SOME GEOLOGICAL ASPECTS OF RADIOACTIVITY:

I THE USE OF BIOTITE IN DETERMINATION OF GEOLOGIC AGE BY THE STRONTIUM METHOD

II THE USE OF LEPIDOLITE IN DETERMINATION OF GEOLOGIC AGE BY THE CALCIUM METHOD

III THE POTASSIUM CONTENT OF ULTRAMAFIC ROCKS AND ITS HEAT CONTRIBUTION

by

WALTER HOLYK

B. A. Sc., University of British Columbia

(1949)

SUBMITTED IN PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

(1952)

Signature of Author . . . .
Department of Geology, May 9, 1952

Certified by . . . .
Thesis Supervisor

. . . .
Chairman, Departmental Committee on Graduate Students

Preface

This report is based upon three independent investigations made by the writer during the period of 1951 to 1952 at the Massachusetts Institute of Technology. The writer's original intention was to work only on the rubidium to strontium decay method of age determinations of rocks using biotite. The feasibility of the method could not be assessed until isotope analyses of the strontium were available. Because of the delay in obtaining isotope analyses, the writer decided to investigate two other problems suggested by Dr. L. H. Ahrens that are related to radioactivity and are of current interest. These are concerned with the feasibility of determination of age by the potassium to calcium decay in lepidolites, and the determination of the amount of potassium in ultramafic rocks.

ACKNOWLEDGEMENTS

The writer is especially grateful to Professor L. H. Ahrens for calling attention to the problems and for his help and suggestions throughout all phases of this work.

Information, help, advice, and material were provided by members of the faculty and staff of the Department of Geology, Massachusetts Institute of Technology.

Many people provided samples essential to this investigation. These include Professor G. Kennedy and Professor J. Thompson of Harvard University; Professor H. W. Fairbairn, Dr. W. H. Dennen, Dr. W. H. Pinson, and Dr. F. B. Whiting all of M. I. T.; Mr. L. Nicolaysen of the Carnegie Institution of Washington; and Dr. J. M. Black of the British Columbia Department of Mines.

Miss Mona Franck and the former Miss Margaret Kearns provided welcome assistance in the laboratory.

A research assistantship granted by the Division of Industrial Co-operation, and a tuition scholarship granted by the Massachusetts Institute of Technology enabled the writer to carry on this research.

The willing co-operation of Mr. L. Herzog and Dr. L. T. Aldrich of the Carnegic Institution of Washington, whose work was essential to part of this investigation, is indeed appreciated.

The writer is gratefully indebted to his wife, Helen, for her encouragement and inspiration during the course of this work, as well as for her indefatigable efforts in bringing this report to a final form.

ABSTRACT

I Further investigations, a continuation of work initiated by Dr. F. B. Whiting (M. I. T. dissertation, 1951), were made into the possibility of extending the strontium method of age determination to the common rock forming mineral biotite.

Strontium enriched concentrates of a number of biotites were prepared by a chemical method involving the use of hydroflouric and perchloric acids. These concentrates were submitted for mass spectrographic analysis in order to determine the proportion of radiogenic strontium.

The proportion of radiogenic strontium to total strontium is now available for 32 biotites; the highest proportion reported is 11.9%. These values are combined with the total content of strontium and rubidium as determined by quantitative spectrographic methods to give geologic ages.

The calculated ages of 18 biotites agree within a factor of two with the geologic ages inferred from field relationships. Larger discrepancies exist for the remaining 14 samples. The closest correlation is obtained for samples in which the proportion of radiogenic strontium exceeds 1%. The discrepancies are not entirely random; a systematic error varying with the total strontium content of the biotite appears to be present.

II The possibility of determining geologic ages by the radioactive decay of K^{40} to Ca^{40} was investigated for the mineral lepidolite.

The calcium content of twenty-five lepidolites was determined by a spectrographic method. Calculations based upon the known geologic ages of the samples indicate that radiogenic calcium ought to comprise from 1 to 40% of the total calcium in the samples. No systematic variation of the total calcium content with geologic time is evident. The determination of geologic age by this method will depend upon the ability to determine the amount of radiogenic calcium by isotope analysis.

III Quantitative spectrographic investigations of some fifty ultramafic rocks indicate that published abundance values of potassium in similar rock types are based upon erroneous chemical determinations and consequently must be drastically reduced. This implies a corresponding reduction in the amount of heat that is produced by the radioactive decay of potassium in these rocks.

All dunites contain about $\leq .001\%$ K. Peridotites, serpentinites, and pyroxenites of the primary peridotite suite contain about $\leq .001\%$ K. Ultramafic rocks of the basaltic magma suite generally contain greater amounts of potassium but, nevertheless, significantly less than indicated by Daly's averages.

ABSTRACT

(cont'd)

The new results cast doubt upon the popular theory that the interior of the Earth is similar in chemical composition to the ultramafic rock dunite. Considerations of the distribution of potassium in the earth as well as the present heat conductivity at the earth's surface strengthen the theory that the mantle is similar in composition to the stony meteorites.

The perspiration from the fingers introduces potassium contamination during any form of handling of the carbon electrodes used in spectrographic analysis. Fortunately, this contamination can be entirely eliminated by heating the electrodes to a red heat for half a minute and avoiding further contact with the hands.

TABLE OF CONTENTS

PART I

PART II

PART III

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

PART I

THE USE OF BIOTITE IN DETERMINATION OF GEOLOGIC AGE BY THE STRONTIUM METHOD

INTRODUCTION

This investigation is a continuation of the work initiated by Whiting (1951) upon the use of biotite for the determination of geologic age by means of the radioactive decay of rubidium to strontium.

Whiting prepared and determined the amounts of rubidium and strontium in some 50 biotite samples. The present investigator attempted to carry the work several stages further to the point where actual geologic ages can be calculated.

A knowledge of the amount of radiogenic strontium in each biotite sample is essential to the age calculations. Isotope analyses were determined by Dr. L. T. Aldrich and Mr. L. Herzog of the Carnegie Institution of Washington, Department of Terrestial Magnetism.

Biotite is a very common mineral in both igneous and metamorphic rocks. Consequently the use of biotite for reliable strontium age measurements would indeed be valuable to geologists. It would be possible to determine the time of crystallization of intrusive rocks as well as to determine the period of recrystallization in metamorphic rocks.

CHAPTER I

GENERAL BACKGROUND

Previous Work

The possibility of determining geologic age by utilization of the radioactive decay of rubidium to strontium was suggested by Goldschmidt (1937) and Hahn and Walling (1938). Considerable investigation and discussion has been carried on since then and age measurements on minerals from pegmatites have been determined by the following investigators: Hahn, Mattauch and Ewald (1943) on pollucite; Ishibashi and Ishihara (1942) on lepidolite; Eklund (1946) on microcline; and Ahrens (1947, 1949 and 1950) on lepidolites. Ahrens (1949) concluded that the method was sufficiently reliable for age determination using lepidolites and discussed the possibilities of extending the method to granite biotites.

Whiting (1951) investigated the possibility of using biotite to determine age by the strontium method. He developed a spectrographic procedure for the measurement of the rubidium and strontium content of biotites, and calculated the theoretical amounts of radiogenic strontium that should be present in some fifty biotites by working backward from the estimated geologic ages of the source rocks as determined from field relationships. On the assumption that the lowest limit of the proportion of radiogenic to total strontium that can be determined on the mass spectrograph is 1%, he concluded that the strontium method was feasible for most of the biotites of Palaeozoic and Precambrian age.

In cooperation with Dr. Aldrich of the Carnegie Institution of Washington who determined the amount of radiogenic Sr, Whiting found the age of a Manitoba biotite to be $(1825 \pm 400) \times 10^6$ years. This age was in general agreement with ages obtained by other methods on material obtained in the same area. Isotope analysis was available for just the above sample so that no further age determinations were made by Whiting. His samples were made available to the present writer who made strontium concentrates of the biotites and in most cases checked the accuracy of Whiting's strontium and rubidium determinations. The results of this investigation are presented herein.

Radioactivity of Rubidium

Rubidium consists of two isotopes, Rb^{85} and Rb^{87}. Only Rb^{87} is β active and decays to form Sr^{87}. This radiogenic strontium is herein labelled as Sr^{87*} to avoid confusion with ordinary Sr^{87}. The abundances of Rb^{85} and Rb^{87} are 72.8 and 27.2% respectively (Hahn, Strassman, and Walling, 1937; Hemmendinger and Smythe, 1937; and Nier, 1950).

The radioactive disintegration of Rb can be expressed by the equation for first order reaction

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

where N_0 is the number of atoms originally present, and N is the number of atoms left after time t. In this case N and N_0 refer to number of rubidium atoms, and from the nature of equation (1) can be expressed in % Rb. λ refers to the decay constant of Rb^{87}.

Ahrens (1949) has shown that in the case of Rb the above equation can be simplified to the form

$$N_0 - N = \lambda t N$$ which can be re-stated as

$$\% \, Sr^{87*} = \% \, Rb^{87} . \lambda . \, t \qquad (2)$$

from which $$\text{Age} = \frac{\% \, Sr^{87*}}{\% \, Rb^{87}} \times \frac{1}{\lambda} \qquad (3)$$

The half life of Rb^{87} has been determined by different investigators (Strassmann and Walling, 1938, 6.3×10^{10} years), Eklund, 1946, 5.81×10^{10} years), and (Haxel, et al, 1948, $6.0 \pm 0.6 \times 10^{10}$ years). The value used in this report is assumed to be 5.9×10^{10} years to correspond with that used by Whiting (1951). The period of half life is equal to $0.693/\lambda$.

The value of λ may be substituted in (3) and re-stated to give

$$\text{Age} = \frac{\%\ \text{total Sr}}{\%\ \text{total Rb}} \times \%\ \text{Sr}^{87*}\ \text{of total Sr} \times \frac{8.51 \times 10^{10}}{.272} \qquad (4)$$

CHAPTER II

PREPARATIONS, SPECTROGRAPHIC AND ANALYTICAL TECHNIQUES

Source of Samples

Preparation of Biotite Samples: Most of the biotite samples used in this investigation were prepared by Whiting (1951). His method of preparation is described elsewhere. The same number scheme that was used by him is retained in this report. Biotites in the range from the number 1 to 60 inclusive were prepared by Whiting. Numbers 61 to 69 were prepared by the present writer and their locations and descriptions are shown in Table 1. The biotite samples used for the chemical concentration of strontium are the larger portions of the samples from which spectrographic analyses have been made.

The procedure followed by the writer in the preparation of his samples is fundamentally the same as Whiting's. The rocks were crushed, split in a Jones riffler, screened, and passed through a magnetic separator. The biotite rich product obtained from the separator was seldom pure. However, repetition of the process innumerable times usually gave a fairly pure product. A clean biotite concentrate was finally obtained by repeated pouring of the sample over an elongated piece of cardboard inclined at 45°. Gentle tapping of the cardboard resulted in the rolling of unwanted rounded grains of feldspars and other minerals rapidly down the incline whereas the flat flakes of biotite adhered to the cardboard and lagged behind.

TABLE 1

LOCATION OF SAMPLES

No.	
61	Biotite, from granite #8, Manitoba. Age - Archean. No Impurities.
62	Biotite, from granite #13, Winnipeg River, Manitoba. Age-Archean, No impurities present.
63	Biotite, from Anorthosite, National Lead Co. property, Tahawus, N. Y. Sample collected by Dr. W. H. Dennen from concentrating table of mine plant. Sample arced contained about 1% plagioclase. Age - Grenville.
64	Biotite, very pure from large sheet approximately 4 x 4 inches. Southern Rhodesia. Age 2000 years.
65	Pure biotite, from granite 11, Nova Scotia. Age - Devonian.
66A	Biotite fraction from two mica schist. Gassetts, Vt. Rock is believed to be Precambrian but period of recrystallization may be Ordovician.
66B	Muscovite portion from rock above.
67	Muscovite, from mica quartzite schist, Deer Leap Summit, Rutland, Vt. Age - Precambrian. Period of recrystallization possibly Ordivocian.
68	Biotite, from dark green mica chlorite schist, Sherburne, Vt. Age - Precambrian. Period of recrystallization possibly Ordovician.

Each individual sample was thoroughly mixed and the material required for spectrographic analysis was obtained by coning and quartering of the larger sample. This portion was ground to a powder in a mechanical agate mortar.

Preparation of Feldspar Fractions: Impure feldspar concentrates of the rocks from which some of the biotite samples were obtained were made available to the writer by Whiting. The concentrates were passed through the magnetic separator. Repeated manipulation of the settings of the separator gave fairly pure concentrates of feldspar.

It was highly desirable that a plagioclase portion could be obtained in rocks containing both feldspars. The reasons for this will be given later. It was occasionally possible to get a plagioclase enriched portion in the magnetic portion of the separator when the maximum current of 1.5 amperes was used. Apparently, as suggested by Whiting, grains of magnetite tend to occur with the plagioclase grains more so than with orthoclase. A method for the complete separation of the two feldspars was not devised by the writer.

Portions of the end sample were ground and used for spectrographic analysis. The remainder was used for chemical concentration of Sr.

Utmost care was taken in the preparation of the biotite and feldspar samples to avoid contamination.

Analysis of Biotite for Rubidium

Choice of Method: The method followed in the spectrographic determination of Rb in the biotites was essentially similar to the internal standard method developed by Whiting with but a few minor modifications. Sodium is used as an internal standard and added to the biotite in the form of the standard albite. The validity of this method has been discussed by Whiting, and need not be repeated here. The intensity ratios of Rb 7947 and Na 5682 were used in construction of the working curves and in the determination of the Rb content in the biotites.

Preparation of Samples for Arcing: The biotites were mixed with two parts of standard albite and mixed in an agate mortar for 5 minutes. The material was loaded into 1/8" pure carbon electrodes having a cavity 1.5 mm. in diameter and 4 mm. in depth. Use was made of a special electrode holder described on page 122 in the loading of the electrodes. A much firmer and more uniform pack of the sample could be made by this method. It was found that a very firm pack of these samples inhibits the loss of material during arcing almost completely. The use of the holder also lessens the possibility of contamination from the fingers.

Preparation of Rubidium Standards: The standards prepared by Whiting were available to the writer. These were made by adding RbCl to a base (consisting of 1 part biotite No. 9 and 2 parts of albite) to give a mixture containing .5% RbCl. Successive dilutions of the RbCl mixture with the pure base gave standards containing .5, .25, .125, .0625, and .031% RbCl.

The writer commenced with Whiting's .25% RbCl mixture and diluted this with the pure base (also prepared by Whiting) to give successive standards containing .25, .0833, .0416, .0208, .0104% RbCl.

It may be pointed out at this point that two batches of the base consisting of biotite No. 9 and albite have apparently been made by Whiting, if the notations on the sample bottles were interpreted correctly. The standards prepared by him were made out of the old batch which was exhausted. The present writer made standards from the new batch but started with Whiting's .25% mixture. It is not known which sample was arced by Whiting to determine the intensity ratio of Rb/Na of the pure base. This point is important as it may explain what is believed by the writer to be about a 100% error in Whiting's determination of the Rb_2O content of the pure base used for the standards.

Both sets of rubidium standards were arced.

Spectrographic Settings: A Hilger prism spectrograph, with interchangeable glass and quartz optics, was used. The right end of the plate holder was set at 8600 A using glass optics. Kodak 1-L plates were cut in half to measure 4" x 5" and the half plates were placed at the right end of the plate holder. With these settings Rb 7947 and Na 5682 were recorded about ½ inch from either end of the plate. Half plates were used as an economy measure only. A rotating 8 step sector, with adjacent steps decreasing by a factor of two, was used to give steps varying from 1 to 1/128 of total exposure. In some samples (as marked on plates) the first two steps were omitted. Six spectra were recorded on each plate.

Arcing Technique: The electrodes were preset before each arcing so that the image of the electrodes on the slit housing showed a gap distance of approximately 1¼ inches. This represented an actual gap between the electrodes of approximately ¼ ". The arc was started by drawing a carbon electrode across the gap in such a manner so as to make a contact. The shutter was kept open at all times.

The reason for such a procedure is twofold. It gives the operator a better control of the arc during the first few seconds of arc and thereby ensures a more standard burn for all samples. It also avoids the several second delay between the making of contact, drawing apart of electrodes, and the opening of the shutter. A firm packing of the sample into the electrode eliminated the loss of material almost entirely.

The samples were arced at 3 amperes and a line voltage of 220 volts to alkali completion. The end of the alkali volatilization is marked by a rapid rise of the voltmeter needle to 50 volts from the normal 30 volts.

Developing of Plates: The plates were developed for 4½ minutes in Kodak D-19 developer at 18°C. They were then placed directly into an acid fix and fixed for 20 minutes after clearing. The plates were washed for ½ hour in running water and finally sponged and allowed to dry.

This method was applied to all the plates developed in this investigation.

Determination of Rubidium in Feldspars

Spectrographic Procedure: A total energy method was used in determination of the rubidium content of the feldspars. The standard granite G-1, containing .061% Rb_2O, was used as the standard.

The ground feldspar samples and the G-1 were mixed with 2 parts of carbon, ground in an agate mortar for 5 minutes, and loaded into carbon electrodes having a cavity of 1.5 x 4 mm. The electrode holder already described was used.

Samples were arced to alkali completion at 3 amperes on the Hilger spectrograph. Settings were identical to those described in the section dealing with the Rb determination of biotites. The usual time required for alkali completion averaged 30 seconds.

The samples were arced in duplicate. A duplicate sample of G-1 was arced on every second plate.

Determination of Strontium in Biotites

Method: The method employed for the determination of strontium in the biotites is essentially that developed by Whiting. Only minor modifications of his method were found necessary.

Barium was added as an internal standard and the validity of its use (also see page 38) is discussed by Whiting. The amount of strontium present in the standards and in the unknowns was determined by measuring the intensity ratio of Sr 4607 and Ba 4726.

Preparation of Samples: The pure powdered biotite was mixed with two parts of a carbon powder mixture containing 3% of very pure $BaSO_4$. The latter mixture is the same as used by Whiting in his investigation and was prepared by him. The resulting material was ground in an agate mortar for 5 minutes and placed in a muffle furnace for 3 minutes at 750°C. It was found that heating of the material greatly improved the arcing characteristics.

The samples were loaded into 1/8" electrodes having the standard cavity of 1.5 mm. in diameter and 4 mm. in depth. The electrode holder was used and thereby a very tight and uniform packing of all samples was ensured. Firm packing eliminated almost entirely the loss of material reported by Whiting.

Preparation of Strontium Standards: The writer prepared new standards for the determination of Sr. The same biotite (No. 50) as used by Whiting was chosen as the base. Pure SrO was added to the base to give a mixture containing .0975% SrO. This mixture was thoroughly ground in the agate mortar. Successive dilutions, as already described elsewhere, gave standards containing .0975, .0487, .0224, .0122, .0061, and .0051% SrO. Two parts of the carbon mixture containing 3% $BaSO_4$ was added to one part of each sample. The same procedure as described above was followed in loading the samples.

Spectrographic Settings: The Hilger spectrograph already described was employed. Glass optics were used with the right end of the plate holder set at 5500 Angstroms.

The sensitivity of the Kodak 1-L plates in stock was considerably greater than of those used by Whiting. More will be said about the variation of sensitivity of 1-L plates in the discussion of K analysis in ultramafics in another part of this report. The greater sensitivity of the plates prevented the writer from following identical procedures described by Whiting.

Preliminary work showed that a slit width of 6 as recommended by the previous investigator made the Sr 4607 line too intense to be measurable on the photometer. The intensity was partly reduced by a slit width setting of 5.

It was also found that the method of superimposing one sample upon another on the same spectrum could not be used because the greater sensitivity gave far too dense a background and Sr 4607 line. Consequently, only one sample was arced per spectrum.

A rotating step sector was used and gave 8 steps decreasing by a factor of 2 covering the range between 1 and 1/128 of total exposure. Six spectra were recorded on each plate. The standard procedure of developing was used.

Arcing Technique: The electrodes were preset and the arc started in the manner described under the section of rubidium analysis. The arc was commenced at 3 amperes and after 5 seconds the current was increased to 6 amps. No material was lost from the electrodes by this method. The practice of pre-arcing the samples for several seconds as reported by Whiting was found unnecessary and hence not employed.

Volatilization tests showed that the completion of Sr and Ca volatilization coincided with a flick of the voltmeter needle which hovered steadily around 50 volts following the alkali completion. The time required depended upon the sample and varied from 18-35 seconds.

Determination of Strontium in Feldspars

Spectrographic Procedure: A total energy method with G-1 as the standard was used for the determination of strontium in the feldspars. G-1 contains ~.02% SrO. The same samples that were prepared for Rb analysis were used to determine the strontium content.

The samples were loaded into standard 1/8 inch electrodes and arced in duplicate. Duplicate samples of G-1 were arced on every second plate.

The settings on the Hilger spectrograph were identical to those described above for the biotite procedure. The method of presetting the electrodes and commencing the arc were also similar.

The samples were arced at 3 amperes until the completion of the calcium. This was indicated by the disappearance of the yellow calcium flame and appearance of a greenish flame after about 1½ minutes of arcing.

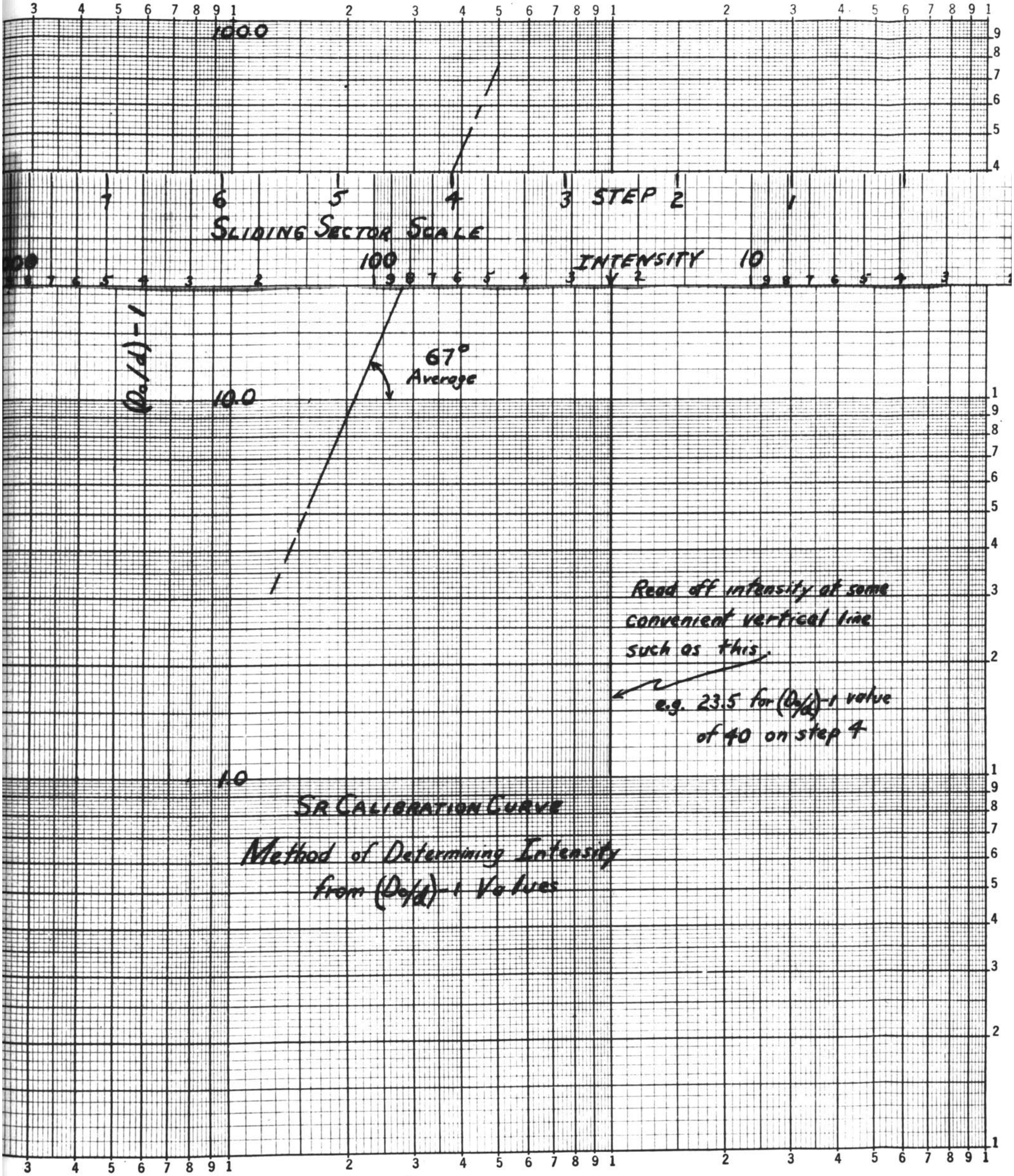
Calculations

General: All measurements of the line densities were obtained on a Hilger non-recording photometer. Galvonometer deflections were obtained for as many steps as possible for each line measured. The values were divided into 50 to give d_o/d values where d_o equals 50 (the deflection for clear glass) and d is the galvonometer deflection of the analysis line.

Rubidium Calculations: The method used in determining the intensities of the Rb in the feldspar and biotite is fairly standard practice although strictly speaking, not entirely accurate. Photometric readings were obtained at the steps which gave deflections between 1 and 15 where possible so that the resulting d_o/d values fell on the straight line portion of the plate calibration curve (see below). The constancy of the slope of the straight line portion was established by obtaining d_o/d values for adjacent sectors from different plates. The d_o/d values were plotted on log log paper against a linear horizontal plot of the step number. A straight line was drawn through the plot of d_o/d against sector number at the predetermined angle. This method is permissible if the deflections obtained fall in the above range without introducing any significant error. The intensities of the lines were recorded by measuring the values on a reversed log log scale at some convenient level.

A similar procedure was used for determining the intensities of the strontium in the feldspars.

FIGURE 1



Read off intensity at some convenient vertical line such as this.

e.g. 23.5 for (Do/d)-1 value of 40 on step 4

SR CALIBRATION CURVE

Method of Determining Intensity from (Do/d)-1 Values

Strontium Calculations: The intensity of the background in the biotite Sr plates was fairly large and hence a background correction was necessary. Values of d_o/d were obtained for as many steps as possible for both the background and Sr and Ba lines on several different plates. Values of $(d_o/d) - 1$ were combined on log log paper to give a calibration curve for the plates. It was found that the same calibration curve was more or less applicable for both the lines and the background on all the plates. The straight line portion of the curve had invariably the same slope for all plates. $(d_o/d) - 1$ values were plotted as this eliminates the drastic toe in the calibration curve obtained by plotting d_o/d values alone.

Deflections were recorded where possible for those steps which gave $(d_o/d) - 1$ values falling on the straight line portion of the calibration curve. Similar deflections were recorded for background. A reversed log log scale with the sectors marked on it was used to determine the intensities. The number of the step for which the deflection was made was placed on the $(d_o/d) - 1$ value as read on the calibration curve and the corresponding intensity was read off at a convenient vertical line. Reference to Figure 1 will make this operation clear.

