- Bridgewater, D., Keto, L. McGregor, V.R. and Myers, J.S. 1976: Archean gneiss complex of Greenland, in: *Geology of Greenland*, ed. A. Escher and W.S. Watt Gfønlands Geologiske Undersøgelse, Copenhagen. pp. 18-75.



- Collerson, K.D., Jesseau, W.C. and Bridgewater, D. 1976: The Archean gneiss complex of Eastern Labrador, in: Early History of the Earth, ed. B.F. Windley, J. Wiley, New York.
- Cumming, G.L. and Richards, J.R. 1975: Ore lead isotope ratios in a continuously changing earth. Earth planet. Sci. Lett. 28, 155-171.
- Cumming, G.L. and Scott, B.D. 1976: Rb/Sr dating of rocks from the Wollaston Lake Belt, Saskatchewan. Can. J. Earth Sci. 13, 355-364.
- Davis, D.W., Grey, J., Cumming, G.L. and Baadsgaard, H. 1977: Determination of the  $^{87}\text{Rb}$  decay constant. Geochim. Cosmochim. Acta. 41, 1745-1749.
- Faure, G. and Powell, J.L. 1972: Strontium Isotope Geology Springer-Verlag, New York.
- Gale, N.H. and Mussett, A.E. 1973: Episodic uranium-lead models and the interpretations of variations in the isotopic composition of lead in rocks. Rev. Geophys. Space Phys., 11, 37-86.
- Hart, S.R. 1964: The petrology and isotopic-mineral age relations of a contact zone in the Front Range, Colorado. J. Geol. 72, 493.
- Heier, K.S. and Compston W. 1969: Interpretation of Rb-Sr age patterns in high grade metamorphic rocks, North Norway. Norsk. Geol. Tidsskr. 49, 257-283
- Heier, K.S. and Brunfelt, A.O. 1970: Concentration of Cs in high grade metamorphic rocks. Earth planet. Sci. Lett. 9, 416-420.
- Heier, K.S. and Thorenson, K. 1971: Geochemistry of high grade metamorphic rocks, Lofoten-Vesteraalen, North Norway. Geochim. Cosmochim. Acta 35, 89.
- Heier, K.S. 1973: Geochemistry of granulite facies rocks and problems of their origin. Phil. Trans. R. Soc. Lond. 273A, 429-442
- Hofmann, A. 1971: Effect of regional metamorphism on radiometric ages in pelitic rocks - preliminary results. Carn. Inst. Wash. Yearb. 70, 242-245.

- O'Nions, R.K. and Pankhurst, R.J. 1974: Rare-earth element distribution in the Archean gneisses and anorthosites, Godthaab area, West Greenland. Earth planet. Sci. Lett. 22, 328-338.
- Papanastassiou, D.A. and Wasserburg, G.J. 1969: Initial strontium isotopic abundances and the resolution of small time differences in the formation of planetary objects. Earth planet. Sci. Lett. 5, 361-376.
- Pidgeon, R.T. and Hopgood, A.M. 1975: Geochronology of Archean gneisses and tonalites from north of the Frederikshaabs Isblink, S.W. Greenland. Geochim. Cosmochim. Acta 39, 1333-1346.
- Roddick, J.C. and Compston, W. 1977: Strontium isotopic equilibrium: a solution to a paradox. Earth planet. Sci. Lett. 34, 238-246.
- Shieh, Y.-N. and Schwarcz, H.P. 1974: Oxygen isotope studies of granite and migmatite, Grenville province of Ontario, Canada. Geochim. Cosmochim. Acta 38, 21-45.
- Tatsumoto, M., Knight, R.J. and Allegre, C.J. 1973: Time Differences in the formation of meteorites as determined from the ratio of  $^{207}\text{Pb}$  to  $^{206}\text{Pb}$ . Science 180, 1279-1283.
- Taylor, P.N. 1975: An early Precambrian age for migmatitic gneisses from Viken I Bø, Vesteraalen, North Norway, Earth planet. Sci. Lett. 27, 35-42.
- Wasserburg, G.J., Albee, A.L. and Lanphere, M.A. 1964: Migration of radiogenic strontium during metamorphism. J. Geophys. Res. 69, 4395-4401.

solutions were covered and heated for at least 6 hours, stirring occasionally. When all of the samples were into solution, the covers were removed and the solutions were evaporated down to about 3 ml. They were then transferred into 15 ml centrifuge tubes. The solutions were allowed to cool for several hours and then the tubes were centrifuged to remove whatever gel had formed. The solutions were decanted back into their respective beakers and the centrifuge tubes rinsed with water to remove the gel.

