USE OF BIOTITE

FOR STRONTIUM AGE MEASUREMENTS

by

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I   ABSTRACT

The strontium method of measuring geological age, using the radioactive decay of rubidium 87 to strontium 87, has in the past been applied only to minerals of pegmatites, principally lepidolite. Here, the possibility of using a common rock-forming mineral has been investigated. Biotite appears to be the most suitable mineral.

Techniques of spectrographic analysis have been devised to measure the amounts of rubidium and strontium present in biotites. An age was estimated for each specimen, based upon the geological relationships of the source rock. The tentative age figure is combined with the measured contents of rubidium and strontium to calculate what proportion of the strontium is likely to be radiogenic, using the formula

$$\% \text{ Sr } 87* \text{ of total Sr } = \text{Age in years x } .272 \text{ x } \% \text{ Rb x } 1.175 \text{ x } 10^{-11} \text{ x } \frac{1}{\% \text{ Sr}} \text{ x } 100 \%$$

To permit actual calculation of the age of biotite, a mass spectrometric analysis of the strontium isotopes is required. Present methods of mass spectrometry can determine with satisfactory accuracy what percentage of the strontium

in a biotite is radiogenic if it is at least 1 % of the total strontium. A tentative working basis for this investigation was therefore adopted, that biotites in which more than 1 % of the total strontium is radiogenic are suited for age measurements.

Thirteen of the 15 Precambrian biotites tested are suitable, as are 5 out of the 7 Palaeozoic ones and 1 out of the 16 Mesozoic-and-younger ones.

One actual age determination has been made. The age of a biotite from southeast Manitoba has been determined as 1825×10^6 years $\pm$ 400×10^6 years. This value agrees in general magnitude with age determinations made by other methods on material from the same area.

The accuracy of the age calculation can be improved by measuring the strontium isotope ratios in a mineral, formed at the same time as the biotite, which has less rubidium and more strontium. Plagioclase feldspar fits these requirements.

General data on the distribution of rubidium, cesium, lithium, strontium, sodium, and potassium are included.

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II ACKNOWLEDGEMENTS

III INTRODUCTION

Up to this time the strontium method of age determination has been applied only to minerals of pegmatites. Used thus, the method is severely restricted because of the relative rarity of pegmatites. If a common rock-forming mineral could be used a huge field of application would be opened up, not only in dating the time of crystallization of innumerable intrusive bodies, but also in determining when some types of metamorphism occurred.

It was thought that, of all the common minerals, biotite would be most suitable for age measurements. The object of this investigation was primarily to discover whether biotite could be used successfully, and secondarily to find out whether any other rock-forming mineral, or the whole rock rather than any fraction of it, was usable.

For such an investigation, accurate methods of determining rubidium and strontium are required. As no such methods were available which could be applied to biotite, it was necessary to develop them. Moreover, it was desired to use methods which would give values accurate enough to use to calculate the age of the samples. As a result, considerable attention has been given here to analytical techniques.

Although the main object of the study was investigation of the possibility of using biotite for age work, observations were made also on the geochemistry of cesium and

lithium in biotite, because this rock mineral is the main host, not only of rubidium, but also of these other two rare alkali metals.

Previous Work

Investigation of the possibility of using the decay of rubidium 87 to strontium 87 as a measure of age started about 15 years ago (Goldschmidt, 6), (Hahn and Walling, 10). The half-life of Rb 87 has been determined with fair precision, (Strassmann and Walling, 27, 6.3×10^{10} years) (Eklund, 5, 5.81×10^{10} years), (Haxel, et al, 13, $6.0 \pm 0.6 \times 10^{10}$ years) and for the calculations in this report is taken to be 5.9×10^{10} years. Age measurements on minerals from pegmatites have been made by several investigators (Ahrens, 2), (Hahn, Mattauch, and Ewald, 9), (Eklund, 5), (Ishibashi and Ishihara, 15). The ages so determined agree in general magnitude with the general geologic ages and with measurements made by the lead and helium methods.

No report of an attempt to employ biotite is known to me.

IV BACKGROUND

The basis of the strontium method is the radioactive decay of rubidium 87 to form strontium 87. The radiogenic strontium is labelled Sr 87*, to avoid confusion with ordinary Sr 87, found in common strontium.

The radioactive disintegration of any radioactive element may be expressed as

$$N = N_0 e^{-\lambda t} \quad \dots \quad (1)$$

where N_0 is the number of atoms originally present, λ is the decay constant, and N is the number of atoms left after the lapse of time t. Here, N and N_0 refer to atoms of rubidium 87. The period of half-life is equal to $0.693/\lambda$. Ahrens (2) has shown that formula (1) may be simplified to the form

$$\text{Age} = \frac{\% \text{ Sr } 87*}{\% \text{ Rb } 87} \times \frac{1}{\lambda} \quad \dots \quad (2)$$

The half-life of Rb 87 is taken as 5.9×10^{10} years. Rubidium 87 is 27.2 % of total rubidium. Formula (2) may therefore be restated in terms of measurements which can be made spectrographically, as follows

$$\text{Age} = \frac{\% \text{ total Sr}}{\% \text{ total Rb}} \times \% \text{ Sr } 87* \text{ of total Sr} \times \frac{8.51 \times 10^{10}}{.272} \quad (3)$$

The proportion of Sr 87 that is radiogenic can be determined by the use of a mass spectrometer. Total Sr and

total Rb can be measured by optical spectrographic methods.
Two general methods of determining the value of the Sr: Rb
ratio can be followed.

    1.   Total Rb and total Sr can be measured
        separately.

    2.   The ratio could be found directly by link-
        ing the ratio of the intensities of Rb
        and Sr lines to the ratio of the concen-
        trations of those elements present in the
        sample arced.

Method 1. was used in this investigation as it gives
measurements of the rubidium and strontium contents of the
samples, which can be checked with other people's measure-
ments for similar material, and which are by themselves
data of general geochemical interest.

Selection of Most Suitable Mineral

Five items which are important in judging the possi-
bility of using a given mineral are discussed below.

    1.   The concentration of total rubidium should
be fairly high. Rubidium is present in all minerals, but
in some is present in quantities that border on the detec-
tion limit. The higher the concentration of rubidium, the
greater is the accuracy of the measurement. The analyti-

cal procedure described in a later section measures the Rb content in biotites in the range 0.03 - 0.30 % Rb_2O with a standard deviation of 5 - 6 %.

2. The concentration of total strontium must be sufficiently large to permit accurate measurement. The analytical method described later measures the content of total Sr in biotites in the range 0.005 - 0.030 % SrO with a standard deviation (or coefficient of variation) of 2%.

3. For accurate mass spectrographic determination of the isotope ratios of strontium, with the method used by L. T. Aldrich at the Carnegie Institution, (Dept. of Terrestrial Magnetism), the amount of strontium in the sample to be analysed should be about 1 % or more. Original material in which the Sr content is of the order of 0.01 % can be used as it is possible to concentrate the strontium easily, by chemical means, by a factor of about 100.

4. If a sample contains at least 1 % total strontium, and at least 1 % of that is radiogenic, the amount which is radiogenic can be measured with suitable accuracy. This requirement that the radiogenic strontium be a considerable proportion of the total strontium imposes certain limits upon which minerals can be used, and upon the age range for which strontium-method age determinations are accurate enough to be significant. For the % Sr 87* to be large, the % Rb and the age must both be large, and the % non-radiogenic Sr fairly low. The following table, and

Plate 1, show how much Sr 87* is produced from various amounts of rubidium in various lengths of time.

Table 1

% Sr 87* Produced

Age in Years

% Rb	10^8	5×10^8	10^9	2×10^9
0.01	0.000003	0.000016	0.00003	0.00006
0.05	0.000016	0.00008	0.00016	0.00032
0.10	0.000032	0.00016	0.0003	0.0006
0.50	0.00016	0.0008	0.0016	0.0032
1.00	0.00032	0.0016	0.0032	0.0064

A mineral of Precambrian age, say 1×10^9 years, with a Rb content of 0.10 %, will contain 0.0003 % Sr 87*, and this will be a measurable amount (1 %) of the total strontium only if the total Sr is less than 0.03 %. For younger minerals, proportionally more Rb and less total Sr should be present for the mineral to be suited for age work.

The ratio of Rb:Sr is evidently critical in judging what materials can be used for age determinations. From equation (3) can be derived an expression for the value of this ratio which must be exceeded for the radiogenic strontium to be over 1 % of the total strontium:

$$\text{% Sr 87* of total} = 0.01 \times \text{% Sr total}$$

$$\text{Ratio} = \frac{\text{% Rb total}}{\text{% Sr total}} = \frac{0.01 \times 8.51 \times 10^{10}}{0.272 \times \text{Age.}}$$

% Sr 87* Generated
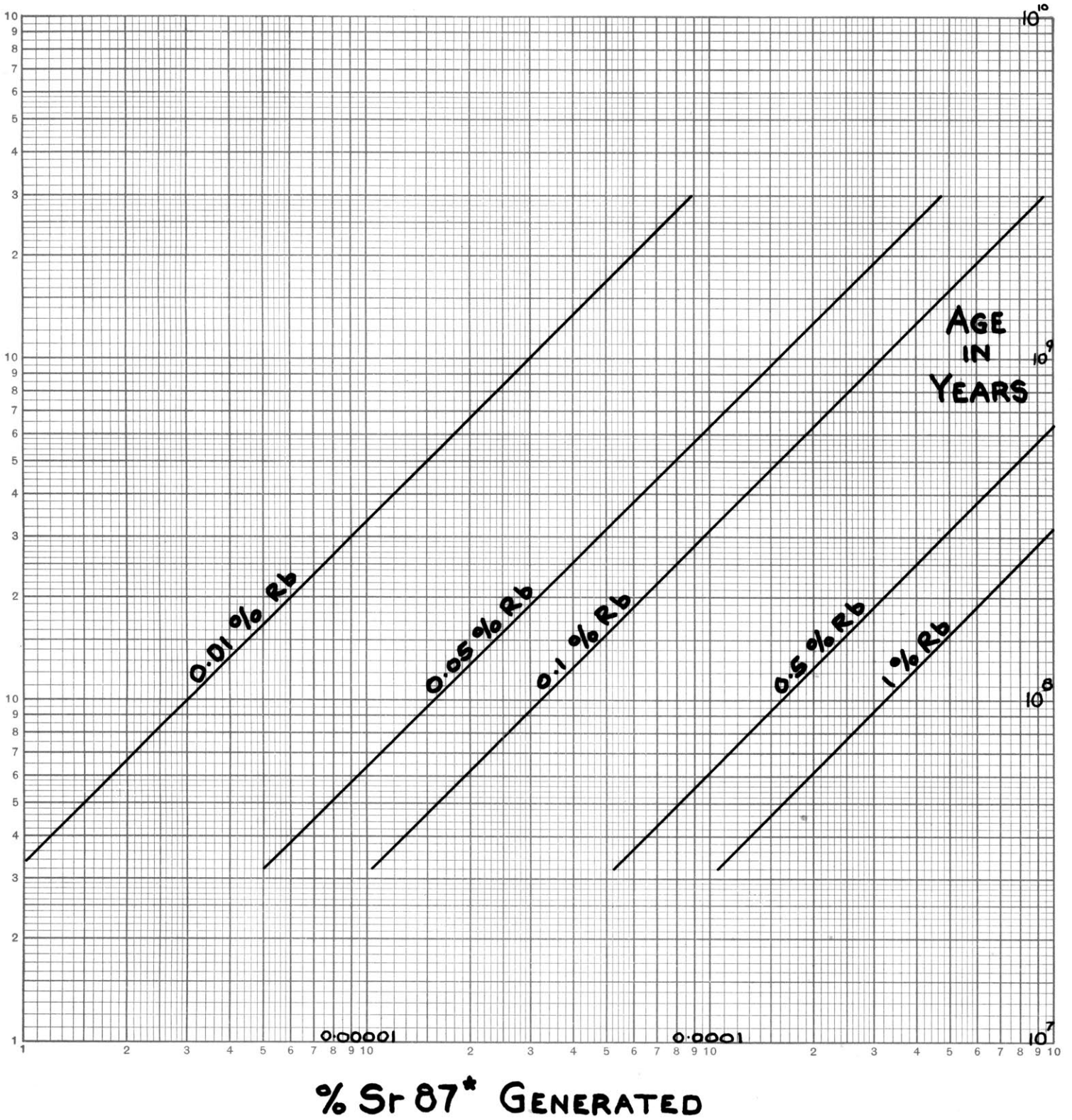
PLATE 1

Plate 2 shows a plot of this ratio against age. Materials plotted above the diagonal cut-off line are suited for use in determining ages by the strontium method.

5. To facilitate chemical concentration of the strontium it is desirable that the mineral should contain enough calcium to act as a carrier for all the strontium present. In general, 0.50 % Ca is sufficient. If the natural content of calcium be less than this amount, some strontium-free calcium could be added to the sample to assist in the co-precipitation.

SUITABLE FOR
AGE WORK

$\dfrac{\% \, Rb}{\% \, Sr}$

NOT SUITABLE

Age in years
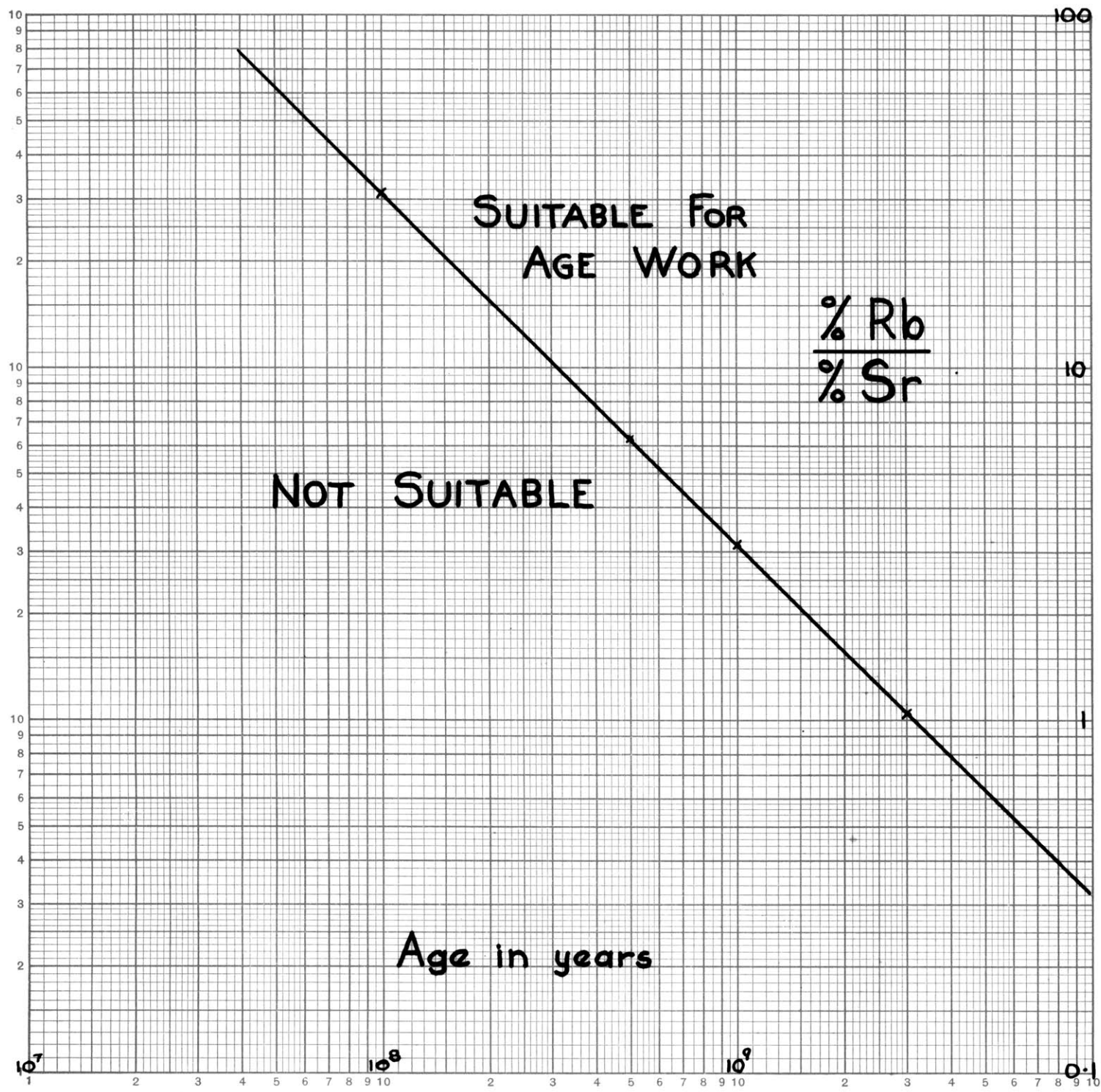
CHANGE OF CRITICAL RATIO

PLATE 2

GEOCHEMISTRY

The distribution of rubidium and strontium in rocks and rock-forming minerals is described below, to show which materials contain amounts of those elements which fit the requirements stated in the foregoing section.

1. **Notes on Geochemistry of Rubidium.**

Rubidium does not form minerals of its own. As it has a positive charge of 1 and an ionic radius of 1.49 A it proxies for potassium (1 + , 1.33 A) with such ease that, when minerals form, all the rubidium is taken up in potassium-rich minerals. As potassium is the smaller ion of the two it is accepted in preference to rubidium in structural sites of growing crystals, with the result that in the minerals of one rock, rubidium is concentrated with respect to potassium in the later-formed crystals. In spite of these variations within one rock, the ratio of K: Rb is approximately constant for the bulk composition of rocks ranging from gabbro to granite. Furthermore, ordinary primary pegmatites have a K:Rb ratio a little lower than the ratio in granites. Only in small-volume residuals such as aplites, granophyres, and the late hydrothermal stage of pegmatites does an enrichment of Rb with respect to K show up in the bulk composition of the rock.*

* Dr. L. H. Ahrens, personal communication.

Rubidium is therefore richer in K-bearing minerals than in Na or Ca minerals. Lepidolite, hydrothermal microcline, and pollucite are especially rich in rubidium. The table below shows typical rubidium analyses of the common rock-forming minerals and of several rocks.

Table 2

Distribution of Rubidium : % Rb

| | Source | | |
	a	b	c
Whole rock	0.047	0.038	0.020 to 0.066
Biotite	0.132	0.081	
Hornblende	0.039	0.024	
Plagioclase	0.0059	0.0067	
Potash Feldspar	0.061	0.068	

a. St. Cloud granite, Sample #43

b. Quartz monzonite porphyry, Sample #42

c. Samples #35, 36, 37, 38.

<center>Source</center>

<center>d.</center>

Whole rock	From not detectable up to 0.08, most near 0.03.
Biotite	0.04 to 0.25, most near 0.15.
Hornblende	From not detectable up to 0.003.
Plagioclase	0.001 to 0.035, most near 0.015.
Potash Feldspar	0.006 to 0.20, most near 0.04.

d. Summary of Caledonian plutonic rocks, (Nockolds and Mitchell, 19) omitting ultra basics and aplites.

<center>Minerals of Pegmatites</center>

Lepidolite	1.0 to 3%
Biotite	0.306, 0.109, 0.137, 0.54*
Muscovite (#29)	0.081
Phlogopite (#18)	0.232
Hydrothermal Microcline	0.5 to 2.0

* Average Rb in pegmatite biotites (Stevens and Schaller, 26).

2. Notes on Geochemistry of Strontium

Strontium (2 +, 1.27 A) has a distribution a little different from that of rubidium. Both metals have ionic radii of about the same size, but the greater charge of strontium causes it to follow the doubly charged, smaller calcium ion (2 +, 1.06 A) rather than potassium. As a minor element, therefore, strontium is found in greatest abundance in calcium-rich minerals. Being larger than calcium, it would be expected to concentrate with respect to calcium in the later-formed minerals.

Because calcium tends to form minerals earlier than does potassium, rubidium and strontium tend to be separated during crystallization. Strontium does follow potassium to a limited extent but, being more highly charged and a little smaller, is concentrated with respect to potassium in early K-minerals whereas rubidium is concentrated preferentially in late K-minerals. This separation of the elements happens to be fortunate, for Rb-rich minerals tend to be Sr-poor. The radiogenic contribution may therefore be a considerable part of the total strontium, possibly enough to be measured accurately.