The deflections for the background were recorded only on one side of the line at a constant position for all spectra measured. Rather than measure the deflection for the background at the step at which the deflection of the line was measured it was decided to measure the deflection at the same relative position in a more intense step where the $(d_o/d) - 1$ value would fall on the straight line portion

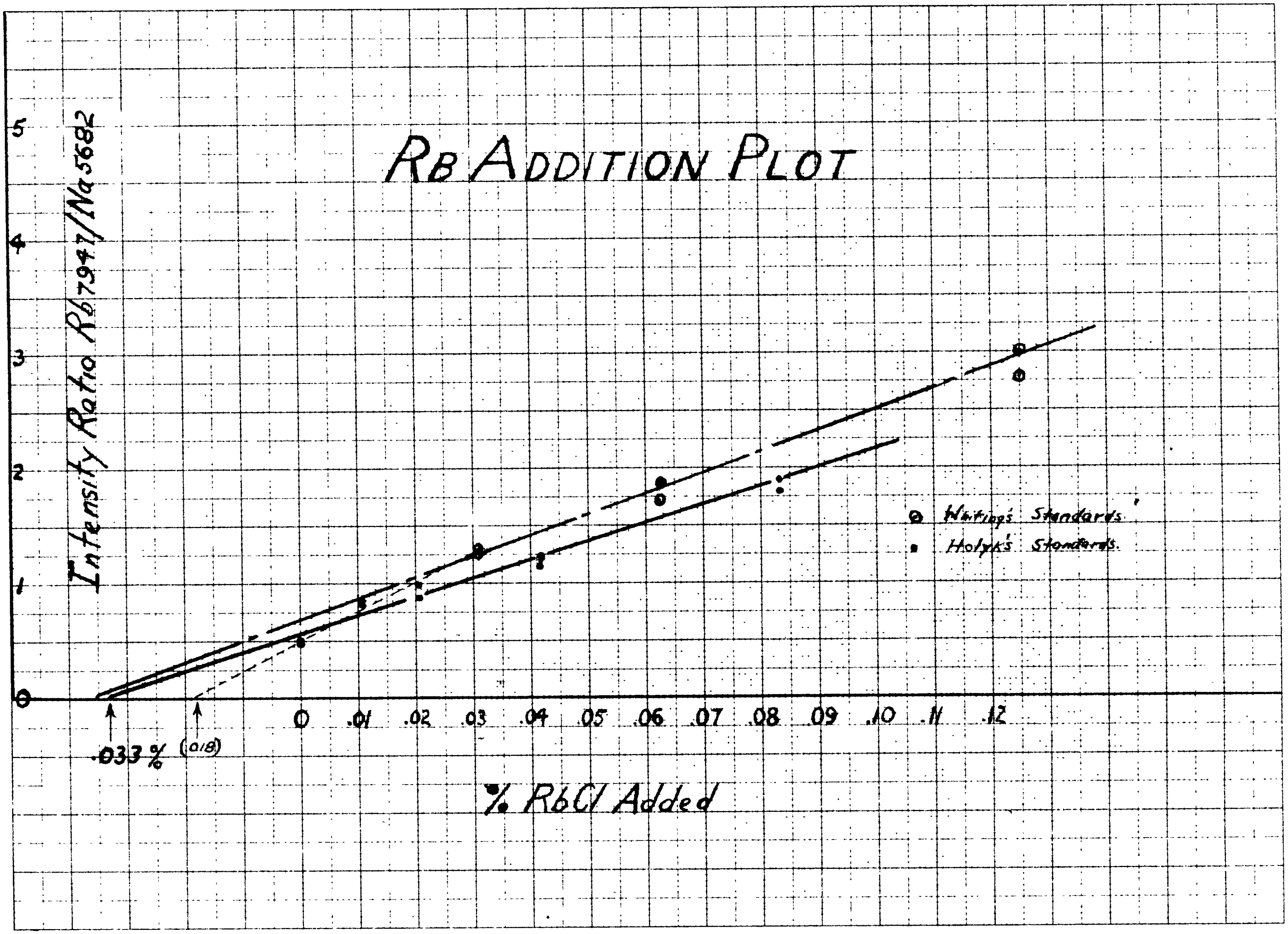
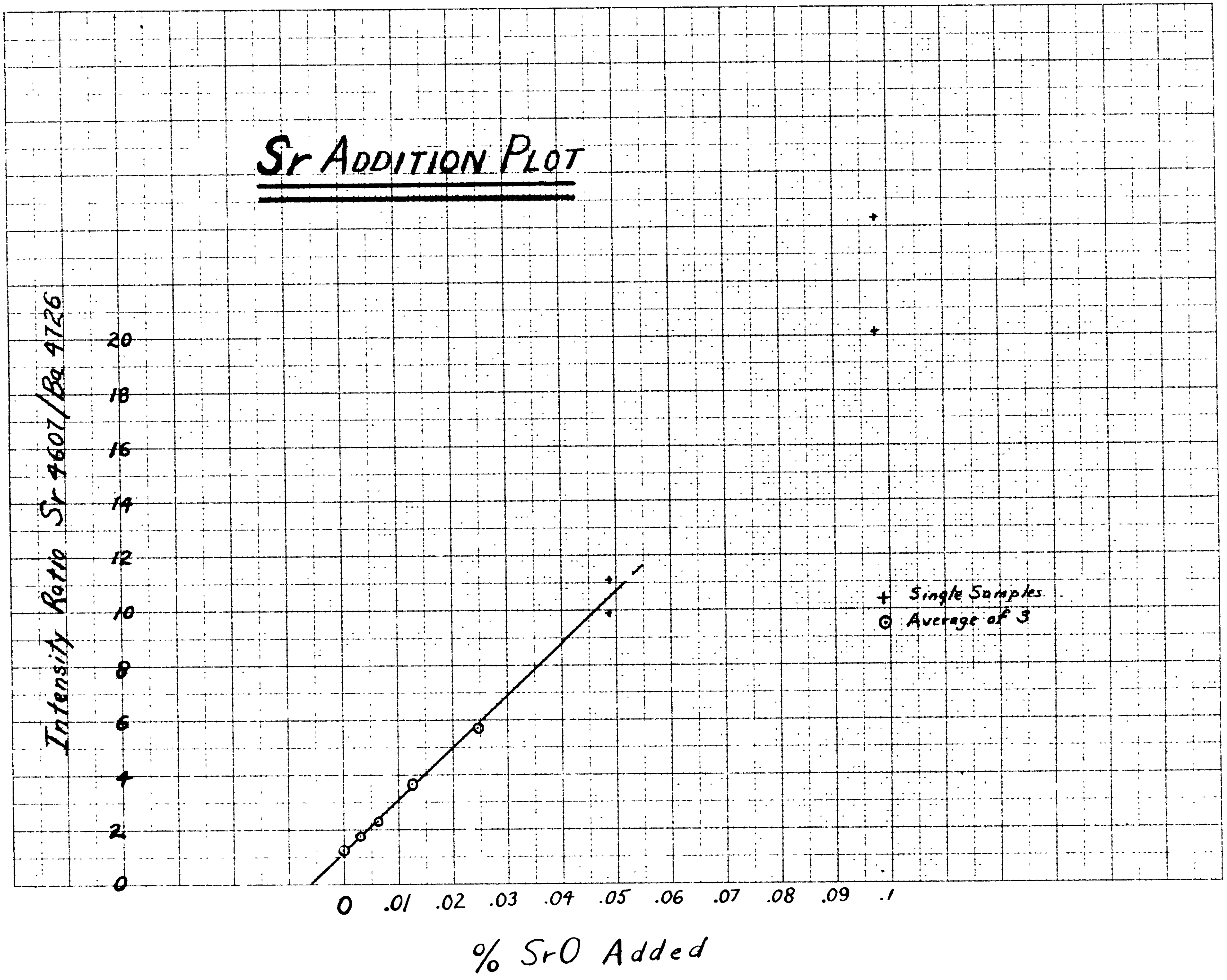

RB ADDITION PLOT
Intensity Ratio Rb 7947/Na 5682
0
1
2
3
4
5
0
.01
.02
.03
.04
.05
.06
.07
.08
.09
.10
.11
.12
.033 %
(.018)
% RbCl Added
Waring's Standards
Holyk's Standards.

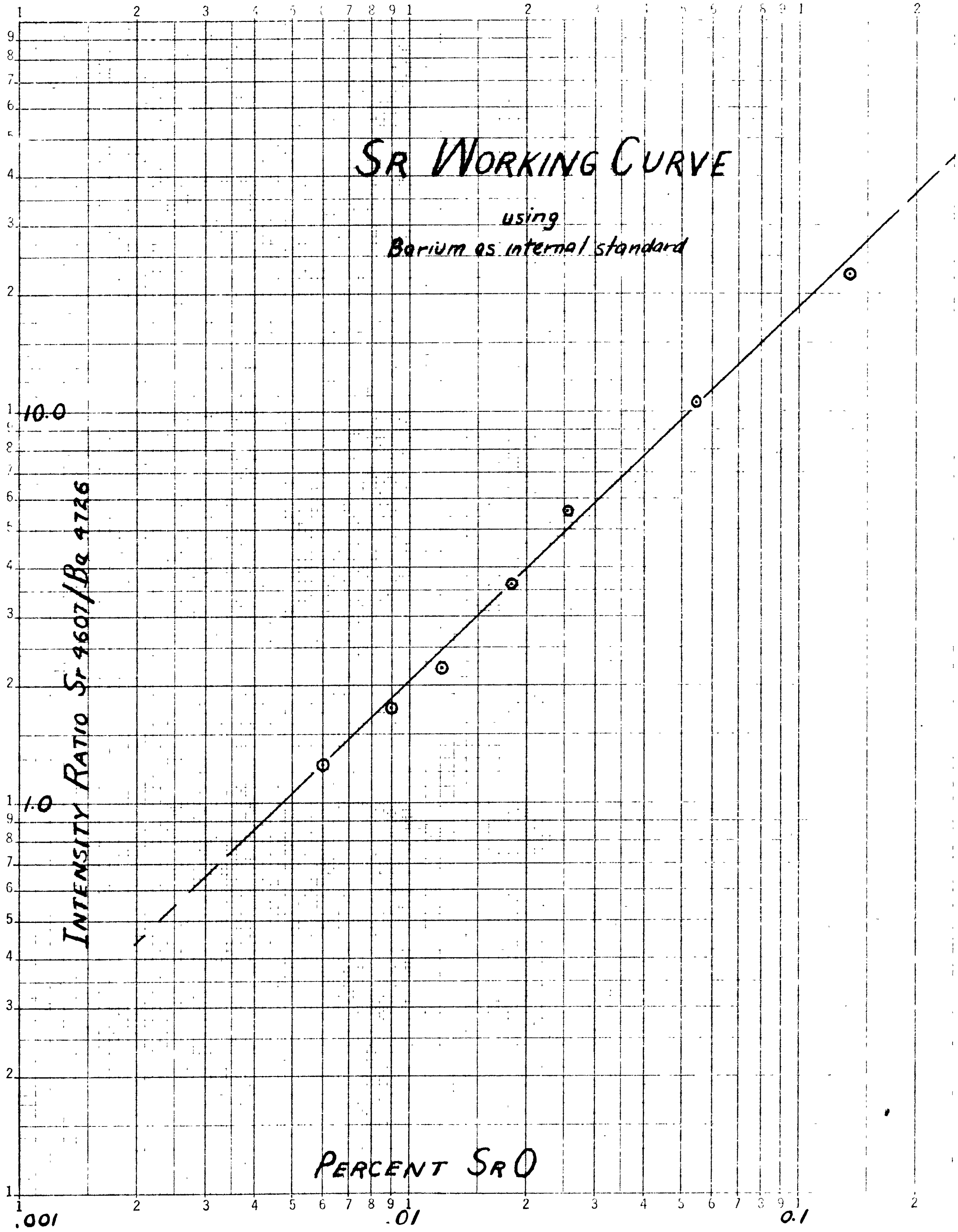
FIGURE 2



Sr ADDITION PLOT

FIGURE 3

FIGURE 4


SR WORKING CURVE
using
Barium as internal standard
INTENSITY RATIO Sr 4607/Ba 4726
10.0
1.0
PERCENT SRO
.001
.01
0.1
MADE IN U.S.A.

of the calibration curve. This would eliminate drastic background corrections which resulted whenever the deflection for background approached that for clear glass.

Addition Plots: Figures 2 and 3 show the addition plots for rubidium and strontium in biotites. They are obtained by plotting the intensity ratios of the analysis lines against the percentage of material added on linear graph paper. Extrapolation of the line to zero intensity indicates the amount of the analysis element present in the pure sample.

Single Point Working Curves: The single point working curves for the determination of Sr and Rb in the feldspars were obtained by drawing a straight line at a slope of 45° through the point represented by the average intensity of the analysis line plotted against the % SrO or % Rb_2O in the standard granite. The amounts of Sr or Rb in the unknown samples were obtained by reading off the percentage vertically below the point at which the intensity of the analysis element in the sample intersects the working curve.

Working Curves: The working curve for the strontium determination is presented in Figure 4. The curve was constructed by re-plotting the intensity ratio of Sr 4607/Ba 4726 against the amount of SrO present. The amount of SrO present was determined by adding the equivalent amount of SrO originally present in the base to the amount of SrO added in the preparation of the standards.

The working curve for Rb was constructed in a similar manner. The RbCl was converted to an equivalent amount of Rb_2O.

The percentage of either material in the unknown samples is determined by applying the calculated intensity ratio to the curve. The percentage is read off vertically below the intersection of the intensity ratio level and the working curve.

Chemical Concentration of Strontium

Method: The writer employed a procedure essentially similar to that described by Ahrens (1951) in the chemical concentration of strontium. The method is based upon different reactions taking place during thermal decomposition of the perchlorates of the metals present in the silicates (see Marwin and Woolaver, 1945).

The silicate is decomposed with mixed hydroflouric-perchloric acid and evaporated to dryness. The silicon is lost as SiF_4 and the excess acid removed by fuming. The dried residue consists of the perchlorates of the elements contained in the silicate.

The perchlorates are ignited to 550° in a muffle furnace. The perchlorates of Mg, Fe, and Al are converted into their corresponding oxides. The alkali metal perchlorates decompose to form chlorides. The alkaline earth perchlorates (including Sr) form mainly chlorides although some oxide may form.

The chlorides are extracted with warm water whereas the insoluble oxides remain as residue. If any iron has escaped conversion to the oxide it may be precipitated at this point with ammonium hydroxide. The excess ammonia must be removed by ignition before further steps in separation be taken.

Perchloric acid is added to the chloride water extract and again taken to dryness. This converts the alkalis and alkaline earths back to perchlorates.

The evaporate is dissolved in anhydrous ethyl alcohol. The perchlorates of K, Rb, and Cs are sparingly soluble and are separated from the Ca, Sr, Na, and Li perchlorates which remain in the extract.

The alcohol solution is evaporated and the evaporate is ignited. The perchlorates of Ca, Sr, Na, and Li are thereby again converted into chlorides.

The chemical concentrate at this point consists mainly of the chlorides of calcium, sodium and lithium and strontium. The concentration of the biotite and feldspar samples was not carried beyond this point.

The concentrates of two biotite samples can be prepared in one day. A greater number can be prepared by having a larger number of samples in different stages of completion and thereby avoiding loss of time during the lengthy periods of evaporation to dryness.

Experimental Procedure: Only limited amounts of the biotite samples analyzed by Whiting were available to the writer. Consequently most of the strontium concentrates were made from about 3 grams of material. Five gram portions were concentrated when available.

Thirty c. c. of HF and 10 c. c. $HClO_4$ were added to 5 grams of biotite in a platinum crucible. The solution was taken to dryness on a hot plate. A wire gauze between the crucible and hot plate eliminated any spattering of the solution which would have otherwise resulted. About 30 c. c. of H. F. was added to the dried residue and the solution was again evaporated to dryness.

The dried residue was leached with 25 c. c. distilled H_2O. The solution was kept warm on a hot plate and all lumps were broken up. The solution was filtered and washed once with 20 c. c. of water. The residue contained the Fe, Al, and Mg perchlorates.
Occasionally it was observed that some Fe may be present in the

extract as indicated by the brownish colour of the solution. When present, the solution was acidified with several drops of HCl, and the Fe was precipitated by the addition of NH_4OH. The resulting $Fe(OH)_3$ was removed by filtering. The extract was evaporated to dryness and ignited to 400°C to remove the excess ammonium hydroxide and decompose the ammonium salts. It was found that all traces of ammonium had to be removed prior to the addition of $HClO_4$. If this was not done then ammonium perchlorate formed by later procedures would decompose explosively upon ignition and invariably cause the loss of the complete sample.

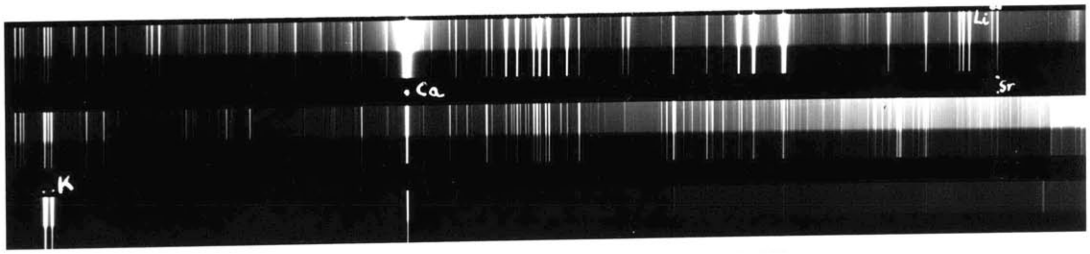
Upon elimination of all traces of ammonia, 20 c. c. of water and 5 c. c. of $HClO_4$ were added to the residue and the mixture was evaporated to dryness. All traces of free perchloric acid were removed by playing a bunsen flame on the inside of the evaporating dishes.

The residue was extracted with 25 c. c. of anhydrous ethyl alcohol. Any lumps were broken in an agate mortar. The solution was filtered. The residue theoretically contained the K, Rb, and Cs. perchlorates whereas the extract contained Sr, Ca, Li, Na and probably a little Fe and Al perchlorates.

The alcohol extract was evaporated to dryness. The evaporate was ignited to 550°C to convert the perchlorates to chlorides. Concentration of the Sr was terminated at this point and the samples were submitted for mass spectrographic analysis of strontium.

The final concentrate generally consisted of several milligrams of material and often occurred only as a coating upon walls of the crucible used in evaporation. Larger concentrates were obtained when

PLATE 1



Chemical Concentrates of Biotite #1

a. "Sr - Ca - Li" concentrate

b. "Al - Mg - Fe" concentrate

c. "K" concentrate

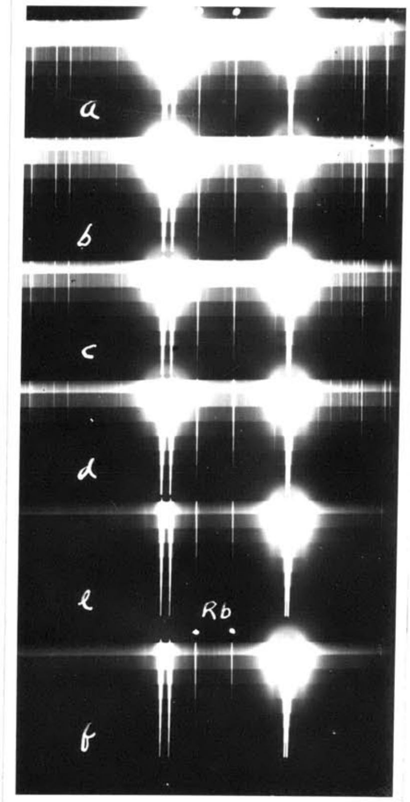
larger amounts of the biotite sample were available.

The procedure described above was also followed for making feldspar concentrates. The NH_4OH stage was omitted because of no iron interference.

Efficiency of Method: All the different steps discussed in the chemical concentration of strontium were verified by spectrochemical analysis of the different residues. The strontium shows a definite enrichment in the theoretical strontium concentrate in comparison to the earlier rejects in which it is absent.

Plate 1 illustrates the extent to which the separation of the elements have been made in the various stages described above.

PLATE 2



COMPARISON OF BIOTITE BASE WITH STANDARD GRANITE

a, b - Standard Granite G - 1

c, d - Base (Biotite 9 2 parts Albite)

e, f - Standard Albite

CHAPTER III

ANALYTICAL RESULTS AND DISCUSSIONS

Rubidium Content of Biotites

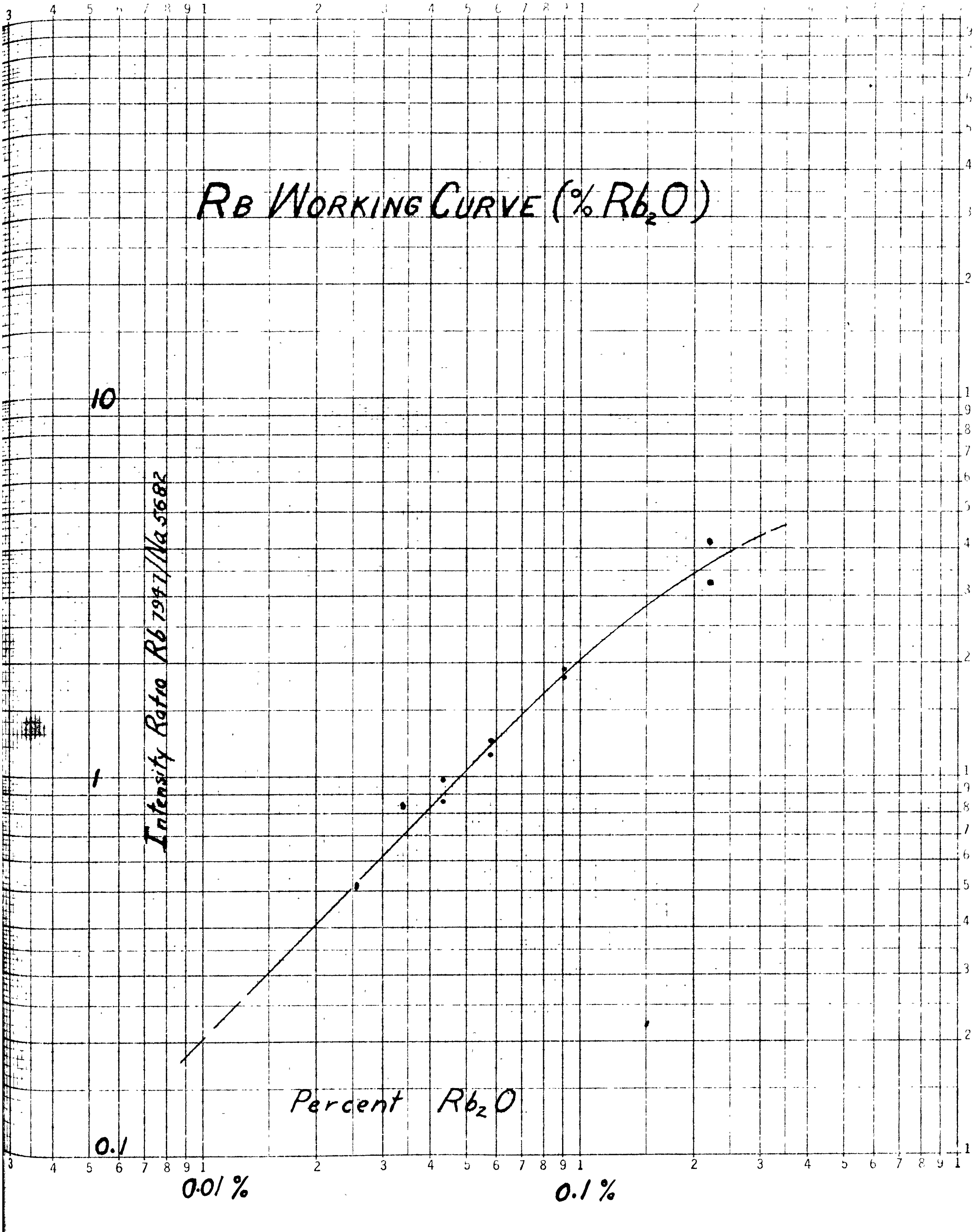
Discussion of Addition Plot: The plot of the intensity ratios of Rb/Na versus the amount of RbCl added to the base shows two distinctly different graphs for the two sets of standards arced. This discrepancy may have its explanation in the apparent fact that two different batches of the base of biotite 9 plus two parts albite were prepared by Whiting. This was discussed in an earlier section. It would appear that the old batch had a slightly higher Rb_2O content. It is not known which mixture Whiting used to establish the intensity ratio of Rb/Na in the pure base.

The extrapolation of the curve to zero intensity gives the equivalent of .033% RbCl originally present in the base (see Figure 2). A similar or higher value would be obtained by extrapolation of the curve obtained from Whiting's standards. This value of RbCl equals .026% Rb_2O.

The extrapolation of the dashed line in Figure 2 to zero intensity indicates the equivalent of .018% RbCl present in the base. These may be the two identical points that Whiting joined in his addition plot to obtain a value of .017% RbCl originally present.

The new base used in preparation of the standards was arced in duplicate in conjunction with a duplicate sample of G-1. Spectra of the two samples are illustrated in Plate 2 for comparison. A single point working curve method indicated .027% Rb_2O in the base on the

FIGURE 5


RB WORKING CURVE (% Rb_2O)
Intensity Ratio Rb 7947/Na 5682
10
1
0.1
Percent Rb_2O
0.01 %
0.1 %

basis that G-1 contains .061% Rb_2O. This is very similar to the value of .026% Rb_2O obtained by the addition method.

On the basis of the two independent results, the value of .026% Rb_2O in the base (consisting of 1 part biotite 9 and 2 parts albite) is considered by the writer to be more accurate than Whiting's results.

A duplicate sample of the standard albite used for dilution with biotite was arced in conjunction with G-1. The albite was found to contain .0045% Rb_2O. All samples arced consisted of one part biotite and two parts albite, and hence it follows that the albite contributes .003% Rb_2O to each sample.

Abundance of Rb_2O in Biotites: The intensity ratios of Rb/Na were applied to the working curve shown in Figure 5 and the percentages of Rb_2O in the samples were read off on the horizontal scale. These values represent the Rb_2O content of biotite mixed with two parts of albite alone. One final correction was made. The value of .003% was subtracted from each of the products to give the final percentage of Rb_2O in the biotite. The amount of .003% was already shown to be the amount of Rb_2O contributed to the mixture by the standard albite.

The values of Rb_2O obtained for the various samples analyzed are presented in Table 2. Whiting's results for the same sample are presented for comparison.

TABLE 2

RUBIDIUM IN BIOTITES

No.	% Rb_2O	% Rb_2O (Using Whiting's Intensity Ratios but Writer's working Curve)	% Rb_2O (Whiting's Results)
1	.083	.075	.047
5	.048	.057	.037
6	-	.231	.15
7	.114	.108	.076
8	-	.237	.17
9	.075	.060	.039
11	-	.210	.141
12	.126	.141	.089
13	.072	.097	.061
14	.219	.327	.22
15	.076	.072	.047
16	-	.183	.118
18	.357	.341	.25
19	.187	.222	.144
20	-	.189	.12
21	-	.342	.255
23	.110	.109	.074
26	.207	.312	.25
27	.204	.273	.188
29	-	.132	.089

TABLE 2 (cont'd)

RUBIDIUM IN BIOTITES
(continued)

No.	% Rb_2O	% Rb_2O (Using Whiting's Intensity Ratios but Writer's Working Curve)	% Rb_2O (Whiting's Results)
30	.111	.120	.077
39	.193	.201	.130
50	.102	.063	.059
51	.163	.135	.085
53	.177	.144	.113
56	.141	.130	.088
60	.129	.117	.073
61	.129		
62	.039		
63	.087		
64	.144		
65	.203		
66 Bi	.125		
66 Musc	.030		
67	.054		
68	.085		

TABLE 3

STRONTIUM IN BIOTITES

No.	% SrO (Internal Standard Method)	% SrO (Total Energy Method)	% SrO (Whiting's Results)
1	.016	.013	.0136
5	.022	.018	.0161
6	-	-	.0119
7	.010	.009	.0104
8	-	-	.0073
9	.017	.012	.0144
11	-	-	.0063
12	.014	.018	.0165
13	.071	.081	0.1
14	.004	.004	.0064
15	.017	.019	.0159
16	-	-	.0151
18	.013	.020	.0124
19	.016	.016	.0144
20	-	-	.0093
21	-	-	.0079
23	.012	.015	.0129
26	.003	.0034	.0068
27	.004	.004	.0082
29	-	-	.0064

TABLE 3 (cont'd)

STRONTIUM IN BIOTITES
(continued)

No.	% SrO (Internal Standard Method)	% SrO (Total Energy Method)	% SrO (Whiting's Results)
30	.010	.010	.0106
39	.020	.024	.0161
50	.006	.008	.0085
51	.011	.007	.0101
53	.003	.002	.0064
56	.004	.005	.0073
60	-	-	.0035
61	.005	.004	-
62	.014	.007	-
63	.037	.039	-
64	.001	.0014	-
65	.002	.0013	-
66 Bi.	.005	.005	-
66 Musc.	.055	.034	-
67	.024	.018	-
68	.012	.011	-

Strontium Content of Biotites

Abundance of SrO using Internal Standards: An addition plot of the intensity ratios of Sr/Ba versus the amount of SrO added indicates .006% SrO present in biotite 50 (See Figure 3). This is somewhat lower than the value of .0085% SrO reported by Whiting.

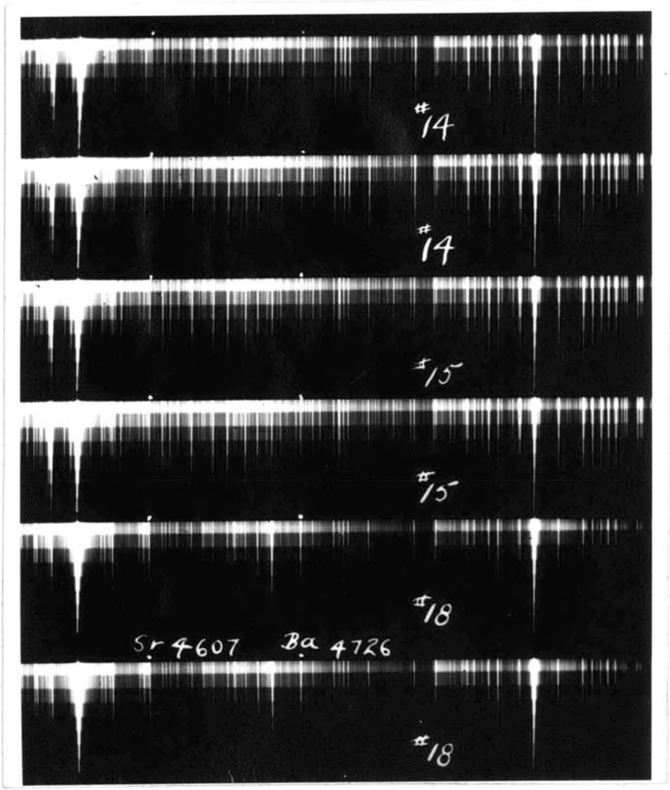
The percentages of SrO found in the biotites arced are shown in Table 3. Whiting's results are also included for comparison.