The solutions were then poured back into the centrifuge tubes and about 5 mg of  $\text{Ba}(\text{NO}_3)_2$  was added to each tube in an almost saturated solution. The  $\text{Ba}(\text{NO}_3)_2$  had been purified by passing through a cation exchange column to remove Sr and Pb. Conc.  $\text{HNO}_3$  was added slowly to each tube until it was half full. The wall of the tube was then rubbed with a Teflon stirring rod for a minute or so until a fine precipitate of  $\text{Ba}(\text{NO}_3)_2$  began to appear. Enough conc.  $\text{HNO}_3$  was then added to bring the solutions to about 14 ml. The tubes were then sealed securely with parafilm and inverted several times to mix the solutions. They were then left overnight to allow the precipitate to equilibrate and settle out. The  $\text{Ba}(\text{NO}_3)_2$  containing the strontium was then centrifuged down and the supernatant liquids were decanted into Pt dishes for the removal of the Rb.

The walls of the tubes containing the  $\text{Ba}(\text{NO}_3)_2$  were washed carefully with water. Several drops of water were then added to the tubes to redissolve the precipitate. About

8 ml of conc.  $\text{HNO}_3$  was then added to the tubes and the sides rubbed once more with a Teflon rod to precipitate the  $\text{Ba}(\text{NO}_3)_2$ . The solutions were left overnight and the precipitates were then centrifuged down and the supernatant discarded. The precipitates were rinsed in about 8 ml conc.  $\text{HNO}_3$ , then recentrifuged and the  $\text{HNO}_3$  discarded. The tubes were carefully inverted so that the precipitates stayed in the tips and then left resting on Kleenex overnight for the precipitates to dry.

A set of ion exchange columns was prepared to separate the barium and the strontium. These were made of Teflon tubing and contained 2 ml Dowex 50W-X12, 100-200 mesh cation exchange resin. The resin was cleaned by passing at least 30 ml of 6N HCl through it, 6 ml at a time. This was followed by 6 ml of 2.5N HCl. The precipitates were redissolved in 1 ml of 2.5N HCl and loaded into the columns. The strontium was eluted using 2.5N HCl in the fraction from 6 to 15 ml.

Since the lead ion tends to coprecipitate with Ba along with the Sr, it was decided during the later separations to attempt the removal of Pb in the columns as well. This was done for sets 7, 8 and 9. Since the Pb exists in solution as an anionic complex, it should pass directly through the cation exchange resin. Accordingly, the first 5 ml of eluate, which would normally have been discarded, was saved in clean glass beakers.

It was found during the first set of separations that a

considerable amount of Rb was still present in the load. Therefore, for all subsequent sets the eluates from the columns were evaporated to dryness, redissolved in 1 ml of 2.5N HCl, reloaded into the same, cleaned Teflon columns and eluted as before. This resulted in negligible Rb on the filament.

The Rb separation was carried out as follows. Five drops of pure conc.  $H_2SO_4$  was added to the nitric acid solutions in the Pt dishes and each solution was stirred with a Teflon rod. The solutions were evaporated to dryness over a Teflon-coated hot plate in the filtered air hood. The dishes were then transferred to bare hot plates inside the regular fume hood and heated at  $550^{\circ}F$  until fuming ceased. Each dish was then carefully heated over a bunsen burner in the fume hood until fuming ceased again. The dishes were then placed over a set of bunsen burners outside the fume hood and the residues ignited at  $900^{\circ}C$  for 15 to 30 minutes.

After cooling, the residues were leached with several drops of water and the solution, about 1/4 to 1/2 ml, transferred to a 3 ml centrifuge tube. Several drops of pure  $HClO_4$  solution were added which resulted in a precipitate of  $KClO_4$  and the coprecipitation of Rb. The tubes were centrifuged and the supernatant poured off. The walls were then rinsed carefully with water. If the precipitate appeared to have caked solidly, it was washed with water but if there was any tendency to crumble this step was avoided.