Some strontium analyses of rocks and minerals are presented in the following table.

Table 3

Distribution of Sr : % Sr

	Source		
	a	b	c
Whole rock	0.017	0.034	
Biotite	0.0122	0.0209	
Hornblende	0.001	0.001	
Plagioclase	0.034	0.034	
Potash Feldspar	0.034	0.034	0.081 to 0.13

a. St. Cloud granite, Sample #43

b. Quartz monzonite porphyry, Sample #42

c. Three granites from Colorado (Bray, 3)

Source

	d	e	f
Whole rock	0.003 to 0.02	most near 0.15	most near 0.008
Biotite		most near 0.009	
Hornblende		most near 0.015	
Plagioclase		most near 0.3	
Potash Feldspar		most near 0.15	

d. Samples #35, 36, 37, 38

e. Summary of Caledonian plutonic rocks (Nockolds and Mitchell, 19), omitting ultrabasics and aplites.

f. Granites and granitic gneisses from Finland (Sahama, 24)

Minerals of Pegmatites

Lepidolite	extremely low			
Biotite	0.0046	0.0079	0.0064	0.0145
Muscovite	0.0054	0.0055[g]	0.0066[g]	0.009[g]
Phlogopite	0.0105	less than	0.001[h]	

g. Bray, 3

h. Noll, 20

3. Preliminary Conclusions

Some differences exist in the reported ranges of Rb and Sr contents for the various minerals. Some of these differences may be analytical errors, others are certain to result from local peculiarities among the rocks. Some general conclusions may nevertheless be drawn from the data in tables 1, 2, and 3.

1. Whole rocks: average Rb 0.04 %, average Sr 0.03 %. Only rocks of Precambrian age would appear to contain enough radiogenic strontium for it to be detectable with present analytical methods. Precambrian rocks rich in rubidium and poor in strontium are most suitable.

2. Hornblende: average Rb 0.01 % (?), average Sr 0.01 % (?). It seems that even the most ancient hornblendes are not suitable.

3. Plagioclase: average Rb 0.01 %, average Sr 0.03 %. Age work is not possible.

4. Potash feldspar: average Rb 0.05 %, average Sr 0.08 %. It is just possible that some of the extremely ancient potash feldspars might be used. Post-Cambrian ones are not suitable.

5. Biotite; average Rb 0.15 %, average Sr 0.01 %. Almost all Precambrian biotites, and many Palaeozoic ones, appear to be suitable for age measurements. Few post-Palaeozoic biotites have the proper ratio of Rb : Sr.

These relationships are shown in Plate 3 on a cut-off

chart similar to that described before (Plate 2).

Potash feldspar and biotite are both potassium-rich minerals, and both are natural hosts for rubidium, containing considerably more rubidium than other minerals do. Potash feldspar contains so much common strontium that the proportion of radiogenic strontium is very low. Strontium replaces potassium, as does rubidium, but more strontium enters the feldspar structure than enters the mica structure.

Quartz generally has less than 0.0001 % of either rubidium or strontium.

According to these preliminary tests, biotite is the most suitable of all the common rock-forming minerals. The table in section VIII, in a later section of this report, gives calculated proportions of radiogenic strontium of total strontium for the full set of biotites, using age figures based upon geological dates.
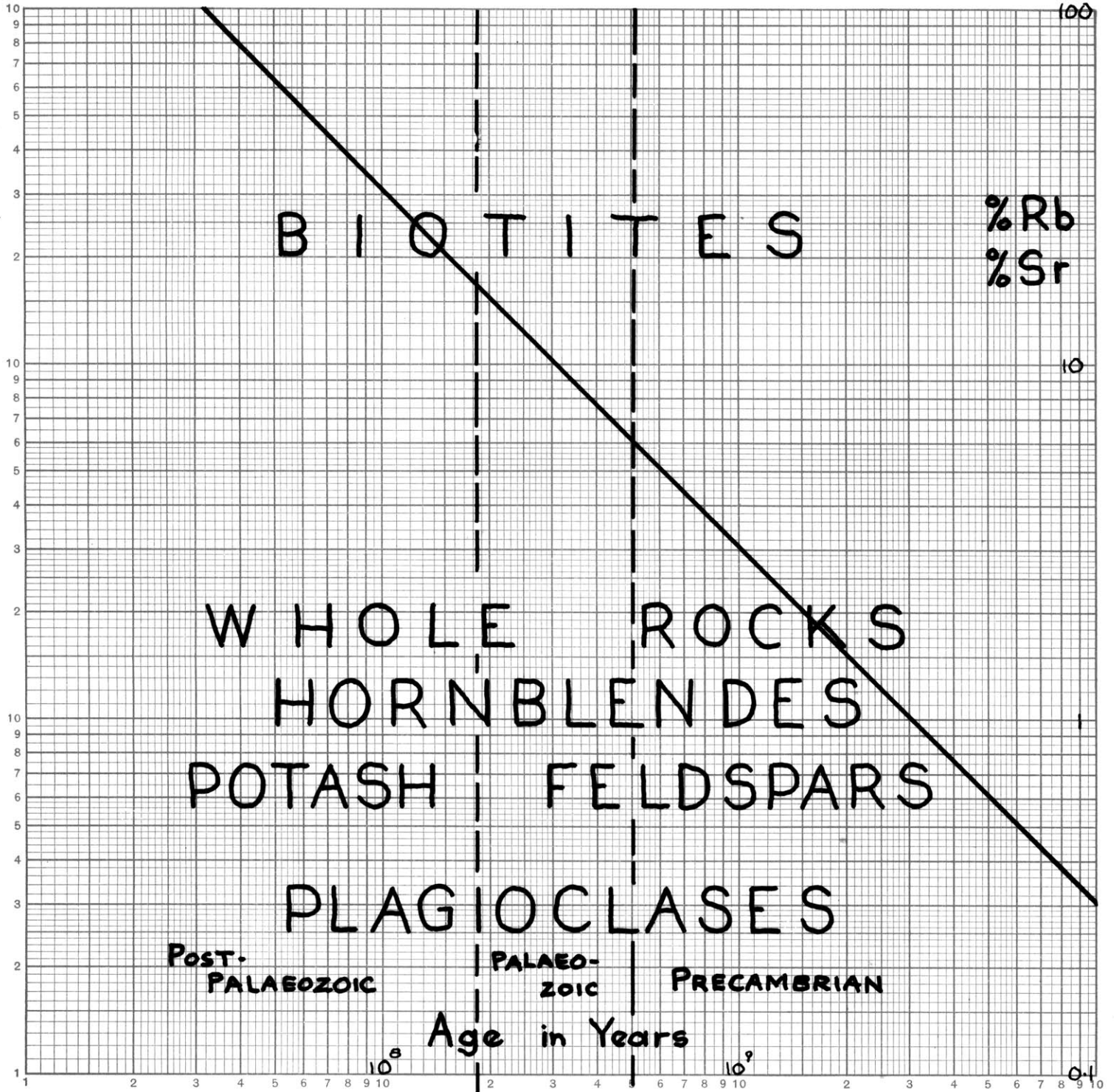
CRITICAL RATIO IN MINERALS

PLATE 3

4. Stability of Biotite

The use of biotite for age measurements is based upon the postulates that no rubidium or strontium has been lost from the mineral by weathering, and that no interchange of constituents has taken place between biotite and its neighbours between the time of formation of the mineral and the time of analysis. Any loss or addition of rubidium or strontium would change the ratio of parent to daughter element, and so invalidate any calculation of age.

Biotite is fortunately a relatively stable mineral. The relative resistances of minerals to weathering is summarized in the following series, in which each mineral is less resistant than those below it. (Reiche, 23)

olivine

augite

Calcic plagioclase

calci-alkalic plagioclase

hornblende　　　　alkali-calcic plagioclase

alkali plagioclase

BIOTITE

potash feldspar

muscovite

quartz

This series is similar to Bowen's reaction series. Here, however, a mineral does not react to form the one next below it in the series; the minerals merely decompose in the order given.

Assuming that relative persistence in sediments is equivalent to relative resistance to weathering, Pettijohn (21) ranks the common heavy minerals in order of decreas-

ing stability:

zircon

tourmaline

monazite

garnet

BIOTITE

apatite

ilmenite

magnetite

staurolite

kyanite

epidote

hornblende

andalusite

topaz

sphene

zoisite

augite

sillimanite

hypersthene

diopside

actinolite

olivine.

From these series it is concluded that biotite is relatively resistant to breakdown by weathering. Degenerative changes can occur, however, and for this reason only rocks that looked fresh were used as source specimens, and the

biotite in each sample was examined for signs of altera-
tion. If the changes are minor in amount and are confined
to tiny spots inside the crystals, no change in the bulk
composition of the biotite should occur.

The internal stability of rubidium and strontium in
biotite seems to be similarly favorable. The ions are
held in the structure by bonds thought to be predominantly
ionic. The daughter element, strontium, is not greatly
different in size or charge from the parent element, so
that no great stress would develop in the structure by the
conversion of a minute fraction of one element into the
other.

5. Use of Secondary Biotite

Where biotite has formed in a sediment or igneous rock during anamorphic metamorphism, for example, in the formation of one of the common quartz-biotite gneisses, it is necessary to consider the effect on the validity of strontium age measurements of the Sr 87* that existed in the original material. Naturally, Sr 87* would have been produced from the rubidium of the source material throughout its existence, both as a sediment and in the rocks from which the sediment was formed. Only a small fraction of this radiogenic strontium follows the Rb into new biotite, however, for it acts just like the other Sr 87 and other Sr isotopes as the ions compete for sites in the growing biotite structures. The situation is therefore completely analagous to that in a solidifying magma. Provided the gneiss is ancient, the contribution of Sr 87* by Rb will be large enough to make insignificant any excess percentage of Sr 87 in the biotite at its time of formation.

V MATERIALS FOR ANALYSIS

A. Selection of Source Rocks

Igneous rocks were chosen as the source of biotite because it is generally possible to determine by geological relationships the time of formation of the rocks with an accuracy sufficient for use in this investigation. A special effort was made to select specimens in which the biotite appeared to be primary and unaltered. Rocks in which the biotite grains were at least 0.5 mm. across were preferred, for these give, on crushing, a product in which the grains are large enough for impurities in the biotite fraction to be seen and, if necessary, removed by hand picking.

Areas from which specimens were obtained are: British Columbia, Manitoba, Nova Scotia, Northwest Territories, Ontario, Quebec, Alaska, California, Colorado, Georgia, Idaho, Maine, Massachusetts, Minnesota, New Hampshire, New Jersey, North Carolina, South Carolina, South Dakota, Texas, Utah, Virginia, the Ural Mountains, and Southern Rhodesia.

The table on the following page shows the number of specimens of each type of source rock, subdivided according to age. Granites predominate in the collection because, as granites are the most widely distributed biotite-bearing rocks, the strontium method would have widest application if granite biotites prove suitable for use.

Table 4

Source Rocks

Type	Number of Specimens		
	Precambrian	Palaeozoic	Post-Palaeozoic
Granite	11	5	4
Syenite	0	2	0
Intermediate	1	0	8
Basic	3	1	1
Lamprophyres	0	0	2
Pegmatites	5	4	1

B. Preparation of Samples for Analysis

1. Separation of Biotite and Plagioclase Feldspar

Each rock sample was split into fragments about one inch square. Clean, unweathered, un-stained lumps were crushed in a Dodge-type jaw crusher, the product being fed through repeatedly until it could all go through a 6-mesh screen. A Jones splitter was used to divide the sample into two fractions, one about eight times as big as the other. From the larger fraction particles between 60 and 115 mesh in size were screened out to form a feed for the Franz isodynamic separator. Any magnetite in this fraction was taken out by a hand magnet as it would clog the separator if not removed. An initial separation by the Franz machine, producing one concentrate rich in biotite and other ferromagnesian minerals, and another concentrate of quartz and the feldspars, could commonly be accomplished by using these settings: slope to horizontal 20° - 30°, tilt 10°, current 0.5 amps. Relatively pure biotite could, for most samples, be extracted from the biotite concentrate by running it through the machine repeatedly with small variations in the current and the degree of tilt. No precise instructions can be given, for each rock presents unique difficulties, and the method which separates biotite from hornblende in one rock with perfect ease may prove totally ineffective when applied to another.

In some rocks, plagioclase feldspar may be separated

from potash feldspar and quartz because a small amount of magnetite, attached to the plagioclase, causes the grains to be slightly magnetic. A setting of slope 15°, tilt 4°, current 1 ampere is recommended for a first attempt.

From some samples, the Franz separator did not give a pure biotite concentrate. A final purification may be effected by shaking the impure concentrate on an inclined sheet of rough paper. Biotite cleavage flakes stick to the paper while more rounded grains roll off.

The purity of each final concentrate was estimated by inspection with a powerful hand lens or binocular microscope. Hand picking of stray grains of unwanted minerals is possible when the grains are of the size range -60 to + 115 mesh.

The final grinding of all samples was done in a motor-driven agate mortar and pestle. One gram of biotite could be reduced to a fine powder in about three hours in this device. One gram of plagioclase feldspar could be powdered in about one hour.

2. Samples of the Whole Rock

The smaller fraction from the Jones splitter, mentioned above, was crushed to -100 mesh in a hand mortar, reduced by coning and quartering to about one gram of material, and was ground in the agate mortar to serve as a sample of the whole rock.

3. Separation of Pure Minerals

Where absolutely pure samples of the minerals in one rock were required, the above techniques were not used. Cleavage flakes were chipped from large crystals of each of the types of feldspar, which were identified by their twinning. Cleavage flakes of hornblende were picked by hand from crushed rock, each flake being examined for presence of 60° cleavage and absence of adhering grains.

The biotite used for comparison with the hornblende and feldspars was the more impure material used for age analysis.

4. Technique for Sheet Mica

Large sheets of mica are difficult to powder by use of mortars. Stiff slabs of clean mica were forced against a rotating drill bit mounted in an ordinary drill press. The powder and shreds were caught on clean paper and the -100 mesh particles were screened out for further comminution in the agate mortar. This is a quick method for use where contamination by the drill bit is not important.

5. Possibility of Contamination by Crusher or Mortars

A notable feature of the strontium method is the lack of importance of any contamination of the sample by the rock splitter, screens, trays, jaw crusher, separator, or mortars. Any elements which might be introduced occur

naturally in the samples in considerable amount, and, in any event, were not to be determined.
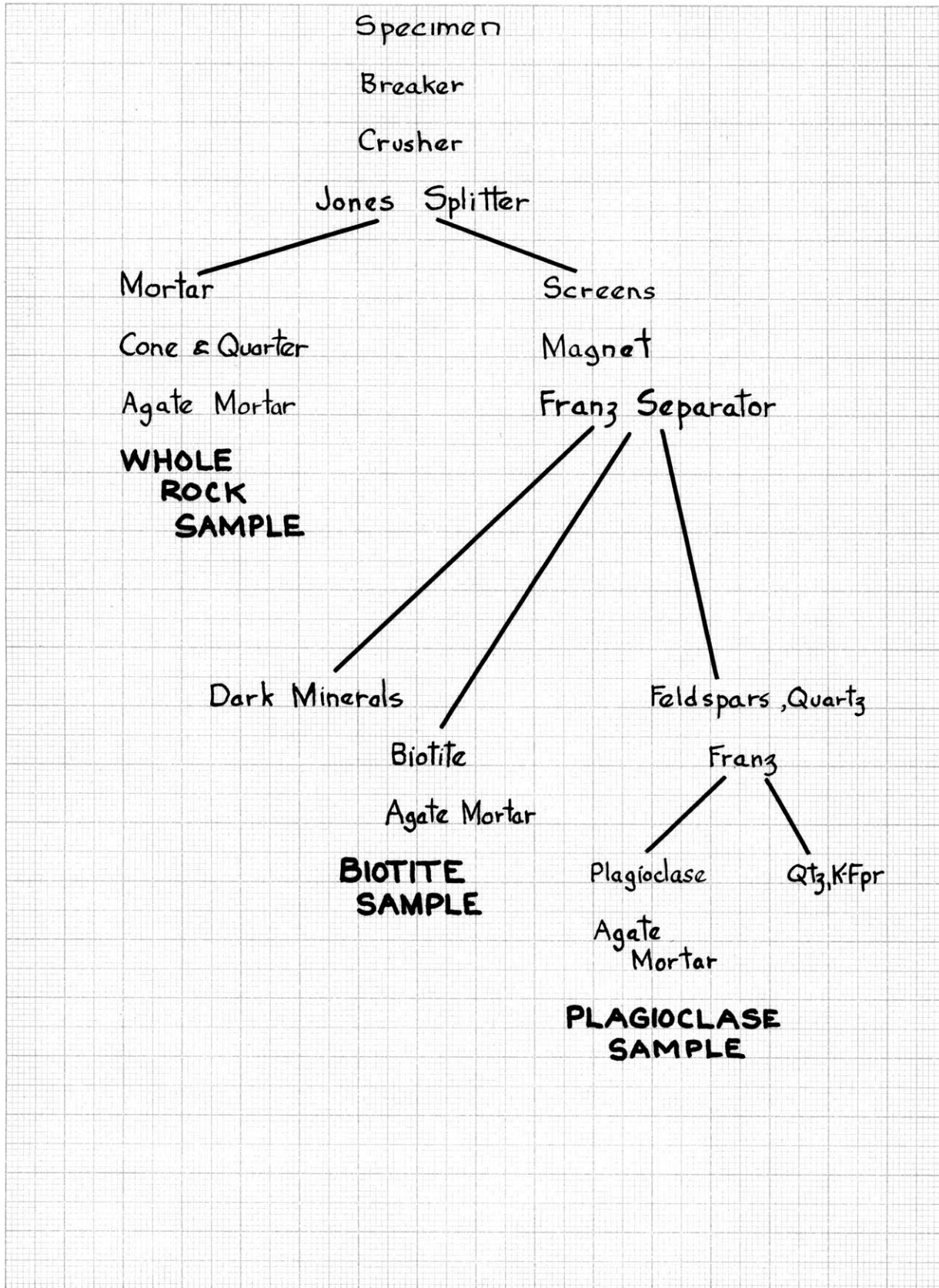
FLOW SHEET

PLATE 4

C. Impurities in the Biotite Concentrate

Small percentages of impurities are present in most
of the biotite concentrates. Generally, a granite having
biotite as its only dark mineral yielded an almost pure
biotite fraction. Rocks having hornblende or augite as
well were apt to have up to 10 % of cleavage flakes of
those minerals, plus a little feldspar, in the concentrate.

These impurities do not harm the validity of the age
measurements. Small percentages of rubidium are present
in all minerals, so that any one, or any combination, in-
cluding the whole rock itself, could be used for age meas-
urements if an analytical method of sufficient precision
could be found. As biotite has the largest percentage of
rubidium it is easiest to use. Inclusion of other miner-
als merely decreases the rubidium percentage a trifle.
Similarly for strontium: although amphiboles, pyroxenes,
and plagioclase can contain a larger amount of total stron-
tium than does biotite the excess of Sr 87 over the normal
7.02 % is still the Sr 87*, attributable to disintegration
of Rb 87. If the percentage of total Sr in the powder be
increased by the impurities in the concentrate, the per-
centage of Sr 87* will be a little less, but not enough
less to decrease markedly the accuracy of the mass spectro-
meter measurements.

Naturally, the reported percentages of lithium, ru-
bidium and cesium refer to the total concentrates, not to

the biotites alone.

Large amounts of calcium can cause inaccuracies in the lithium determinations, but in most biotites the content of calcium is less than 1 or 2 %, too little to interfere.

VI   ANALYTICAL PROCEDURES

A.   Rubidium Analysis

1.   Apparatus

The optical spectrograph used was a Hilger prism spectrograph, equipped with interchangeable glass and quartz prisms. The glass prism was used, giving a dispersion of approximately 30 A/mm at 7000 A. The wavelength range from 4900 A to 10,000 A can be recorded on one 10" plate.