The Validity of using Barium as an Internal Standard: Some doubt is held by the writer concerning the validity of the use of barium as an internal standard for the determination of strontium in biotites. Whiting developed his method on the basis that the variation of barium content within the biotites was insignificant in comparison to the 3% $BaSO_4$ mixture added. Reference was made by him to the range of 0.1 to 0.8% barium in biotites of Caledonian rocks investigated by Nockolds and Mitchell (1948).

The addition of 2 parts of carbon containing 3% $BaSO_4$ to one part of biotite would give a mixture containing from 1.2 to 1.4% barium on the assumption that the barium content of the biotites lies in the range of 0.1 to 0.8%. This range is small and perhaps may be disregarded, but it does introduce a deviation of 15%.

It seems, however, an unwarranted step to extend the variation of barium within the Caledonian igneous rocks to all the biotites in this investigation. Barium has an ionic radius of 1.43A and is readily caught up in potassium minerals chiefly orthoclase, biotite, and muscovite. According to Rankama and Sahama (1950) up to 9% Ba

PLATE 3



VARIATION OF INTENSITY OF BARIUM

Spectra of 3 mica samples showing variation of Barium Intensity. Note that the barium intensity of sample 18 is at least twice that of samples 14 and 15.

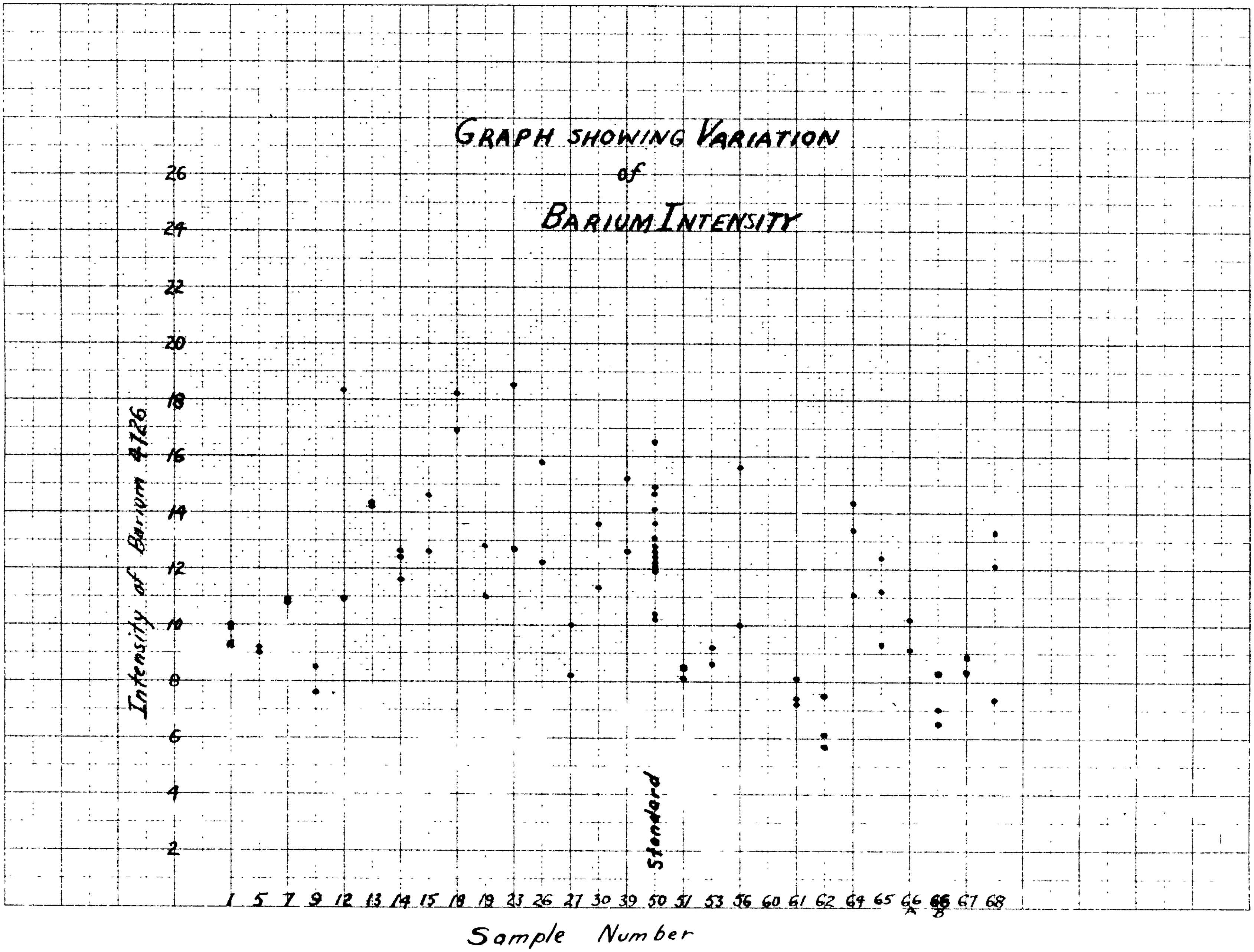

GRAPH SHOWING VARIATION of BARIUM INTENSITY

FIGURE 6

can occur in barian muscovite and as much as 6.16% Ba is contained in barian biotites. The bulk of barium is held in biotite in diorites, and in biotite and potash feldspars in alkaline rocks. In view of this possible variation one may question the validity of the method used by Whiting.

Examination of both Whiting's and the present writer's plates show a rather poor reproducibility of Ba 4726 from sample to sample. This can be observed visually as well as determined by photometer measurements. The intensity of the strongest Ba line seen in any samples is about 3 times that of the weakest sample. This variation may also be observed on the same plate (see Plate 3) and hence cannot be attributed entirely to procedure. A much better reproducibility, however, is evident for arcings of the same sample. It must be pointed out that sample 18 shown on Plate 3 is a phlogopite.

The extent of the poor reproducibility is shown in Figure 6. It is seen that the intensities of Ba 4726 are reasonably similar in the different arcings of the base (No. 50) and also in the duplicate or triplicate arcings of other samples. The intensities from sample to sample, on the other hand, vary considerably. For instance, the intensity of the barium line of sample 18 is 3 times that of sample 62. This variation seems to be rather high to be attributed to procedure and may very well be inherent in the samples themselves. Actual determination of the barium in the biotites would seem in order before the use of it as an internal standard is justified.

FIGURE 7

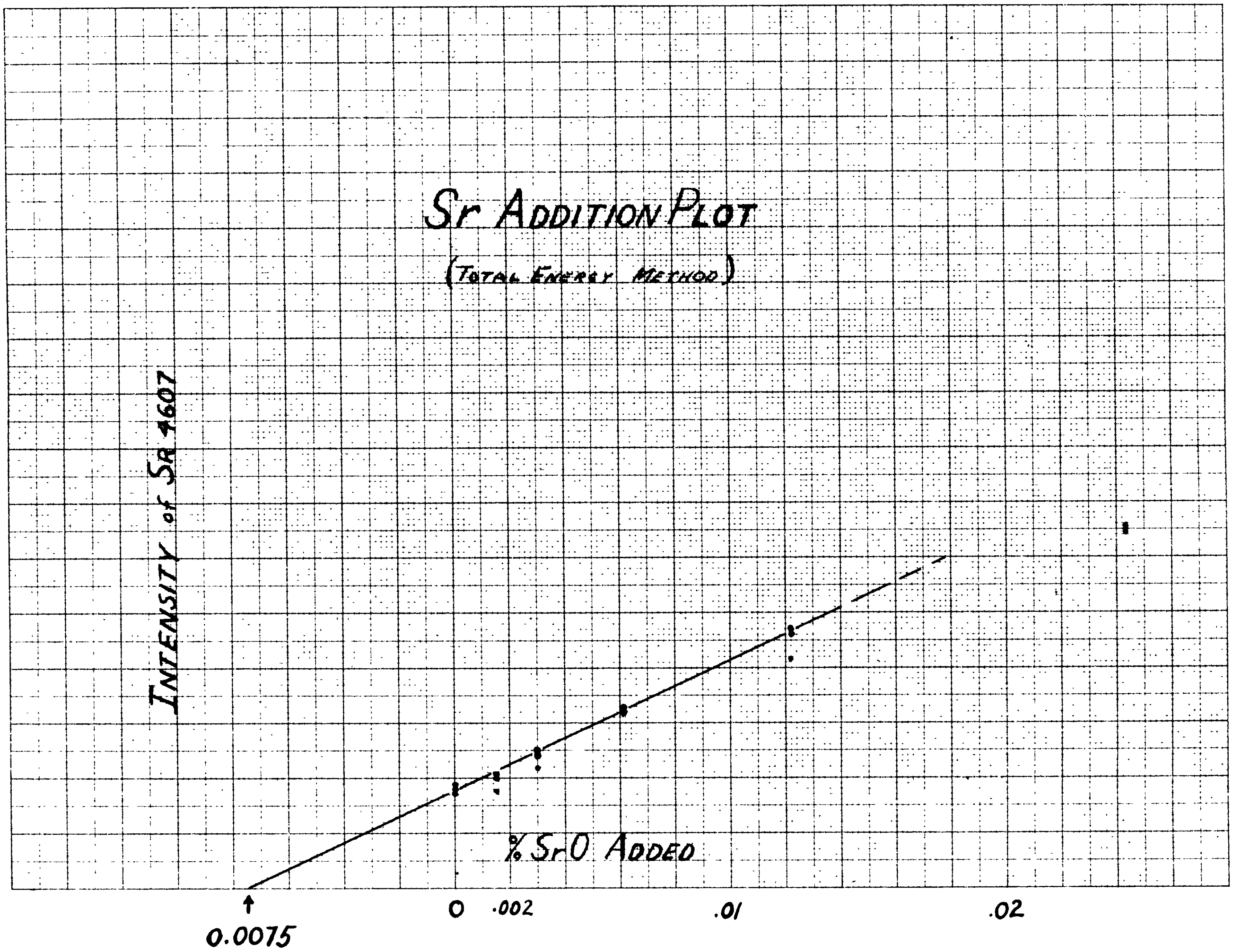

Sr ADDITION PLOT
(TOTAL ENERGY METHOD)
INTENSITY of SR 4607
% SrO ADDED
0.0075
0
.002
.01
.02

FIGURE 7a

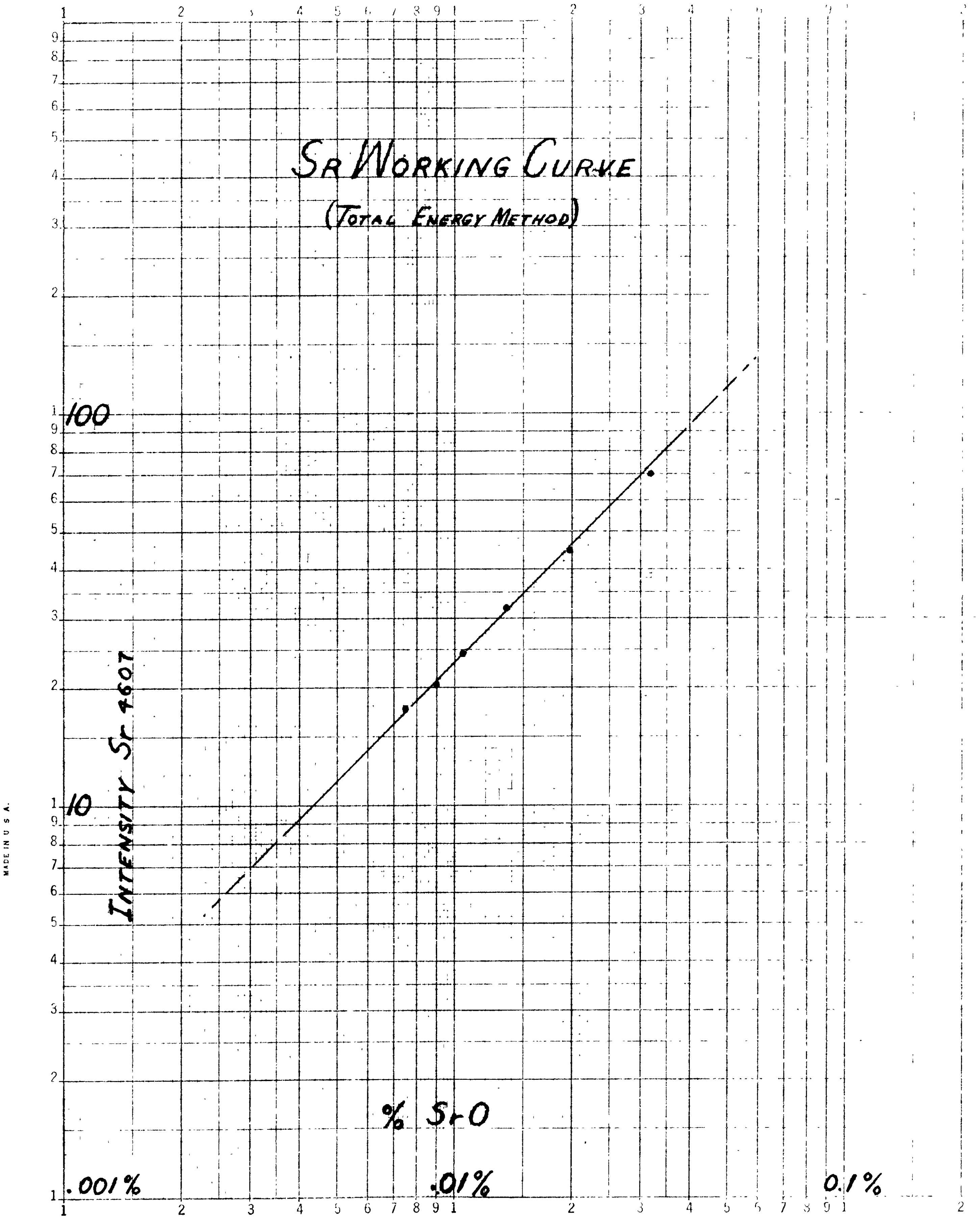

Sr Working Curve
(Total Energy Method)
100
10
Intensity Sr 4607
% SrO
.001%
.01%
0.1%
MADE IN U.S.A.

TABLE 4

STRONTIUM AND RUBIDIUM IN FELDSPAR FRACTIONS

Sample	% SrO	% Rb_2O
1	.033	Tr
5	.07	.04
6	.031	.048
7	.044	Tr
8	.165	.12
9	.040	.018
11	.006	.105
12	.042	.017
14	.052	.058
15	.093	.011
19	.021	.043
21	.019	.075
23	.044	.003
26	.019	.071
27	.020	.060
30	.046	Tr
31	.021	.019
40	.031	Tr
41	.061	.056
51	.018	.0045

TABLE 4

(continued)

Sample	% SrO	% Rb_2O
52	.019	.055
53	.009	.047
62	.0007	.049
63	.068	Tr
65	.014	.01
68	.006	Tr

TABLE 5

CALCULATED GEOLOGIC AGES

No.	Percentage (Sr87* of Total Sr)	Age x 10^6 Years (Internal Standard Method)	Age x 10^6 Years (Total Energy Method)	Age x 10^6 Years (Whiting's Results)	Age x 10^6 Years (Geologic)
1	6.8	3800	3100	5700	1000
5	1.67	2200	1750	2000	300
6	.44			100	100
7	.79	200	170	280	110
8	.15			20	270
9	.17	110	75	110	1000
11	1.19			150	240
12	.46	150	190	180	200
13	0	0 - 280	0 - 320	0 - 560	50
14	1.14	60	60	95	900
15	.4	260	290	400	240
16	.79			290	900
18	6.1	650	990	870	900
19	.42	105	105	120	900
20	.45			100	280
21	1.89			170	210
23	1.18	375	470	590	900

TABLE 5 (cont'd)

CALCULATED GEOLOGIC AGES

No.	Percentage (Sr87* of Total Sr)	Age x 10^6 Years (Internal Standard Method)	Age x 10^6 Years (Total Energy Method)	Age x 10^6 Years (Whiting's Results)	Age x 10^6 Years (Geologic)
26	11.9	500	570	920	210
27	7.3	420	420	910	1050
29	.35			70	280
30	.61	150	150	240	700
39	.6	175	210	210	100
50	4.4	750	1000	1800	2000
51	1.6	315	200	550	1000
53	3.37	165	110	550	280
56	0	8	10	24	80
60	.78		110		2000
62	3.67	3800	1900		2000
63	2.63	3400	3500		1000
64	.7	15	20		2000
66 Bi.	1.81	210	210		350
66 Mus.	.29	1600	1000		350

Abundance of SrO using Total Energy Method: An addition plot of strontium 4607 intensities (see Figure 7) indicates .0075% SrO present in biotite 50 (cf. .0085% - Whiting; .006% - Holyk; by intensity ratio Sr/Ba). The working curve for the total energy method is shown in Figure 7a. The 45° slope of the working curve adds support to the reliability of the total energy method.

The total intensities of strontium 4607 of the samples arced by the present investigator are applied to the working curve and new values of % SrO were obtained. These values and the new calculated ages are shown in Tables 3 and 5. It is seen that a better correlation between the calculated and geologic ages is generally obtained by using the strontium content as determined by the total energy method.

Strontium and Rubidium Content in Feldspars

The standard granite is assumed to contain .061% Rb_2O and .02% SrO. Total energy methods using G-1 as the standard gave the SrO and Rb_2O contents in the feldspars as tabulated in Table 4.

Radiogenic Strontium in Biotites and Feldspars

Thirty-two of the 40 biotite and 14 of the 25 feldspar concentrates have been analyzed on the mass spectrograph for radiogenic strontium. The determinations available at the present time are shown in Tables 5 and 6. The probable error of the determinations is reported by Herzog to be about the absolute value of ± .1%.

Calculated Geologic Age

The ages for the different samples were calculated using the following equation:

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

The derivation of this formula has been discussed in an earlier section.

The ages calculated on the basis of the writer's results are shown in Table 5. The ages calculated on the basis of Whiting's results are also included. The probable geologic ages are likewise shown for the different samples.

Reliability of Assumed Geologic Age

The best way of evaluating the use of biotite for age work can of course be made by comparison of the calculated ages to the ages inferred by field relationships of the rocks or established by some other method of geochronometry.

Such a comparison is made in Table 5. It must be point out that this is only an approximate comparison. It is rather unfortunate that the choice of material in this investigation was more or less random but, of course, necessitated by the material available in the petrology collection. The exact location, geologic field relationships, and also exact geologic ages are unknown for most of the samples. The geologic ages used in this report are those reported by Whiting who in turn probably established them from consideration of geographic location, field relationships as reported in the literature, or from opinions of other geologists.

The mere fact, for instance, that a rock comes from the Canadian Precambrian Shield does not conclusively make the rock of Precambrian age. Even consideration of field relationships does not necessarily give the correct age of the rock in question. Many a controversy has raged in the past over the ages of different rocks. The question of granitization only helps to complicate the problem of age determination.

Sample 12 may be cited as an example. This granite from Mount Airy, North Carolina, has been assumed to be possibly Precambrian in the past and Whiting assigned an age of 900×10^6 years. More recent work (as reported by Chayes to Herzog, personal communication) shows that the rock is probably late Palaeozoic. This would give a geologic age of about 200×10^6 years which is similar to the calculated age of $150 - 190 \times 10^6$ years.

Another case that may be mentioned is number 64, a biotite from a pegmatite in Southern Rhodesia. The pegmatite is believed to be about two billion years old whereas the calculated age is about 15-20 million years. The radiogenic strontium is 0.7%. On this basis it follows that all the strontium would have to be radiogenic to increase the age from 15 to 2000 million years. The sample could indeed be very much younger than the age assumed.

Number 27, Llano granite, Texas, has been determined to be 1050 million years by two measurements using helium and lead methods (Whiting, 1951). This age is at least twice the age calculated by the present writer and is comparable to Whiting's results. The calculated age of sample 5, on the other hand, is 6-7 times the assumed geologic age. This sample is biotite from the Salem gabbro whose age is reasonably well known to be early Paleozoic.

It is seen from Table 5 and Figure 8 that more than half of the calculated ages correspond to the assumed geologic ages within a factor of two. In view of negative evidence to the contrary the assumed geologic ages will be considered to be true for further discussion. The possibility of erroneous assumptions, however, cannot be overlooked.

FIGURE 8

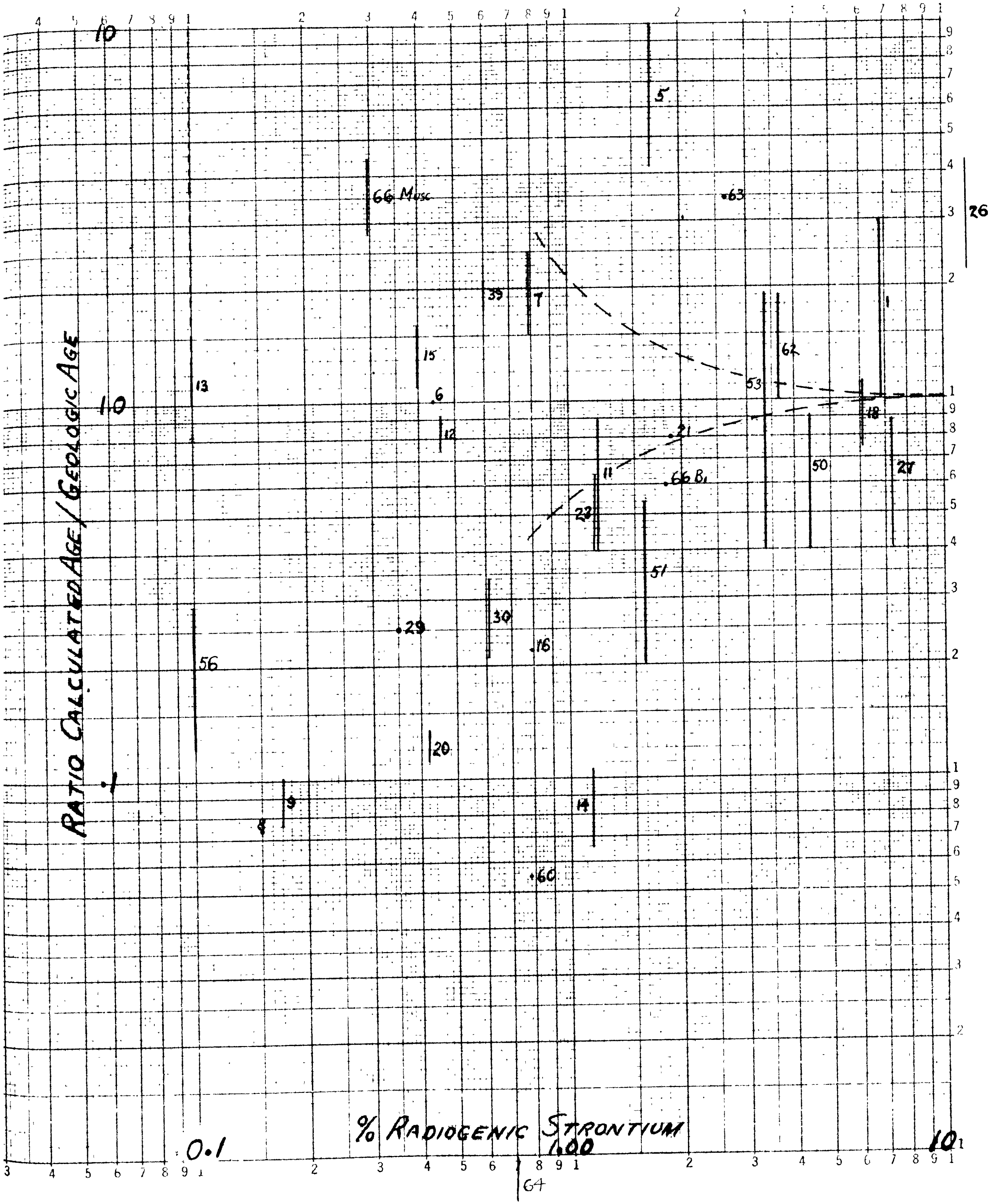
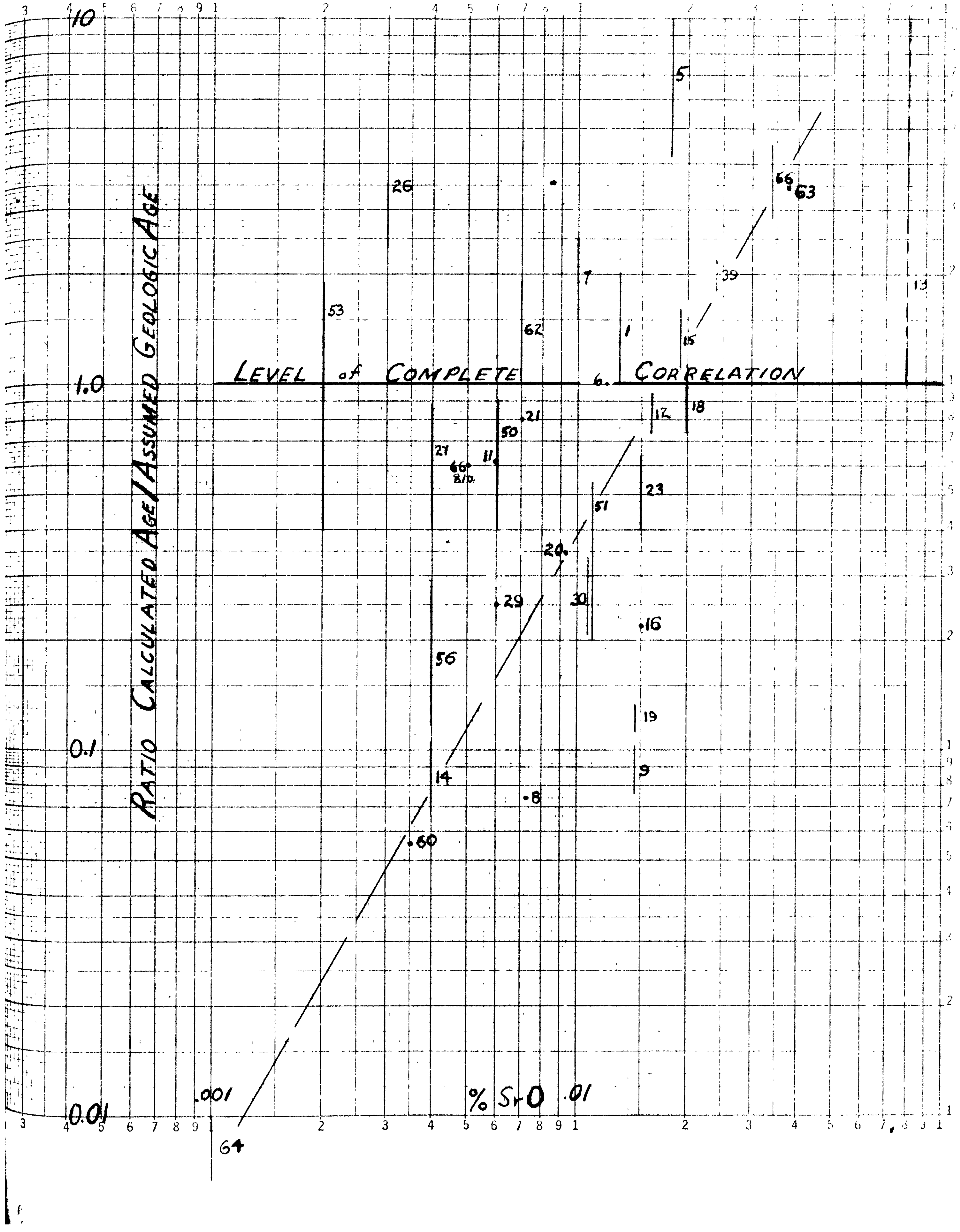

10
1.0
0.1
1.00
10
RATIO CALCULATED AGE / GEOLOGIC AGE
% RADIOGENIC STRONTIUM
5
66 Musc
63
26
39
7
1
62
15
53
13
6
18
12
21
50
27
11
66 B₁
23
51
30
29
16
56
20
1
9
8
14
60
64

FIGURE 9


10
1.0
0.1
0.01
RATIO CALCULATED AGE / ASSUMED GEOLOGIC AGE
LEVEL of COMPLETE CORRELATION
.001
% SrO
.01
64
5
26
66
63
39
7
13
53
62
1
15
6
12
18
21
50
27
66
8/0
11
23
51
20
29
30
16
56
19
9
14
8
60

Variation of Age Discrepancies with Radiogenic Strontium

The ratio of the calculated age to the geologic age is a measure of the error made whatever its cause may be. This ratio would equal unity if complete correlation between the calculated and the geologic ages were obtained.

Figure 8 shows a plot of these ratios against the amount of radiogenic strontium on log log paper. Points indicate that only one age and hence only one ratio are available. A line represents the range of the ratios of the calculated to geologic ages on the basis of the three sets of results shown in Table 5.