A drop or two of water was added to the tube and the residue shaken to redissolve some of it. The tube was then capped and labeled.

Two sets of normal lead separations were also carried out. About 1 g of sample was dissolved in HF and HNO<sub>3</sub> as in the Rb-Sr procedure. The samples were then evaporated to dryness. The residues were redissolved in 10-15 ml 4N HCl and the beakers capped and heated for 1-2 hours just below the boiling point. The solutions were poured into centrifuge tubes, cooled and the silica gel was centrifuged off. The supernatants were transferred back into their respective beakers and evaporated to dryness.

The quartz columns to be used for the Pb separation contained AG1-X8, 200-400 mesh anion exchange resin. The resin was cleaned with 20 ml 9N HCl passed through 10 ml at a time. About 1/2 to 1 ml of 1N HCl plus 4 ml or less of 1N HBr were added to each beaker and the solutions warmed to dissolve the residues. They were then loaded into the columns. After these solutions had passed through, 2 ml of 1N HBr was added, 1 ml at a time, to rinse the resin then 12 ml of 1N HBr was added and passed through. This was followed by 3 ml of 2N HCl. Finally the lead was eluted with 10 ml of 9N HCl into small Teflon beakers.

The Sr was loaded onto the filament according to the following procedure. The eluate from the columns was first evaporated gently to dryness so as not to char the organics. The sample was taken up in a drop of water and the solution

evaporated down to a very small drop, just enough to fit inside a small capillary drawn from a clean glass tube 3 mm in diameter. The sample was carefully blown onto the rim of the Teflon beaker and carefully evaporated under the heat lamp until it occupied about 2 cm of the capillary. Meanwhile a Ta single filament had been oxidized by heating it just below the glow point until a layer of oxide appeared in the center. The sample was carefully loaded onto the filament a droplet at a time while warming gently. After the sample was fully loaded and dried, the current was raised gradually to just below the point where the filament had been oxidized and then decreased to zero. This was to ignite any organics which may be on the filament and which could react explosively with perchloric acid. A small droplet of perchloric acid was loaded onto the filament from another capillary. The temperature of the filament was then raised until the perchloric acid fumed off. The temperature was further increased until the point where the sample began to fuse. The sample fuses into a bead and becomes agitated on the filament for a minute or two, finally becoming inert. The filament was then glowed briefly and the current reduced to zero.

Rubidium was loaded onto the sides of a triple rhenium filament. Enough of the saturated solution in the centrifuge tube was taken up to fill the capillary. The sample was then loaded, drop by drop, onto one of the side filaments, heating gently to evaporate. When all the sample had been

loaded, the temperature was raised gradually until it began to fuse. The procedure was repeated with the other side filament. Finally the capillary was rinsed and filled with water and used to wash the center filament, which usually had some sample spattered onto it.

The lead was loaded onto a single rhenium filament using the silica gel technique. The sample was first evaporated to dryness, then redissolved in  $H_2O$ . This was evaporated down to a drop and taken up in a large capillary. It was then loaded and evaporated on the filament. A droplet of silica gel and phosphoric acid mixture was then placed on the sample and the filament warmed gently. The silica gel becomes cloudy initially as the water evaporates. The current through the filament was raised gradually to about one amp until the silica gel begins to liquify and become clear again. As the current is gradually raised over a period of an hour or two, the sample should redissolve in the liquid. Finally at about 1.8 amp the liquid becomes cloudy again and begins to dry out. At about 2 amp the phosphoric acid fumes off. Finally, the filament was glowed so that the organics were ignited and the load had a white, waxy appearance.

Most of the operations were carried out in a filtered air hood. The water used had been purified by passing it through a mixed bed ion exchange column then distilling it twice beneath the boiling point. The first distillation was done in a glass still and the second in a quartz one. All



acids were vapour distilled except the  $\text{HClO}_4$  and  $\text{H}_2\text{SO}_4$  which were of the highest grade commercially available. The Sr spike used was NBS SRM-988 which had been individually aliquoted into glass vials. Each vial contained 0.6042  $\mu\text{g}$  of spike.