The film used was Eastman Kodak type I-L, on glass, measuring 4" x 10", and giving a satisfactory medium sensitivity for wavelengths between 3000 and 10,000 A. The film was developed $4\frac{1}{2}$ minutes at 18° C in Kodak D.19 developer, washed briefly, fixed in acid hypo for 10 minutes after the plate cleared, and washed from 30 minutes to one hour in moving water. In hot weather the wash water was cooled by ice cubes to prevent the emulsion from peeling off the glass.

The arcing was carried out with anode excitation with a direct current of 3 amperes. The line voltage was about 225 volts. A rotating step sector with adjacent steps increasing the exposure by a factor of two was used to provide six steps, from 1/4 to 1/128 across a slit height of 14 mm. The slit width was kept constant at 0.025 mm. Five spectra were recorded on each plate. The sector ro-

tated at well over 500 rpm., so that no intermittency effect enters.

Pure carbon electrodes 1/8" in diameter were used, with a cavity drilled in one end 1/16" by 1/4". The sample powder was packed in as tightly as was possible without breaking the walls of the cavity. The biotite powder was diluted with two parts of Bureau of Standards "Albite". Most analyses were run in triplicate. Where extra accuracy was desired, for example with samples 50 and 60, several extra arcings were made.

2. Rubidium Standards

Preliminary experiments carried out by analysts in the Cabot laboratory under the direction of Dr. L. H. Ahrens indicated that accurate analyses for rubidium could be made based upon the use of sodium as an internal standard.

The normal Na_2O content of biotites ranges from 0.30 to 1.78 %, according to analyses culled from the literature (Heinrich, 14), (Nockolds, 18). Analyses in duplicate of samples #1 - #16 by Geraldine Sullivan, using a flame photometer, showed a variation from 0.23 to 1.35 %, with most of the samples containing close to 0.80 % Na_2O. See table 5, next page. The Na_2O content of a random biotite could not be assumed to be this latter value, however, without introducing an error of perhaps 50 %. To

Table 5

MAJOR ELEMENT CONTENTS

Sample	% K_2O	% Na_2O
1	6.22	1.03
2	3.74	1.54
3	9.29	0.54
4	5.42	1.23
5	3.56	1.35
6	7.24	0.78
7	8.10	0.55
8	6.80	0.88
9	5.69	0.94
10	4.97	1.01
11	5.06	0.99
12	8.40	0.65
13	8.35	0.77
14	8.56	0.23
15	6.20	0.70
16	7.59	0.69

Each analyses is the average of duplicate flame photo-meter measurements, performed by G. R. Sulliven of the A.P.I. staff at M.I.T.

assure that all the samples contained essentially the same content of sodium, two parts of a standard albite were added to each. This albite contains 10.73 % Na_2O. Two parts of it combined with one part of the biotite reduced the possible variation in the Na_2O percentage in the diluted sample to the range 21.8 to 23.3 %. The extreme error from the mean in assuming the soda content as invariable is therefore $\pm$ 3.5 %.

The material used as a base for mixing standards should be as similar as possible to the material to be analysed. Any difference in composition or structure is apt to introduce considerable systematic error. For this reason a natural biotite was selected as the base. Five biotites, selected at random, were arced on one plate. The one that seemed to contain the lowest percentage of Rb_2O was selected for use in the preparation of standards. Several grams of this biotite, #9, were mixed thoroughly with two parts of the albite.

Although potassium is an excellent internal standard for rubidium, it was not used because the potassium content of biotites varies excessively. Even if the biotite is diluted with two or three parts of potash feldspar, the potassium content of the mixture is too variable.

The rubidium contents of a random group of biotites were thought to range between 0.01 % Rb_2O and 0.50 % Rb_2O. A set of standards was planned to cover this range for ru-

bidium and for cesium and lithium, so that the amounts of those elements might be determined as well.

A mixture was prepared as follows, each weighing being within ± 0.05 mg.

$$30.0 \quad mg \quad Li_2CO_3$$

$$30.0 \quad mg \quad RbCl$$

$$\underline{30.0 \quad mg \quad CsClO_4}$$

Total: 90.0 mg of a 1:1:1 mixture.

This mixture was diluted with 180.0 mg of the standard albite, giving a 2:(1:1:1) mix. The 2:(1:1:1) mix was added to the biotite-albite base in amount sufficient to produce the first standard, containing 0.50 % $RbCl$ and equal %'s of Li_2CO_3 and $CsClO_4$. Part of the new mixture was diluted with more of the biotite-albite mix to give another standard, containing 0.25 % of each of the compounds mentioned. Similar dilutions were carried out to make the rest of a set of standards containing 0.50, 0.25, 0.125, 0.0625, and 0.031 % of each compound.

The advantage of this method of mixing standards is that smaller amounts of the base are needed, and the resulting mixtures are more accurate, than had each standard been mixed separately by weighing out tiny amounts of $RbCl$, Li_2CO_3, and $CsClO_4$ to add individually to the base material.

3. Selection of Analysis and Internal Standard Lines

A pair of sensitive Rb lines, at wavelengths 7800.2
and 7947.6 A were examined as possible analysis lines.
Both are atom lines, with excitation potentials of 1.6
volts.

Rb 7947 is the weaker of the doublet and, for all the
biotites arced in preliminary runs with albite, seemed to
have the most suitable intensity. With the selection of
steps available on stepped sectors the other line was oc-
casionally too dense to be measured. Furthermore, being
weaker, Rb 7947 should be less afflicted by self-absorp-
tion.

The sodium "D" doublet was far too dense to be meas-
urable, so Na 5682.7, the weaker component of a pair
Na 5682.7 and Na 5688.2 was used. This line is about 3.5
inches away from the rubidium line.

Cesium has a sensitive line at wavelength 8521.1 A,
about an inch away from the Rb line. With most biotites
this line is not dense enough to measure accurately, owing
to the dilution of the biotite with albite. The cesium
analyses given in the tables are not particularly reliable.

Li 6103 was used for measurements of the lithium con-
tent of the samples. The calcium line 6102.7 can cause
interference when the Ca percentage is high. For most bio-
tites the Ca content is less than 1 - 2 % and no interfer-
ence would be expected. In all the biotite analyses, the
arc was cut off as soon as all alkali metals had been vol-

atilized, and before the period of maximum emission of cal-
cium. In addition, all lithium determinations based on
Li 6103 were checked by visual comparison with the spectra
of the standards, using the strong line Li 6707 and the
very weak one Li 8126.5, both of which are free from inter-
ference. With some samples the lithium line was so weak
that large background corrections had to be applied. The
measurements are not all particularly reliable.

4. Purity of Reagents

The RbCl, CsClO$_4$, Li$_2$CO$_3$ were "chemically pure" but
do contain small amounts of impurities, none of which were
present in quantities sufficient to prohibit their use in
making up the set of standards.

The albite used to dilute the biotite and provide ex-
cess sodium was tested for rubidium and was found to con-
tain $\sim$ 0.0012 % Rb$_2$O. This amount is insignificant compared
to the magnitude of the common rubidium percentage in bio-
tite. A small correction was made, however, by determining
the intensity ratio Rb 7947 : Na 5682 in pure albite and
subtracting this from the intensity ratios of those lines
in the standards, before constructing the working curve.

5. Self-absorption of the Analysis Line

It is seen by examination of the curve on plate11 that
self-absorption is present when the Rb$_2$O content of the

arced material (1 part biotite plus 2 parts albite) is
0.05 % or greater. Most of the Rb_2O contents were found
to be less than 0.05 %, but a considerable number are
greater. These are considered to be less accurate.

6. Volatilization

To investigate the behavior in the arc of the elements
to be measured a volatilization run was made, using biotite
#50 mixed as usual with two parts of albite. The spectrum
is shown in plate 5. Total exposure time is about 1 minute
50 seconds, the plate being racked down 1 mm. per 2 seconds.
Practically all of the K, Na, Li, Rb, and Cs volatilize dur-
ing the first stage. The exhaustion of these constituents
takes place almost simultaneously and instantaneously. The
analysis arcings were cut off immediately the alkalis had
volatilized, to stop background from building up.

7. Arcing in Triplicate

Plate 6 shows three spectra from Sample #50, slightly
enlarged.

8. Cesium Analyses

The analyses for cesium were made in three ways. For
all the biotites, cesium lines that were dark enough to
give reliable readings on the microphotometer were measured
by use of that machine, and the contents of Cs_2O determined
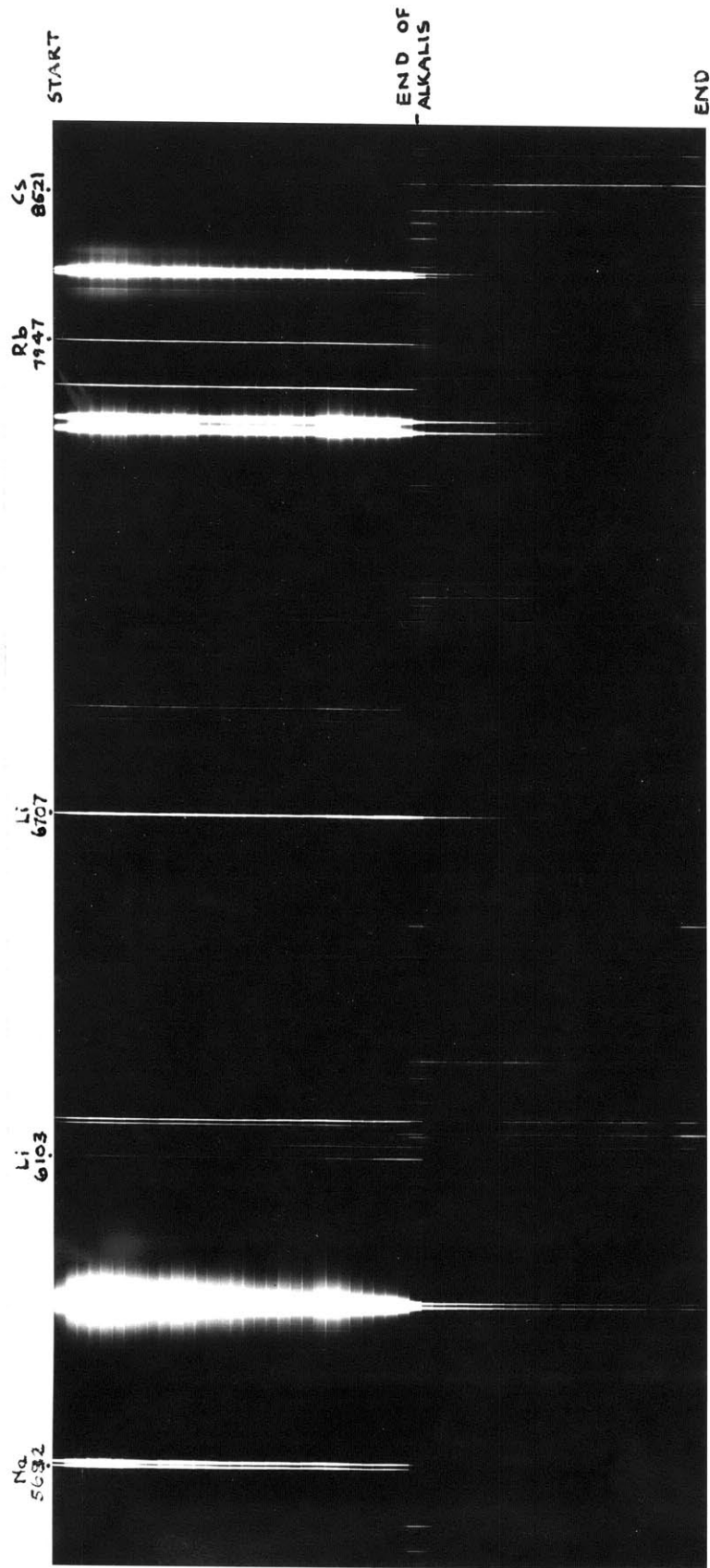
Volatilization Test, Rubidium Analysis

Sample #50 with 2 Parts of Albite
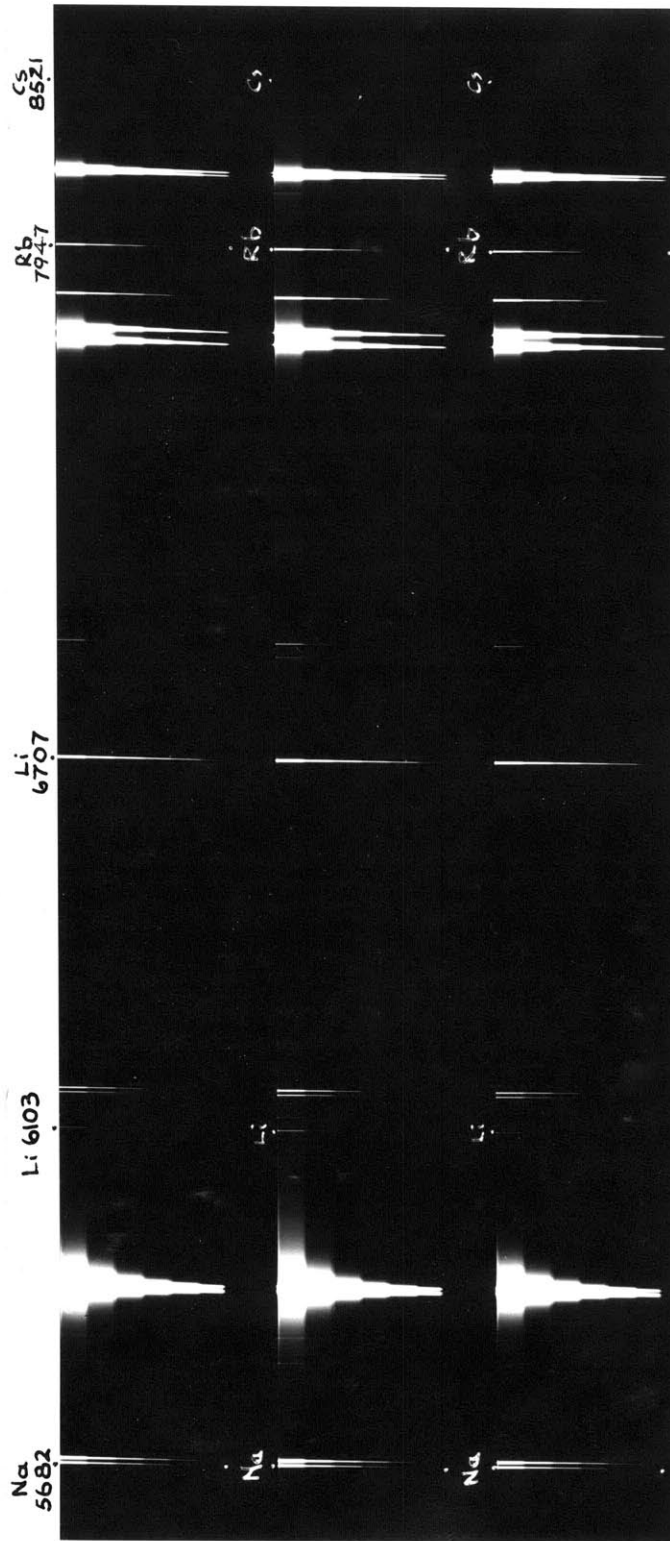
PLATE 5

Triplicate Spectra of Sample #50 with Two
Parts Albite

PLATE 6

by use of the cesium working curve. Percentages represent-
ed by lines too weak to measure were estimated by visual
comparison of those lines with stronger lines in other
spectra. Cesium percentages in the mineral separates and
in the granites were estimated by visual comparison of the
spectra with triplicate spectra of the standard granite,
which was taken to contain 0.00025 % Cs_2O.

B. Strontium Analysis

1. Apparatus

The spectrograph used for rubidium measurements was used also for strontium. Glass optics were used as before, with the plate holder set to record the wavelengths from 4500 A to 8000 A. With this setting, the sensitive line Sr 4607 is $1\frac{1}{8}$ inches from one end of the plate, and Rb 7947 $1\frac{1}{2}$ inches from the other end. The spectra were recorded on Eastman Kodak I-L plates, developed and fixed as before.

Anode excitation (6 amperes) was employed. Before each arcing, the specimen was sintered for a few seconds at 3 amperes to prevent spurting-out of powder when the electrodes were separated. Line voltage was between 225 and 235 volts. A rotating step sector was set to give six steps, recording 1/4 to 1/128 of the total emission across a slit height of 10 mm. Slit width was kept constant at approximately 0.025 mm. Seven spectra could be recorded on each plate. Numbering and identifying of lines followed the pattern established previously.

Pure carbon electrodes similar to those used in analyses of rubidium were used for the strontium samples.

The dispersion in the 4600 A region is about 7 A/mm.

2. Strontium Standards

The technique used for rubidium could not be applied to strontium because the albite which had served to improve

the arcing qualities of the biotite and reduce the varia-
tion in the soda content of the samples contained more
strontium than is usually present in biotite. Undiluted
biotite does not arc well; the silicate bead which forms
is apt to fly from the electrode cavity before arcing is
complete. Some diluting material was needed, and carbon
powder seemed to hold most promise. Not only is it ob-
tainable in a state of extreme purity, but in arcing it
tends to make the strontium and barium behave similarly
during volatilization.

Numerous trials were made, with varying amounts of
added carbon. With all the mixtures, spurting of the pow-
der during some stage of the arcing caused loss of mater-
ial. To drive off the water thought to be responsible for
this spurting, samples were heated to a bright red heat
for varying lengths of time. It was found that three min-
utes of heating to 750 - 800° C in a muffle furnace was
sufficient to produce a mixture that arced well. Although
a little powder was lost in almost every arcing, this loss
occurred just as the electrodes were separated and before
the slit was opened. No preferential loss of any consti-
tuent occurred, merely a slight decrease in the total
amount left to be arced. After the initial loss the sam-
ples burned smoothly, without appreciable wandering of the
arc.

Volatilization tests, one of which is illustrated in

plate 7, showed that the strontium and barium volatilize almost simultaneously, and that a cut-off after 17 or 18 seconds of arcing at 6 amperes would separate the Sr and Ba lines from the background that would build up on the plate in a longer exposure.

Preliminary arcings led to a suspicion that the SrO added to the biotite to form a set of standards volatilized in a flash, separately from Sr held structurally within the biotite. A test of one standard, similar to the test described above, showed that this does not happen, but that instead the strontium comes off very steadily. The working curve should therefore be valid.

Dr. Ahrens suggested that, as the spectrum from a single arcing was weak, spectra of two samples of each unknown be superimposed. This was done. The resulting spectra are almost ideal with respect to density of lines and lack of background.

Plate 8 shows triplicate spectra for Sample #6 with carbon and barium sulphate. The 10-inch plate is long enough to record the barium line 7780.4 and the rubidium line 7947 as well as the strontium and barium lines. The possible use of the high-wavelength barium line to act as a "bridge" between Sr 4607 and Rb 7947 is discussed under "Recommendations for Further Research."