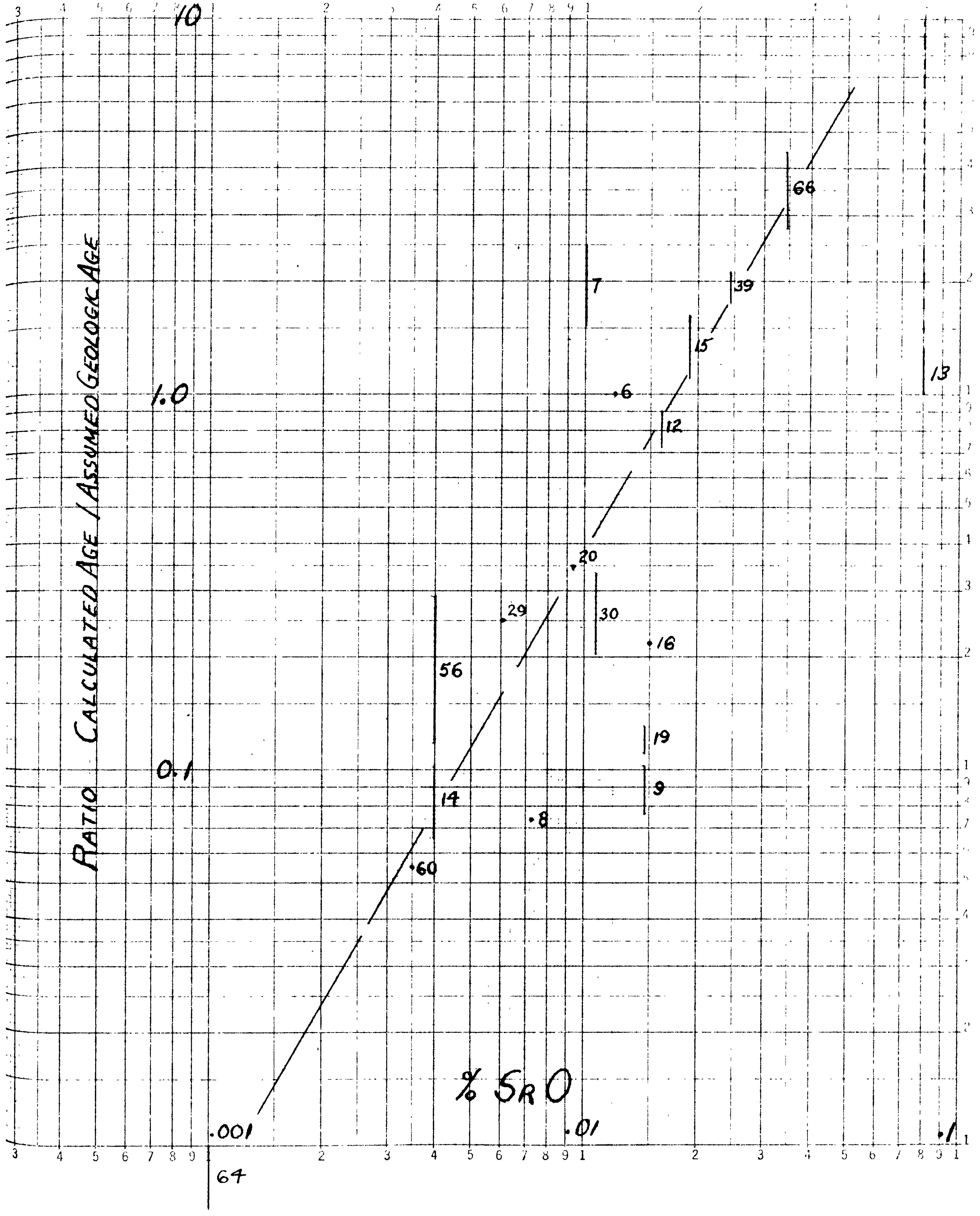
This plot shows that the discrepancy between calculated and assumed geologic ages is generally least for those samples which contain more than 1% radiogenic strontium. With some imagination (and excluding samples 5 and 26 even if wrongfully) one can draw in a curve that more or less reflects the decrease of accuracy with decrease of the amount of radiogenic strontium. This general trend may indeed be significant and show that ages obtained from samples containing less than 1% radiogenic strontium using the present procedure are open to question.

Possibility of Systematic Error

The ratios of the calculated ages to the assumed geologic age for each sample are plotted against the total % SrO in the sample in Figure 9.

Several general statements can be made concerning this graph. The samples containing the most amount of strontium show calculated

FIGURE 10


RATIO CALCULATED AGE / ASSUMED GEOLOGIC AGE
10
1.0
0.1
% SrO
.001
.01
.1
66
7
39
15
13
6
12
20
29
30
16
56
19
9
14
8
60
64

ages greater than the geologic ages. The samples showing the least amount of strontium give ages that are generally lower than the assumed geologic age. Those samples which contain more than 1% radiogenic strontium give the closest correlation between calculated and assumed geologic ages.

A suggestion of a definite pattern is evident in the graph. This is more evident if one considers only those samples which contain less than 1% radiogenic strontium (see Figure 10). The dashed line indicates what the writer considers to be the general trend of the points or lines representing the ratios.

There are insufficient points on this graph to warrant the statement that there is a definite pattern. The apparent pattern may indeed be fortiutous rather than systematic.

However the possibility of a systematic error in the determinations cannot be overlooked. If the apparent trend as indicated by the dashed line is correct then the ratio of the calculated/geologic age would vary as the n'th power of the % SrO. The equation would be of the form

$$\text{Ratio} = k\ (\%\text{SrO})^n$$

The value of "n" would be determined by the slope of the dashed line. The value of k can be determined from calculated geologic ages of some biotite for which the age has been determined by other methods of geochronometry. The actual geologic age for the rock could thus be determined from the calculated geologic age.

As already mentioned the evidence is much too scant so that in effect the above discussion of correction of the systematic error is but speculation and need not be pursued farther. However, it would be extremely interesting to have a larger number of age determinations using exactly the same methods to determine whether or not the apparent pattern has any significance.

Errors in Spectrographic Determinations

The writer considers his determinations of rubidium to be more accurate than those obtained by Whiting. It has already been pointed out that it seems the latter investigator may have made an error in the determination of the rubidium content of the biotite used for the standards. If so then all of his rubidium determinations would be subject to correction. A more reliable result can perhaps be obtained by applying Whiting's intensity ratios to the new working curve. At any rate, the discrepancies for the samples checked do not as a rule exceed 100%.

The strontium determinations made by the writer are not significantly different in most cases from Whiting's results. The validity of the use of barium as an internal standard is in doubt and hence the determinations by the total energy method may be more reliable. It must be pointed out, however, that the background on the strontium plates is rather intense so that the results may be somewhat in error. It may also be pointed out that these determinations were made only in duplicate. It would seem, however, because of the general similarity of the results of both investigators that the average of the two or three sets of results may be considered accurate to within a factor of 2. This would be, indeed, a generous maximum probable error. The extremities of the lines shown in Figures 8 and 9 denote the maximum and minimum ratios of the calculated/geologic ages obtained from the results shown in Table 5. It is extremely probable that the true ratio (assuming the geologic age to be correct) for the different samples fall somewhere along their respective lines. In other words, errors in spectrographic determinations of strontium and rubidium can contribute only to discrepancies falling inside the range indicated by the lines.

It follows then that errors in spectrographic determination may account for discrepancies between calculated ages and geologic ages falling within a factor of 2. However, errors in spectrographic determinations cannot possibly account for the large discrepancies that exist for about one half of the samples.

Possibility of Strontium Contamination

The presence of strontium in the reagents used for chemical concentration of the biotites would introduce an error to the calculated ages. This error would be systematic if uniform amounts of sample and reagents were used throughout.

The reagents HF, $HClO_3$, and NH_4OH which were used in the chemical concentration were tested for blank errors spectrographically. Pure carbon electrodes were soaked in each of the reagents for five minutes and arced on the spectrograph. Strontium was not detected in any of the reagents tested. The detection limit for Sr in rocks is about .0001% and would probably be less in the present case. Ahrens (1949) also reports the absence of strontium in hydroflouric acid.

Strontium may of course be present in amounts below the detection limit. Such an amount would probably be insignificant for most samples containing about .01% Sr.

The possibility of Sr contamination from the reagents used could be checked by a method such as the following. Strontium concentrates should be prepared from four or five equal portions of the same sample for which known but varying amounts of reagents have been used. Mass spectrographic determinations could then be made on each of the portions. If the amounts of radiogenic strontium remain constant for all portions then no contamination is present. If the amount of radiogenic strontium decreases with the increased amount of reagents used then strontium contamination is present.

The presence of normal strontium in the reagents would dilute the Sr^{87*} in the chemical concentrate and consequently the reported values of $Sr^{87}*$ would be too low. This in turn would give ages that are too low and hence the ratios of the calculated age/geologic age would be consistently less than unity.

No such systematically low ratio is evident in Figure 9. It must be concluded therefore that although the possibility of some Sr contamination from reagents exists, it seems unlikely that any such contamination would account for some of the large anomalies between the calculated and geologic ages that are present.

Accuracy of Determination of Radiogenic Strontium

According to Herzog (personal communication) the determinations of radiogenic strontium were originally obtained by measuring variations in the Sr^{87}/ Sr^{86} ratios. Later work showed that the Sr^{86}/ Sr^{88} ratio varied by as much as 5% from sample to sample both for biotites and celestites. Such variations necessarily introduced an error in the determinations of radiogenic strontium. This method was subsequently abandoned and further determinations were made by measuring the excess of Sr^{87} over 7.02% of total strontium. The value of 7.02% is the ratio of Sr^{87} to total strontium at the present time in the so-called normal strontium (Eimer and Amend Chem. Co., $SrCO_3$ - probably a California celestite of (?) Tertiary Age).[1]

The latter method of determining the amount of radiogenic strontium is based on the assumption that the amount of Sr^{87} remains constant at 7.02% throughout geologic time. From considerations of the abundance

---

[1] Herzog, L., Personal Communication

of strontium and rubidium Ahrens (1948) stated that the amount of radiogenic strontium in the earth's crust is about 0.8%. He presently believes that this amount may have to be increased to 1.4% (personal communication) from consideration of revised abundance values. This would mean that at the time of formation of the earth the ratio of Sr^{87} to total strontium would be about 5.62% instead of 7.02%. If this is so then a considerable error could be introduced in assuming that the excess of Sr^{87} over 7.02% of total strontium in biotites of all ages is radiogenic. This error would be increasingly large for reported values of radiogenic strontium below 1% of total strontium and especially so for those of Precambrian age.

Fluctuations in the isotope ratios do occur as found by Herzog in both biotite and celestite. There is no reason to suppose why the figure of 7.02% for Sr^{87} should not vary with geologic age. The fact that negative amounts of Sr^{87} were reported for the feldspar fractions indicate that the amount of Sr^{87} at the time of formation of the rock was less than 7.02%.

As pointed out by Whiting, (1951) the amount of Sr^{87} present when the rock was formed can be found graphically by determining the ratio of Sr^{87} for two fractions of a rock, one of which is high in rubidium and the other rubidium poor, and extrapolating to zero amount of rubidium. Isotope analyses were made of feldspar fractions. Unfortunately many of the feldspar fractions had a rubidium content comparable to the biotite and consequently an accurate extrapolation could not be made. Herzog believes that the results indicate

TABLE 6

RADIOGENIC STRONTIUM IN FELDSPARS

Sample No.	% Radiogenic Strontium
5	.07
6	- .03
7	- .10
8	- .10
9	- .09
11	- .02
12	.01
14	1.14
15	- .09
18	- .05
23	- .03
26	.13
51	- .04
63	- .16

the relative amount of Sr ^{87}to be less than 7.02% for older rocks but that the amount will be considerably less than 1.4%. The amounts of radiogenic strontium in the feldspars are shown in Table 6. (See Herzog - 1952, for discussion of variation of Sr^{87} in feldspars with time.)

As the matter stands the variation of the ratio of Sr^{87} to total strontium with geologic time is not completely known. Any fluctuation of the values with respect to the assumed value of 7.02% will introduce an error into the radiogenic strontium analysis.

The exact knowledge of the amount of Sr^{87} becomes critical when the amount of radiogenic strontium falls below 1%. Any fluctuation of the amount of Sr^{87} from 7.02% of total strontium will be reflected in discrepancies in calculated age. This becomes extremely important for rocks of Precambrian age. Reference to Figure 8 shows that the discrepancies between the calculated and assumed geologic ages generally increase as the ratio of radiogenic strontium falls below 1%.

The calculated age of biotite 64 is puzzling. This is a pegmatite mica from Southern Rhodesia believed to be about 2000 years old. This biotite is exceptionally pure having been obtained from a large single sheet of mica. The spectrum of the biotite shows a very weak, diffuse Sr 4607 line. It is so weak, and ill-defined that the writer doubted for a while whether or not it is a Sr line. The line seems to be out of focus in comparison to the Sr 4607 lines in other plates whereas no difference is evident for the lines of other elements.

If this biotite is 2000 years old then nearly all of this strontium should be radiogenic (see Table 5). However, a value of only 0.7%

radiogenic strontium is reported.

An answer to the anomalous results of this biotite may be that required to explain many of the inconsistencies in ages obtained for the remainder of the biotites.

Possibility of Loss of Radiogenic Strontium

It would be wise to consider the possibility of loss of radiogenic strontium from biotite. Such a loss could account for some of the very low ages obtained in comparison to the assumed geologic ages.

Biotite is a relatively stable mineral with respect to weathering (Pettijohn,1941). Whiting chose rocks that looked fresh and examined the biotite portions of each rock for alteration. The alteration is presumably negligible in the biotites used in this investigation.

The rubidium and strontium in biotite are thought to be tightly held in the structure by ionic bonding. Rubidium has an ionic radius and charge similar to potassium and will therefore probably occupy potassium positions in the biotite structure. The daughter element, strontium 87, would likewise occupy the alkali position upon its formation. Strontium is considerably smaller in size than rubidium but is doubly charged so that a certain amount of strain will develop at the structural site of rubidium following its decay to strontium. Only a small portion of rubidium, however, will have decayed even in oldest biotites because of the very long half life, and consequently the strain imparted in the biotite structure may be insignificant. (see Ahrens, 1949, p261, for more detailed discussion.)

It is not known what position ordinary strontium occupies in biotite. From consideration of the ionic charges and radii of the elements (revised by Ahrens, 1952)

Rb^{+}	1.47 A
K^{+}	1.33 A
Sr^{2+}	1.12 A
Ca^{2+}	0.99 A
Mg^{2+}	0.66 A

it would seem that a diadochy could exist between strontium and either, or both, potassium and calcium within the structure. The position of Sr would then depend, in part at least, on the position of calcium. Evans (1948) states that the cations which may occur in 6-fold coordination in biotite (that is occupying the Mg position) include Al^{3+}, Fe^{3+}, Mg^{2+}, Fe^{2+}, Mg^{2+}, Li^{+} while the alkali metal position, although most commonly potassium, may be Na^{+} or Ca^{2+}. In margarite, the brittle mica, the divalent Ca^{2+} ion occurs in the alkali position. It seems very unlikely that Sr^{2+} would occupy Mg^{2+} positions because of the large discrepancy in size even though there is a possibility that a diadochy between Ca^{2+} and Mg^{2+} may occur.

As already mentioned, some strain will be developed at the structural site of radiogenic strontium. However, some strain may also be inherent in the alkali positions that are occupied by ordinary strontium ions. If this were so then the strain at the positions of both radiogenic strontium and ordinary strontium may be similar and there should be no reason why radiogenic strontium should be leached in preference to ordinary strontium. The ratio of radiogenic strontium to ordinary strontium should remain the same even if a significant amount of strontium was lost from the biotite.

Ahrens (1949, p290, 263) discussed the possibility of loss of strontium from lepidolites and considers that the loss should be negligible, and very small in comparison to the lead and helium method of age determination where the possibility of loss for parent or daughter element is potentially great.

His reasoning, however, was based upon consideration of older ionic radii (Sr^{+2} being 1.27 A) and hence his conclusions may be subject to revision in the light of his revised ionic radii (1952).

Comments on Metamorphic Rocks

Only three samples of mica schists were investigated. These rocks are from Vermont and are of Precambrian age but the period of recrystallization may be late Ordovician (W. F. Brace, personal communication). The available data for the samples is presented in Table 7.

TABLE 7

CONTENT OF STRONTIUM AND RUBIDIUM IN METAMORPHIC ROCKS

Sample	% Rb_2O	% SrO	Y[1]	Calculated Age	Geologic Age (of recrystallization)
66 Biotite	.125	.005	1.81	210	350
66 Muscovite	.030	.055	.29	1000	350
67 Biotite	.054	.024			
68 Biotite	.085	.012			
68 (Feldspar + Quartz)	Tr	.006			

The significant factor is that detectable amounts of both strontium and rubidium as well as radiogenic strontium are present in the micas of metamorphic rocks. It seems possible therefore that the use of biotite for age measurements (once put on a firmer basis) can be extended to metamorphic rocks and determinations of the period of metamorphism determined.

Several interesting points arise from consideration of the available data. It is seen that during recrystallization most of the

---

1. Denotes percent radiogenic strontium of total strontium.

rubidium entered the biotite structure in preference to muscovite (sample 66) or the feldspar and quartz fraction (sample 68). Strontium, on the other hand, shows a ten fold enrichment in the muscovite fraction relative to the biotite fraction (sample 66) and a two fold enrichment in the biotite relative to the feldspar and quartz fraction of sample 68. The ratio of feldspar to quartz has not been determined.

The radiogenic strontium would be produced by the decay of rubidium throughout the history of the metamorphic rocks (i. e. before and after formation of the secondary mica). The ability to date the age of metamorphism will depend upon the determination of the amount of Sr^{87} present in the rock at the period of recrystallization just as in the case of igneous rocks.

CHAPTER IV

CONCLUSIONS

The most important conclusion that may be drawn from this investigation is that radiogenic strontium is definitely present in biotites. Mass spectrographic determinations by Herzog and Aldrich on biotite concentrates show the presence of radiogenic strontium ranging from 0 to 11.9% of the total strontium in the biotite samples. The use of biotite for age determinations thus seems feasible.

Ages have been calculated for 32 samples of biotite. The ages of eighteen samples do not vary by more than a factor of 2 from the assumed geologic ages. The maximum age determined for any sample is 5700 years on the basis of Whiting's determinations of the strontium and rubidium content of biotites. The maximum age obtained on the basis of the writer's results is 3500 years. The maxima in both cases were obtained for rocks of Precambrian age.

The best correlation between calculated and presumed geologic ages is obtained for samples containing more than about 1.5% radiogenic strontium. The ages determined for samples containing less than 1% radiogenic strontium are generally either too high or too low.

Some of the samples arced by Whiting were checked by the writer for the rubidium and strontium content. An error is believed to have been made by Whiting in his determinations of the rubidium content of the biotite he used for the preparation of his standards. This would introduce an error into his determinations of the rubidium content of the different samples. The discrepancies between the writer's and Whiting's results do not differ by more than a factor of two, except for several samples.

The present method of using barium as an internal standard for the determination of strontium in biotite is probably not valid. The presence of barium in biotite appears to be significant in some samples. A considerable variation of the intensities of Ba 4726 was observed from sample to sample; this variation is greater than can be attributed to procedure alone. Determinations of the strontium content by the total energy methods differed somewhat from those using the internal standard method. In most cases the values obtained by the total energy method decreased the discrepancy between the calculated and the geologic ages.

Generally speaking, the calculated age is greater than the geologic age in those samples containing a larger amount of strontium; and the calculated age is less than the presumed geologic age for those samples having a very low strontium content. A plot of the ratio of the calculated age/ geologic age against the total % SrO in the biotite shows the possibility of a systematic error being present which affects the results of those samples having less than 1% radiogenic strontium. There is a possibility that the relation between the ratio and the strontium content is of the form:

$$\frac{\text{Calculated Age}}{\text{Geologic Age}} = k\,(\%\ \text{SrO})^n$$

However, sufficient data is lacking and this apparent variation may be fortuitous.

Errors in spectrographic determinations would be of importance where the discrepancy between the calculated and geologic ages are within a factor of two. On the other hand the large discrepancies for about half the biotites cannot possibly be attributed to spectrographic errors. Errors other than spectrographic must be sought.

Spectrographic checks on the reagents HF, $HClO_3$, and NH_4OH indicated the absence of strontium. It does not seem possible, therefore, that contamination of ordinary strontium from the chemical reagents would explain the anomalous results.

The writer is not competent to judge the reliability of the determinations of radiogenic strontium but will leave this for a specialist in mass spectrography to decide. It seems, however, that further investigations concerning the variation of isotope ratios and especially the variation of Sr^{87} with geologic time are in order.

The case of the pegmatitic biotite from Southern Rhodesia (Number 64) is indeed puzzling. It would seem that either the biotite should consist almost entirely of radiogenic strontium or that the biotite is of Tertiary rather than Precambrian age.

Micas from metamorphic rocks contain both strontium and rubidium as well as measurable amounts of radiogenic strontium. Once the discrepancies brought out in this investigation are explained and corrected for, there seems to be no reason why the biotite method should not be extended to metamorphic rocks.

CHAPTER V

RECOMMENDATIONS FOR FURTHER RESEARCH

The most vital aspect that requires further investigation before the merits of the biotite method of age determination can be evaluated is the variation of Sr^{87} with geologic time. There is no doubt that the amount of Sr^{87} increased throughout the geologic history but the extent of this variation is not sufficiently known. More isotope analyses of ancient rocks which contain insignificant amounts of rubidium are therefore needed. Precambrian anorthosites would be most admirably suited for this purpose. [1]

An important problem omitted from this investigation because of time limitations is that concerning the question of whether the biotite in the granite is primary or secondary. If the biotite of the rock is primary then the calculated age of the rock using biotite would theoretically correspond to the period of intrusion and crystallization of the rock. On the other hand, such correlation would be lacking between the calculated age and geologic age as inferred from field relationship if the biotite were secondary and formed at some period of metamorphism later than the period of crystallization of the intrusive mass. Biotite is a very common mineral in rocks affected by low grade regional metamorphism (Turner and Verhoogen, 1951) and hence could very well be secondary in many granites in which case the calculated age

---

[1] The possibility of using anorthosite was suggested by Dr. L. H. Ahrens during a discussion of this matter.

PART II

THE USE OF LEPIDOLITE IN DETERMINATION OF GEOLOGIC AGE BY THE CALCIUM METHOD

INTRODUCTION

The ultimate object of this investigation is to develop a method of measuring geologic age by means of the natural radioactive decay of K^{40} to Ca^{40} in lepidolites.

Such a method is desirable for several reasons. It would offer an alternate method of obtaining geologic age and hence serve as a check upon age determinations by the strontium method. Having determined the age of lepidolite by the calcium method one can check the decay constant of rubidium which is believed to be known with an accuracy of about ±15% (Ahrens, 1949). The half life of K^{40} is now believed to be reasonably reliable (Birch, 1951). Finally, the development of such a method would rest upon the identification and determination of radiogenic Ca^{40} in the lepidolite. This would be very convincing evidence to the effect that K^{40} to Ca^{40} decay plays an active part in geologic processes.

An accurate means of determining the calcium content is an essential step in such a method and hence most of the attention in this investigation was devoted to the development of a spectrochemical method for the determination of calcium in lepidolites. No positive ages have as yet been determined by the decay of K^{40} to Ca^{40} although several efforts have been made.

Brewer (1937) tried to establish an upper limit for the age of the earth by assuming that all of the calcium of the crust was formed by β decay. Actually, as will be shown below, Ca^{40} does constitute about 97% of all the calcium in the earth. Brewer's results showed that all the calcium could be generated in about 2 x 10^9 years using the half life of potassium as 170 x 10^6 years. This figure was increased to 15 x 10^9 years by using a half life approximately equal to that accepted at present (Brewer, 1938). Birch (1951) questioned the method on the basis that a large amount of the Ca^{40} is doubtless primitive.

Festa and Santagelo (1950) applied Brewer's method to meteorites and established an upper limit of the age of the earth as 6.4 x 10^9 years using the short half life of 350 million years. The validity of their assumptions is again questioned by Birch (1951).

The calcium content of 26 lepidolites was determined spectroscopically by Ahrens and Evans (1948). They report an error of ±30% for specimens having between .01% and .03% Ca because of a blank error caused chiefly by the presence of calcium in the spectrographic electrodes. The calcium determinations for lepidolites containing less than .01% Ca were obtained from spectrographic determinations of hydroflouric acid residues of the lepidolites. The possibility of blank errors caused by chemical reagents and carbon electrodes would be of greater concern for lepidolites containing less than .01% Ca. Ahrens (1951) calculated that the proportion of radiogenic calcium in lepidolites should be in the range of 1 - 30% of total calcium.

Ahrens (1951) discussed the problem and concluded that a calcium method for determining geologic age seemed entirely feasible but emphasized that the method would probably be confined to lepidolites and possibly pegmatitic muscovite of Precambrian age because of geochemical reasons.

CHAPTER VI

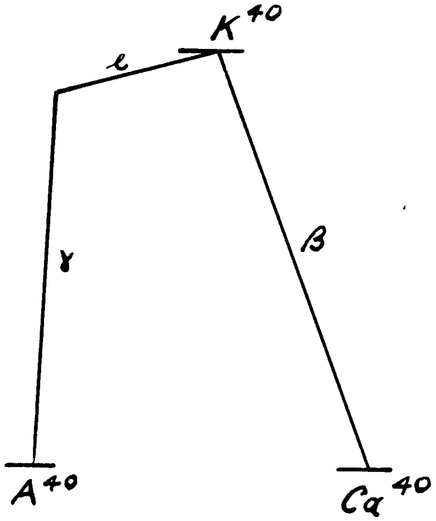
GENERAL BACKGROUND

Decay Scheme for K^{40}

The radioactive disintegration of potassium by the spontaneous emission of electrons, or β-decay, was discovered in 1905 (Campbell and Wood). The radioactive isotope was identified as K^{40} in 1937 by Smythe and Hemmendinger. The possibility of a dual decay scheme for K^{40} was discussed theoretically by Fermi (1934), Sitte (1935), Moller (1937), and von Weizsacker (1937).

Thompson and Rowlands (1943) reported the first experiemental evidence for electron capture (K-capture, with K referring to orbit) in 1943. Other work has contributed to the general understanding of potassium decay. The decay scheme for K^{40} is shown in Figure 11 which is reproduced after Sawyer and Wiedenbeck (1950).

Figure 11



Branching Ratio of K^{40} Decay

The branching ratio is the ratio of electron captures to β decays in the disintegration scheme of potassium. Thompson and Rowlands (1943) estimated the ratio to be about 3 or 4. Bleuler and Gabriel (1947) gave a value of 1.9 for the branching ratio on the basis of observations of X-rays produced in the capture process. Harteck and Suess (1947) reported a value of less than 0.1 as a result of analysis for A^{40} in potassium salts and granite. Aldrich and Nier (1949) made mass spectrographic analysis of argon in potassium minerals and found a ratio of the order 0.02 to 0.09. Ahrens and Evans (1948) suggested a value of 1.4 from calcium determinations of lepidolite but without making isotopic analysis of the calcium. Sawyer and Wiedenbeck (1950) gave a value of 0.135 as a result of their observations of secondary (Auger) electrons associated with the X-rays. Ceccarelli, Quarcini, and Rostagni (1950) offered a value of 0.07 from an improved X-ray method. Inghram, Brown, Patterson and Hess (1950) established a value of 0.1263 ± 0.0027 from mass spectrometer analysis of the ratio of A^{40}/Ca^{40}.

Birch (1951) summarizes the work of the above investigators and believes the branching ratio established by Sawyer and Wiedenbeck to be the most probable solution. He chooses 0.13 as the most probable value. This means that during the decay of K^{40} about 12% will decay to A^{40} and 88% to Ca^{40}.

Isotopic Abundances of Potassium and Calcium

Potassium consists of three isotopes K^{39}, K^{40}, and K^{41}. The isotopic abundances are shown in Table 8. (after Rankama and Sahama, 1950, p53). Isotope abundances have been obtained and compared for a variety of samples by different investigators (Suess, 1938 and 1939; Schumb, Evans, and Leaders, 1941, on meteoric and terrestrial potassium; Smythe - 1939, on granites from a depth of 2500 feet and surface samples; Brewer - 1939, on clay soils and Vesuvius lava) and no significant differences were found. It appears that the potassium originated at the same time with an universal isotopic abundance.

Calcium consists of 6 isotopes which are listed in Table 8. Two sets of values by Nier (1938) and White and Cameron (1948) are given and a slight discrepancy of about 3% in the Ca^{40}/Ca^{44} ratio is evident between the two sets of values. Ahrens (1949 - 50, 1951) suggested the possible presence of Ca^{40} in sylvite from Stassfurt, Germany and reports that this has been verified by means of the mass spectrograph (Inghram, Brown, Patterson and Hess, 1952).

TABLE 8

ISOTOPIC ABUNDANCES OF POTASSIUM AND CALCIUM

Isotope	%	%
K^{39}	93.38	
K^{40}	0.012	
K^{41}	6.61	
	After Nier	After White & Cameron
Ca^{40}	96.96	96.92
Ca^{42}	0.64	0.64
Ca^{43}	0.14	0.13
Ca^{44}	2.06	2.13
Ca^{46}	0.0033	0.0032
Ca^{48}	0.19	0.18

Decay Constants of K^{40}

The values for the decay constants of K^{40} have undergone a considerable amount of fluctuations. These fluctuations are sufficiently dampened at the present time to give a reasonably accurate half life for K^{40} of 1.3×10^{9} years, with an uncertainty factor of approximately 10% (Birch, 1951).