Data sets 1 and 2 were done by spiking separate aliquots of sample for Rb and Sr as was sample 271D in set 5. All the rest were done by double spiking the same aliquot. Sr and Rb blanks were measured during set two by performing the separation procedure on the spikes alone. A Sr blank of 3 ng and a Rb blank of 4 ng were measured. A blank check on the double spike procedure during set 5 gave a Sr blank of 5 ng and a Rb blank of 72 ng. The Rb blank was measured in one of the Sr spikes and found to be about 2 ng. It was also measured in about 5 mg of  $\text{Ba}(\text{NO}_3)_2$  and again found to be about 2 ng. This barium nitrate had only been in use for sets 7 and 9 inclusive, however, since the old barium had been exhausted. It is therefore possible that the old barium had been contaminated with Rb. A Rb blank correction of 70 ng was made on all double spiked analyses before set 7. Repeats on four of the samples were measured during set 6 and are listed in Table X. The repeats were all done by the double spiking procedure and are corrected for a Rb blank of 70 ng. They are in reasonable agreement for all samples except 47A which has a 2.9% discrepancy in the  $^{87}\text{Rb}$  measurement. This may be due to failure to obtain a representative portion of the whole rock, since the sample

## Rb-Sr Sample Repeats

No.	Sample	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Rb} \dagger$	$^{86}\text{Sr} \dagger$
1-1	75-291D	0.8547	3.543	655.1	184.9
	Uivak II	$\pm 0.0006$			
6-1	"	0.8561	3.530	655.3	185.7
		$\pm 0.0001$			
	Difference:	-0.16%	0.37%	-0.03%	-0.43%
1-5	75-287D	0.7584	1.193	416.3	349.0
	Uivak II	$\pm 0.0001$			
6-2	"	0.7590	1.202	419.3	349.0
		$\pm 0.0003$			
	Difference:	-0.13%	-0.75%	-0.72%	0.00%
3-3	74-47A	0.7552	1.0156	266.1	262.1
	Late Syn. Gr.	$\pm 0.0001$			
6-4	"	0.7555	0.9866	259.2	262.7
		$\pm 0.0001$			
	Difference:	-0.04%	2.90%	2.63%	-0.23%
4-2	75-285C	0.7833	1.756	95.67	54.50
	Nulliak Assemb.	$\pm 0.0002$			
6-6	"	0.7837	1.744	96.04	55.08
		$\pm 0.0001$			
	Difference:	-0.05%	0.69%	-0.39%	-1.06%

† Units are nanomoles/gram.

aliquots used were often very small, although in this case a correlated variation in radiogenic  $^{87}\text{Sr}$  would be expected. The discrepancy may also be due to an unusually large Rb blank.

The Rb measurements were done on a 12 inch, 90° instrument using a Faraday cup collector. The accelerating voltage was maintained at 5 kv and peak switching was accomplished by varying the magnetic field. Data was

collected and analyzed using a TI980A computer. The source holder and draw-out plates were cleaned between each run and periodic checks for Rb contamination were done by running blank filaments. Fractionation corrections were determined by running samples of normal Rb. The correction factor by which the measured  $^{87}\text{Rb}/^{85}\text{Rb}$  value was multiplied to give the true value was 1.00275.

The Sr and Pb samples were run on a Micromass-30 using Faraday cup collection and an accelerating voltage of 8 kv. Data collection, correction to the peaks for electrometer decay, and analysis were accomplished using a HP 9825 computer.

Fractionation corrections for the lead were determined by running NBS SRM-981 standards. All samples were run at  $1400^{\circ}\text{C}$  as determined by an optical pyrometer. The correction factors by which the measured values were multiplied to give the true values were:  $^{206}\text{Pb}/^{204}\text{Pb} - 1.001708$ ;  $^{207}\text{Pb}/^{204}\text{Pb} - 1.002813$ ;  $^{208}\text{Pb}/^{204}\text{Pb} - 1.004569$ .

The errors quoted for the lead ratios and the  $^{87}\text{Sr}/^{86}\text{Sr}$  values are internal standard errors and should represent a 1 sigma variation. In all cases for the repeats, the two Sr ratios fall outside their quoted errors. This may again be due to non-representative sampling. It is difficult to estimate the error in the  $^{87}\text{Rb}/^{86}\text{Sr}$  ratio because of the possible sources of systematic error such as mass discrimination and blank. The ratios are taken to be accurate to 1% at the 1 sigma level.