3. Use of Barium as an Internal Standard
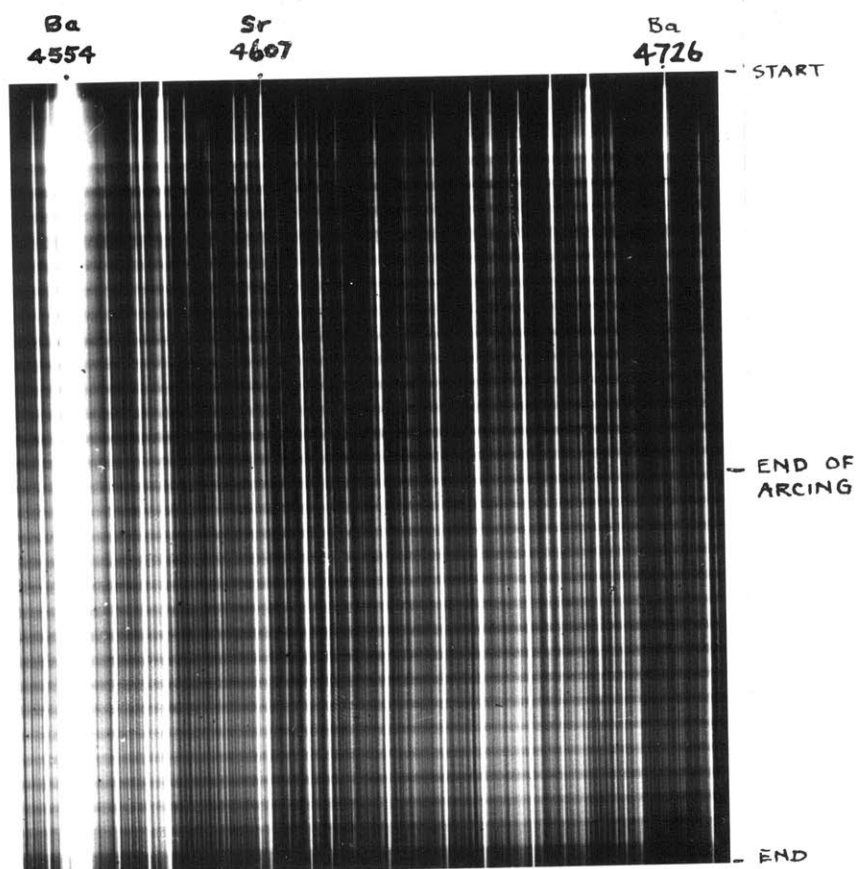
Volatilization Test, Strontium Analysis
Sample #50 with Carbon and BaSO$_4$

PLATE 7
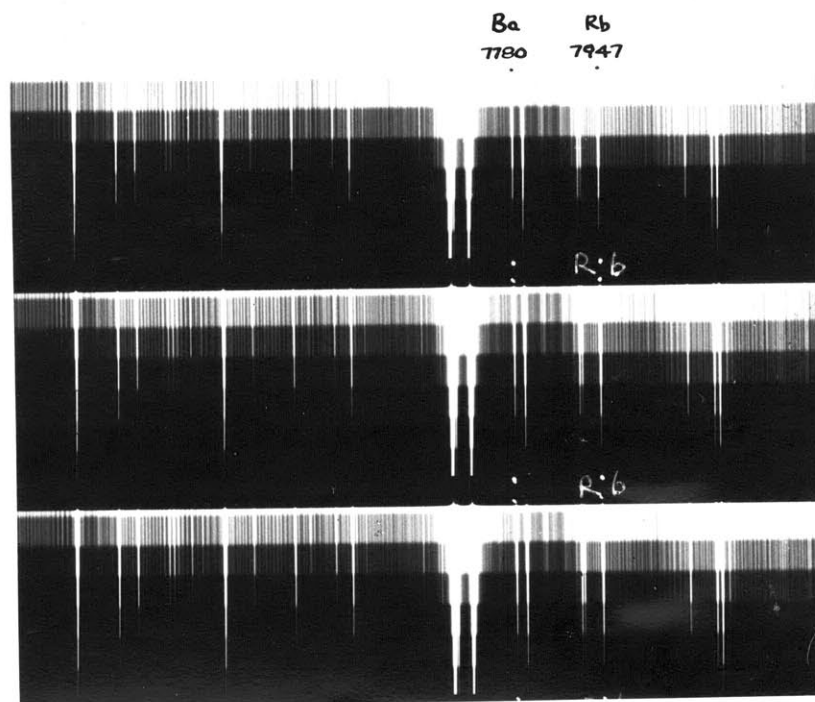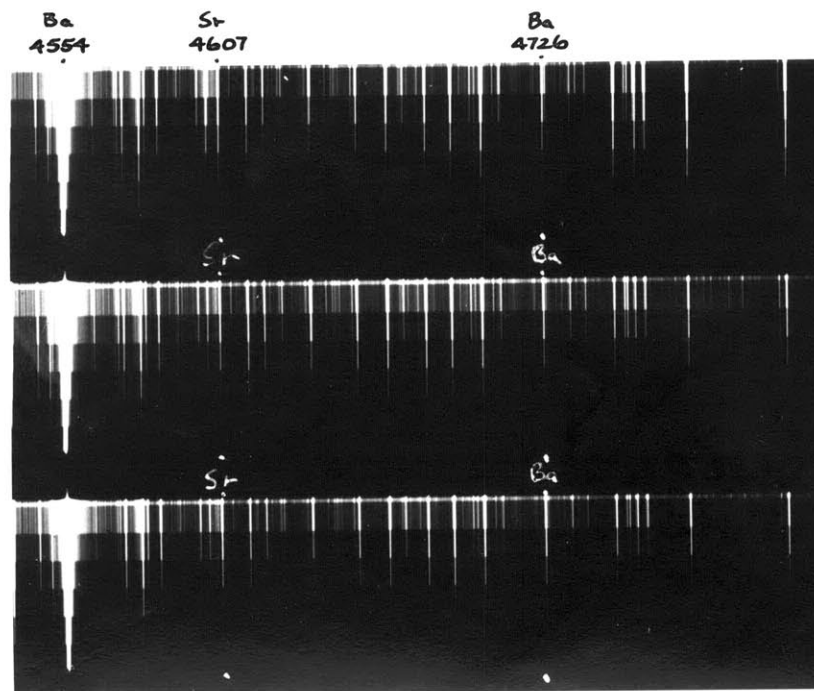
Triplicate Arcing of Sample #6
with Carbon and BaSO₄

PLATE 8

Several characteristics of barium make it especially useful as an internal standard for measuring the strontium content of biotite. When carbon powder is added to the sample, the elements volatilize together. Barium lines of appropriate sensitivity occur in the region of the Sr sensitive line. A barium salt can be obtained in a high state of purity. One barium line was found, close to Sr 4607, that did not appear in the spectrum of any one of six biotites arced in the preliminary tests. When 2 - 3 % $BaSO_4$ is added to the sample this line appears in the spectrum, almost equal in intensity to Sr 4607.

The barium content of biotites is low, ranging between 0.1 % and 0.8 % according to data published by Nockolds and Mitchell (19); the mean is close to 0.3 % Ba. For analysis arcings, all samples were mixed with two parts of pure carbon powder that carried 3 % $BaSO_4$. This procedure introduced an excess of barium, reducing the probable range of Ba content in the arced mixture to between 2.1 % and 2.5 %. This variation is negligible.

The internal standard line, Ba 4726 is 1½ inches away from the analysis line Sr 4607.331.

Sr 4607 was chosen as analysis line because it is the most sensitive strontium line. No interfering lines are strong enough in biotite to cause trouble.

A set of strontium standards was prepared. Pure carbon was mixed thoroughly with 3 % of its weight of pure

barium sulphate. Half a gram of Sample #50 was mixed with
enough SrO to give a mixture carrying 5 % SrO, and part of
this was diluted with enough Sample #50 to reduce the SrO
content to 0.050 %. Successive further dilutions gave suc-
ceedingly lower SrO contents for the mixtures. The final
products were:

1. Pure Sample 50, which is pure biotite.

2. Sample 50 + 0.0005 % SrO

3.   "   "   + 0.001 % SrO

4.   "   "   + 0.002 % SrO

5.   "   "   + 0.005 % SrO

6.   "   "   + 0.010 % SrO

7.   "   "   + 0.020 % SrO

8.   "   "   + 0.050 % SrO

Each standard was mixed with two parts of the carbon
which contained 3 % $BaSO_4$.

The percentage of SrO originally in the pure biotite
#50 was determined by the "addition" method described under
"Methods of Calculation."

4. Reproducibility

Calculations based on seven double arcings of Sample
#50 show that the coefficient of variation in any one
double arcing is about 3 %. The coefficient for the aver-
age of three such arcings is $3/\sqrt{3}$ or approximately 2 %.
This is extremely good reproducibility, about as high as

can ever be obtained using a D. C. arc. Two contributing
factors are: the excellent internal standardization of
strontium provided by barium, and the smooth burning qual-
ities of the mixture. The actual agreement between the
three analyses of each sample was found to be excellent
for most samples.

5. Purity of Reagents

All ingredients used in making up the standards were
tested for purity. SrO mixed with pure carbon, BaSO4 with
carbon, pure SrO, pure BaSO4, and mixtures with biotite
were arced repeatedly to determine what effect one consti-
tuent had on lines of another.

The BaSO4 was prepared in a state of extreme purity
by Dr. L. H. Ahrens, by precipitating it from a solution
of BaCl2 with sulphuric acid. The barium chloride was ob-
tained from Johnson-Mathey, London, and is certified spec-
trographically pure. The spectrum obtained by arcing un-
diluted BaSO4 does not include Sr 4607, and as a result,
no contribution to the density of the analysis line could
be made by impurity in the added barium sulphate.

The spectra of the SrO contains the barium lines 4554
and 4934, but none of the weaker lines. The two mentioned
are sensitive lines, much more so than the internal stand-
ard line 4726. The minute amount of SrO added in prepar-
ing standards could not therefore contribute to the density

of Ba 4726.

Carbon powder to dilute the biotite was made from carbon rods of the highest available purity, the same type used as electrodes.

6. Self-absorption of the Analysis Line

The curvature of the upper portion of the SrO working curve shows that self-absorption of the analysis line starts to take place at a SrO concentration 0.020 % and increases strongly as the SrO content goes up to 0.05 %. The curve is not considered valid outside of the limits 0.005 % SrO to 0.03 % SrO as self-absorption is apt to occur erratically above the upper limit stated.

7. Technique for Materials other than Biotite

The sensitive line Sr 4607 is extremely dense in the spectra of all the whole rocks. Fortunately, the weaker Sr line 4832.1 is recorded on the plates, so that estimation of the SrO content by comparison with the SrO-rich standards (0.02 - 0.1 %) could be checked with reasonable accuracy.

The rocks and minerals were arced without dilution in the standard type of pure carbon electrodes.

Estimation of SrO contents of the minerals was done visually, by comparison of line densities with five spectra of the G-1 standard granite, assumed to have an SrO content

of 0.02 %. As the line Sr 4607 is too dense for accurate measurement where the SrO content is that high, all the recorded values were checked by comparison of Sr 4832.

C. Methods of Calculation

A Hilger non-recording microphotometer was used to measure the relative densities of the analysis line and internal standard line for Sr measurements. A Jarrel-Ash microphotometer was used for the Rb, Li, and Cs measurements.

The line densities were recorded for one, two, or three steps of the spectrogram, as many steps as possible being read for each line. Each density was divided into the density reading for the clear plate, and the resulting figure was plotted on a vertical logarithmic scale against the steps on a linear horizontal scale. The intensities of lines can be compared by measuring either the separation of the lines horizontally, or by measuring each line on a reversed logarithmic scale at any convenient level. Plate 9 will make these operations clear.

The percentage of each constituent in the base and in each of the standards was determined by making "Addition Plots." The intensity ratio of analysis line to standard line in each mixture was plotted against amount added. Projection of the curve through the resulting points to the limit where the intensity ratio was zero gave an intercept on the base line which was a measure of the content of the element concerned in the pure biotite.

A new curve was then plotted, using the same intensity ratio, but with the total content of each element being

used instead of just the amount added. A conversion factor
was applied to change the percentage present from terms of
the chloride, carbonate, and perchlorate to the respective
oxides. The resulting curves were "Working Curves." Plates
10 - 17 are the "Addition Plots" and "Working Curves" for
Rb_2O, SrO, Cs_2O, and Li_2O.

In analyses of unknowns, the intensity ratios for
Sr/Ba, Rb/Na, Cs/Na, and Li/Na were taken to the respective
working curves and % Rb_2O, % SrO, % Cs_2O, and % Li_2O were
read off the horizontal scale in each case. For Rb_2O, Cs_2O,
and Li_2O, the resulting measurements had to be multiplied
by three to give the percentage of each constituent in the
biotite, as the curve records the percentage in the 2:1
mixture with albite.

CLEAR PLATE
LINE READING

CLEAR PLATE
LINE READING

Ba 4726

Sr 4607

$$\frac{I \text{ Sr } 4607}{I \text{ Ba } 4726} = \frac{38}{72} = 0.527$$

STEPS

PLATE 9

PLATE 10

$\dfrac{\text{I Rb } 7947}{\text{I Na } 5682}$

2·0

1·0

0·017

0

0·05

0·1

0·15

% RbCl Added $\times \dfrac{187}{242} = \% \, Rb_2O$
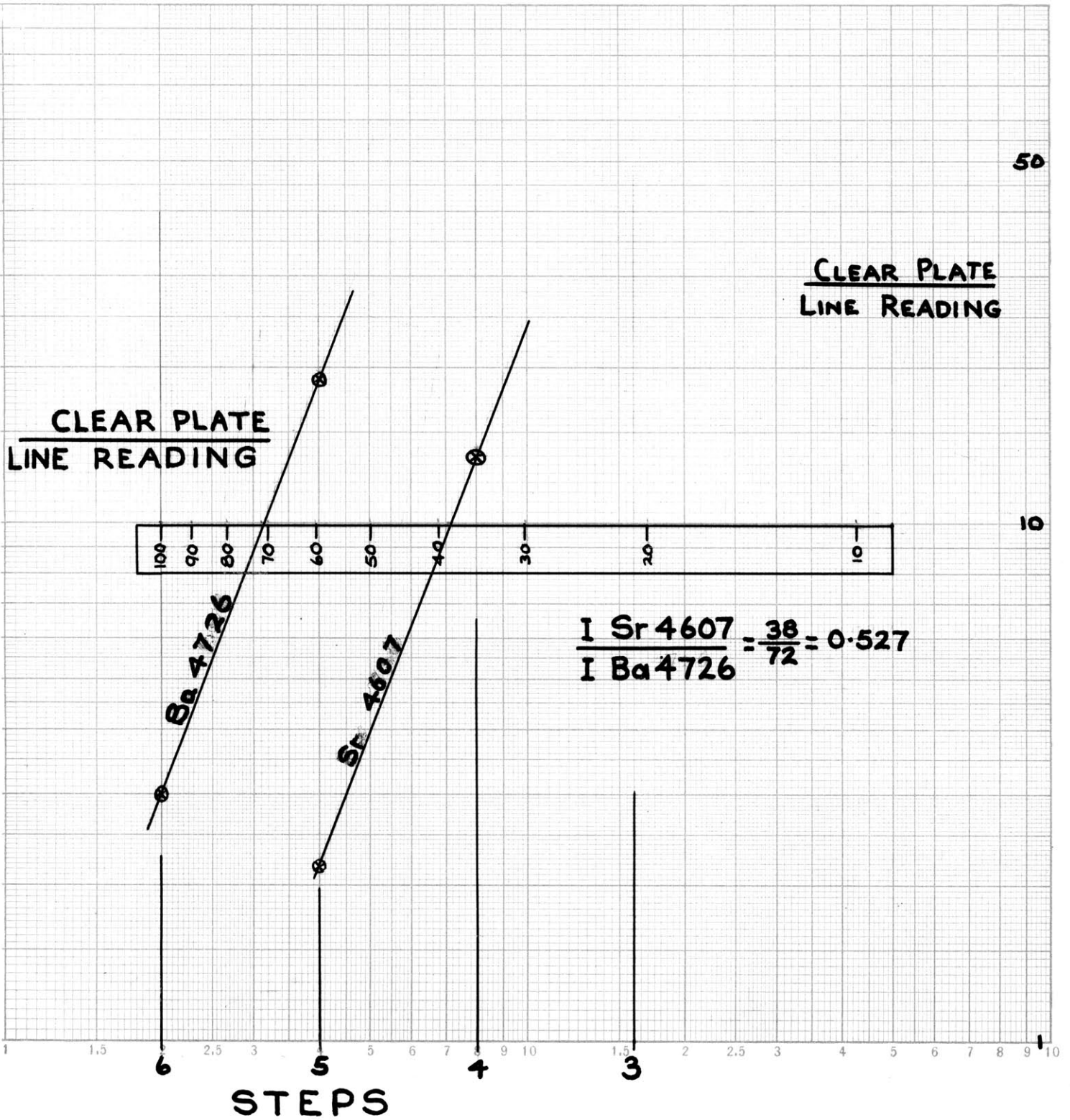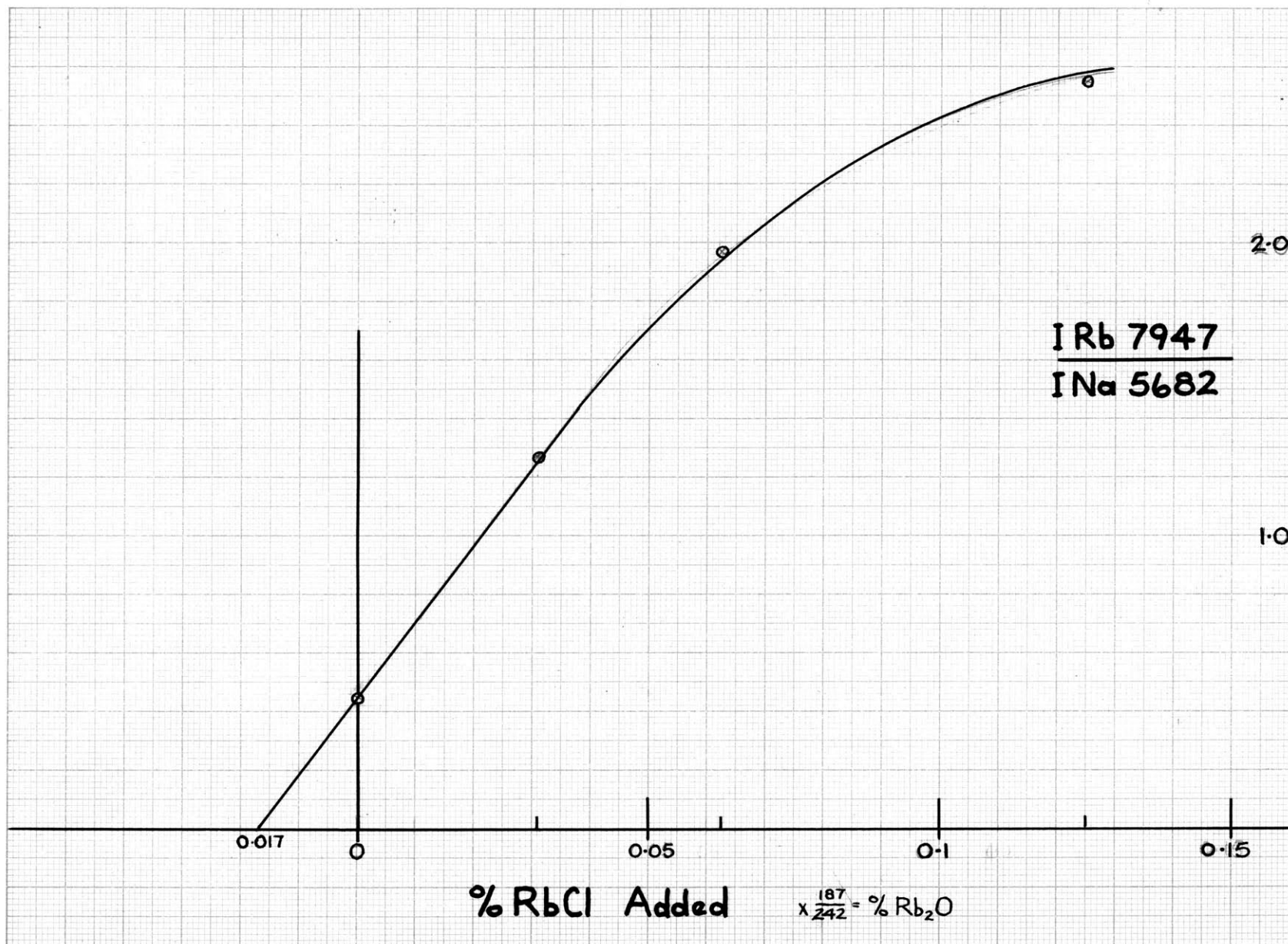
Rb ADDITION PLOT