The method of obtaining the decay constants from consideration of the β emission and isotopic abundance of K^{40} is discussed by Birch (1951, p113). According to the results of Sawyer and Wiedenbeck (1950) the total disintegration constant of K^{40}, λ, is 0.548×10^{9} per year. The half life of K^{40} is given by the value $\frac{.693}{\lambda}$.

Calculation of Radiogenic Calcium

The amount of radiogenic calcium produced by the radioactive disintegration of K^{40} can be calculated by the standard exponential formula for first order reactions:

$$N = N_o e^{-\lambda t} \qquad (5)$$

where N_o = number of atoms of K^{40} originally present

N = number of atoms of K^{40} left after time t

t = elapsed time in years

λ = decay constant = 5.48×10^{-10}

The atomic abundance of K^{40} is 1.19×10^{-4} (Nier, 1950). About 88% of a given amount of K^{40} will decay to Ca^{40} (Birch, 1951). The amount of K_2O in lepidolites generally varies from 9.5 - 10.5% but can be assumed to be nearly constant at 10% (Ahrens, 1951), or 8.29% K, for the purposes of this investigation.

The amount of K^{40} originally present, N_o, can be determined from equation (1). This formula can be simplified to

$$\begin{aligned} N_o &= (.000119)\ (8.29)\ e^{(5.48 \times 10^{-10})t} \\ &= .000985\ e^{(5.48 \times 10^{-10})t} \qquad (6) \end{aligned}$$

by substitution of appropriate constants and expressing the values of N and N_o in percent. The value of N_o is obtained by substituting the assumed geologic age for t and solving the exponential formula. The percentage of radiogenic Ca^{40} is therefore given by the value of $.88\ (N_o - N)$.

CHAPTER VII

EXPERIMENTAL AND ANALYTICAL TECHNIQUES

Preparation of Samples

Many of the lepidolite samples used in this investigation were obtained in the prepared state. These were examined for impurities which were removed if present by the method described below.

Other samples were prepared by crushing of the raw pegmatite samples in a percussion mortar. The crushings were screened and the coarser material removed for further crushings. The very fine powdered screenings were rejected because of the difficulty that would be involved in making any further purification. The screened portion was passed through a magnetic separator innumerable times at different settings. A fairly pure concentrate of lepidolite could be obtained in this way. The settings on the separator would vary from sample to sample and hence no specific details need be given.

The lepidolite concentrate was then passed over an inclined sheet of paper. Gentle tapping of the paper resulted in the rapid rolling of the rounded grains down the incline whereas the flat lepidolite flakes lagged behind. An almost pure concentrate of lepidolite could be obtained in this way by repeated efforts.

All samples analyzed were examined under a binocular microscope for impurities. A very small portion of each sample was examined at a time and any foreign particles present such as quartz or feldspar were removed by a sharpened damp toothpick. This was a tedious process but gave a very pure sample of lepidolite as far as could be ascertained by visual inspection.

Choice of Method

In view of the small amounts of calcium in the lepidolites it was decided that a total energy method of spectroscopic analysis using the pure material if possible would be preferable. Such a method would avoid any unnecessary amount of handling of the sample and thereby minimize the risk of Ca contamination.

Subsequent work precluded the use of the pure lepidolite. The samples were consequently mixed with 2 parts of carbon and arced in 1/8" pure carbon electrodes having a cylindrical cavity of 1.5 x 4 mm. using anode excitation. More detailed information follows in the succeeding sections.

Preparation of Samples for Arcing

Powdered lepidolite was loaded into both carbon and graphite electrodes of different sizes and arced as such. The burn was entirely unsatisfactory as a globule formed in the early stages of arcing and hopped out very frequently. Electrodes of different shapes were tried in order to prevent the globule from hopping out but were unsuccessful.

The burning characteristics were greatly improved by adding two parts of carbon to the powdered lepidolite. It was found that considerable material would often be lost in the early period of arcing. This was probably caused by sudden release of gases such as water vapour. The carbon and lepidolite mixtures were heated to 750°C for

3 minutes in a muffle furnace and it was found that this improved the arcing qualities immensely. This procedure was adopted for all the samples analyzed.

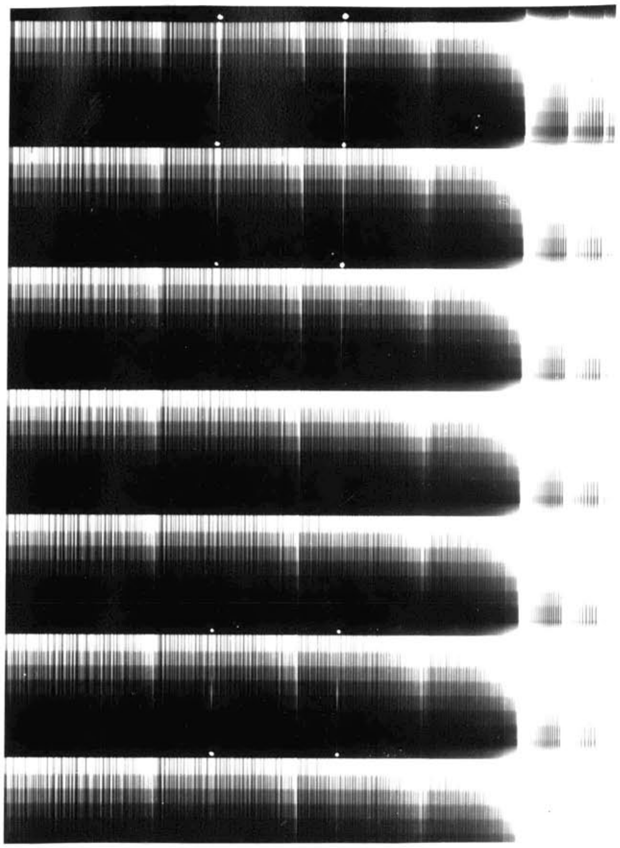
Large (1/16") electrodes caused an intense CN background in the vicinity of Ca 3968 and therefore could not be used. The use of 1/8" electrodes gave a much lower background. The intensity of Ca 3968 in the samples arced was sufficiently large to enable the 1/8" electrodes to be used.

Preparation of Standards

Preliminary arcing of ten lepidolite samples chosen at random showed the lepidolite from San Diego to contain the least amount of Ca. The San Diego lepidolite was therefore chosen as the base.

The standard diabase W - 1, assumed to contain about 7.80% Ca (Fairbairn et al, 1951) was added to the pure base to give a mixture containing 1% Calcium. Subsequent dilutions of this mixture with the pure lepidolite gave standards containing .0625, .03125, .0156, .0078, .0039, and .0019 % Ca.

PLATE 4



CALCIUM CONTAMINATION IN ELECTRODES

a. impure electrode

b. impure electrode, "purified"

c. impure electrode, "purified"

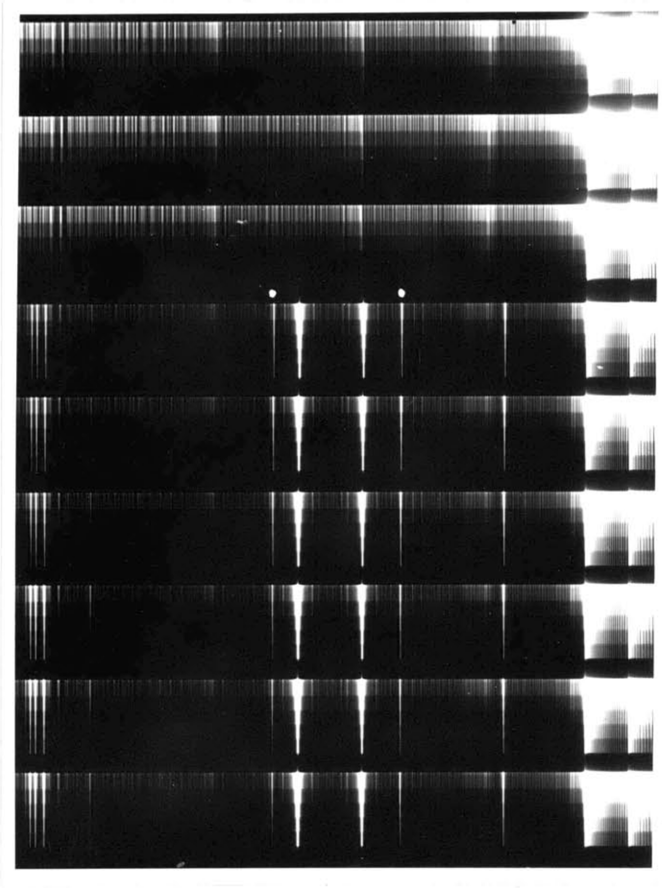
d. pure electrode

e. pure electrode

f. pure electrode, "purified"

g. pure electrode, "purified"

PLATE 5



COMPARISON OF CALCIUM CONTENT

OF ELECTRODES AND LEPIDOLITES

a, b, c, Pure electrode arced for 40 seconds

d, e, f, Lepidolite, Pala, California

g, h, i, Lepidolite, Nigel Claims

Calcium Impurities in Electrodes

Previous investigators (Ahrens and Evans, 1948) reported some difficulty with the presence of calcium in the pure electrodes. The 1/8" electrodes used for the lepidolite analysis were loaded with pure carbon powder and arced for 40 seconds which is the usual time required for calcium volatilization. Examination of the plates showed only a trace of Ca 3968.

An attempt was made to purify the carbon electrodes by steeping in acid. Both pure and impure carbon electrodes were steeped in a 1:1 mixture of HNO_3 and HCl for 6 days in separate evaporating dishes. The solutions were kept warm over a low hot-plate and changed each day. The electrodes were washed thoroughly with distilled water and dried in a muffle furnace at 750°C. The electrodes were loaded with carbon powder obtained by crushing one of the treated electrodes and arced for 40 seconds.

The results of this treatment are shown in Plate 4. It is seen that about $\frac{1}{4}$ of the calcium in the impure electrodes was removed by this procedure. On the other hand Ca 3968 appears more intense in the treated pure electrodes. It is possible that the chemically pure reagents used possessed a certain amount of Ca. The intensity of calcium of the pure electrodes is negligible in comparison to the calcium content of the lepidolites (see Plate 5). Consequently, it was decided to use the pure carbon electrodes without any further purification.

Spectrographic Procedure

A Wadsworth grating spectrograph was used in this investigation. It has been adequately described in other reports (Dennen, 1949).

The plate holder was centered at 3800 A at a focus of 15.7. Only one plate (Eastman 103-O) was required and it was placed in the central portion of the holder being slightly offset in the direction of increasing wavelength.

A rotating step sector with adjacent steps decreasing by a factor of 2 gave 5 steps ranging from 1/8 to 1/128 of full exposure. The sector was set in such a manner so as to omit the first three steps.

The arc was started by bringing the electrodes together and separating them upon contact. The shutter was kept open at all times. The arc was shielded from the slit with the palm of the hand during the interval between making contact and total separation of the electrodes. An alternate method would be to keep the shutter closed until the electrodes were separated. The latter method is somewhat awkward with the present layout of the spectrograph.

The sample was arced at 3 amps. for about 5 seconds and at 6 amps. until the calcium was volatilized. Anode excitation was employed. Preliminary arcing at 3 amperes prevented the material from being blown out of the electrode as invariably happened if the arc was started at 6 amperes. The samples were arced in triplicate. Nine exposures could be obtained on each plate.

The plates were developed as a single batch using the standard developing procedure described elsewhere in this report.

The reader is cautioned of excessive use of the red safe-light in the darkroom. A series of plates were loaded into the plate rack for developing purposes using the safe light for illumination. The plates were exposed to the safe light for approximately five minutes and were found to be strongly fogged upon being developed and could not be used.

Calculations

A Hilger non-recording photometer was used in the determination of the calcium intensities. The deflections obtained from several steps of each line were converted into $(d_o/d) - 1$ values. These were plotted on log log paper against the step number and the relative intensities determined by a reversed log scale as already described.

Background deflections were obtained on either side of the line but free from its halation. The average deflection was converted into a $(d_o/d) - 1$ value from which the intensity of the background was determined. The absolute intensity of the line was obtained by subtracting the intensity of the background from that of the line.

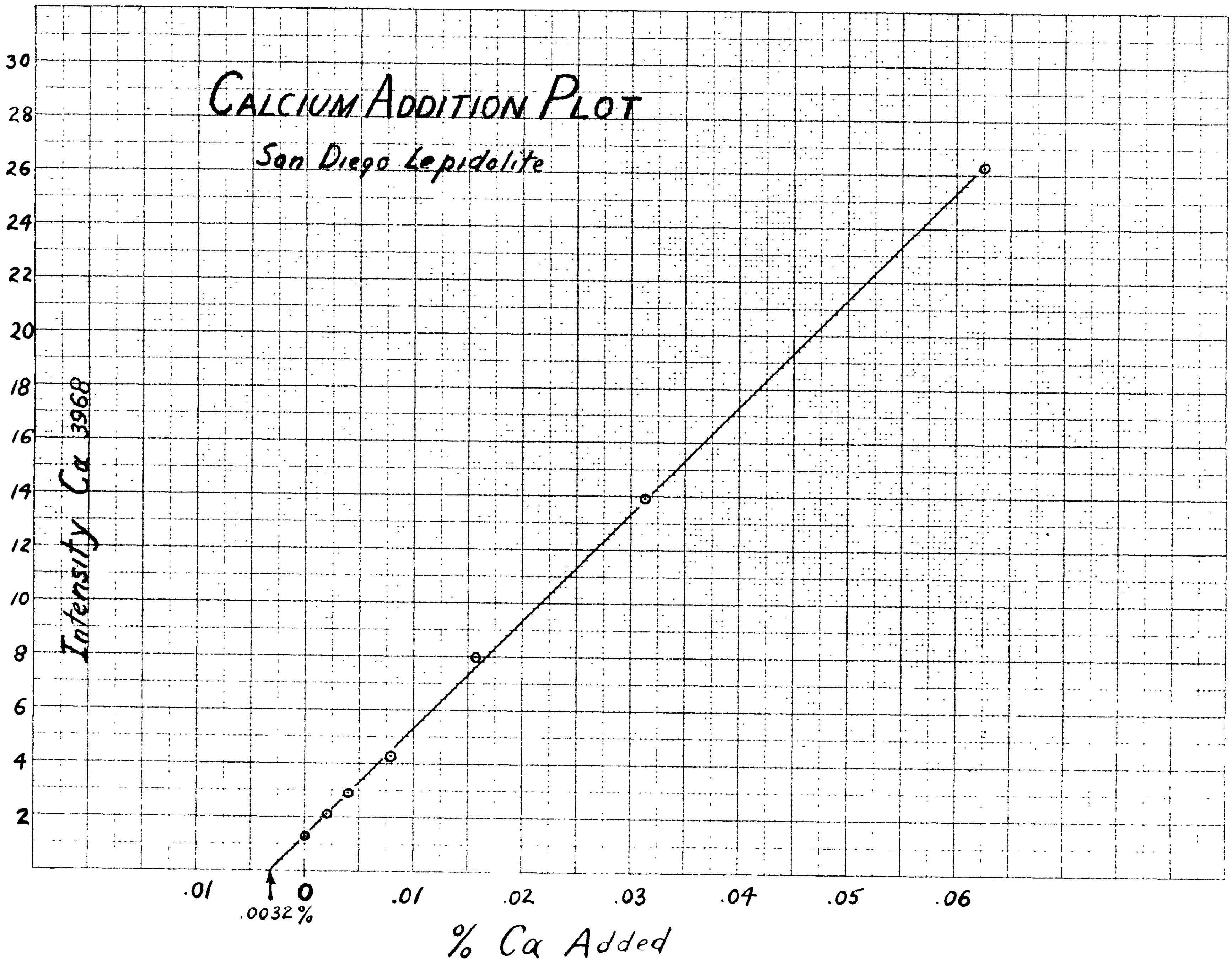

CALCIUM ADDITION PLOT
San Diego Lepidolite
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
Intensity Ca 3968
.01
0
.01
.02
.03
.04
.05
.06
.0032%
% Ca Added

FIGURE 12

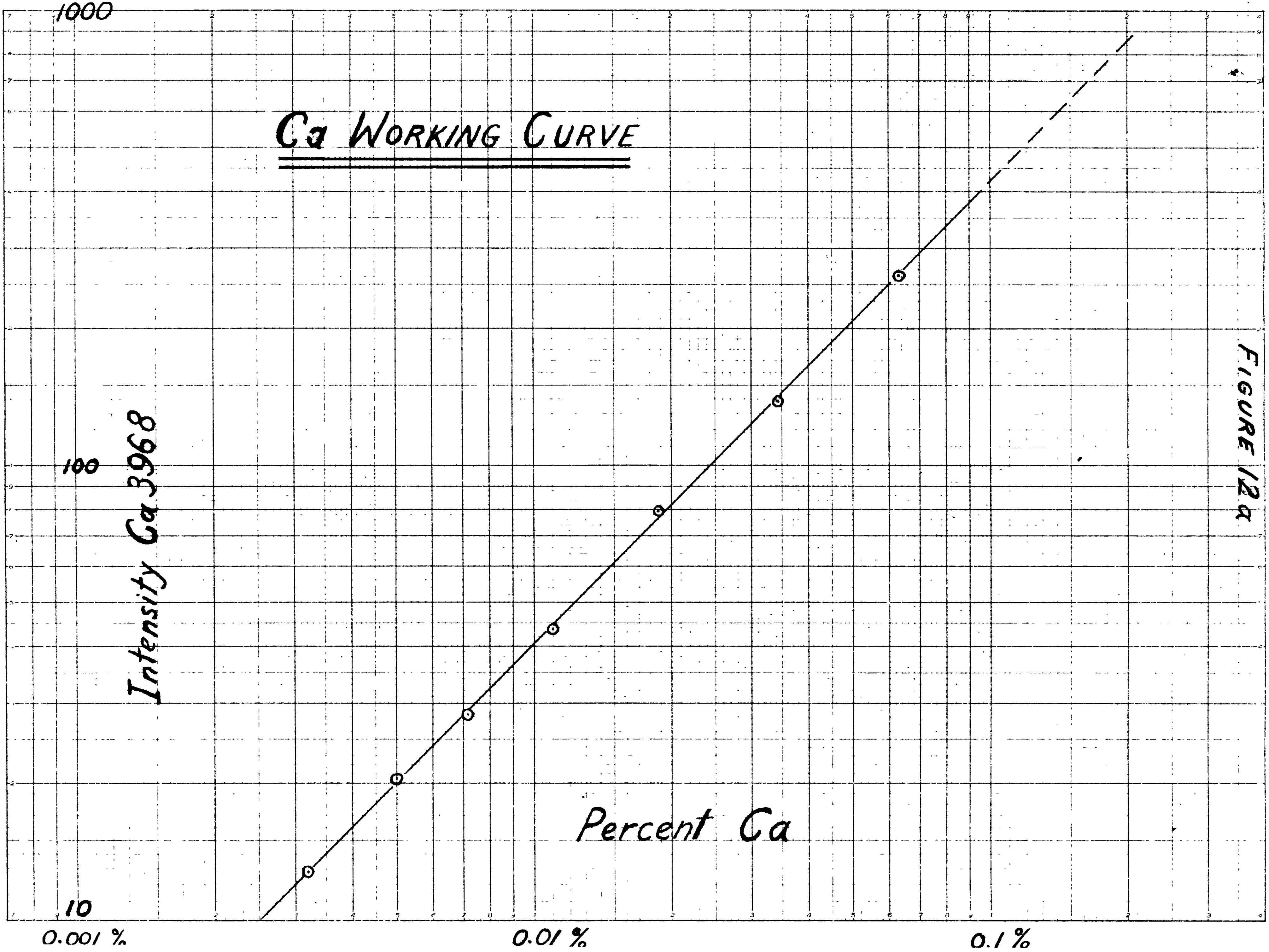

Ca WORKING CURVE
1000
100
10
Intensity Ca 3968
Percent Ca
0.001 %
0.01 %
0.1 %

FIGURE 12a

TABLE 9

CALCIUM CONTENT OF LEPIDOLITES

Location	% Ca	Age (x 10^6 yrs.)	% Ca^{40} (Calculated)	% Ca of Total Ca
N 38, N'dara, S.Rhodesia	.0043	2000	.00171	40
N 45, Bikita, S.Rhodesia	.006	2100	.00183	30
N 58, Forfar, S.Rhodesia	.0040	2000	.00171	43
N 68, Filabusi, S.Rhodesia	.0123	2000	.0071	14
Wiston Farm, S.Rhodesia	.0050	2000	.00171	34
Nigel Claims, S.Rhodesia	.0132	2000	.00171	13
"C" Lutope Tin Mine, S. Rhodesia	.0295	2100	.00183	6
Willie 481, Letaba, Transvaal	.0120	2000	.00171	14
Jakkalswater, Namaqualand (1)	.0050	900	.00055	11
Jakkalswater, Namaqualand (2)	.0026	900	.00055	21
Kubuta, Swaziland	.060	2000	.00171	2.8
Mozambique, P.E.A. (1)	.0036	500 (?)	.00027	7
Mozambique, P.E.A. (2)	.0043	500 (?)	.00027	6
Nampeyo Hill, Uganda	.0040	500 - 1000	.00027 - .00062	7 - 15
Ruhuma, Uganda	.0033	500 - 1000	.00027 - .00062	8 - 18
M'gale, Uganda	.0035	500 - 1000	.00027 - .00062	8 - 18
F 36, Lunya, Uganda	.0073	500 - 1000	.00027 - .00062	4 - 8
No 2. S.W. Africa	.0120	700	.00040	3.3
Australia	.0073	500	.00027	3.8

TABLE 9 (cont'd)

Location	% Ca	Age (x 10^6 yrs.)	% Ca^{40} (Calculated)	% Ca of Total Ca
Portland, Conn.	.0047	270	.00014	3
Black Mtn. Quarry, Maine	.0044	270	.00014	3.2
San Diego, California	.0032	100	.000044	1.2
Ingersoll, Black Hills, South Dakota	.0093	800	.00046	5
Shuswap, British Columbia	.0114	270	.00014	1.2
Winnipeg River, S. E. Manitoba	.0196	2400	.00237	12

CHAPTER VIII

ANALYTICAL RESULTS AND DISCUSSION

Calcium Content of Lepidolites

Addition Plot: The straight line in Figure 12 represents the locus of the intensities of Ca 3968 plotted against the amounts of calcium added. Extrapolation of the line to zero intensity indicates the presence of .0032% Ca in the pure San Diego lepidolite.

Working Curve: The intensities of Ca 3968 were replotted against the absolute amounts of calcium present in the base to give the working curve shown in Figure 12a. The absolute amounts of calcium in the standards were obtained by the addition of the amount of .0032% to the percent of calcium added to the base. It will be noticed that the working curve has the theoretical 45° slope.

Calcium Content of Samples: The amounts of calcium present in the samples were obtained by applying the corresponding intensities to the working curve and reading of the % Ca on the abscissa. The calcium content of the lepidolites is presented in Table 9. The calcium contents of the lepidolites are of the same general magnitude as reported by Ahrens (1951, p314).

The standard deviation calculated from 6 arcings of the San Diego lepidolite equals ± 7%.

Calculations of Radiogenic Calcium

The theoretical amounts of radiogenic calcium present in the lepidolites can be calculated from equation 6 and the assumptions made on page 81 if the ages of the samples are known. The ages for most of the lepidolites are established by the Rb - Sr method (Ahrens 1951, and personal communication).

The theoretical amounts of radiogenic calcium determined on the basis of the above assumptions are presented in Table 9.

Comments on Determination of Radiogenic Calcium

The proportion of radiogenic calcium may be determined by mass spectrographic analysis. Ca^{40} forms about 97% of ordinary calcium. The second most abundant isotope is Ca^{44} which forms about 2.06 - 2.13% of common calcium (see Table 8). The amount of radiogenic Ca^{40} can be established by measuring the variation of the ratio of Ca^{40}/Ca^{44}. Accurate determination of the proportion of radiogenic strontium would be somewhat difficult because of the very high proportion of Ca^{40} in ordinary calcium. Ahrens (1951) believes that the lowest ratio of radiogenic calcium to total calcium that can be measured may be of the order of 1 - 5%.

A chemical concentration similar to that described in Part I for biotites can be followed to obtain a calcium concentrate suitable for mass spectrograph analysis.

Ahrens (personal communication) reports that preliminary work on a hydroflouric acid residue of a lepidolite from Manitoba failed to show the presence of radiogenic calcium although the theoretical proportion of radiogenic to total calcium was approximately 30%. The entire problem is at present being investigated by Dr. L. T. Aldrich of the Carnegie Institution of Washington.

The possibility of a blank error caused by the chemical reagents was investigated. Pure carbon electrodes were soaked in the reagents and arced on the spectrograph. Calcium is absent in the HF, NH_4OH, and $HClO_4$.

CHAPTER IX

CONCLUSIONS

The calcium content of lepidolites can be determined by a simple spectrographic method. The possibility of calcium contamination is reduced by the elimination of any preliminary chemical treatment of the sample. Blank errors due to the presence of calcium in the electrodes appear to be insignificant.

The calcium content of twenty-five lepidolites analyzed varied from .0026 - .06%. A plot of the calcium content shows no systematic variation with geologic age. It may however be pointed out that some of the oldest lepidolites contain the highest content of calcium. This trend may be due, however, to the possible presence of traces of impurities such a plagioclase in the samples.

The proportion of radiogenic calcium to total calcium in the samples falls in a range of 1 - 40% on the basis of theoretical calculations. Most of the lepidolites of Precambrian age (over 500×10^6 yrs.) contain more than 5% radiogenic strontium. It would appear therefore that the calcium method of age determination should be feasible for lepidolites of Precambrian age.

CHAPTER X

RECOMMENDATIONS FOR FURTHER RESEARCH

The present work indicates that up to 40% of the calcium in lepidolites ought to be radiogenic. Similar estimates were made by Ahrens (1951). However, as mentioned in a previous section, preliminary work has failed to show the presence of radiogenic calcium in a Precambrian sample of lepidolite from Manitoba. In fact, radiogenic calcium has been reported present in but one sample of sylvite. It would seem that the ability to determine the amount of radiogenic calcium by isotope analysis is the most important aspect requiring investigation. Explanations other than analytical technique, however, may offer the answer to the apparent absence of radiogenic calcium.

PART III

THE POTASSIUM CONTENT OF ULTRAMAFIC ROCKS AND ITS HEAT CONTRIBUTION

INTRODUCTION

One of the most fundamental problems amongst geologists and geophysicists is that concerning the source and distribution of heat in the interior of the Earth. The scientists concerned with this problem place much emphasis upon the heat produced in the mantle by the disintegration of K^{40}, the radioactive isotope of potassium. This investigation is concerned with the abundance of potassium in ultramafic rocks and is directly related to the amount of heat generated within the mantle of the Earth.

The problem of the internal structure of the earth is much too broad a problem to be considered here. The reader is referred to a text such as "The Internal Constitution of the Earth" by Gutenberg (1951) for a comprehensive discussion. It will suffice to mention briefly the popular theories (Birch, 1951) regarding the composition of the mantle. The first theory supposes that the mantle resembles the ultrabasic rock dunite (Adams and Williamson, 1925) and the second theory supposes that the mantle resembles the average stony meteorite in composition (Washington, 1925; Daly, 1943).

The amount of potassium present in dunite is commonly assumed to be about 0.03% which is based upon Daly's averages (1933, see below). Recent work by Pinson (1951) indicated that the reported values of potassium content in ultramafic rocks as determined by chemical analysis may have to be drastically revised. This work was undertaken, therefore, to determine the amounts of potassium in ultramafic rocks by spectrographic methods in order to check the reliability of the chemical analyses referred to in geologic literature.

CHAPTER XI

PREVIOUS WORK

Chemical Analyses: Numerous investigators have determined, reported, and compiled chemical analyses of ultramafic rocks from various countries (such as Clarke, 1889; Clarke and Hillebrand, 1897; Harker, 1889 and 1904; Washington, 1903; Daly, 1910, 1914, 1933; Clarke and Washington, 1922 and 1924). Chemical analyses are often included in many transactions, proceedings, or other publications of geological societies, in scientific journals, and in official government survey publications. No attempt was made to search all the literature for chemical analyses.

The mean chemical composition of various types of igneous rocks were compiled by Daly in 1933. His values for the average potassium content of ultramafic rocks are listed in Table 10.

Chemical analyses of serpentine usually fail to show an analysis for potassium. Daly does not give any averages for serpentine. The general magnitude of the potassium content in these rocks is shown in Table 11 which are taken from compilations by Clarke and Washington (1924).

TABLE 10

Daly's Averages

Rock Name	% K_2O
Cortlandite	0.54
Amphibole Peridotite	0.36
Wehrlite	0.57
Harzburgite (Saxonite)	0.13
Lherzolite	0.21
Dunite	0.04
Mica Peridotite	4.90
Websterite	0.35
Bronzitite	0.11
Diallagite	0.49
Augitite	1.92
Saxonite	0.13
Anorthosite	.74
Norite	.79

TABLE 11

Potassium in Serpentinites

Location	% K_2O
Blandford, Mass.	.10
Middlefield, Mass.	.08
Rowe, Mass.	.16
Russell, Mass.	none
North Blandford, Mass.	none
Chester, Mass.	none
Mount Diablo, Calif.	.16 (average of 8)
Boulder Creek, Ore.	none
Iron Mountain, Ore.	.05
Three Brothers, Wash.	.10

Recent contributors to the general problem of radioactivity of potassium have assumed a potassium content in dunites not significantly different from Daly's averages (Birch, 1951, 0.03% K; Gutenberg, 1951, 0.01% K; Urry, 1949, 0.01% K). To the writer's knowledge Daly's averages for potassium in ultramafic rocks have remained essentially unchallenged until Pinson's work (1951) showed that these values may have to be drastically reduced.

Pinson made spectorgraphic determinations of a number of ultramafic rocks and his values are reproduced in Table 12.

Occurrence of Potassium in Igneous Rocks: The geochemistry of potassium has been recently discussed by Rankama and Sahama (1950) and the reader is referred to their excellent book for detailed information.

It seems well established that magnesium and iron silicates such as olivine or pyroxenes are the first minerals to crystallize from an igneous melt. The ionic radii of Mg^{+2} and Fe^{+2} are 0.66A and .74A respectively. Potassium, on the other hand, forms a univalent positive ion having an ionic radius of 1.33A. It is very strongly lithophile in character.

It could be inferred, from considerations of Goldschmidt's rules, that the large disparity in size and difference of charge would make itself felt and consequently little or no substitution of K^{+1} for Mg^{+2} or Fe^{+2} would take place. The magnesium and iron would enter the structures of early formed minerals such as olivine or pyroxene and the K^{+} would be rejected into the residual melt of a crystallizing magma.

Such is actually the case. Potassium is strongly enriched in the late crystallates and is present only in small amounts in the early formed fractions. Clarke (1924) estimates that feldspar forms about 60% of the minerals of igneous rocks. These feldspars are either pure alkali feldspars or contain variable amounts of the alkali components. The bulk of potassium is contained therefore in the feldspars. Alkali feldspars such as orthoclase, microcline, sanidine, and adularia are peculiar to the last stages of magmatic differentiation.

Potassium is also enriched in feldspathoids, potash micas, and to a minor extent in alkali pyroxenes and amphiboles. The feldspathoids and micas are also generally formed in the later stages of magmatic differentiation. Some ultramafic rocks, however, contain a considerable amount of biotite (e. g. kimberlite, and mica peridotite) and consequently a large amount of potassium, comparable to that in granite.

CHAPTER XII

SOURCE OF MATERIALS

The object of this investigation was to work only on ultramafic rocks such dunites, peridotites, and serpentinites. Unfortunately, specimens of such rocks were of limited supply.

Some of the ultramafic rocks were obtained from the M. I. T. petrology and mineral deposits collections. Eight specimens of ultramafics were obtained from the petrology collection at Harvard University. A suite of ultramafic rocks from S. E. Alaska was obtained from Professor G. Kennedy of Harvard University. Seven specimens of well known ultramafic rocks were acquired from Dr. W. H. Pinson (1952) who in turn acquired them from Davis and Hess (1949) of the Carnegie Geophysical Laboratory. Two specimens were obtained from Dr. J. M. Black of the British Columbia Department of Mines. Professor H. W. Fairbairn supplied two dunite samples from Russia and New Zealand.

The location and a very brief megascopic description of the samples are outlined in the following section. The names and locations of the rocks obtained from the M. I. T. and Harvard collections are those appearing on the corresponding collection cards. The rocks were not examined microscopically except for several specimens. The given locations of the samples are assumed to be correct, and with the exception of sample 36 there was no reason to doubt the accuracy of assigned rock name on the basis of visual examination. The reader is referred to Davis and Hess (1949) for detailed petrographic descriptions of the samples obtained from them.

Location and Description of Samples

1. Serpentinite (M. I. T.) Bell Mine, Thetford, P. Q. A dull, greenish-grey serpentine with a porcelain-like texture. Several grains of pyroxene up to 2 mm. in size occur in the fine grained groundmass.

2. Serpentinite (P 141 - Davis and Hess), Geiger's Quarry, Wash. Sample obtained from Pinson in crushed state. For petrographic description see report by Davis and Hess (1949).

3. Dunite (43AK 142 - Kennedy) Blashke Islands, S. E. Alaska. A highly altered, black dunite cut by numerous veinlets of serpentine.

4. Dunite (P 145 - Davis and Hess) Twin Sisters Mtn., Whateon, Wash. A massive, fresh, light greenish-grey dunite, coarse grained, contains traces of euhedral chromites.

5. Lherzolite (1316 - M. I. T.) Sudbrook Park, Maryland. A fresh, dark greenish-brown rock in which crystals of pyroxene up to 10 mm. in length can be observed. Light grey crystals of plagioclase are scattered throughout and form about 5% of the rock.

6. Pyroxenite (43-AK-478, Kennedy) Mt. Burnett, S. E. Alaska. A fresh specimen of massive, coarse grained pyroxene.

7. Peridotite (43-AK-530, Kennedy) Mt. Burnett, S. E. Alaska. A medium grained, light brown, granular specimen consisting of olivine grains and about 5% disseminated magnetite.

6. Pyroxene (43-AK-435, Kennedy) Mt. Burnett, S. E. Alaska. The pyroxene portion of a dunite dike containing large crystals of

Pyroxene. (see sample 11).

9. Wehrlite (43-Ak-74, Kennedy) Blashke Islands, S. E. Alaska A non-homogeneous specimen consisting of coarse grained pyroxene and fine grained, brown olivine. Specimen is partly weathered.

10. Serpentinized Dunite (p320, Davis and Hess) King's Mine, Thetford, P. Q. Consists of granular olivine intersected by a network of serpentine veinlets. Serpentine forms about half of specimen.

11. Dunite (43-AK-435, Kennedy) Mt. Burnett, S. E. Alaska. Dunite portion of dunite dike containing large crystals of pyroxene (see sample 8).

12. Lherzolite (Sc10 - M. I. T.) Baltimore, Md. Rock contains about 5% plagioclase crystals. Specimen appears similar to number 5.

13. Hypersthenite (1306 - M. I. T.) Oakwood, Md. A granular pyroxenite with grains up to 5 mm. in size. Interstices are occupied by plagioclase which forms about 5% of rock. Specimen appears partly weathered.

14. Anorthosite (M. I. T.) Cartierville, P. Q. A fresh, massive, medium grained rock consisting of plagioclase and trace of sulphides. According to Saull the field outcrop may be a large boulder.

15. Wehrlite (43-AK-112, Kennedy) Blashke Islands, S. E. Alaska. A medium grained rock composed mainly of dark brown pyroxene grains. A few grains of bluish-green olivine are present. Rock contains large phenocrysts of clear, green diopside.

16. Websterite (p369, Davis and Hess) Webster, N. C. A medium grained, granular, somewhat friable rock consisting of light brown pyroxene and bright green olivine in approximately equal amounts. Fresh appearance.

17. Pyroxenite (43-AK-75, Kennedy) Blashke Islands, S. E. Alaska. Specimen consists almost entirely of coarse grained diopside with few crystals of olivine.

18. Pyroxene-Olivine Rock (2409 - M. I. T.) 4 miles N. W. of Duluth, Minn. A coarse grained rock consisting of pyroxene crystals and serpentine. A few flakes of biotite are present.

19. Serpentinite (5770 - M. I. T.) Thetford, P. Q. A dark green, dense serpentine, described as grading into altered peridotite 5771 - sample 44.

20. Pyroxenite (43-AK-107, Kennedy) Blashke Islands, S. E. Alaska. From a pyroxenite dike. Consists essentially of pyroxene grains up to 15 mm. in size with some black specks believed to be serpentine. Fresh appearance.

21. Dunite (43-AK-525, Kennedy) Mt. Burnett, S. E. Alaska. Specimen consists of fresh, fine grained, light greyish-brown olivine.

22. Mica Pyroxenite (43-AK-452, Kennedy) Mt. Burnett, S. E. Alaska. A medium grained, granular, friable rock consisting of pyroxene and about 2% biotite flakes.

23. Mica Augite Peridotite (S49, M. I. T.) Murfreesboro, Ark. A dull, greenish-brown, altered rock containing about 2% biotite.

24. Pyroxenite (S57, M. I. T.) Webster, N. C. Consists of fresh, coarse grained orthorhombic pyroxene. Contains about 1% bright green specks which may be olivine.

25. Serpentinite (1319, M. I. T.) Bare Hill, Md. A dull, yellowish-green serpentine, somewhat granular in appearance. Contains traces of magnetite.

26. Anorthosite (S44, M. I. T.) Split Rock, Minn. Massive, coarse grained rock consisting of light grey plagioclase. Very fresh appearance.

27. Serpentine (p318, Davis and Hess) Belvedere Mts., Vt. Hess and Davis report rock as being 87 % serpentinized. Specimen obtained from Pinson in crushed form.

28. Dunite (p391, Hess and Davis) Addie, N. C. A fresh, fine grained rock consisting of polygonal olivine grains and about 2% chromite.

29. Dunite (43-AK-47, Kennedy) Blashke Islands, S. E. Alaska. Very fine grained, partly weathered olivine, crisscrossed with iron stained fractures.

30. Saxonite (M. I. T.) Riddle, Oregon. Specimen obtained in crushed form from Pinson.

31. Dunite (p140, Davis and Hess) Balsam Gap, N. C. A sugary textured, medium grained, light green rock consisting of olivine and minor chromite.

32. Cumberlandite (4791, Harvard) Cumberland, R. I. Specimen consists of serpentine and olivine which has been replaced by about 40% magnetite.

33. Dunite (867, Harvard) Nelson, New Zealand. Massive light yellowish-green olivine, very fresh in appearance. Contains 1% disseminated chromite.

34. Peridotite (6464, M. I. T.) Dump of new pit (8/6/28) Asbestos Corporation Mine, Thetford, P. Q. A fresh, greenish grey rock in which about 10% pyroxene grains occur in a finer grained groundmass.

35. Peridotite (1170, Harvard) Cortlandt Series, Montrose Pt., N. Y. A black, medium grained rock consisting essentially of pyroxene. Contains traces of pyrrhotite.

36. Not arced, specimen appears to be improperly labelled.

37. Wehrlite (4955, M. I. T.) Dickerson Hill, Westpoint, N. Y. Fresh, medium grained rock consisting of pyroxene and olivine. A few specks of biotite are present.

38. Dunite (10194-11 M. I. T.) Nizhni Taguil, Russia. A partly serpentinized fine grained dunite containing 1% chromite.

39. Serpentinite (9216-10, M. I. T.) Saranovskoye, Russia. A massive, dark green serpentine, somewhat granular, contains 5% chromite.

40. Mica Pyroxenite (43-AK-437, Kennedy) Mt. Burnett, S. E. Alaska. A friable specimen consisting of equal amounts of medium grained pyroxene and biotite.

41. Peridotite (3131, Harvard) Bakerville, Mitchell County, N. C. A fine grained, somewhat weathered rock, consisting of granular olivine and about 5% pyroxene.

42. Pyroxenite (9149, M. I. T.) Rhodesia, Very fresh, medium grained, orthorhombic pyroxene.

43. Anorthosite (4006, Harvard) St. Jerome, P. Q. A fresh specimen of protoclastic plagioclase containing black streaks of ilmenite.

44. Peridotite (5771, M. I. T.) Black Lake, P. Q. Specimen is described as a typical specimen of Black Lake peridotite. A fine grained rock containing about 10% pyroxene grains up to 3 mm. in size, very fresh appearance.

45. Pyroxenite Norite (M. I. T.) Lydenburg District, Merensky Reef, Transvaal. A medium grained rock consisting of pyroxene and 5% plagioclase in interstices.

46. Dunite (10194, M. I. T.) Nizhni Taguil, Russia. Very fresh specimen of fine grained, dark green olivine, contains 1% chromite.

47. Hortonolite Dunite (M. I. T.) Lydenburg District, Transvaal. Fresh, coarse grained olivine, dark brown colour, sub-metallic lustre.

48. Lherzolite (4003d, Harvard) Lac Lherz, Pyrenees. Massive fine grained, fresh rock consisting of olivine and pyroxene with traces of magnetite.

49. Bronzitite (20580, Harvard) E. Side Bighorn Mts., on Buffalo-Tensleep road. Consists of fresh, coarse grained pyroxene.

50. Serpentinite (9171, M. I. T.) Fontoche Mine, New Caledonia. A dull green serpentine in which several grains of pyroxene are present.

51. Dunite (Fairbairn) Dun Mountain, N. Z. Consists of yellowish green, glassy, medium grained olivine, contains 1% chromite. Specimen is portion of drill core.

52. Dunite (Fairbairn) Krasny Ural Mine, Urals, Russia. Fresh mottled green olivine, contains about 5% chromite in disseminated patches.

53. Peridotite (Black) Atlin, B. C. Appears to be serpentine in hand specimen. Thin section shows serpentinized olivine with minor amphibole.

54. Amphibole-Olivine Rock (Black) Atlin, B. C. Hand specimen consists of essentially of radially fibrous amphibole.

CHAPTER XIII

PREPARATIONS, EXPERIMENTS, AND ANALYTIC PROCEDURES

Preparation of Samples

The amounts of material available from the rock collection specimens were necessarily small as it was not desirable to pulverize the entire specimens. Ten to 100 gram chips were broken off the specimens in a screw vice. Weathered or dirty surfaces were carefully removed off the chips by means of the screw vice or a hammer. The chips were washed and scrubbed in running water and dried in an air blast.

The writer fully realizes the inadequacies of the small chip samples obtained in turn from collection specimens to be representative samples of the rock masses in the field. A large sample from 5 to 10 lbs. would have been preferable but, unfortunately, was unavailable. With the exception of some specimens from S. E. Alaska, all the specimens were fairly homogeneous in texture and mineral content. The writer believer, therefore, that the chips analyzed are adequately large and the results are indicative of what would be found by more elaborate sampling in the field.

The chips were crushed in a steel percussion mortar which was carefully cleaned before each sample. Contamination from the mortar itself offered no problem as the only element sought was K and the amount contributed from the steel presumably negligible. The crushed sample was coned and quartered to yield a 5 gram portion which was ground in a mechanical agate mortar. Grinding for $\frac{1}{2}$ hour was usually sufficient to bring the sample to a powdered stage.

Spectrographic Procedures

Method: It was decided that a total energy method of analysis would be most suitable for the determination of K because of the difficulty in choosing a suitable internal standard. Any alkali, of course, would make an admirable internal standard. Sodium and lithium could not be used because of their variable abundance in the ultramafic rocks. Rubidium or cesium would be suitable because of their low content in the ultramafic rocks. However, it would be extremely difficult to obtain a salt of these elements which would be absolutely free of traces of potassium.

It was felt that a total energy method would be sufficiently accurate provided that all procedures were standardized. Consequently the writer endeavoured to maintain the same degree of uniformity throughout the various stages of the investigation.

Pinson (1952) reported a very low concentration of K in the ultramafics he analyzed. In view of this it was highly desirable that the most sensitive line of K (7664.9) be used. This precluded the possibility of using the grating spectrograph which does not cover this range of the spectrum and the Hilger spectrograph was used instead. Further details regarding the latter instrument will be given in a later section.

<u>Preliminary Experiments</u>: A preliminary investigation was made to determine what size and type of electrode would give the best burning qualities. It was found that the pure samples of ultramafic rocks would not burn satisfactorily in either carbon or graphite electrodes. The arc would wander greatly and give a very irregular burn. Many of the pure samples also formed a glass bead which had a tendency to fly out of the electrode in the early stages of arcing. A mixture of the sample with one part of carbon improved the burn somewhat.

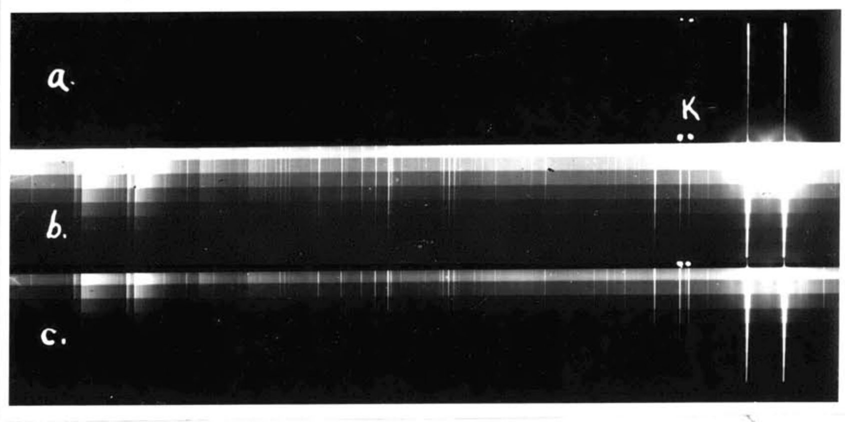
A mixture of the rock sample mixed with two parts of carbon was found to give a very smooth burn in carbon electrodes.

Some difficulty was encountered with the serpentine samples. These samples, even though mixed with two parts of carbon, showed a strong tendency to be blown out of the electrode after several seconds of arcing. A very satisfactory burn was obtained by heating the packed electrodes over the bunsen flame for about 30 seconds.

It was hoped that large electrodes could be used in order that larger amounts of sample could be arced. Fifty to sixty milligram samples could be packed into the large electrodes whereas only 10 milligram samples were the maximum load in the small electrodes. Subsequent work prohibited the use of both 3/16" graphite and carbon electrodes because they gave rise to intense CN background in the region of the most sensitive K line. This is rather unfortunate in view of the low K content of the rocks.

A common way of reducing or eliminating background is by the addition of an alkali salt. Such a method could not be used, however,

PLATE 6



BACKGROUND USING COPPER ELECTRODES

a - Copper Electrode, arced for 10 seconds.

b - Copper Electrode, sample 24, arced for 3 minutes.

c - Copper Electrode, sample 24, arced for 1 minute.

because of the ubiquitous presence of K in all alkali salts.

The background could not be eliminated entirely with the use of either carbon or graphite electrodes. It was established, however, that it could be reduced to a minimum by arcing a mixture of 1 part sample with 2 parts carbon powder to the completion of alkali volatilization in 1/8" carbon electrodes at 3 amperes.

The background is strong even though at a minimum. It places a lower limit of about .003% on the accurate determination of K. Values below this amount can of course be estimated but are less reliable.

Use of Copper Electrodes: A possible method of eliminating the CN background detrimental to the determination of low potassium contents may be sought in the use of copper or some other metal electrodes. Several experiments on their use have been carried out by the writer.

Several copper electrodes were fashioned out of 1.8" copper wire. Pure powdered pyroxenite (sample 24) was loaded into the electrodes and arced at 3 amperes using anode excitation. The use of a copper cathode gave a very irregular burn. However, the use of a carbon electrode for the cathode gave a fairly smooth burn and the CN background was completely eliminated. The extent to which the background is removed is shown in Plate 6.

A possible difficulty that may arise in this method is that the copper fuses and envelopes the sample. This may inhibit the volatilization of the elements sought. One avenue of approach would be to use larger electrodes with thicker walls and a small cavity or some other alloy having a higher melting point. Mixture of the sample with 2 parts of the carbon would cause a more rapid volatilization of K. It seems doubtful to the writer if the carbon mixture would give rise to any significant CN background as the burn using copper electrodes would be relatively cool and thereby lessen the development of background.

The copper electrodes used in these tests showed the most sensitive K lines and hence would not be useful for K analysis of the ultramafics. However pure electrolytic copper could doubtlessly be obtained wherein K was entirely absent.

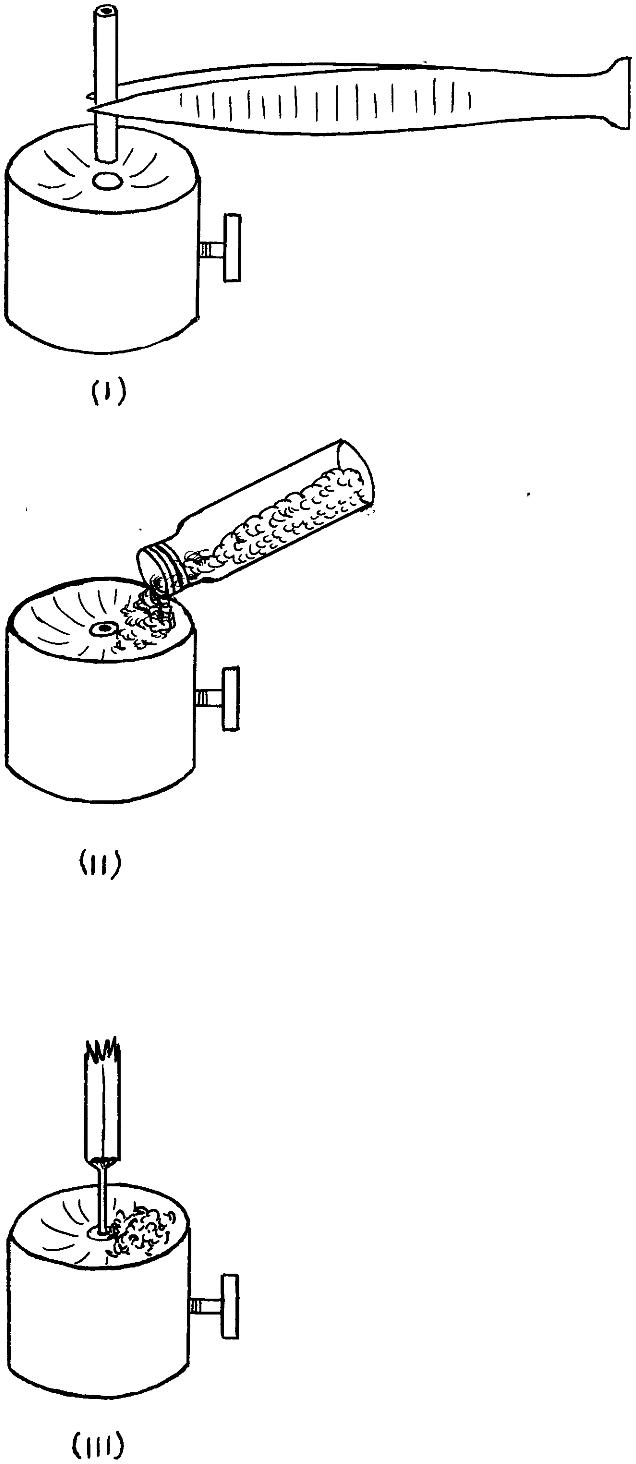
The object of these experiments was to determine whether or not any strong K line could be detected in the sample of pyroxenite which showed only a trace of K[1] when arced in carbon electrodes. As the writer did not establish how much of the K was contributed by the impure copper electrodes no further work was carried out in this line.

---

1. More recent work by the writer on K contamination shows that the presence of potassium in the copper electrodes may be in part attributed to contamination by the perspiration from the fingers during handling of the electrodes.

FIGURE 13

METHOD OF LOADING ELECTRODES



(I)

(II)

(III)

Spectroscopic Settings: The Hilger spectrograph described in Part I of this report was used in the analysis of the ultramafics. Glass optics were used with the right end of the holder set at 9500A. This setting enabled the most sensitive K lines as well as Na and Li to be recorded on one half of a normal photographic plate. The slit width was kept constant at position 6 (~.025 mm.). A rotating step sector with adjacent steps decreasing by a factor of 2 was used to give 8 steps ranging from 1 to 1/128 of total exposure. The sector was rotating about 500 r. p. m. Anode excitation was employed and the samples arced at 3 amps. and a line voltage of 220 volts. Kodak 1-L plates (emulsion number 484, 423) measuring 4" x 5" were used. The plates were developed following the standard procedure described on page 11.

Loading of Electrodes: A special electrode holder made by John Solo of the Geology Machine Shop was used in loading the sample into the carbon electrodes. The holder was made out of stainless steel and a sketch of its design is shown in Figure 13. The holder serves a dual purpose. It permits a much firmer and more uniform packing of the sample without breaking the walls of the electrode. It also prevents the contact of the electrode with the fingers which are a definite source of contamination. The latter was important because contamination was a big problem in this investigation.

Ten samples of ultramafics were chosen at random and loaded into the electrodes in duplicate using the holder. It was found that the weight of material packed did not vary by more than ± 2% from.010 grams.

PLATE 7

VOLATILIZATION OF POTASSIUM

Sample 12 (containing .03% K) mixed with 2 parts of carbon and arced at 3 amperes. Each step represents 5 seconds.

It was also found that loss of material from the electrode during arcing was eliminated almost entirely. Loss of material was always an important factor when the electrodes were held in the fingers and loaded with a spatula.

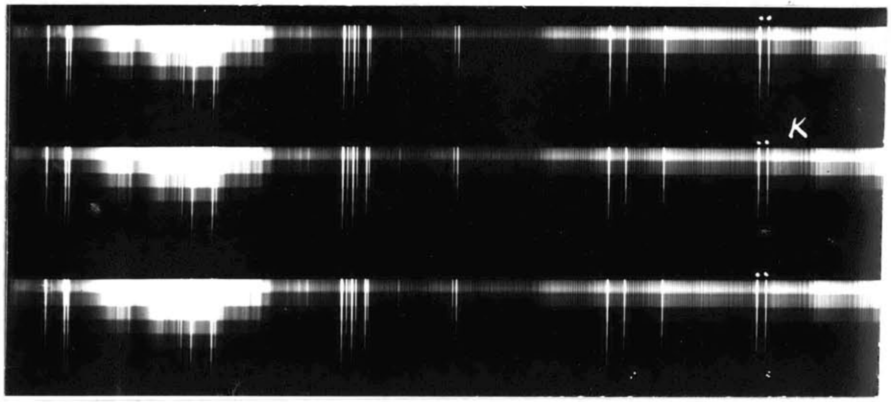
Starting the Arc: The electrodes were always set at predetermined positions so that their image on the slit housing upon arcing measured about 1¼ inches. This position was established by viewing the slit in relation to the electrodes through the focusing lens on the spectrograph. The arc was started by drawing a carbon electrode across the gap. The shutter was kept open at all times.

An alternate method of arcing commonly practised is to bring the electrodes in contact, separate them, and finally opening the shutter. This method was abandoned for the two reasons which follow.

Volatilization tests (see Plate 7) showed that the bulk of K was volatilized in the first 5 seconds of arcing. It was felt that a considerable portion of the K may be volatilized in the 2 or 3 second delay occurring between the sparking of electrodes and opening of the shutter. Secondly, the method of presetting the electrodes gives the operator a much better control of the orientation and the gap distance of the electrodes in the first few seconds of arcing.

It was felt that both of these factors were very important considerations in the total energy method of analysis used. These seemingly small points are therefore stressed for that reason.

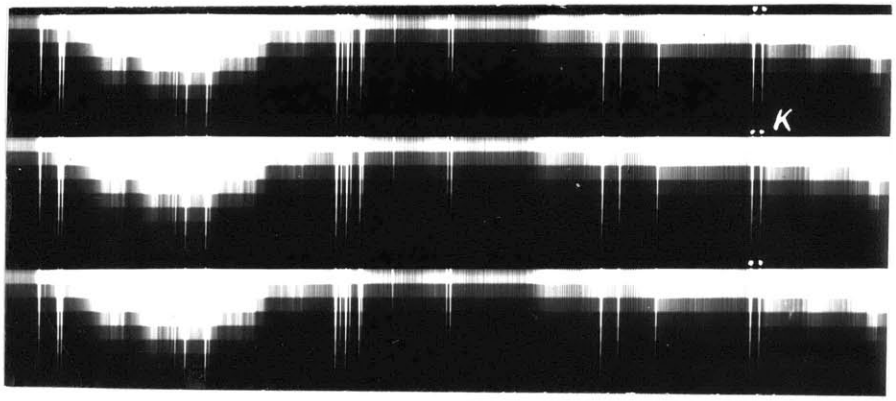
PLATE 8



1 - L plate, emulsion 484, 423.

Sample 22, double exposure.

PLATE 9



1 - L plate, emulsion 484, 839.

Sample 22, single exposure.

VARIATION OF SENSITIVITY WITH EMULSION

Volatilization of K: The dilution of the sample with two parts of carbon caused a relatively rapid volatilization of the K. Plate 7 shows that the K was completely volatilized in the first 20 seconds of arcing.

All samples were arced to alkali completion. This point is indicated by a rapid fluctuation of the voltmeter to 50 volts from the normal reading of 30 volts during the period of alkali volatilization. The time required varied with the samples and ranged from 20 to 35 seconds.

Variation in Emulsion of 1-L Plates: A work of caution concerning the emulsion number on 1-L plates would be in order. It was found in the course of arcing that the sensitivity of the plates varied greatly with different emulsion numbers. The techniques devised and employed in this investigation are based on 1-L plates having an emulsion number 484,423. Plates having different emulsion numbers could not be used with the working curve presented in this report without introducing considerable error.

Plates having the emulsion number 485,839 were found to be far too sensitive for the methods used. The CN background is much more intense relative to the K line in these new plates as compared to the older plates. Examination of plates 8 and 9 will make this clear. Plate 8 is a double exposure on the older emulsion number and plate 9 is only a single exposure of the same sample. Both of the samples were arced without altering any of the instrument settings. This same evidence is available for some 30 different samples.