Rb Working Curve
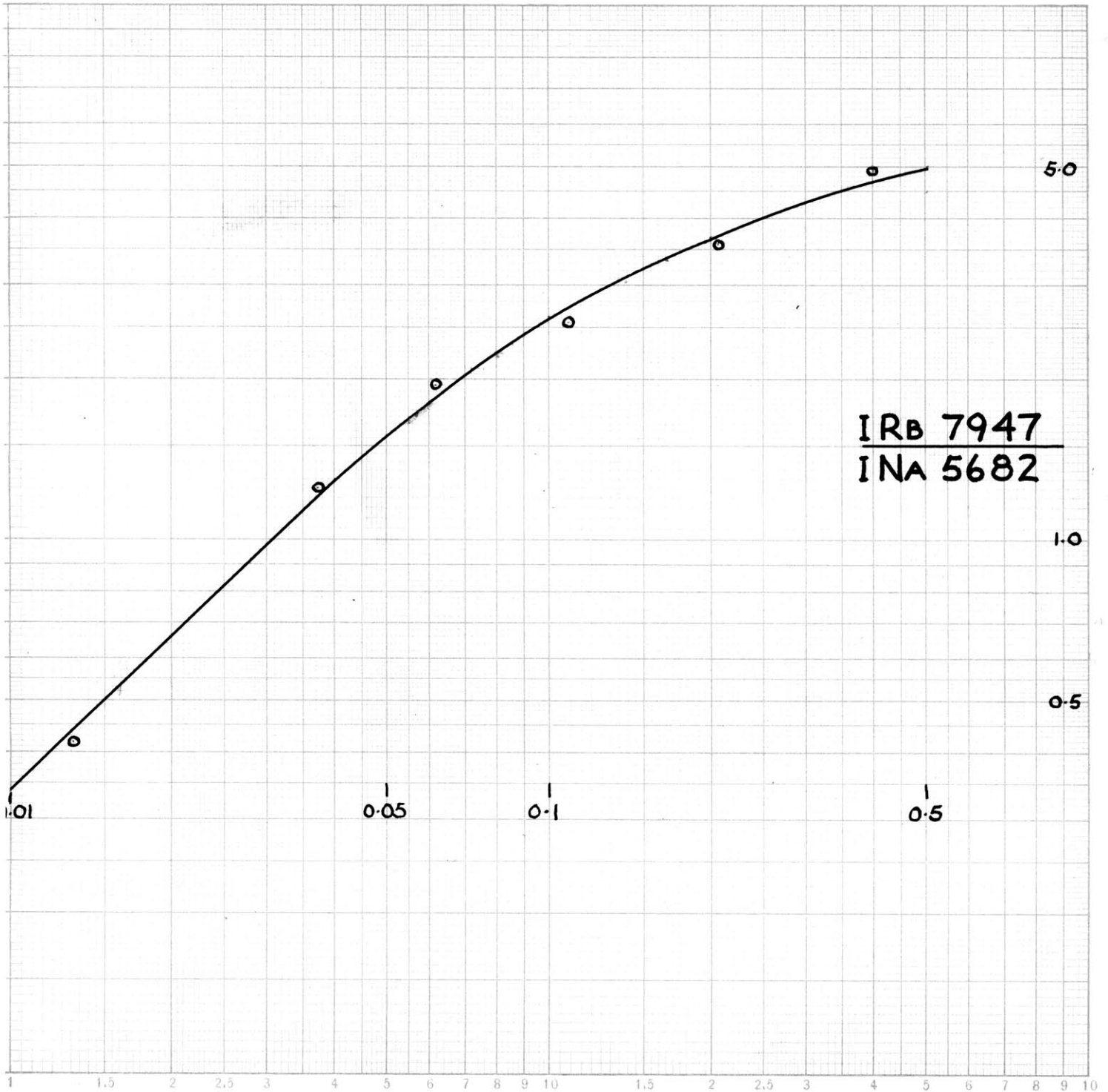
$$\frac{I\,R_B\ 7947}{I\,N_A\ 5682}$$

% Rb₂O in 2:1 Mix with Albite

PLATE 11

PLATE 12

Sr ADDITION PLOT

ISr 4607 / IBa 4726

% SrO Added

0.0085   0   0.0005   0.001   0.002   0.005   0.01

Sr Working Curve

$$\frac{I\ S_R\ 4607}{I\ B_A\ 4726}$$

3·0

2·0

1·0

0·5

0·3

0·01

0·005   0·01   0·02   0·05   0·10

1   1.5   2   2.5   3   4   5   6   7   8   9 10   1.5   2   2.5   3   4   5   6   7   8   9 10
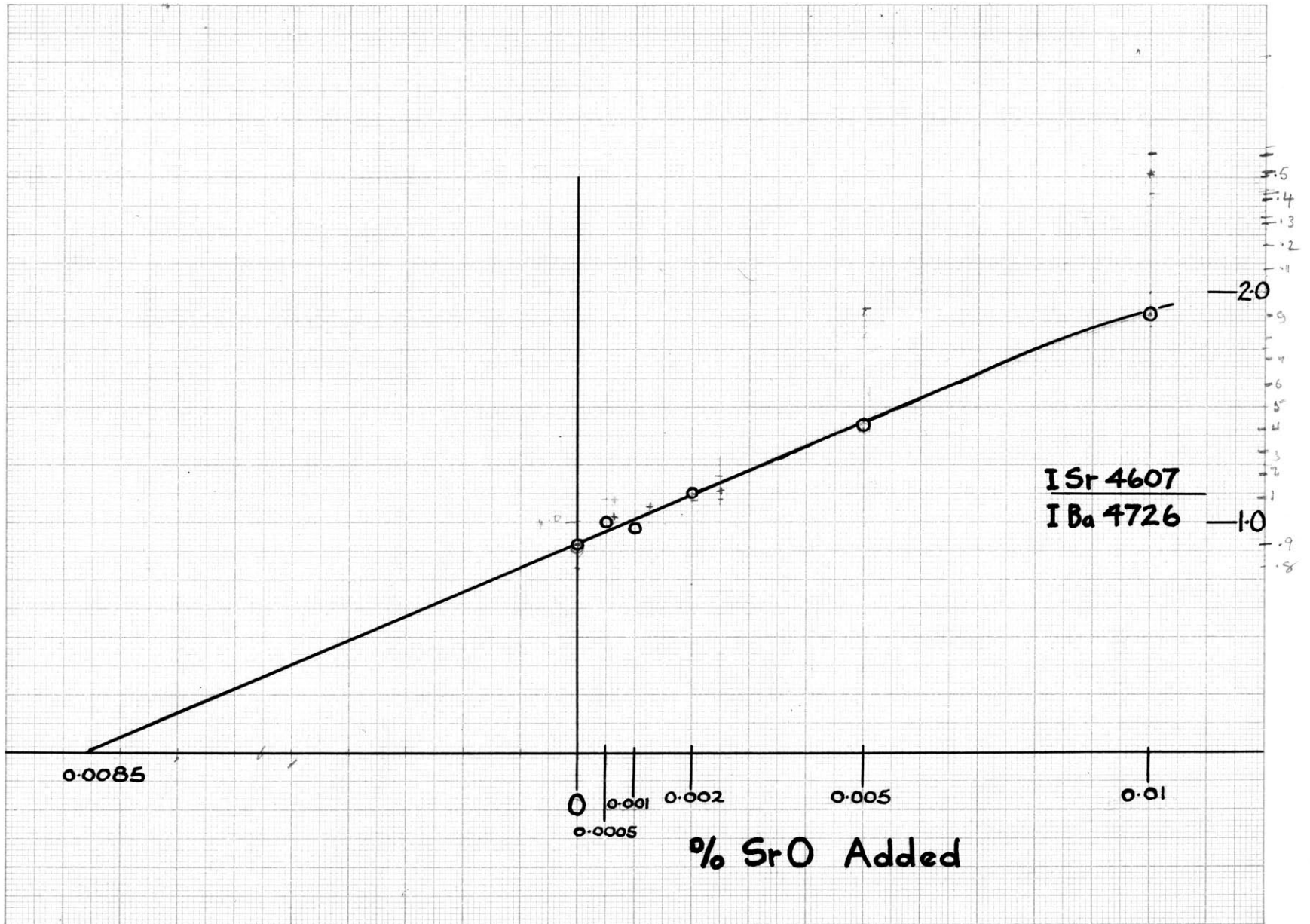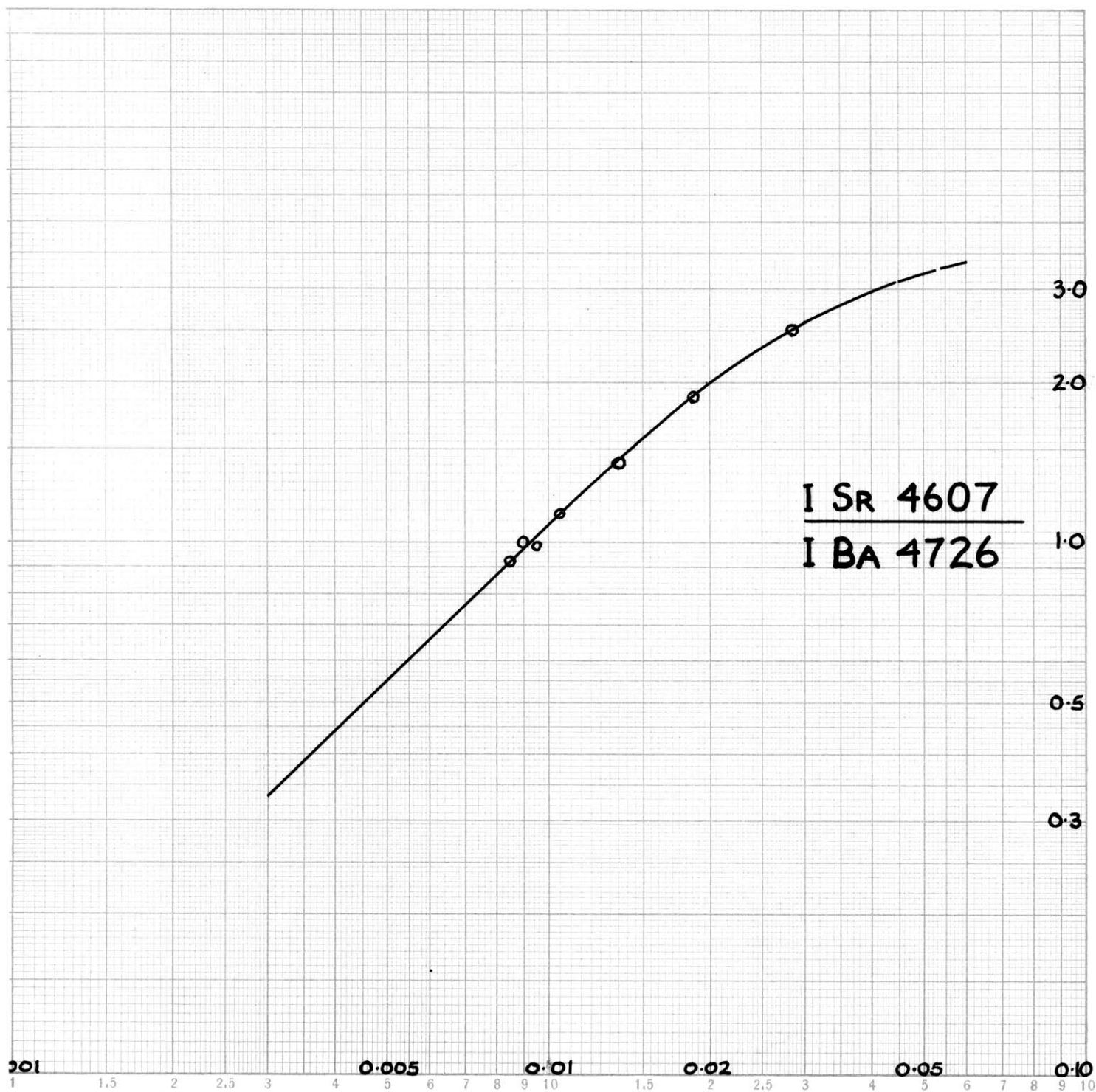
% SrO in Biotite
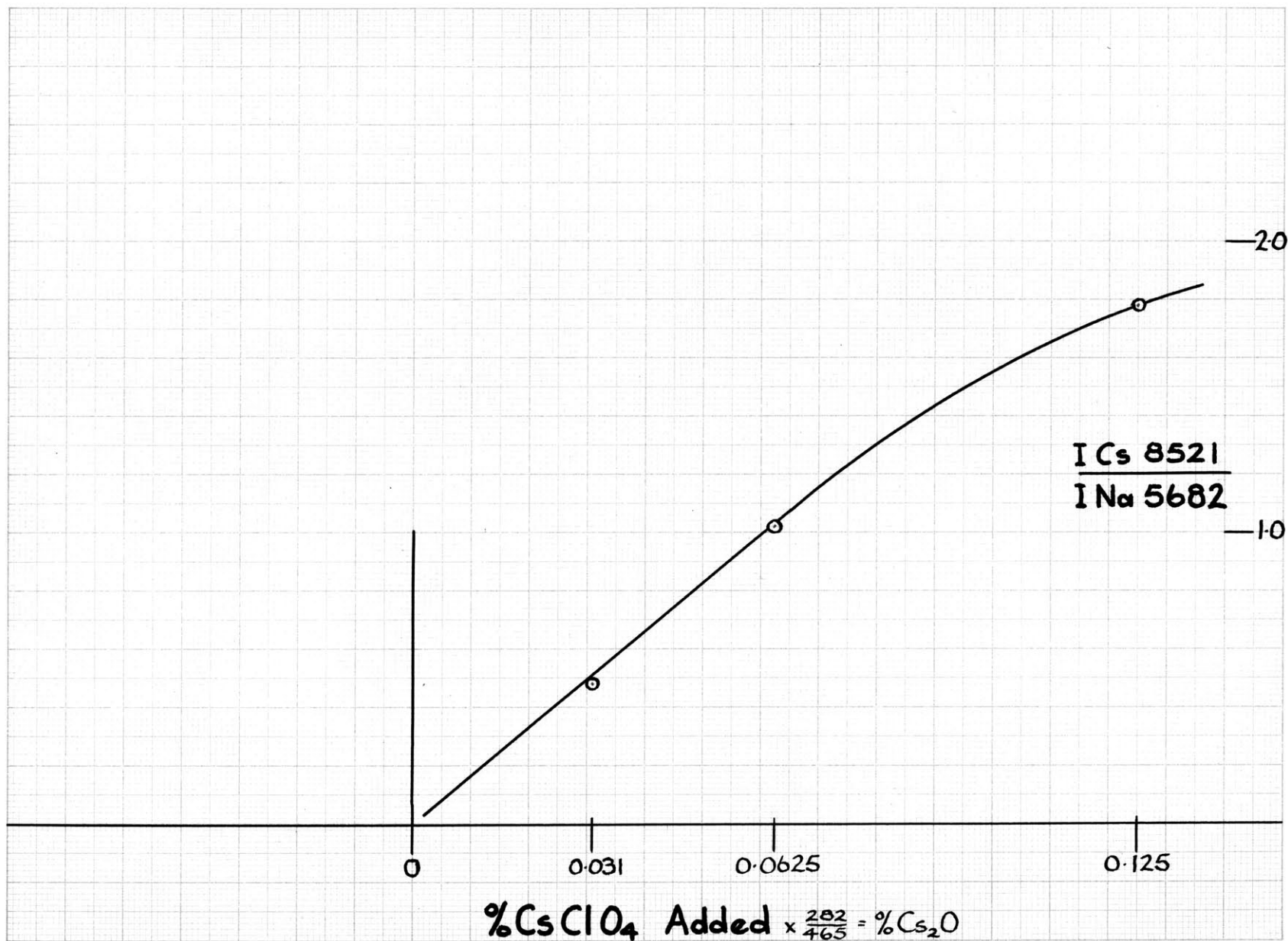
PLATE 13