The great difference of the sensitivity of the 1-L plates is attributed only to the difference of emulsions on the plate.

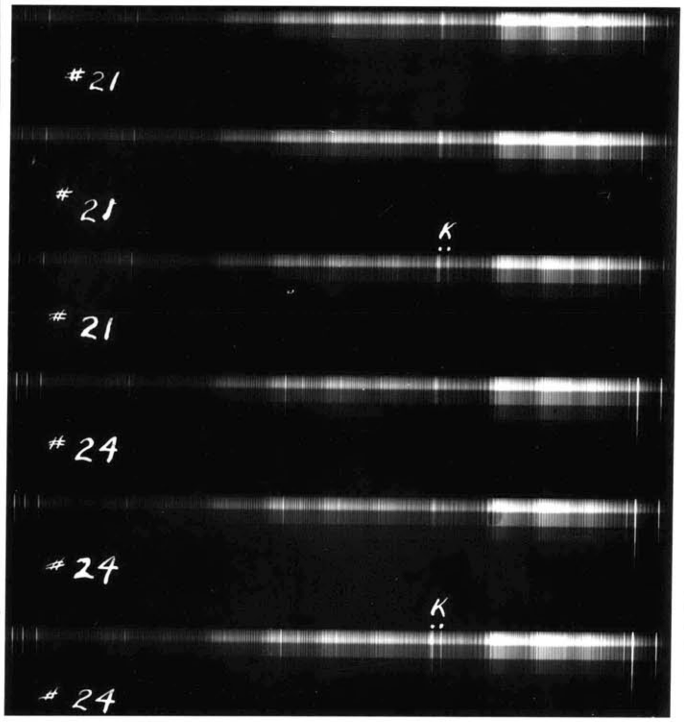
K Contamination in Electrodes: The pure carbon electrodes were tested for the presence of K. Pure carbon powder was loaded into the standard electrodes and arced for 30 seconds which was the average time required for the rock samples arced. A very faint line was visible at the K 76649 position and the writer could not ascertain if it was due to K or to a CN line. As the line was very weak it was felt that it may be disregarded and consequently some 50 samples were arced in triplicate.

Examination of these plates revealed an extremely poor reproducibility which could not be readily explained as the conditions of arcing were uniform. In the arcing of these plates the writer followed the customary procedure of using a long sharpened carbon for the cathode. The carbon was wiped off after arcing, resharpened, and used again for the next sample. Blank carbon electrodes were arced with the used carbons for the cathode and it was found that these re-used electrodes were contributing to K contamination.

The samples were re-arced using sharpened carbon electrodes about an inch long for the cathode. Two burns of each sample were superimposed on the same exposure and three spectra were obtained for each sample.

Much better reproducibility was observed on these plates. However, many of the samples showed inconsistent results. It was

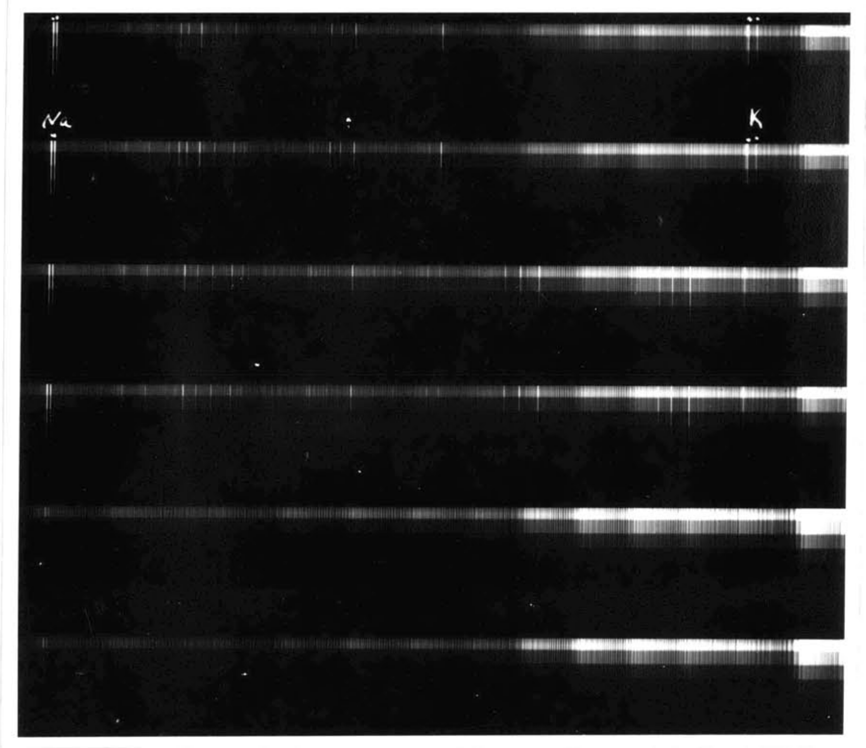
PLATE 10



EFFECT OF K CONTAMINATION

Note the inconsistent potassium doublet in both samples 21 and 24.

PLATE 11



ELIMINATION OF K CONTAMINATION

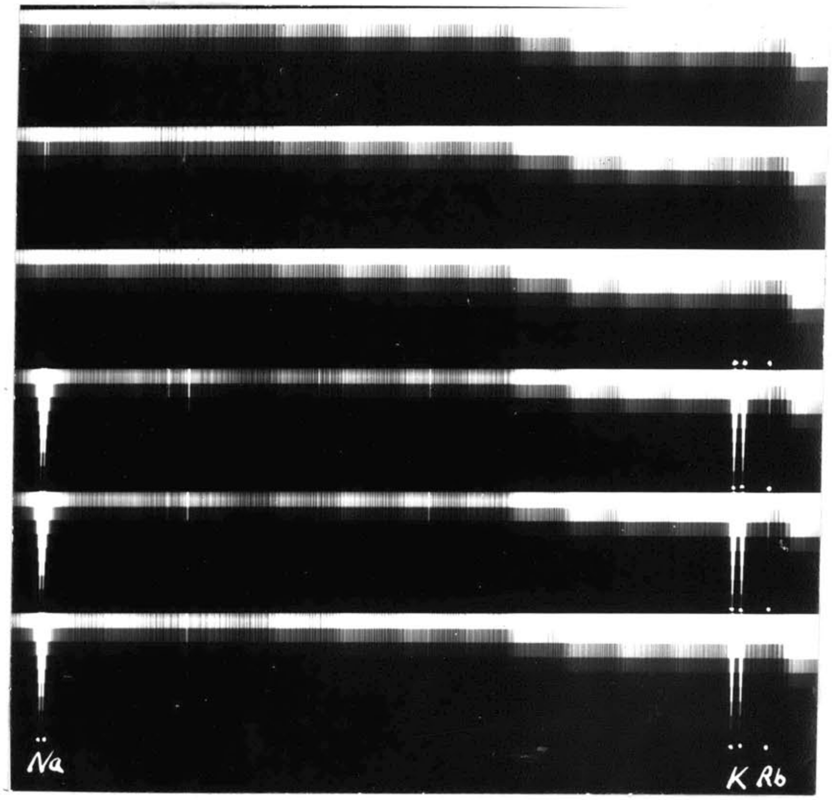
a, b, sample 54 .01% K

c, d, sample 28 .001% K

e, f, pure carbon electrodes, heated to red heat for $\frac{1}{2}$ minute, and arced for 30 seconds.

Note that the K doublet is almost non-existent in c, d. The visible single line is not a potassium line. (c. f. a, b)

PLATE 12



K CONTAMINATION FROM PERSPIRATION

a, b, c, - pure carbon electrodes

d, e, f, - pure carbon electrodes, handled in perspiring fingers for about ½ minute.

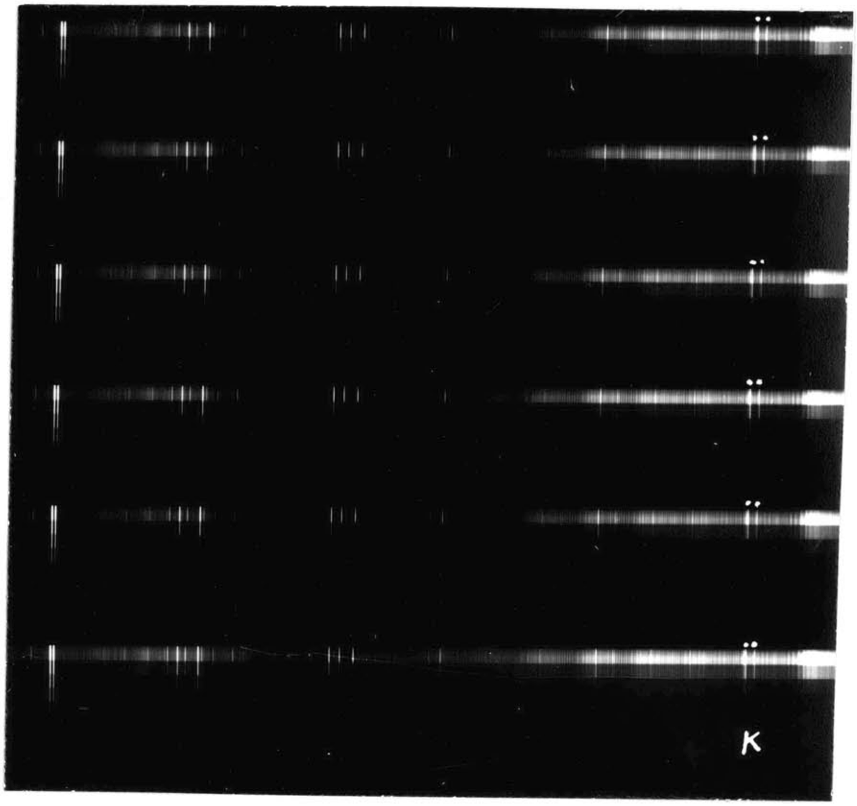
common to find, for instance, that two spectra may show merely a trace of K whereas the third spectrum would show a K line visible for as many as 5 steps. These inconsistent results are illustrated in Plate 10. These anomalous results could be explained only by contamination as it seemed statistically improbable that 4 out of 6 burns would show a mere trace of K whereas the remaining burns would show as much as a 20 fold enrichment of K.

Subsequent experiments showed that the K contamination could be eliminated entirely by heating both the cathode and anode electrodes to a red heat for 30 seconds over a bunsen burner. The contamination could be removed regardless of whether the electrodes were heated prior to or after the sample has been loaded. The electrodes were handled by tweezers and contact with the fingers was avoided. It would seem that the potassium was present in the form of a volatile salt such as the chloride.

The extent to which the K contamination is removed from the carbon electrodes is shown in Plate 11. It is seen that not a trace of K 7664.9 remains in the electrodes after heating the electrodes.

The probable source of the potassium contamination has since been determined by the writer. It is believed to be introduced from perspiration of the fingers during the cutting, sharpening, or loading of the electrodes. Plate 12 illustrates the degree to which K contamination may occur. The top three exposures are pure carbon electrodes arced for 20 seconds after heating to a red heat. The bottom three exposures are pure carbon electrodes which had been heated to red heat for 30 seconds, subsequently handled in perspiring

PLATE 13



EFFECT OF HEATING SAMPLES

a, b, c, Heated to white-red heat for one minute.

d, e, f, Electrodes preheated before loading sample.

fingers, (most of the perspiration obtained from forehead) for about half a minute, and arced for 30 seconds.

Effect of Heating Samples in Electrodes: It was established that no potassium contained in the sample was lost during the heating of the loaded electrodes to red heat for 30 seconds. Several different lines of evidence prove this.

The samples have been arced at least three different times - once by heating the electrodes to red heat and twice without heating. There is no detectable differences in the intensities of the K lines for most of the samples, if the occasional anomalous spectrum is disregarded. It has already been shown that the anomalous results were caused by contamination.

The standards were subjected to the same heat treatment. A plot of the intensity versus the % K gives a straight line having a slope of 45° indicating that no K is lost by heating.

Several samples were loaded into preheated electrodes and corresponding samples were loaded into electrodes and then heated. No difference in the intensities of the K line were observed. Reference to Plate 13 will support this claim. The first three samples have been heated to a white-red heat for 1 minute. The last three samples were loaded into preheated electrodes. No difference in intensity is evident.

Preparation of Standards: The material to be used as a base in the preparation of standards should be as similar as possible to the samples to be arced. Any difference in composition or structure of the mineral components may tend to introduce a systematic error which may be considerable. The preliminary arcing of the samples established that sample 34, a fresh peridotite (#6464, M. I. T. collection) from the Asbestos Corporation dump in Quebec, had but a trace of potassium. The peridotite therefore formed an admirable base as the mineral components would be most closely similar to the variety of dunites, peridotites, pyroxenites, and serpentines to be arced.

A set of standards was prepared to cover the range from 1% to .0004% K. A standard containing 0.1% K was obtained by adding .0227 grams of standard granite (G-1) to 1 gram of peridotite. The standard granite contains 5.42% K_2O or 4.5% K. The mixture was thoroughly mixed and successive dilutions with the peridotite gave standards containing 0.1, .05, .025, .0125, .00625, .00315, and .00157% K. Later investigations showed that standards in excess of 0.1% K were required and consequently standards containing 1 and 0.5% K were prepared in a similar manner.

Calculations

The same Hilger microphotometer as described in Part 1 was used to determine the line densities. The deflections for as many steps as possible were obtained for different lines and background on about 10 different plates. "d_o/d" values were plotted on log log paper to give the calibration curve shown in Figure 15.

The deflections were obtained on those steps of K 7664.9 which gave d_o/d values between 5 and 40 where possible. Such values fell on the straight line portion of the working curve.

Background corrections were necessary and consequently applied to all readings. In view of the unequal background development on either side of the K line it was decided to measure the background on the left side (as viewed in the photometer) of the line only, but free from its halation. The same relative position was picked for all spectra. The use of such a system may not be perfectly valid. However, just what to do with the background is indeed a problem. This method was used both for the samples and the standards and hence it is highly probable that no significant error was introduced.

The working curve shown in Figure 14 is drawn for double exposures on one spectra. Therefore the intensities obtained for single exposures must be multiplied by 2 to determine the % of K present in the sample. The working curve was constructed in a similar manner for the standards containing more than 0.1% K.

CHAPTER XIV

ANALYTICAL RESULTS AND DISCUSSION

Addition Plot and Working Curve: The intensities of K 7664.9 in the standards were plotted against the respective amounts of K added on log log paper. It can be seen from Figure 14 that the locus of these points forms a straight line in the range between .00315 and .1% K. The slope of this line is 45° and equals the theoretical slope. It a appears therefore that the amount of K in the peridotite has little effect on the intensity values of K in the range between .00315 and .1%.

The departure of the graph from linearity above the concentrations of .1% K is probably caused by self absorption.

The intensity values determined for the potassium concentrations below .00315% show extreme spreading. The background intensity plays an important role at these low concentrations and hence the points cannot be considered too reliable.

The apparent toe in the curve at these low concentrations may be caused by two reasons. The chief reason is the presence of a trace of K in the base material. The second was already mentioned previously as being the impossibility of assessing the role of background accurately.

A method commonly used to determine the amount of the analysis element in the base is by means of the addition plot. (Ahrens, 1950). In this case a projection of the 45° slope to zero intensity would indicate a zero amount of K. The spread is too great in the low concentrations to warrant the use of an addition plot.

The average of the intensities obtained for the pure material was

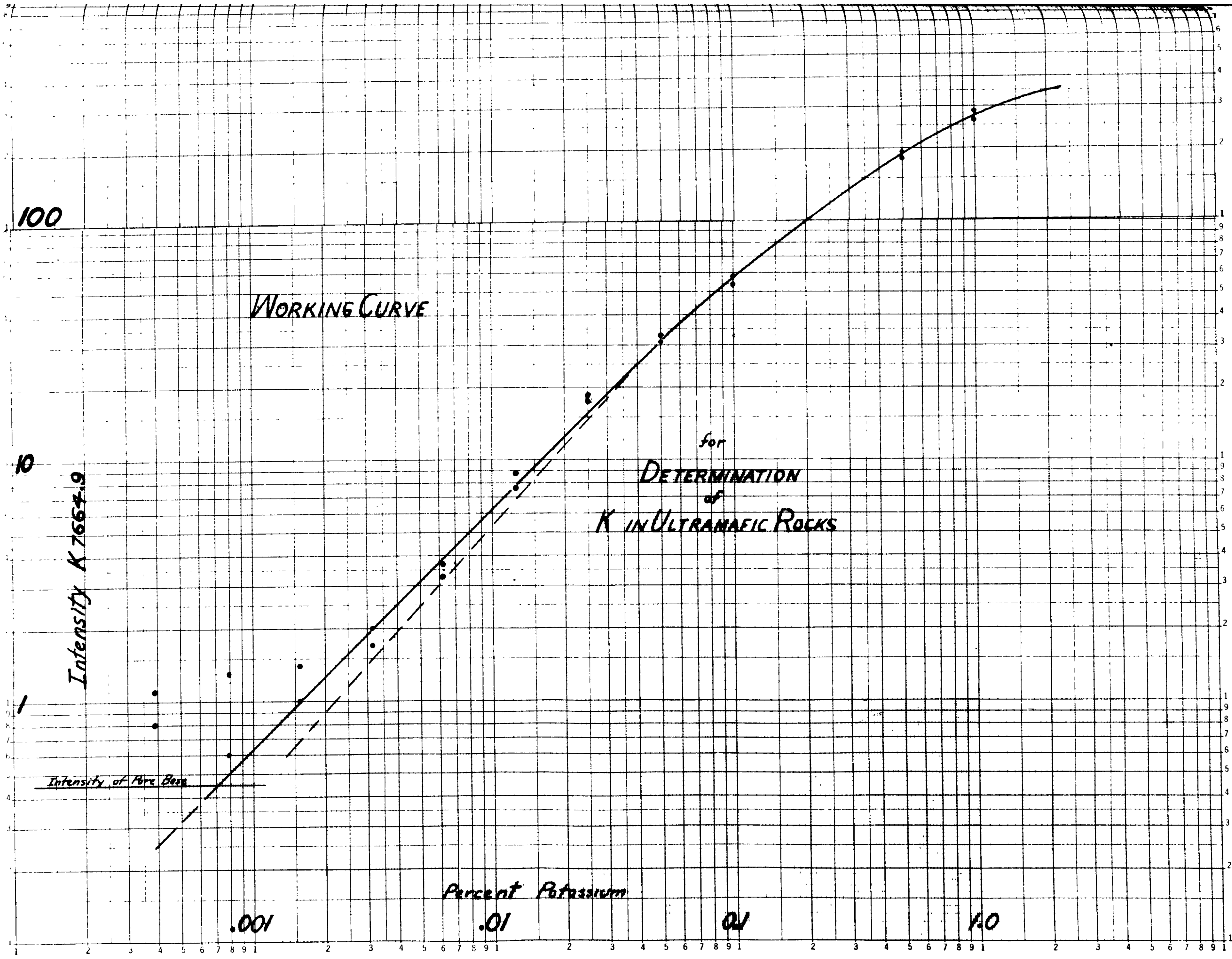
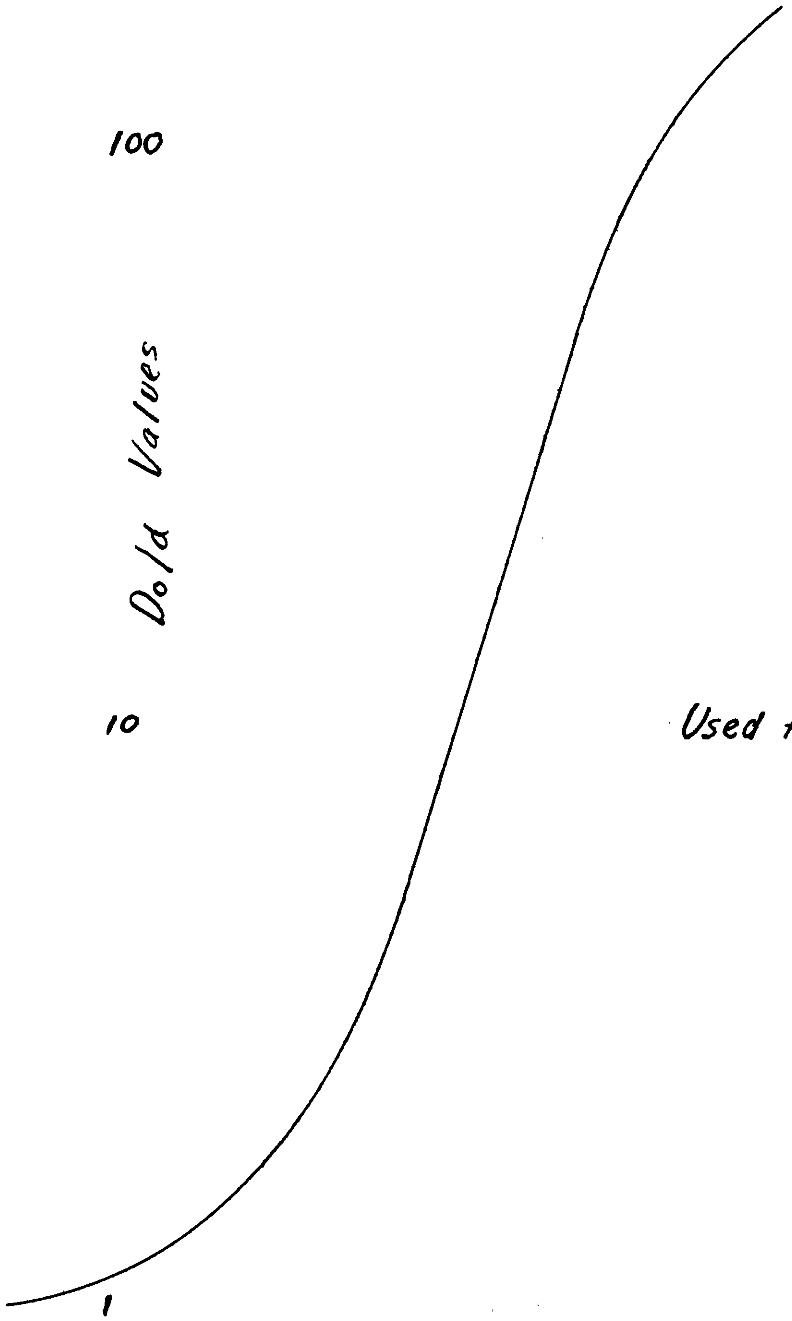

WORKING CURVE
for
DETERMINATION
of
K IN ULTRAMAFIC ROCKS
Intensity K 7664.9
Intensity of Pure Base
Percent Potassium
100
10
1
.001
.01
0.1
1.0

FIGURE 14

FIGURE 15

CALIBRATION CURVE
of
I-L PLATES



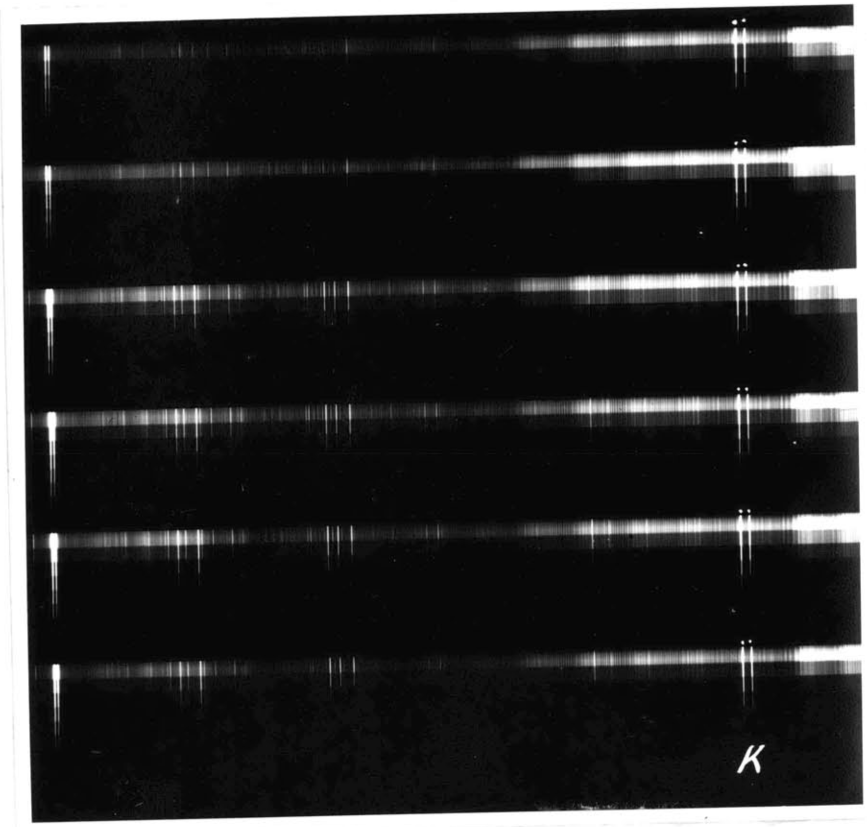
Used for determination of
K intensity

0.45. If no traces of the trace element were present in the base then the plot of the intensity ratios would theoretically form a straight line at 45°. It is evident from the shape of the curve and also from the plates that the amount of K in the base must be less than .003%. It is also seen that no self absorption is evident till the concentration exceeds .1%. The position of the intensity for .05% K added (Figure 14) would be displaced an insignificant amount if the amount of potassium in the pure base (~ .001% K) were taken into account. Therefore, the theoretical amount of potassium in the base should be indicated by the intersection of a 45° line drawn through this position and the intensity level of the pure base. This intersection on the graph indicates .0007% K.

A working curve can be constructed by plotting the intensity ratio against the adjusted amount of K present (i. e. the % K in the base plus the % K added to the standard). Such a curve is indicated by the dashed line in Figure 14. It is seen that the slope of the resulting working curve exceeds the theoretical 45°. It seems, therefore, that the .0007% K indicated may be high for the content of K in the base. As mentioned before, not too much faith can be placed in the intensity values obtained for the low concentrations because of the relatively strong background.

Visual examination of the pure peridotite spectra would indicate an intensity of one half the intensity for the .00039% standard. If this is correct then the K content would be about .0004%. Even the value of .0004% would have the effect of increasing the slope of the curve in excess of 45°. It seems very possible then that the K content

PLATE 14



COMPARISON OF ULTRAMAFIC STANDARDS
AND STONY METEORITES

a, b, Peridotite 34, containing 0.1% K

c, d, Homestead Meteorite

e, f, Kernouve Meteorite

may be as low as .0001% which would have no appreciable effect on the slope of the working curve.

No definite value can be assigned to the K content of the peridotite but it should lie in the range from .0001 to .001% K.

Because of the inability to assign any definite value to the K content of the peridotite it would seem best to use the addition plot also as a working curve. The actual K content of the samples analyzed may therefore be greater than the value quoted by an amount ranging from .0001 to .001%. This range may be large but the results obtained for the K content are nevertheless significant.

Accuracy of Results: Two chondrites were arced to check the general accuracy of the method used in this investigation. The potash contents of these chondrites have been previously determined by Pinson by spectrographic methods and checked by G. Sullivan by flame photometer methods (see Pinson, 1951, p 25).

The potassium contents determined by the three different methods are as follows:

Chondrite	% K_2O Present (Spectrograph)	% K_2O Pinson (Spectrograph)	% K_2O Sullivan (Flame photometer)
Homestead	0.115	0.11	0.12
Kernouve	0.115	0.11	0.10

It is seen that the potassium determinations by the three methods are consistent. A comparison of the spectra for the two meteorites in relation to the 0.1% K standard is shown in Plate 14.

The values of potassium reported as ≤ .001% were obtained by visual comparison of the spectra of the different samples to that of sample 34, which was used as the base for the standards. This range of ≤ .001% is believed to be correct.

The reported values greater than .002% K may be subject to a maximum correction of about +.001% K. This follows from the fact that the amount of potassium present in the pure peridotite (sample 34) could not be assigned a definite figure and hence was not considered in construction of the working curve (see page 139 for further discussion).

The relative intensities obtained from 6 samples of number 42 containing .008% K are of the following magnitude: 23.5, 20, 20, 24, 19, 22. (These intensities are relative only and obtained on new 1-L plates so cannot be applied directly to the working curve shown in Figure 14). Because of the 45° working curve these values are directly proportional to the amount of potassium present. The relative deviation is ± 8% on the basis of the above intensities.

Potassium Content of Ultramafics

For discussion purposes it would be convenient to sub-divide the ultramafic into three groups, each of which have distinctive chemical and mineralogical differences as well as different field relations. The classifications used by Davis and Hess (1949) will be satisfactory for this purpose.

1. Ultramafic Rocks of the Basaltic Magma Suite. This class of ultramafics is one of the most clearly recognized forms of igneous intrusion (Turner and Verhoogen, 1951, p234) and is represented by banded gabbro-peridotite sheets or lopoliths such as the Bushveld or Stillwater complex. The ultramafics appear to be differentiates of a basaltic magma.

Much less distinct but similar ultramafic rocks occur as minor associates of granite or granodiorite masses along fold mountain regions and may be differentiates (Turner and Verhoogen, 1951, p239).