Cs ADDITION PLOT

PLATE 14

Cs WORKING CURVE

% Cs$_2$O IN 2:1 MIX WITH ALBITE

PLATE 15

PLATE 16

Li ADDITION PLOT

I Li 6103
────────
I Na 5682

% Li₂CO₃ Added   × $\frac{30}{74}$ = % Li₂O

2·0

1·0

0·03   0   0·1   0·2   0·3

65

Li Working Curve

$\dfrac{I\,Li\ 6103}{I\,Na\ 5682}$
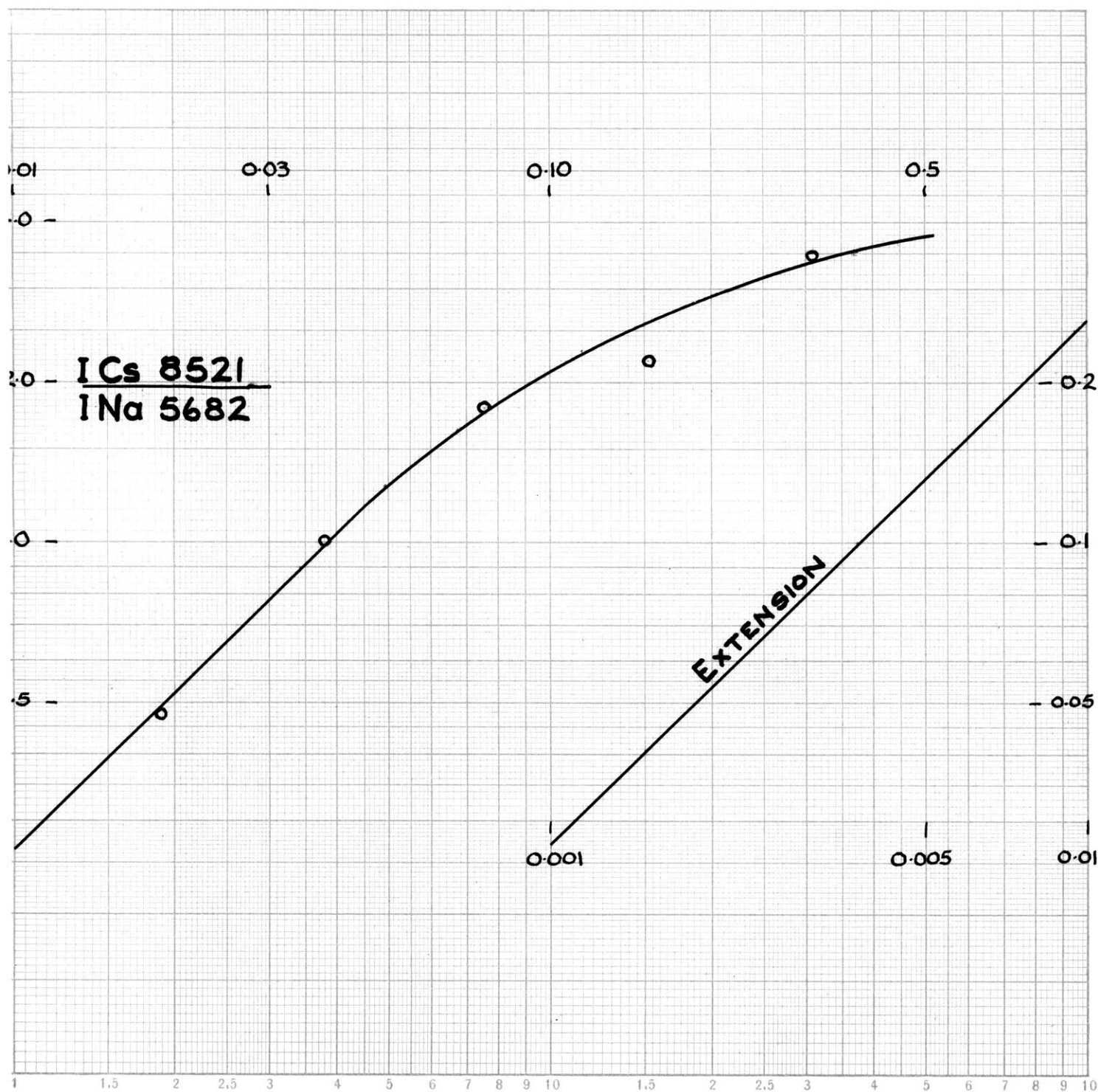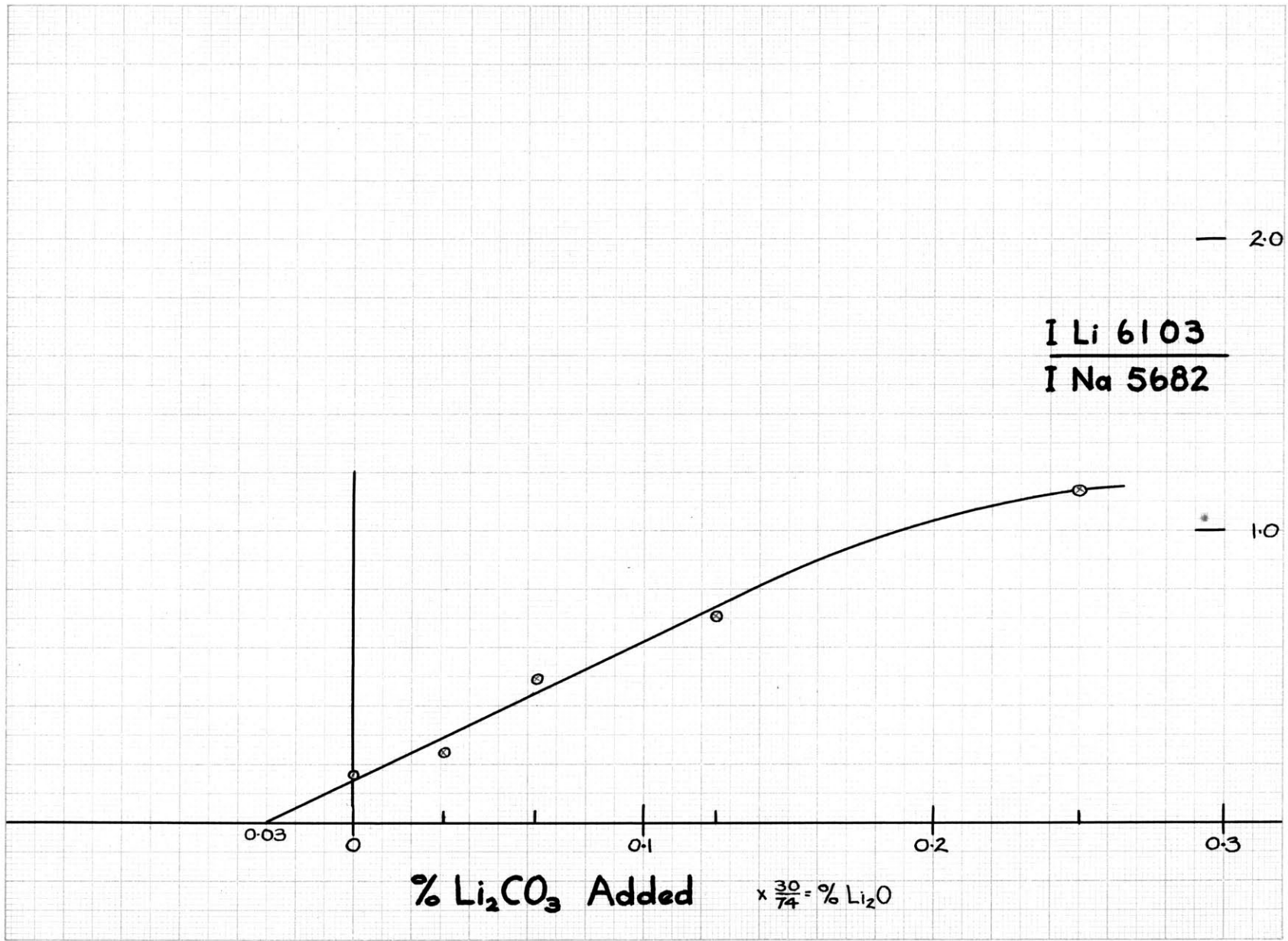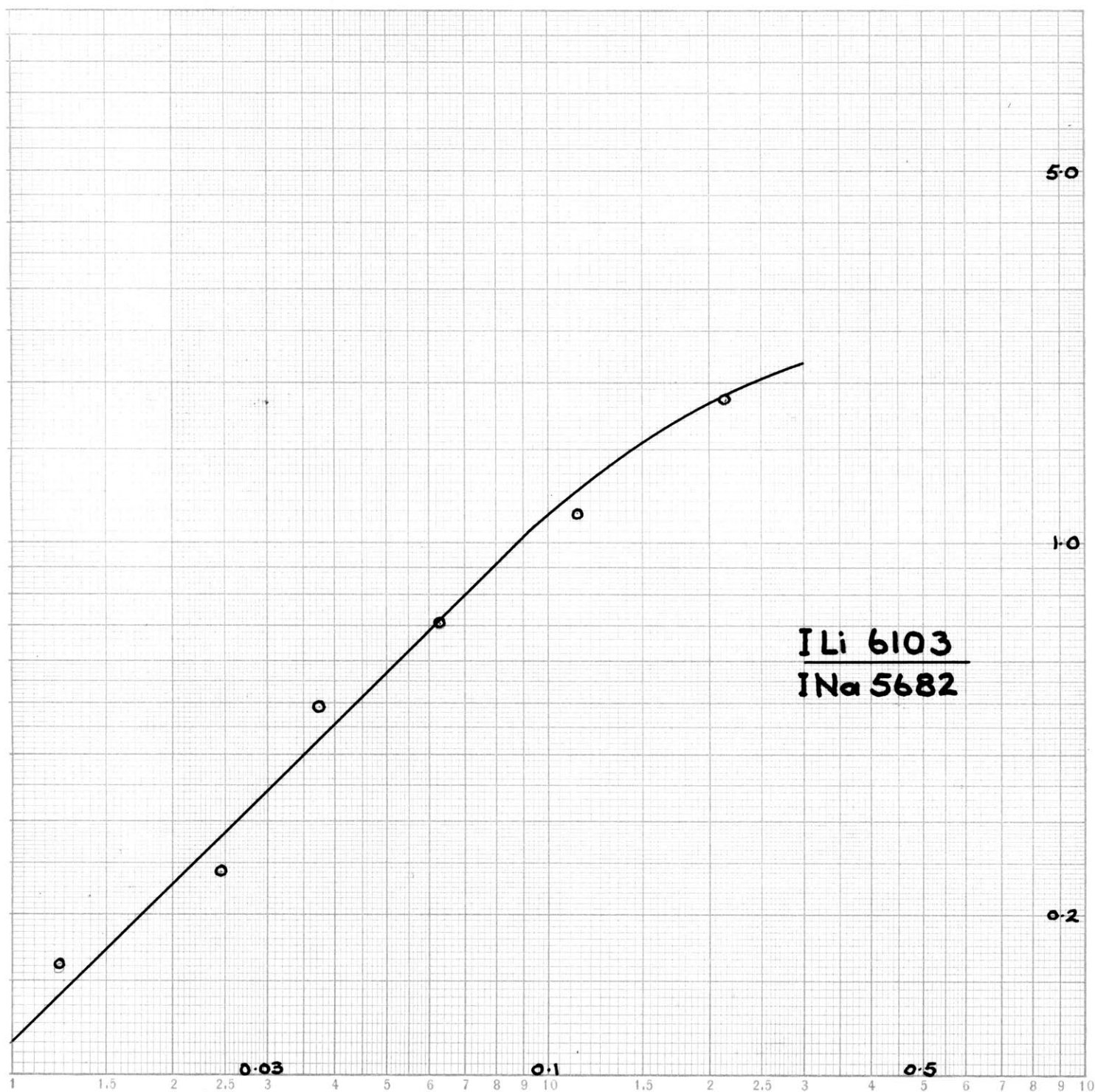
% Li$_2$O in 2:1 Mix with Albite

PLATE 17

D. Chemical Concentration of Strontium

The richer the sample is in strontium, the more accurately can the isotope ratios be measured. The total strontium content of biotites is about 0.01 %, a concentration which is too low for mass spectrometric analysis. The method outlined briefly below concentrates this strontium by a factor of about 100.

The method makes use of the selective thermal decomposition of perchlorates. The sample is fumed with H F (to remove silica) and $HClO_4$ and the residue is ignited and leached with water. Iron and aluminum are removed, and a final concentrate of calcium and the alkali metals is obtained, from which calcium oxalate is precipitated. The precipitate carries down the strontium oxalate as well. The mixture of oxalates is ignited to convert it to a mixture of oxides which is suitable for mass spectrometric analysis.*

The final precipitate can be used most easily as the carbonate or sulphate, or any compound which will decompose at arc temperature to an oxide. Chlorides cannot be used, for Rb Cl and $SrCl_2$ volatilize simultaneously. Since both Sr 87 and Rb 87 have the same mass they will react the same in producing a reading in the mass spectrometer, and any Rb in the sample will increase the Sr 87 percentage. If chlorides are not used the Rb volatilizes at a different time than the Sr, so the two can be separated.

*Information supplied by Dr. L. H. Ahrens.

VII   ANALYTICAL RESULTS

A.   Tables of Analyses and Descriptions of Samples

Table 6 gives SrO and Rb_2O analyses for samples #1 -
#60. For each sample, the three individual analyses are
given, as well as the mean. Individual analyses for SrO
vary less from the mean than do Rb_2O analyses, reflecting
the difference in the coefficients of variation of the
two methods: 5 - 6 % for Rb_2O and 2 % for SrO. Descrip-
tions of the samples are given in table 7. Explanation
of the symbols * and *** is provided at the end of table
10.

Table 6

MINOR ELEMENT CONTENTS

Sample	% Rb$_2$O Triplicates	Average	% SrO Triplicates	Average
1	0.054 0.046 0.043	0.047	0.0135 0.0135 0.0138	0.0136
2	0.041 0.041 0.034	0.039	0.0144 0.0153 0.0158	0.0152
3	0.173 0.153 0.153	0.160	0.0104 0.0099 0.0095	0.0099
4	0.173 0.126 0.082	0.127	0.0133 0.0127 0.0127	0.0129
5	0.032 0.043 0.036	0.037	0.0168 0.0163 0.0152	0.0161
6	0.17 0.15 0.13	0.15	0.0121 0.0118 0.0117	0.0119
7	0.060 0.084 0.084	0.076	0.0107 0.0102 0.0103	0.0104
8	0.17 0.16 0.19	0.17	0.0074 0.0075 0.0070	0.0073
9	Standard	0.039	0.0142 0.0143 0.0147	0.0144
10	0.144 0.132 0.108	0.128	0.0096 0.0095 0.0100	0.0097
11	0.144 0.135 0.144	0.141	0.0065 0.0067 0.0057	0.0063
12	0.080 0.087 0.100	0.089	0.0157 0.0172 0.0165	0.0165

Sample	Rb$_2$O		SrO	
	Triplicates	Average	Triplicates	Average
13	0.054 0.063 0.067	0.061	>0.1	>0.1
14	0.23 0.23 0.21	0.22	0.0061 0.0067 0.0065	0.0064
15	0.056 0.044 0.041	0.047	0.0172 0.0155 0.0150	0.0159
16	0.11 0.12 0.12	0.118	0.0153 0.0143 0.0157	0.0151
17	0.44 0.28 0.28	0.33	0.0048 0.0057 0.0057	0.0054
18	0.24 0.26 0.26	0.25	0.0124 0.0123 0.0126	0.0124
19	0.137 0.153 0.143	0.144	0.0147 0.0142 0.0142	0.0144
20	0.14 0.11 0.11	0.12	0.0093 0.0091 0.0096	0.0093
21	0.25 0.25 0.27	0.255	0.0079 0.0081 0.0078	0.0079
22	0.17 0.15 0.16	0.150	0.0075 0.0080 0.0072	0.0075
23	0.068 0.076 0.077	0.074	0.0128 0.0130 0.0128	0.0129
24	0.135 0.117 0.128	0.126	0.0172 0.0173 0.0167	0.0171
25	0.064 0.058 0.064	0.062	0.0315 0.0335 0.0355	0.0335

Sample	Rb₂O Triplicates	Average	SrO Triplicates	Average
26	0.28 0.23 0.24	0.25	0.0067 0.0066 0.0070	0.0068
27	0.192 0.180 0.193	0.188	0.0082 0.0084 0.0081	0.0082
28	Off curve, Estimated	2.1	0.0067 0.0066 0.0065	0.0066
29	0.0855 0.102 0.078	0.089	0.0064 0.0062 0.0065	0.0064
30	0.082 0.076 0.074	0.077	0.0112 0.0100 0.0107	0.0106
31	0.074 0.067 0.068	0.070	0.0086 0.0089 0.0089	0.0088
32	0.054 0.068 0.056	0.059	0.0118 0.0118 0.0123	0.0120
33	0.044 0.040 0.055	0.046	0.0142 0.0150 0.0156	0.0149
34	0.153 0.112 0.118	0.128	0.0103 0.0103 0.0099	0.0102
35	***	0.022	*	~ 0.018
36	***	0.061	*	~ 0.003
37	***	0.072	*	~ 0.02
38	***	0.050	*	~ 0.018
39	0.138 0.120 0.133	0.130	0.0163 0.0162 0.0157	0.0161
40	0.050 0.043 0.047	0.047	0.0102 0.0108 0.0108	0.0106

Sample	Rb$_2$O Triplicates	Average	SrO Triplicates	Average
41	0.090 0.094 0.078	0.088	0.0250 0.0245 0.0246	0.0247
42	***	0.042	*	~ 0.04
43	***	0.051	*	~ 0.02
44	***	0.026	*	~ 0.002
45	***	0.0073	*	~ 0.04
46	***	0.076	*	~ 0.04
47	*	0.035	*	~ 0.001
48	***	0.067	*	~ 0.04
49	***	0.0064	*	~ 0.04
50	0.0555 0.0562 0.0525 0.0630 0.0661 0.0609	0.0593	Standard by addition method	0.0085
51	0.091 0.094 0.071	0.085	0.0098 0.0102 0.0102	0.0101
52	0.091 0.089 0.089	0.090	0.0074 0.0080 0.0075	0.0076
53	0.111 0.119 0.108	0.113	0.0063 0.0065 0.0065	0.0064
54	0.067 0.088 0.072 0.075	0.075	0.0094 0.0093 0.0087	0.0091
55	0.080 0.068 0.088 0.071	0.077	0.0078 0.0077 0.0083	0.0080

| | Rb$_2$O | | SrO | |
Sample	Triplicates	Average	Triplicates	Average
56	0.088		0.0057	
	0.091		0.0098	
	0.088		0.0063	
	0.085	0.088		0.0073
57	0.119		0.0081	
	0.099		0.0079	
	0.114		0.0084	
	0.108	0.110		0.0081
58	0.082		0.0095	
	0.075		0.0107	
	0.078		0.0101	
	0.078	0.078		0.0101
59	0.139		0.0037	
	0.185		0.0042	
	0.170		0.0036	
	0.136	0.158		0.0038
60	0.067		0.0023	
	0.071		0.0037	
	0.084		0.0036	
	0.071		0.0035	
	0.072	0.073	0.0043	0.0035
Standard Granite G-1		0.061		0.02

Table 7

Descriptions of Samples

1. Granite from Robillard township, on boundary between lots 10 and 11, Temiskaming district, Ontario. Age: Early Archean. Donated by W. Johnston.

2. Diabase dike from Medford, Massachusetts. Age: Thought to be Triassic, for it cuts sediments commonly classed as Carboniferous. Biotite fraction contains 10 % of other ferromagnesian minerals.

3. Granite from lot 13, concession IV, Bastedo township, Nipissing district, Ontario. Age: Late Archean, probably near 800 million years.

4. Creighton granite, just south of Creighton, Ontario. Age: Probably pre-Killarney, and therefore near 800 million years.

5. Salem gabbro-diorite from Arlington, Massachusetts. Age: Post-Cambrian and pre-late Devonian, probably early Devonian. Biotite fraction contains 10 % of other ferromagnesian minerals.

6. Granite from the House Mountain range, west central Utah. Age: Laramide, between Cretaceous and early Tertiary. Donated by M. L. Jensen.

7. Granite from Lake Tahoe, California. Age: Cretaceous.

8. Oliverian syenite. A series of domes of this rock outcrop along a belt running from New Hampshire to

southern Connecticut. Age: Probably late Devonian.

9. Granite from Charlton Road, 1/8 mile east of Tamrack Creek, Truax township, Temiskaming district, Ontario. Age: Early Archean.

10. Richardson Island granite from Contact Lake, south of Great Slave Lake, N. W. T., Canada. Age: Middle Precambrian; rock intrudes Echo Bay complex and Snare River complex. Biotite fraction contains 5 % quartz and feldspar.

11. Conway granite, a sub-alkaline type which is thought to be Mississippian in age as it is post-Acadian Revolution and is overlain by Pennsylvanian rocks. Biotite fraction contains 5 % feldspar.

12. Mount Airy granite, from North Carolina. Age: Possibly Precambrian. Biotite fraction contains 2 % feldspar.

13. Minette from Los Animas county, Colorado. Age: Early Tertiary. Biotite fraction contains about 1 % of impurities, mainly feldspar.

14. Platte Canyon granite from Colorado. Age: Presumably early Precambrian. Biotite fraction contains 1 % feldspar.

15. Syenite from Salem Willows, Massachusetts. The rock is considerably altered. Age: As this is Beverly syenite, part of White Mountain Magma Series, the age is considered to be Mississippian. Biotite fraction contains

5 % feldspar.

16. Granite, 1½ miles south of Marten River. Sisk township, Nipissing district, Ontario. Age: Late Archean.

17. Pegmatite from Topsham, Maine. Age: Late Palaeozoic. The sample consists of pure sheet biotite. No impurities. Lepidolite age by Sr method is 200 x 10^6 years. Other methods suggest age is slightly more, between 200 and 300 million years.

18. Phlogopite from pegmatite from Hadderspell township, Quebec. Age: Believed to be Grenville. No impurities.

19. Granite from St. Cloud, Minnesota. Age: Precambrian, possibly very old, somewhere between 500 - 2000 million. Biotite fraction contains 5 % feldspar and 5 % hornblende.

20. Biotite from Miask, Ural Mountains. Apparently from pegmatite. Age: Possibly 270 - 300 million years. No impurities.

21. Pacolet granite from South Carolina. Age: Late Palaeozoic or Precambrian. Biotite fraction contains 1 % feldspar.

22. Pegmatite from Ruggles quarry, Grafton, New Hampshire. The sample consisted of coarse crystals of biotite and muscovite. No. 22 is pure biotite. No. 29 is pure muscovite. Age by lead method: 280 million years.

23. Aberdeen granite from Gunnison county, Colorado.

Age: Precambrian. Biotite fraction contains 3 % quartz
and feldspar.

24. Pegmatite from Black Hills, South Dakota. Age:
Precambrian. Biotite fraction contains 1 % limonite, 1 %
feldspar. Strontium ages from lepidolite from this area
range from 800 - 1500 million years.

25. Camptonite from Franklin Furnace, New Jersey.
Age: Not known; may be Triassic or Precambrian. Biotite
fraction contains 5 % ferromagnesian minerals.

26. Stone Mountain granite, from Georgia. Age: Dis-
puted, but possibly late Palaeozoic. Biotite fraction con-
tains 1 % muscovite, 1 % feldspar.

27. Llano granite, from Llano uplift, Texas. Age:
Precambrian. Two measurements by helium and lead methods
give 1050 million years.

28. Siderophyllite from an unusual pegmatite on
Brooks Mountain, Alaska. Siderophyllite is a brittle,
dark green mica in which the FeO content is about 30 %,
with almost no magnesia present. Area is on Seward Penin-
sula, in the central part of the York Mountains. The peg-
matite is a sill associated with a stock of coarse-
grained porphyritic alaskite about two miles in diameter.
Reference: Coats and Fahey, American Mineralogist, Vol.
29, pp. 373 - 377. Age: Cretaceous.

29. Pegmatitic muscovite. See No. 22.

30. Beerbachite, a fine-grained gabbro from Sudbury,

Ontario. The biotite seems to be concentrated near pyrrhotite in this rock. Age: Precambrian.

31. Granodiorite from area between Hollyburn ridge and Burrard Inlet, north of Vancouver, British Columbia. Age: Not known exactly; rock is part of Coast Range batholithic complex usually referred to late Jurassic - Cretaceous. Biotite fraction contains 1 % feldspar, 1 % hornblende.

32. Bytownite gabbro from Duluth, Minnesota, part of Duluth gabbro. Age: Precambrian, possibly Keweenawan. Biotite fraction contains 1 % feldspar and 5 % pyroxene.

33. Olivine gabbro from Iron Mountain, near Cripple Creek, Colorado. Sample contains 5 % pyroxene, 5 % olivine. Age: Possibly Algonkian.

34. Biotite from Ridgeway, Virginia. Donated by W. T. Schaller. The biotite is in the country rock at a contact with a pegmatite. Age: Precambrian (?).

35. Whole rock sample from rock described under No. 1.

36. Whole rock sample from rock described under No. 11.

37. Whole rock sample from rock described under No. 26.

38. Whole rock sample from rock described under No. 27.

39. Monzonite from Ymir, British Columbia. Age: Presumably Laramide. Sample contains 10 % chlorite.

40. Quartz diorite from along Capilano river, north of intake, near Vancouver, British Columbia. Part of Coast Range batholithic complex. Age: Late Jurassic to Creta-

ceous.

41. Quartz monzonite porphyry from Chaffee county, Colorado. Age: If late intrusive, near 60 million years; possibly Precambrian and therefore near 800 million years.

42. Whole rock sample of rock described under No. 41.

43. Whole rock sample of rock described under No. 19.

44. Hornblende from rock described under No. 41.

45. Plagioclase feldspar from rock described under No. 41.

46. Potash feldspar from rock described under No. 41.

47. Hornblende from rock described under No. 19.

48. Potash feldspar from rock described under No. 19.

49. Plagioclase feldspar from rock described under No. 19.

50. Biotite from granite boulders enclosed in the sediments of the Rice Lake Series, southern Manitoba. The Rice Lake sediments are thought to be the oldest Precambrian sediments of that part of the shield area. Pegmatites bearing lepidolite associated with a later granite which intrudes the Rice Lake Series give strontium ages near 2200×10^6 years. Age: Probably a little more than 2000 million years. Impurities in biotite fraction: none.

51. Hornblende gneiss from Grondines Map-area, Grenville subprovince, Quebec. Age: In dispute, presumed to be early Archean. Biotite fraction contains 5 % hornblende.

52. Pegmatite close to No. 51. Age: Presumably ear-

ly Archean. The biotite is slightly altered to sericite, etc.

53. Granite from Nova Scotia. No. 1712 A in Helium-Age Record system. Age: Late Devonian. Biotite fraction contains 3 % chlorite, quartz, feldspar.

54. Palisade granite near Vancouver, British Columbia. Age: Presumed to be late Jurassic to Cretaceous. Biotite fraction contains 10 % feldspar, hornblende. Composite of samples R90C, 73C, 70C, 185A.

55. Dark granodiorite from Idaho batholith. Age: Cretaceous. Less than 1 % impurities.

56. Medium granodiorite from Idaho batholith. Age: Cretaceous. Less than 1 % impurities.

57. Little Cottonwood Stock, Utah. Age: Tertiary. Pure biotite.

58. Quartz monzonite from Idaho batholith. Age: Cretaceous. Pure biotite.

59. Granite of South California batholith. Age: Middle Cretaceous. Biotite fraction is 98 % greenish mica, 2 % brown mica.

60. Pegmatitic biotite from Southern Rhodesia. Strontium age measurements on lepidolite from this area give figures around 2000 million years.

B.   Discussion of Rb_2 Analyses of Table 6

The range of Rb_2O content in 20 biotites from gran-
ites is 0.039 - 0.255 %.   Seven lie between 0.039 and
0.10 %, 6 between 0.10 and 0.15 %, 4 between 0.15 and
0.20 %, and 3 between 0.20 and 0.255 %.   No change in the
Rb_2O content with age was evident.

The biotites from two syenites of Palaeozoic age con-
tain 0.047 and 0.170 % Rb_2O.

Nine analyses of biotites from intermediate types of
igneous rocks range between 0.047 and 0.130 % Rb_2O.   Seven
analyses are between 0.047 and 0.10 %; the other two are
0.11 and 0.13 % Rb_2O.   Owing to the small number of samples
no conclusions could be drawn as to any shift in Rb_2O con-
tent with age.

Five biotites from basic rocks contain 0.037, 0.039,
0.046, 0.059, and 0.077 % Rb_2O.   A tentative conclusion is
that basic rocks contain less rubidium than do acidic
rocks, possibly about one-half as much.

Two biotites from lamprophyres have low Rb_2O contents:
0.062 and 0.061 %.

Data in table 6 on Rb_2O in whole rocks and in miner-
als other than biotite were included in table 2 and were
discussed in section IV, 3.

Distribution of Rubidium between Biotite and Potash Feldspar

For age work, biotites high in rubidium are preferred

to biotites low in rubidium. Some factor or combination of factors must control the concentration of rubidium in biotite. Temperature, grain size, and the presence of a potassium-rich mineral other than biotite are some possible controls.

To examine the distribution of rubidium among the potassium-rich minerals of a rock, two sets of new analyses of individual minerals and their source rocks have been combined in graph form with six similar sets for the Caledonian rocks (Nockolds and Mitchell, 19). The number of samples is so small that the conclusions reached below can be no more than tentative, yet a rough pattern may be discerned.

Figure 1, plate 18, shows that the proportion of the total rock rubidium which is held within the biotite increases as the percentage of biotite increases. This relationship is normal if biotite is the preferred host.

Figure 2 shows that no distinct correlation exists between the concentration of rubidium in the biotite and the amount of biotite in the rock. Some factor other than the abundance of biotite must control how much rubidium is packed into the biotite structure. The temperature of formation may be critical. To examine the effect of the presence of another possible host for rubidium, figures 3 and 4 were constructed. Potash feldspar, being rich in potassium, is another natural host for rubidium, so the proportion of

PLATE 18
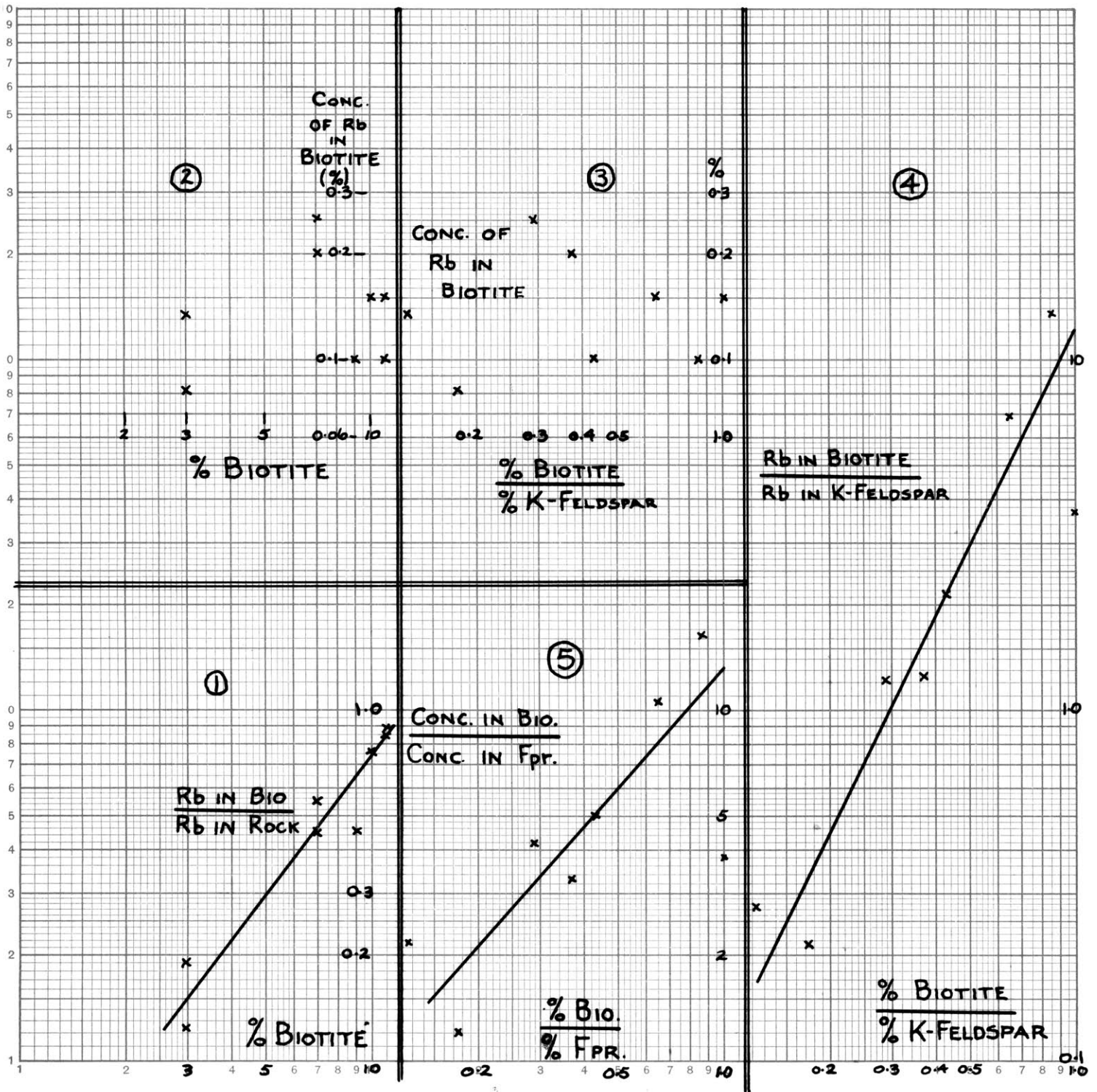
biotite to potash feldspar is used as one variable.

Figure 3 shows that the concentration of rubidium in biotite does not vary regularly with the ratio of biotite to potash feldspar in the rock.

Figure 4 shows that an increase in the relative amount of biotite with respect to feldspar increases the relative amount of the total rubidium held in the biotite. This is accomplished not by raising the concentration in the biotite, but by lowering the concentration in the feldspar. The concentration in biotite is controlled by some unknown factor; the concentration in feldspar is controlled by the amount of biotite present which acts as the preferred host. Biotite seems to accept only a certain amount of rubidium; any excess rubidium is forced into the feldspar structure.

Figure 5 suggests that as the amount of biotite increases with respect to feldspar, the concentration in biotite increases with respect to the concentration in feldspar. As before, this is caused, not by an enrichment in biotite but by an impoverishment in the feldspar.

A final, tentative conclusion is that where the percentage of biotite is low, the biotite is not necessarily rich in rubidium and hence not necessarily more suited for age determinations.

C. Discussion of SrO Analyses

The range in SrO content of 20 biotites from granites is 0.0038 to 0.0165 %. Five lie between 0.0038 and 0.0075 %, 6 between 0.0075 and 0.010 %, 7 between 0.010 and 0.015 %, and 2 between 0.015 and 0.0165 %. No change with age was evident.

The biotites from two Palaeozoic syenites contain 0.0073 and 0.0159 % SrO.

Nine analyses of biotites from rocks of intermediate composition range between 0.0073 and 0.0247 % SrO. Four lie between 0.0073 and 0.010 %, 4 between 0.010 and 0.020 %, and one is 0.0247 % SrO.

Five biotite concentrates from basic rocks contain 0.0106, 0.0120, 0.0149, 0.0152, and 0.0161 % SrO. A tentative conclusion is that basic rocks contain a little more strontium than do more acidic rocks.

Two biotites from lamprophyres contain 0.0073 and 0.0159 % SrO.

Data in table 6, but not discussed above, were included in table 3 and were discussed in section IV, 3.

These analyses for SrO in biotites agree closely with analyses of biotites in the Caledonian rocks (Nockolds and Mitchell, 19).

VIII   CALCULATIONS FOR PROPORTION
OF RADIOGENIC STRONTIUM

To determine which biotites of the analysis group could be expected to contain sufficient radiogenic strontium for the Sr 87* to be 1 % of the total Sr, ages were assumed for all the samples and the % Sr 87* of total Sr has been calculated, using the measured contents of total Rb and total Sr.

The formulae used are:

$$\% \text{ Sr 87* generated} = 0.272 \times \% \text{ Rb} \times \text{age} \times 1.175 \times 10^{-11}$$

$$\% \text{ of Sr that is radiogenic} = \frac{\% \text{ Sr 87* generated}}{\% \text{ total Sr}} \times 100 \%$$

The values are given in table 9.

The values for % Rb in this table are derived from table 6, each percentage of Rb_2O being multiplied by $\frac{171}{187}$ to convert oxide to element. A factor of $\frac{87.6}{103.6}$ changes % SrO to % Sr.

Plate 19 is a plot of the ratio of Rb/Sr in all the biotites against age, on a cut-off chart similar to plates 2 and 3.

Table 8

Time Scale Used in Calculations for % Sr 87*

			Millions of Years
Cenozoic		Pliocene	0 - 12
		Miocene	12 - 22
		Oligocene	22 - 35
		Eocene	35 - 48
		Palaeocene	48 - 60
Mesozoic		Cretaceous	60 - 125
		Jurassic	125 - 175
		Triassic	175 - 185
		Permian	185 - 215
		Pennsylvanian	215 - 235
		Mississippian	235 - 255
		Devonian	255 - 310
		Silurian	310 - 350
		Ordovician	350 - 430
		Cambrian	430 - 510
	Late		520 - 750
Precambrian			
	Early	Late Archean	750 - 1000
		Grenville	1000
		Early Archean	over 1000

Table 9

Proportion of Radiogenic Strontium in the Samples

Number	Age in 10^6 Years	% Rb	% Sr 87* x 10^6	% Sr	% of total that is radiogenic
1	1000	0.043	137	0.0115	1.2
2	170	0.0357	19.4	0.0129	0.15
3	800	0.146	373	0.0084	4.4
4	800	0.116	296	0.0109	2.7
5	300	0.0338	32.4	0.0136	0.24
6	100	0.137	43.8	0.0101	0.43
7	110	0.0695	24.4	0.0088	0.28
8	270	0.155	134	0.0062	2.2
9	1000	0.0357	114	0.0122	0.94
10	600	0.117	224	0.0082	2.7
11	240	0.129	99	0.0053	1.9
12	800	0.0814	208	0.0140	1.5
13	50	0.0558	8.9	>0.085	<0.0105
14	900	0.201	578	0.0054	10.7
15	240	0.043	33	0.0135	0.24
16	900	0.108	311	0.0128	2.4
17	230	0.302	222	0.00457	4.9
18	900	0.229	660	0.0105	6.3
19	900	0.132	380	0.0122	3.1
20	280	0.11	98.5	0.0079	1.2
21	210	0.233	156	0.0067	2.3

Number	Age in 10^6 Years	% Rb	% Sr 87* x 10^6	% Sr	% of total that is radiogenic
22	280	0.137	123	0.00635	1.9
23	900	0.0677	195	0.0109	1.8
24	1300	0.115	478	0.0145	3.3
25	180	0.0567	32.6	0.0284	0.11
26	210	0.229	154	0.00576	2.7
27	1050	0.172	577	0.00695	8.3
28	100	1.92	614	0.0056	11.0
29	280	0.0814	72.6	0.0054	1.3
30	700	0.0705	158	0.0090	1.7
31	125	0.064	25.5	0.00745	0.34
32	550	0.054	95	0.0102	0.93
33	800	0.042	107	0.0126	0.85
34	800	0.117	299	0.00865	3.5
35	1000	0.0201	64.3	~0.015	0.43
36	240	0.0558	42.8	~0.0025	1.7
37	210	0.066	44.3	~0.017	0.26
38	1050	0.0457	153	~0.015	1.0
39	100	0.119	38	0.0136	0.28
40	100	0.043	13.7	0.0090	0.15
41	60	0.0805	15.4	0.0209	0.045
42	60	0.0384	7.4	~0.034	0.022
43	900	0.0466	134	~0.017	0.79
44	60	0.0238	4.6	~0.0017	0.27
45	60	0.0067	1.3	~0.034	0.0038

Number	Age in 10^6 Years	% Rb	% Sr 87* x 10^6	% Sr	% of total that is radiogenic
46	60	0.0695	13.3	~0.034	0.039
47	900	0.032	92	~0.00085	11.0
48	900	0.0614	177	~0.034	0.52
49	900	0.0059	17	~0.034	0.05
50	2000	0.0543	347	0.0072	4.8
51	1000	0.0778	249	0.0086	2.9
52	1000	0.0823	263	0.0064	4.1
53	280	0.103	92.3	0.0054	1.7
54	100	0.0686	21.9	0.0077	0.28
55	80	0.0705	18	0.0068	0.27
56	80	0.0805	20.6	0.0062	0.33
57	50	0.101	16.1	0.0069	0.23
58	80	0.0713	18.2	0.0086	0.21
59	110	0.145	51	0.0032	1.6
60	2000	0.0668	427	0.00296	14.4
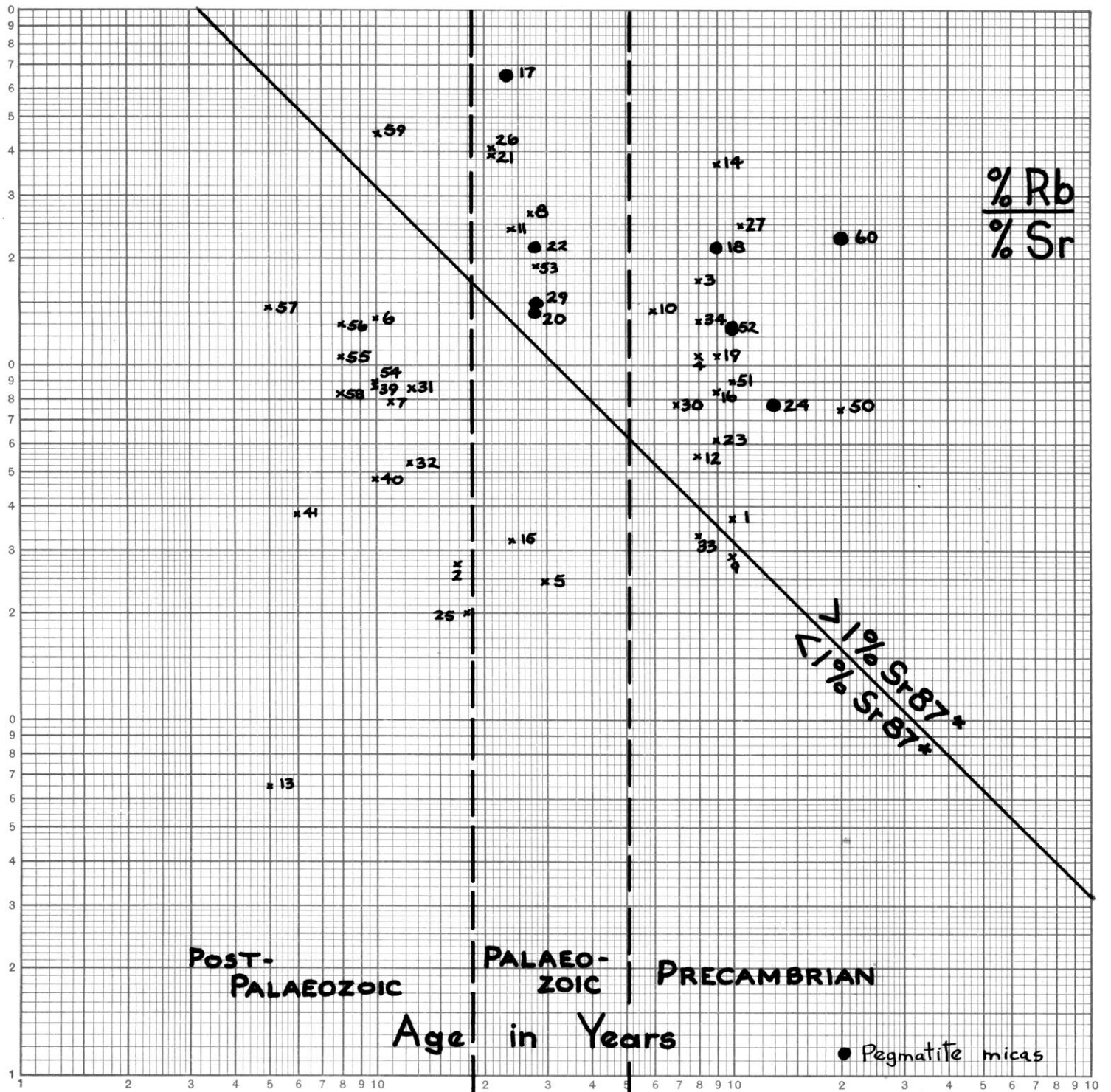
CRITICAL RATIO in BIOTITE

PLATE 19

IX CONCLUSIONS

The following conclusions are based upon the postulate that a mineral, for use in strontium age measurements, should have at least 1 % of its strontium radiogenic.

1. Most common-rock biotite from pre-Mesozoic rocks appear to be suitable for use in strontium age measurements. Thirteen of the fifteen Precambrian biotites fitted the requirements, and the other two were close to being suitable. Five of the seven Palaeozoic biotites were usable, as was one of the sixteen Mesozoic ones. Comparison of biotites from different types of source rocks shows that biotites from granitic rocks are more suitable than biotites from basic rocks.

2. All the micas from pegmatites which were analysed are suitable, regardless of age.

3. A favorable ratio of radiogenic to total strontium was found in one of the three Precambrian whole rocks, in one of the two Palaeozoic rocks, and not in the one Mesozoic-or-later rock. Study of the reported ratios of Rb : Sr in Caledonian plutonic rocks (Nockolds and Mitchell) indicates that no rock type in the series gabbro-granite is especially more favorable than any other. Age, rather than rock type, seems to be the controlling factor. Aplites, being high in rubidium and low in strontium are generally

suitable for age work.

4. None of two plagioclase feldspars and two potash feldspars was suitable, a result that agrees with analyses in the literature. Ancient hornblende might possibly be used, judging from the low contents of strontium found in the two samples analysed.

5. The high content of Sr in plagioclase, and the low content of Rb, make that mineral especially useful for determining what percentage of the total strontium was the isotope Sr 87 at the time the minerals formed. If plagioclase be absent from the rock, any other fraction free of biotite might be used. See section XI.

6. The methods of analysis for rubidium and strontium are sufficiently accurate for the percentages to be used in age calculations.

If less than 1 % of radiogenic strontium could be measured accurately in the isotope analysis, younger biotites could be used for age work, and other materials might be usable as well, particularly the whole rock rather than any one mineral.

X AGE DETERMINATION

At the time this report was written only one isotope measurement had been made. Dr. L. T. Aldrich of the Carnegie Institution of Washington, Department of Terrestrial Magnetism, was the analyst. He reported that, in the sample supplied to him,

$$\frac{\%\ Sr\ 87*}{\%\ common\ strontium} = 0.046 \pm 0.005$$

Therefore % Sr 87* of total strontium = 4.4 %.

The sample analysed by Mr. Aldrich was a concentrate of biotite #50, from granite boulders in the Rice Lake Series, southeastern Manitoba. The age may be calculated from equation (3):

$$Age = \frac{\%\ total\ Sr}{\%\ total\ Rb} \times \%\ Sr\ 87*\ of\ total \times \frac{8.51 \times 10^{10}}{.272}$$

$$= \frac{0.0072}{0.0543} \times 0.044 \times \frac{8.51 \times 10^{10}}{.272}$$

$$= 1825 \times 10^{6}\ years.$$

The latitude possible in this measurement, considering all the errors which might be contained in the analyses of rubidium, strontium, and strontium isotopes, is thought to be $\pm$ 400 x 10^6 years.

The age as calculated is about the right magnitude.

The Rice Lake Series is the oldest sedimentary series in the Precambrian of southeastern Manitoba, and is intruded by younger granite. Lead ages and strontium ages of pegmatites associated with the younger granite are around 2000 to 2300 x 10^6 years. Material in the sediments must be older than the pegmatites. For this reason it is thought that the biotite age as calculated is a little low. Nevertheless, the general practicability of the use of biotite is demonstrated.

XI ACCURATE MEASUREMENT OF RADIOGENIC STRONTIUM

At present, Sr 87 is 7.02 % of total strontium
(Ahrens, 2). For a first approximation, one that results
in an age calculation that may be slightly low, the ex-
cess of Sr 87 over 7.02 % in a biotite may be regarded as
the radiogenic strontium contributed by rubidium since
the biotite was formed. This 7.02 %, however, includes
all the radiogenic Sr 87 produced since geologic time be-
gan. What is critical in any age measurement is the Sr
87 added by Rb 87 to the amount present when the biotite
formed.

$$Present\ Total\ Sr = (\ Sr\ 88 + Sr\ 87 + Sr\ 86 + Sr\ 84)_1$$
$$+ Sr\ 87*_2 + Sr\ 87*_3$$

Terms in 1 are the amounts of each isotope at the be-
ginning of geologic time.

Term 2 is the Sr 87* produced from Rb 87 up to the
time of formation of the biotite.

Term 3 is the critical term in age measurements, the
Sr 87* made from the rubidium in the biotite
since the biotite formed.

The amount of radiogenic strontium added by rubidium
since the rock was formed may be found easily and accurate-
ly once two isotope analyses have been made, one on a frac-

tion rich in Rb and one on a fraction low in Rb. The amounts of Rb and Sr in the samples must be measured, as well.

The amount of Sr 87* increases linearly with the amount of Rb present, regardless of the age. The isotope measurement of % Sr 87 of total Sr can be plotted against the % Rb for each fraction, and the line connecting these two points can be projected to the limit where % Rb equals zero. The intercept of this line on the % Sr 87 scale is the amount of Sr 87 present when the rock formed. Part of that may be radiogenic; whether it is or not is unimportant. The difference between this % original Sr 87 and the % Sr 87 in the biotite fraction is the amount contributed by the rubidium since the biotite formed.

These relationships are illustrated by plate 20.

The above method of finding the % Sr 87* can be used only where the necessary isotope analyses can be made with high accuracy. Plagioclase feldspar from the same source as the biotite is most useful because the Rb content is low in plagioclase compared to the SrO content. Furthermore, isotope measurements on plagioclase can be made accurately as the % Sr (total) is high. If a plagioclase fraction is not available, any other fraction poorer in rubidium than the biotite can be used, but as a higher Rb % will move the second point further from the 0 % Rb boundary the determination will be less acurate.

PLATE 20

%Sr 87 of Total Sr

%Sr 87* from Rb in biotite

% Rb in Plag.

% Rb in Bio

% Rb
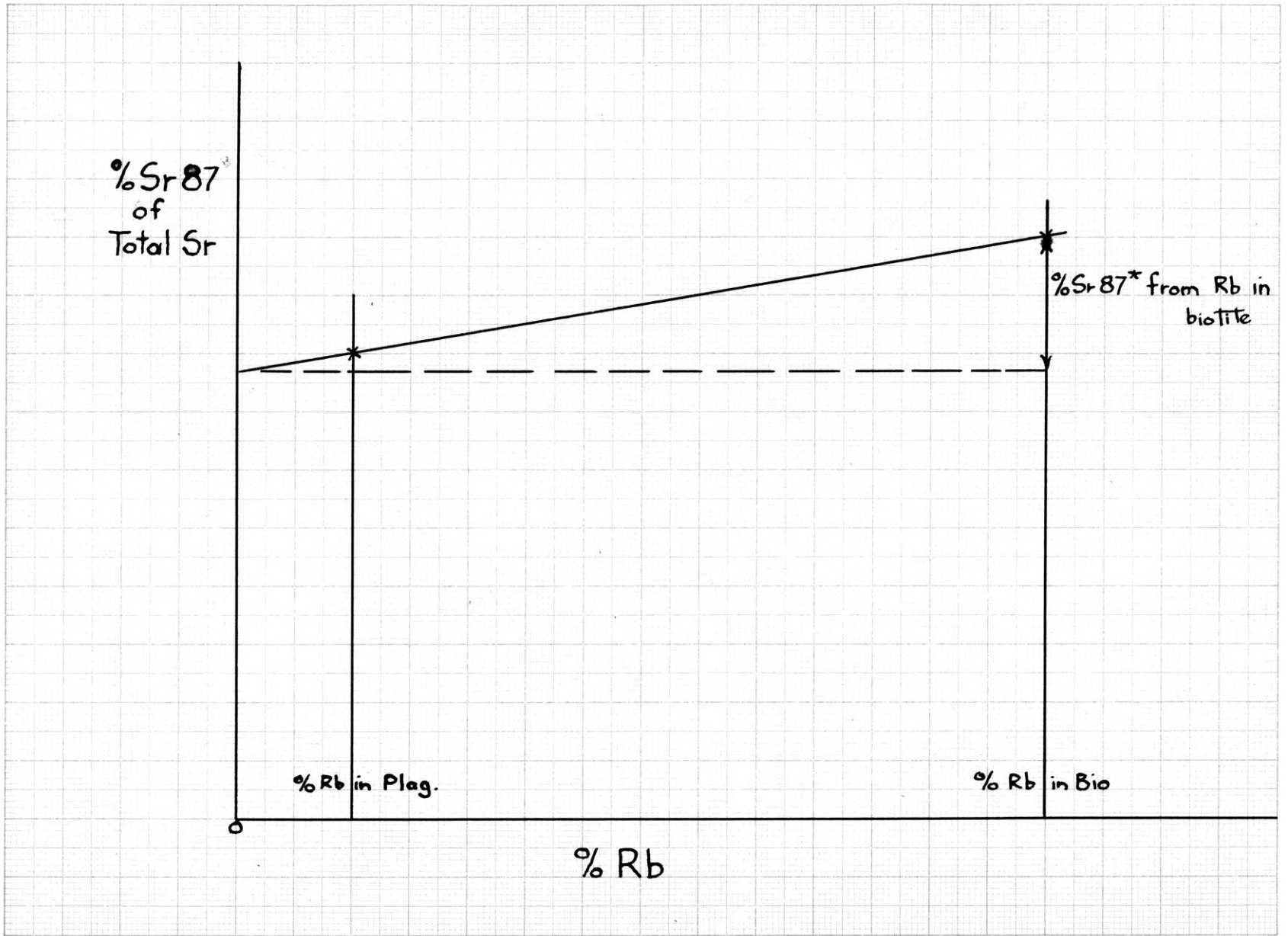
If only biotite is available, an approximate age may
be calculated by assuming some value for the original per-
centage of Sr 87 in the total Sr, possibly 7.0 %.

XII   RECOMMENDATIONS FOR FURTHER RESEARCH

1.   The accuracy of the method of analysing for rubidium in the biotite should be improved.   Changes in the composition of the samples arced, or in the shape or size of the electrodes might be helpful.   A large part of the error is attributed to the wide separation of Rb 7947 and Na 5682 on the plate.   This defect might be avoided by using barium as the internal standard for rubidium as well as for strontium.   Separate analyses for Rb and Sr might still be necessary.   However, it might be possible to measure both elements at once by using barium as a "bridge" to calculate the ratio of Rb/Sr directly.   Ba 4726 is close to Sr 4607, and Ba 7780 is close to Rb 7947.

$$\frac{\% \ Rb}{\% \ Sr} = \frac{Intensity \ Rb \ 7947}{Intensity \ Sr \ 4607}$$

$$\frac{I \ Rb \ 7947}{I \ Sr \ 4607} = \frac{I \ Rb \ 7947}{I \ Ba \ 7780} \ x \ \frac{I \ Ba \ 7780}{I \ Ba \ 4726} \ x \ \frac{I \ Ba \ 4726}{I \ Sr \ 4607}$$

Changes in the value of the ratio I Ba 7780/ I Ba 4726 would compensate any errors introduced by the wide separation of Sr 4607 and Rb 7947 on the plate.

2.   Accurate techniques for measuring the content of Rb and Sr in the plagioclase fraction should be devised.

3.   A more extended study of biotites could be carried out, to provide better information on the Rb : Sr ratio in

biotites from rock types other than granites, and from areas other than North America.

4.   More analyses of hornblendes are needed. The preliminary study suggested that the ratio Rb : Sr might be favourable even though the rubidium content is low, because the strontium content is extremely low. The writer's analyses do not agree well with those of Nockolds and Mitchell (19). Some further checks are desirable. Hornblende might be more suitable than biotite in basic rocks.

XIII   APPENDIX

A.   Lithium and Cesium in the Samples

Table 10 gives Cs_2O and Li_2O contents of the samples.
Many of the analyses are no more than approximations, for
the set of standards did not cover adequately the full
range of concentration of either oxide.

1.   Cesium in the Biotites

According to these analyses the range of Cs_2O content
in biotites from granites is from less than 0.002 % to
0.02 %.   Four samples have less than 0.002 %, 9 between
0.002 and 0.005 %, 5 between 0.005 and 0.01 %, and two be-
tween 0.01 and 0.02 % Cs_2O.   The biotites from two syenites
contain $<$0.002 % and 0.012 % Cs_2O.   Of the 9 biotites from
rocks of intermediate composition, 5 have 0.002 % Cs_2O or
less, and 4 lie between 0.002 and 0.01 %.   In basic rocks,
all the biotites analysed have less than 0.002 % Cs_2O.   The
biotites from two lamprophyres both have less than 0.002 %
Cs_2O.   Micas in pegmatites vary widely in their content of
Cs_2O, from less than 0.002 % to 0.017 %.   The iron-rich
mica, siderophyllite, has about 0.109 % Cs_2O.

In general, biotites having a high content of Rb_2O
have a high content of Cs_2O as well.   Cesium and rubidium
proxy for potassium and hence compete for sites in the
mica structure.   Apparently the presence of large amounts

of one does not tend to exclude the other. Instead, when conditions are such as to give a high concentration of rubidium they are also favourable for admission of large amounts of cesium.

2. Lithium in the Biotites

In biotites from granite the range of Li_2O contents found is from 0.027 % to 0.14 %. Of twenty samples, 7 lie between 0.027 and 0.050 %, 6 between 0.050 and 0.10 %, and 7 between 0.10 and 0.14 % Li_2O. The biotites from two syenites contain 0.117 % and 0.018 %. Of nine biotites from rocks of intermediate composition 6 have between 0.012 % and 0.05 % Li_2O, one between 0.05 % and 0.10 %, and 2 between 0.1 and 0.2 %. Five biotites from basic rocks contain between 0.006 and 0.036 % Li_2O, considerably lower than the range from granites. Some pegmatite micas are rich in Li_2O: the siderophyllite contains about 3 %. Other pegmatite micas range from 0.030 % to 0.32 % Li_2O.

3. Lithium and Cesium in Samples other than Mica

The information in this table on the distribution of these elements elsewhere than in the micas is too fragmentary to warrant discussion.

Table 10

MINOR ELEMENT CONTENTS

Sample	% Cs_2O Triplicates	Average	% Li_2O Triplicates	Average
1			0.037	
			0.034	
	*	<0.002	0.035	0.036
2	*	<0.002	*	~0.018
3	0.0102		0.041	
	0.0099		0.039	
	0.0084	0.0095	0.040	0.040
4			0.050	
			0.050	
	*	~0.005	0.077	0.059
5			0.025	
			0.024	
	*	<0.002	0.016	0.022
6	0.0102		0.150	
	0.0093		0.162	
	0.0085	0.0093	0.114	0.14
7	*	<0.002	**	0.027
8			0.118	
			0.117	
	**	0.012	0.115	0.117
9			0.030	
			0.060	
	*	~0.002	0.050	0.047
10			0.048	
			0.050	
	**	0.008	0.051	0.050
11			0.126	
			0.133	
	**	0.013	0.130	0.130
12			0.110	
			0.118	
	*	~0.003	0.110	0.113
13	*	<0.002	**	0.012

Sample	Cs$_2$O Triplicates	Average	Li$_2$O Triplicates	Average
14			0.12	
			0.116	
	*	~0.003	0.109	0.115
15	*	<0.002	*	~0.018
16			0.059	
			0.057	
	*	<0.002	0.058	0.058
17	0.011		0.0174	
	0.014		0.0183	
	0.015	0.013	0.0170	0.176
18	0.014		0.119	
	0.21		0.123	
	0.016	0.017	0.107	0.116
19			0.101	
			0.099	
	**	0.006	0.094	0.098
20			0.032	
			0.027	
	*	<0.002	0.03	0.030
21			0.105	
			0.099	
	*	~0.003	0.136	0.113
22	0.016		0.029	
	0.013		0.031	
	0.015	0.015	0.037	0.32
23			0.032	
			0.032	
	*	<0.002	0.032	0.032
24	0.013		0.056	
	0.011		0.062	
	0.012	0.012	0.045	0.053
25	*	<0.002	**	~0.02
26			0.078	
			0.079	
	*	~0.003	0.077	0.078
27			0.097	
			0.106	
	**	0.02	0.111	0.105

	Cs_2O		Li_2O	
Sample	Triplicates	Average	Triplicates	Average
28	0.108 0.109 0.110	0.109	*	~3.0
29	*	~0.002	0.080 0.087 0.085	0.084
30	*	~0.002	0.035 0.037 0.035	0.036
31	*	<0.002	*	~0.18
32	*	<0.002	*	0.015
33	*	<0.002	*	~0.006
34	*	~0.006	0.112 0.096 0.109	0.105
35	*	<0.0003	*	~0.007
36	*	<0.0003	*	~0.006
37	*	<0.0003	*	~0.0045
38	*	~0.0003	*	~0.005
39	**	0.01	*	~0.012
40	**	0.008	*	~0.03
41	**	0.005	*	~0.04
42	*	~0.0003	**	~0.018
43	*	~0.0003	**	~0.024
44	*	<0.0001	**	~0.0045
45	*	<0.0001	**	~0.0007
46	*	~0.0002	**	~0.0011
47	*	~0.0005	**	~0.0045
48	*	~0.0003	**	~0.0015
49	*	<0.0001	**	~0.0023

Sample	Cs_2O Triplicates	Average	Li_2O Triplicates	Average
50	**	0.004		0.03
51			0.032 0.024	
	*	~0.002	0.032	0.029
52			0.033 0.042	
	*	~0.003	0.033	0.037
53			0.126 0.133	
	*	0.007	0.130	0.130
54			0.076 0.072 0.059	
	*	~0.002	0.076	0.069
55			0.047 0.042 0.043	
	*	<0.002	0.045	0.044
56			0.047 0.047 0.038	
	*	<0.002	0.056	0.047
57			0.085 0.074 0.090	
	*	~0.006	0.083	0.083
58			0.092 0.12 0.11	
	*	~0.002	0.097	0.105
59			0.071 0.062 0.083	
	*	~0.003	0.083	0.075
60			0.059 0.092 0.073 0.073 0.055	
	*	<0.002	0.092	0.074

	Cs_2O		Li_2O	
Sample	Triplicates	Average	Triplicates	Average
Standard Granite G-1		0.00025		0.0045

* Value estimated by visual comparison of spectra.

** Values taken from extensions of curves derived from standards. The standards chosen did not cover a range wide enough to include all values found, so the curves were projected to give approximate percentages.

*** Minerals were compared with the standard granite G-1 by arcing undiluted and comparing the intensities of the analysis lines to similar lines in the spectrum of the standard granite. For Rb_2O in minerals, G-1 had intensity of 25.9 for content of 0.061 % Rb_2O. For Rb_2O in granites, a similar method was used, with G-1 $\frac{I\ Rb}{I\ Na}$ taken as .433 for 0.061 % Rb_2O, and all granites were diluted with two parts of albite to keep sodium content invariable.

B. Biographical Note

The writer was born at Traynor, Saskatchewan, Canada, on November 19, 1923. He received his early schooling in Saskatchewan and British Columbia. He attended the University of British Columbia from 1942 to 1946 and graduated as Bachelor of Applied Science (Geological Engineering). In the winter of 1947-48 he started graduate studies in geology at McGill University, Montreal, and received the degree Master of Science. Further post-graduate work was started at the Massachusetts Institute of Technology in 1949.

His professional experience has been confined largely to the summer months between sessions at the universities, and includes periods spent in the service of the Geological Survey of Canada, International Mining Corporation, Hedley Mascot Gold Mines, Canadian Explorations, and New Jersey Zinc Explorations Ltd.

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