2. Ultramafic Rocks of Secondary Peridotite Suite. This class of rocks consists of pipes or irregular intrusions of ultramafic composition which cut across the Stillwater and Bushveld complex. Bowen and Tuttle's (1949) recent work indicates that these may be caused by hydrothermal replacement of the older rocks.

3. Ultramafic Intrusives of the Primary Peridotite Suite. This is a major group of ultramafic intrusives which are associated with orogenic belts the whole world over. These belong to the class which were considered by Hess (1938) to represent a primary peridotite magma.

The amount of potassium contained in the ultramafic rocks as determined in this investigation is shown in Table 12.

TABLE 12

ULTRAMAFIC ROCKS OF BASALTIC MAGMA SUITE OR OF UNCERTAIN CLASSIFICATION

Sample No.	Rock Type	Location	% K (average)	% K (Pinson)
3	Dunite	S.E. Alaska[1]	.002	
11	Dunite portion (cf.8)	S. E. Alaska	≤ .001	
21	Dunite	S. E. Alaska	≤ .001	
29	Dunite	S. E. Alaska	≤ .001	
5	Lherzolite	Sudbrook Park, Md.	.035	
7	Peridotite	S. E. Alaska	.004	
9	Wehrlite	S. E. Alaska	.009	
12 (Sc 10)	Lherzolite	Baltimore County, Md.	.034	~ .015
15	Wehrlite	S. E. Alaska	.002	
18	Pyroxene-Olivine Rock	Duluth, Minn.	.034	
23	Mica Peridotite	Arkansas	> 3.5	~ 4.6
32	Cumberlandite	Rhode Island	.005	
35	Peridotite	Cortlandt Series, N. Y.	.18	
37	Wehrlite	West Point, N.Y.	.16	
6	Pyroxenite	S. E. Alaska	.005	
8	Pyroxene portion (cf.11)	S. E. Alaska	≤ .001	
13	Hypersthenite	Oakwood, Md.	.006	

---

[1] The specimens from S. E. Alaska are from a dunite-pyroxenite-gabbro suite in which the amount of gabbro is of the same order of magnitude as the ultramafic fraction. They are placed in the basaltic magma suite by the writer but may not rightfully belong here. (See Davis and Hess, 1949, p867; Kennedy and Walton, 1946).

TABLE 12 (cont'd)

Sample No.	Rock Type	Location	% K (average)	% K (Pinson)
17	Pyroxenite (Olivine bearing)	S. E. Alaska	.006	
20	Pyroxenite	S. E. Alaska	.005	
22	Mica Pyroxenite	S. E. Alaska	.15	
40	Pyroxenite, Biotite bearing	S. E. Alaska	> 3.5	
42	Pyroxenite	Rhodesia	.008	
49	Bronzitite	E. Side, Big Horn Mountains	.011	
45	Pyroxene Norite	Merensky Reef, Transvaal	.059	
14	Anorthosite	Cartierville, P.Q.	.23	
26	Anorthosite	Split Rock, Minn.	.25	
43	Anorthosite	St. Jerome, P.Q.	.25	
	Secondary Peridotite Suite			
47	Hortonolite Dunite	Transvaal	≤ .001	
	Ultramafic Rocks of Primary Peridotite Suite			
1	Serpentinite	Thetford, P.Q.	≤ .001	
2 (P141)	Serpentinite	Geiger's Quarry, Wash.	≤ .001	∼ .0005
19	Serpentinite (grades into sample 34)	Thetford, P.Q.	≤ .001	

TABLE 12 (cont'd)

Sample No.	Rock Type	Location	% K (average)	% K (Pinson)
25	Serpentinite	Bare Hill, Md.	≤ .001	
27 (P318)	Serpentinite	Belvedere Mt., Vermont	≤ .001	~ .003
39	Serpentinite	Saranovskoya, Russia	≤ .001	
50	Serpentinite	New Caledonia	≤ .001	
4 (P145)	Dunite	Twin Sisters Mt. Wash.	≤ .001	~ .0005
10 (P320)	Dunite	Thetford, P.Q.	≤ .001	~ .003
28 (P391)	Dunite	Addie, N. C.	≤ .001	~ .004
31 (P140)	Dunite	Balsam Gap, N.C.	≤ .001	~ .001
33	Dunite	Nelson, N. Z.	≤ .001	
38	Dunite	Nizni Taguil, Russia	≤ .001	
46	Dunite	Nizni Taguil, Russia	.002	
51	Dunite	Dun Mt., N. Z.	≤ .001	
52	Dunite	Krasny Urals Mine, Russia	≤ .001	
16 (P369)	Websterite	Webster, N. C.	.003	~ .011
30	Saxonite	Riddle, Oregon	≤ .001	
34	Peridotite	Thetford, P. Q.	≤ .001	
41	Peridotite	Bakerville, N.C.	.002	
44	Peridotite	Black Lake, P.Q.	≤ .001	

TABLE 12 (cont'd)

Sample No.	Rock Type	Location	% K (average)	% K (Pinson)
48	Lherzolite	Lac Lherz, Pyrenees	≤ .001	
53	Peridotite	Atlin, British Columbia	≤ .001	
54	Amphibole-Olivine Rock	Atlin, British Columbia	.01	
24	Pyroxenite	Webster, N. C.	≤ .001	~ .001

Comments on Chemical Determinations of Potassium

The results of this investigation would indicate that a large number of the potash determinations in ultramafic rocks as reported in geologic literature are entirely erroneous.

Previous investigators have also reported similar discrepancies. Wahl (1950) checked the alkali content of some meteorites and concluded that some of the high alkali values reported depend upon erroneous analytical results. Pinson (1951) made spectrographic analyses of some ultramafic rocks and meteorites and reports a considerably lower potash content than that generally assumed.

The alkali determinations have been considered to be accurate in the past. This may be illustrated by a pertinent statement made by Clarke and Washington (1924) in their discussion of chemical averages:

> "With such proper care as is assumed to have been taken in making the analyses here used for soda and potash, especially as since the Lawrence Smith method is now generally employed, there is little liability to error in their determination, so that, so far as the analyses are concerned, we may consider the averages for them very trustworthy."

This may explain why the potash determinations in ultramafic rocks have not been seriously challenged in the past.

Apart from any obvious error that may have been introduced, Ahrens (1952) points out the possibility of a blank error which may be systematic or random. He quotes an example reported by Groves (1951) wherein a blank determination of 0.11% K_2O was found in an "A. R." grade of $CaCO_3$ and NH_4Cl used in the Lawrence Smith method of alkali determination.

A recent co-operative investigation by numerous analysts (Fairbairn et al, 1951) shows that the accuracy of the determinations using spectrochemical methods is usually superior to that using chemical methods for elements which are present in low concentrations.

In view of the drastic discrepancies between the spectrochemical determinations of potassium in ultramafic rocks as found in this investigation and reported chemical determinations, it seems that chemical determinations of less than about 0.5% K_2O may be of little significance and any interpretations based on such results entirely misleading.

Heat Generation by Potassium

The mean energy released by the radioactive decay of ordinary potassium is now believed to be 27 x 10^{-6} cal/year gram K (Birch 1951, after Alburger, 1950; Sawyer and Wiedenbeck, 1950). A summary of the earlier estimate of the energy release is shown in Table 13, taken after Birch (1951).

Table 13

Date	Authority	Energy Release in 10^{-6} cal/year gm. K	Half Life of K^{40} in 10^9 years
1926	Holmes and Lawson	124	0.18
1933	Holmes	20	1.6
1941	Evans and Goodman, Urry	5 ± 2	1.6
1942	Bullard	8	1.5
1947	Gleditsch and Graf	38	0.24
1948	Ahrens and Evans	26	0.45
1948	Borst and Floyd	20	0.4 to 1.2
1948	Graf	22 ± 3	0.5
1950	Jeffreys	22.6 ± 3.6	0.49 to 0.8
1951	Alburger, Sawyer and Wiedenbeck	27 ± 3	1.27 ± 0.1

A mantle of dunite, (see below for further discussion) having a mass of about 4000 x 10^{24} grams, would therefore produce about .01 x 10^{20} calories/year at the present time on the basis of the revised potassium content of .001% K as determined in this investigation. The heat production on the basis of 0.033% K (Daly's average) is about 0.35 x 10^{20} calories/year (Birch, 1951).

Chemical Composition of the Mantle

It would be interesting to speculate upon the composition of the mantle in the light of the very low potassium content of dunites as determined in this investigation. A few preliminary words regarding the theories held up to the present time would be in order.

Many hypotheses of the structure and chemical composition of the Earth's interior have been presented. According to Birch, (1951) the two most popular theories held at present concerning the chemical constitution of mantle are (1) that it resembles the ultramafic rock dunite and (2) that it resembles the stony meteorite.

Adams and Williamson (1925) proposed a mantle essentially consisting of material resembling dunite in composition. Their theory was based entirely on measured and observed velocities of seismic propogation and entirely independent of radioactivity considerations.

The possible similarity of the earth and the meteorites has been widely discussed ever since the French scientist, A. Boisse, suggested in 1850 that the bulk composition of the earth was comparable to the meteorites. According to Hevesy (1933) the composition of the earth corresponds approximately to 55 parts of stony meteorites, 40 parts of iron meteorites, and 5 parts of troilite. The minerals found in meteorites are similar or identical to those found on earth; moreover, the exclusively meteoric minerals are becoming fewer in number (Neuerberg, 1949). Harrison Brown and Patterson (1948) concluded that meteorites originated in a planetary body similar to the earth. Pinson (1951) put the similarity on a more concrete basis by showing that the K/Rb ratio is nearly constant for both meteorites and common igneous rocks thus suggesting a similar origin. Shand (1949, p342) aptly summarizes the thoughts on meteorites by the statement:

> "meteorites bring to our notice a type of rock existing in the Solar System but different from anything that occurs in the outer shell of our planet, and this material has just the composition that petrology, geophysics, and astronomy combine to indicate as likely to be found in the interior of the earth."

The meteorite hypothesis is offered some support from the present investigation. Let it be assumed that the composition of stony meteorites is comparable to the total composition of the crust and mantle before differentiation. The average potassium content of meteorites is taken to be 0.1% (Pinson, 1951). The crust may be assumed to have a mean thickness of 33 km. (Birch, 1951). The average potassium content of the crust is 2.6% (Rankama and Sahama, 1950). The potassium content of the core is believed to be negligible because potassium is very strongly lithophile in character and is not present in the metallic phases of meteorites (Pinson, 1951). On the basis of these figures about 2.85 x 10^{24} grams of potassium should be present in the mantle (see Table 14). On the other hand, a mantle of dunite composition would contain only .04 x 10^{24} grams of potassium. This leaves a total of 2.8 x 10^{24} grams of potassium unaccounted for; and this amount is more than twice the abundance of potassium present in the crust. These calculations, although admittedly crude, are of interest because they cast some doubt upon the theory that the mantle is similar in composition to dunite.

Table 14

Distribution of Potassium in the Earth

	Mass(10^{24}g.)	K%	Mass of K(x10^{24}g.)
Undifferentiated Mantle and Crust	4047	0.1	4.05
Crust	47	2.6	1.2
Mantle	4000		2.85
Dunite Mantle	4000	.001	.04
K unaccounted for			2.8

A somewhat different approach to the chemical composition of the mantle may be had by consideration of heat production and conductivity. Birch(1951) calculated the production of heat from the different regions of the earth on the basis that dunites contain an average of .033% K (Daly's averages) and the silicate phase of meteorites averages 0.20% K (Brown, 1949). Some of his calculations are tabulated below in Table 15.

Table 15

	% K	Heat (10^{20} cal/year)
Ocean	0.038	--
Sedimentary Rocks	3	--
Crust	2.6	0.32
Mantle (dunite)	0.03	0.35
Mantle (meteorite)	0.17	1.8

He further estimates the present rate of conduction of heat to the earth's surface is 2 x 10^{20} cal/year. About one half of this heat lost by conduction is accounted for by the uranium and thorium of the crust alone. This would leave about 10^{20} cal/ year to be accounted for by potassium and any other source. This is of the same order of magnitude as the calculated amount of heat produced by potassium alone as shown in Table 15. Birch points out that the amount of heat produced on the meteorite hypothesis is about twice as much as the amount of heat lost by conduction assigned to the potassium and any other sources such as initial heat. This, he believes, is an indication that the mean potassium content of the mantle should not exceed about 0.1 percent.

If the value of .001% K in dunites is substituted for the erroneously high value of 0.033% then the heat contribution from a dunite mantle becomes about .01 x 10^{20} cal/year. This, by the same reasoning as followed by Birch, would indicate that about three times as much heat is being lost through conduction as that produced by potassium. This may indicate that the mantle does not consist of dunite.

A very significant bit of information was recently reported by Ahrens, Pinson, and Kearns (1952). As a result of their investigation they concluded that old abundance values were unreliable and that a new abundance value of 0.1% K should be accepted for silicate meteorites. This is remarkably similar to the value of 0.1% K that Birch indicated as a probably upper limit to the mean potassium content of the mantle.

CHAPTER XV

CONCLUSIONS

The amount of potassium in ultramafic rocks is considerably lower than that indicated by published chemical analyses. Daly's averages for the potassium content of most of these rocks appear to be based on entirely erroneous chemical determinations.

The ultramafic rocks commonly associated with orogenic belts and belonging to the primary peridotite suite (as defined by Davis and Hess, 1949) show the lowest potassium content. Out of twenty-five samples of serpentinites, dunites, and peridotites belonging to this class that were investigated, twenty-one had a content of ≤ .001% K; one dunite from Russia had .002% K; a websterite from North Carolina .003% K; a peridotite from Bakerville, N. C. .002% K; and an amphibole olivine rock from Atlin, British Columbia showed .01% K. None of the samples had as high a potassium content as indicated by Daly's averages.

In general, the ultramafic rocks of the basaltic magma suite or those of uncertain classification show higher potassium contents than the preceding class. The potassium contents are, nevertheless, lower than Daly's averages with the exception of mica peridotites which are comparable. Biotite or plagioclase crystals were observed in seven out of ten samples which contained over 0.01% K. All dunites investigated showed ≤.001% K with the two exceptions already mentioned. Three samples of anorthosite were investigated and showed a potassium content of about 0.25%.

If one assumes that the bulk composition of the mantle and the crust is similar to that of the stony meteorites then it seems very unlikely that the mantle of the earth is similar in chemical composition to the ultramafic rock dunite. If this were so then we would have difficulty in accounting for the whereabouts of more than twice the amount of potassium that is now present in the earth's crust.

Considerations of the heat flow of the earth in view of the greatly reduced potassium content of ultramafic rocks would also indicate that the mantle does not consist of dunite. Both of these arguments strengthen the theory that the interior of the earth is more similar in composition to the stony meteorites rather than ultramafic rocks.

Potassium contamination is a major problem in spectrographic investigations such as this where very small amounts of potassium are present. Any form of handling of the sample or the electrodes with bare hands introduces potassium contamination. The source of the contamination is believed to be caused chiefly by body perspiration and introduced by means of the hands. The contamination can be eliminated by heating and avoiding subsequent contact with the fingers.

The detection limit of the method employed is about 0.001% K. This detection limit can be decreased if some means of reducing or eliminating the CN background is developed.

CHAPTER XVI

RECOMMENDATION FOR FURTHER RESEARCH

It would be highly desirable to confirm the preliminary findings of this investigation by more spectrographic determinations of the potassium content in ultramafic rocks. Equal emphasis should be placed on both the primary peridotite and basaltic magma suites. It may prove possible to distinguish these two classes on the basis of the potassium content.

The determination of the potassium content of the ultramafics should be correlated with microscopic investigation of the rocks. It was observed in this investigation that plagioclase or biotite were present in most specimens containing more than .01% K. It would seem probable that the amount of potassium in the ultramafics could be estimated with considerable accuracy from thin section examination of ultramafic rocks.

The use of copper electrodes to reduce CN background should be investigated further. The use of copper electrodes and larger amounts of sample may enable one to assign definite figures to potassium contents falling below .001%.

It was noticed in the course of this investigation that the sodium and lithium contents of most ultramafic rocks were fairly low. The sodium content may also be considerably less than reported in Daly's averages. The Na "D" lines and Li are recorded on the writer's plates. There seems to be no reason why the sodium content of the ultramafic rocks could not be determined from the writer's plates once the amount of Na contributed by the pure carbon electrodes is evaluated. The lithium lines are weak and absent in most of the ultramafic rocks showing small smounts of potassium so that a different technique using the more sensitive lithium line may have to be devised.

Further consideration of the sodium and lithium contents of the ultramafic rocks in comparison to their content in meteorites should prove interesting in speculations about the earth's interior.

BIBLIOGRAPHY

Adams, L. H., and Gibson, R. E., (1926) The compressibilities of dunite and of basalt glass and their bearing on the composition of the earth. Proc. Nat. Acad. Sci., 12.

- - - - - - - and Williamson, E. D. (1925). The composition of the Earth's interior, Smithsonian Rep't for 1923, pp 241 - 260.

Ahrens, L. H. (1947) The determination of geological age by means of the natural radioactivity of rubidium: a report of preliminary investigation, Geol. Soc. S. Africa, Tr. Vol. L, pp 23 - 54.

- - - - - - - (1948) The geochemistry of radiogenic strontium, Mineral. Mag., vol. XXVIII, p 277 - 295.

- - - - - - - (1949) Measuring geologic time by the strontium method. Bull. Geol. Soc. Am. 60, p 217 - 266.

- - - - - - - (1949 - 1950) Exhibit B in Rep. Com. Meas. Geol. Time, (N. R. C. Washington).

- - - - - - - (1950) Spectrochemical Analysis, Addison - Wesley Press, Cambridge.

- - - - - - - (1951) The feasibility of a calcium method for the determination of geological age. Geochimica et Cosmochimica Acta, Vol. 1, p 312 - 316.

- - - - - - - (1952) The use of ionization potentials Part 1. Ionic Radii of the elements. Geochimica et Cosmochimica Acta, Vol. 2, p 155 - 169.

- - - - - - - and Evans, R. D. (1948) The radioactive decay constants of K^{40} as determined from the accumulation of Ca^{40} in ancient minerals. Phys. Rev. 74, 279.

- - - - - - - , Pinson, W. H., and Kearns, M. M. (1952) Association of rubidium and potassium and their abundance in common igneous rocks and meteorites. Geochimica et Cosmochimica Acta (In press).

Alburger, D. E., (1950) Phys. Rev. 78, 629.

- - - - - - - (1951) Heat Production in Potassium, Phys. Rev. 81, 888.

Aldrich, L. T. and Nier, A. O. (1949) Argon 40 in potassium minerals. Phys. Rev. 74, 876.

Birch, F. (1951) Recent work on the radioactivity of potassium and some related geophysical problems. Jour. Geophys. Res. 56, 107.

Bleuler, E. and Gabriel, M., (1947) Dualer Zerfall der Kalium 40, Helv. Phys. Acta, 20, 67.

Borst, L. B., and Floyd, J. J., (1948) The radioactive decay of K^{40}, Phys. Rev. 74, 989.

Brewer, A. K., (1938a),Isotopes of Potassium, Ind. Eng. Chem., 30, 893.
- - - - - - - - - (1938), A mass spectrographic determination of the isotope abundance and of the atomic weight of rubidium, Am. Chem. Soc. Jour., 60, 691.
- - - - - - - - - (1939), Constancy of K^{40}, Phys. Rev., 55, 669.

Brown, H. and Patterson, C. (1947), The composition of meteoric matter: I. The composition of the silicate phase of stony meteorites, Jour. Geol. 55, 405.
- - - - - - - - - (1947a), The composition of meteoric matter: II.The composition of iron meteorites and of the metal phase of stony meteorites, Jour. Geol. 55, 508.
- - - - - - - - - (1948), The composition of meteoric matter: III. Phase equilibria, genetic relationships and planet structure, Jour. Geol. 56, 85.

Buddington, A. F., (1943), Some petrological concepts and the interior of the Earth. Am. Mineralogist, 28, 119.

Bullard, E. C., (1942) Radioactive heat generation in rocks. R. Astron. Soc., Monthly Nat. Geophys. Supp. 5, 41.
- - - - - - - - - (1945) Thermal history of the Earth. Nature 156, 35. With references.

Campbell, N. R. and Wood, A. (1906), The radioactivity of the alkali metals. Proc. Camb. Phil. Soc. 14; 15.

Ceccarelli, M., Quarcini, G., and Rostagni, A. (1950), On the radioactivity of potassium, Phys. Rev. 80, 909.

Clarke, F. W., (1889), The relative abundance of the chemical elements. Philos. Soc. Wash. Bull. 11:131.
- - - - - - - - - (1891), The relative abundance of the chemical elements. U. S. Geol. Survey Bull., 78:34.
- - - - - - - - - (1920), The data of geochemistry. U. S. Geol. Survey Bull., 605:33.
- - - - - - - - - (1924), The evolution and disintegration of matter. U. S. Geol. Survey Prof. Paper, 132-D: 76.
- - - - - - - - -and Hillebrand, W. F., (1897), Analyses of rocks, with a chapter on analytical methods, laboratory of the United States Geological Survey, 1880 - 1896. U. S. Geol. Survey Bull. 148.
- - - - - - - - -and Washington, H. S., (1922), The average chemical composition of igneous rocks. Proc. Matl. Acad. Sci. U. S. 8, 108.
- (1924), The composition of the Earth's crust. U. S. Geol. Survey, Profess. Paper 127.

Daly, R. A., (1910) Average chemical compositions of igneous-rock types. Proc. Am. Acad. Arts Sci. 45.
- - - - - - - - - (1914) Igneous rocks and their origin. New York and London.

Daly, R. A., (1933) Igneous rocks and the depths of the Earth. New York and London.

- - - - - - - (1943) Meteorites and an Earth model. Bull. Geol. Soc. Am. 54.

Davis, G. L., and Hess, H. H., (1949) Radium content of ultramafic igneous rocks: II. geological and chemical implications,. Am. Jour. Sc., Vol. 247.

Dennen, W. H., (1949) Spectrographic investigation of major element variations across igneous contacts. M. I. T. dissertation.

Eklund, S., (1946) Studies in nuclear physics: Excitation by means of X-rays: Activity of Rb 87: Arkiv. Mat., Astron. Fysik., Vol. A 33, no. 14.

Evans, R. C., (1948) Crystal Chemistry, Cambridge University Press.

Fairbairn, H. W. (1949) Structural Petrology of Deformed Rocks, Addison-Wesley Press Inc.

- - - - - - - -and others, (1951) A co-operative investigation of precision and accuracy in chemical, spectrochemical and modal analysis of silicate rocks, U. S. Geol. Survey. Bull. 980.

Fermi, E. (1934) Zs. Physik, 88, 161.

Festa, C., and Santagelo, M. (1950) Ann. di Geofisica, 3, 95.

Gleditsch, E. and Graf, T., (1947) On the Gamma Rays of K^{40}, Phys. Rev. 72, 640.

Goldschmidt, V. M., (1937) Geochemische der Elemente und der Atom, Skrifter Norske Videnskaps - Akad. Oslo 1, Mat. - Naturv. Klasse No. 4.

Graf, T., (1948) Significance of the radioactivity of potassium in geophysics. Phys. Rev. 74, 831.

- - - - - - - - -(1948a) On the total half lie period of K^{40}, Phys. Rev. 74, 1199.

Gutenberg, B., (1939) Physics of the Earth: VII Internal Constitution of the Earth, McGraw Hill.

- - - - - - - (1951) Internal constitution of the Earth, Dover Publications Inc.

Hahn, O., Mattauch, J., and Ewald, H., (1943) Geologische Alterbestimmungen mit dem strontium methods: Chem. Ztg., 67, no. 5-6, 55.

Hahn, O., Strassmann, F., and Walling, E., (1937) Herstellung wagbarer Mengen des Strontiumisotopes 87 als Umwandlungprodukt des Rubidiums aus einen Kanadischen Glimmer, Naturwiss, 25, 189.

- - - - - and Walling, E., (1938) Uber die Moglichkeit geologischer Alterbestimmungen rubidium-haltiger Mineralen und Gesteine: Zeit. Anorg., Allgem. Chem., 236, 78.

Harker, A., (1899) On the average composition of British igneous rocks. Geol. Mag. 4:6, 220.

- - - - - - - - -(1904) The Tertiary igneous rocks of Skye, Mem. Geol. Surv. Un. King.

Harteck, P., and Suess, H., (1947) Der Argongehalt Kalihaltiger Minerale und die Frage des dualen Zerfalls von K^{40}, Naturwiss., 34, 214.

Haxel, O., Houtermans, F. G., and Kemmerich, M., (1948) Phys. Rev. 74, 1886.

Hess, H. H., (1938) A primary peridotite magma. Am. J. Sc., 5 series, 35.

Hevesy, G., (1933) Die Zusammensetzung der Erde. Handbuch der Geophysik. 2, Berlin.

Holmes, A., (1933) The thermal history of the earth. Jour. Wash. Acad. Sci., 23, 165.

- - - - - - and Lawson, R. W. (1926) The radioactivity of potassium and its geological significance, Phil. Mag. 2, 1218.

Inghram, M. G., Brown, H., Patterson, C., and Hess, D. C., (1950) The branching ratio of K^{40} Radioactive Decay, Phys. Rev. 80, 916.

- (1952, in press) The branching ratio of K^{40} radioactive decay. Phys. Rev.

Ishibashi, M., and Ishihara, T., (1942) Chemical studies of micas. Chemical constituents of lepidolite and its meaning from the standpoint of geochemistry and chemical sources. Chem. Soc. Japan, Jour. 63, 767.

Jeffreys, H., (1950) Ann. Geophys. 6, 10.

Kennedy, G. C., and Walton, Jr., M. S., (1946) Geology and associated mineral deposits of some ultrabasic rock bodies in Southeastern Alaska, U. S. Geol. Surv. Bull. 947-D, p 65-84.

Marwin, G. R., and Woolaver, L. B., (1945) Thermal decompositions of perchlorates, Ind. Eng. Chem., Anal. Ed. 17, 474.

- - - - - - - - - - - - - - - - - - (1945a) Determination of sodium and potassium in silicates, Ind. Eng. Chem. Anal. Ed. 17, 554.

Moller, C., (1937) Phys. Rev., 51, 84.

Neuerberg, G. J., (1949) A second note on exclusively meteoric minerals, Pop. Astron. 57, 342.

Nier, A. O., (1938) The isotopic constitution of radiogenic leads and the measurement of geological time. 11, Phys. Rev. 55, 153.

- - - - - - - - -(1950) A redetermination of the relative abundances of the isotopes of neon, krypton, rubidium, xenon, and mercury. Phys. Rev. 79, 450.

Nockolds, S. R., and Mitchell, R. L., (1948) Geochemistry of Caledonian plutonic rocks, Roy. Soc. Edinburgh LXI.

Oldham, R. D.,(1919) The interior of the Earth. Geol. Mag. 56:21.

Pettijohn, F. J., (1941) Persistence of heavy minerals and geologic age, Jour. Geol. vol. 49, p 610-625.

Rankama,K. &Sahama, Th. G., (1950) Geochemistry, Univ. of Chicago Press.

Sawyer, G. A., and Wiedenbeck, M. L., (1950) Decay constants of potassium. Phys. Rev. 79, 490.

Schumb, W. C., Evans, R. D., and Leaders, W. M., (1941) Radioactive determination of the relative abundance of the isotope K^{40} in terrestrial and meteoric potassium. J. Am. Chem. Soc. 63, 1203.

Shand, S. J., (1949) Eruptive Rocks, Woodbridge Press.

Sitte, K. (1935) Zs. Physik, 96, 593.

Smythe, W. R.,(1939) Cosmic rays and radioactive potassium. Phys. Rev. 55, 316.

- - - - - - - and Hemmendinger, A., (1937) The radioactive isotope of potassium. Phys. Rev. 51, 178.

Strassmann, F., and Walling, E., (1938) Die Abscheidung des reinen Strontium-Isotops 87 aus einen alten rubidium-haltigen Lepidolith und die Halbwertszeit des Rubidiums, Ber. Deut. Chem. Ges. 71, Abt. B, 1.

Suess, H., (1938) Bemer Kungen zum Meteoritenproblem: Die Radioaktivitat des Kaliums als Mittel zur Bestimmung des relativen Alters der Elemente. Naturwiss., 26, 411.

- - - - - - - -(1939) Die Radioaktivitat des Kaliums als Mittel zur Bestimmung des relativen Alters der Elemente in Meteoriten. Naturwiss., 27, 702.

Thompson, F. C., and Rowlands, S., (1943) Nature, 152, 103.

Turner, F. J., and Verhoogen, J., (1951) Igneous and metamorphic petrology, McGraw Hill.

Urry, W. D., (1949) Thermal history of the Earth, Trans. Amer. Geoph. Union, 30, 171.

Wahl, W., (1950) A check on some previously reported analyses of stony meteorites with exceptionally high salic contents, Geochimica et Cosmochimica Acta 1, p 28-32.

Washington, H. S., (1903) Chemical analyses of igneous rocks, published from 1884 to 1900, with a critical discussion of the character and use of analyses. U. S. Geol. Survey, Prof. Paper 14.

- - - - - - - (1925) The chemical composition of the Earth. Am. Jour. Sci. 9

White, J. R., and Cameron, A. E., (1948) The natural abundance of isotopes of stable elements. Phys. Rev. 74, 991.

Whiting, F. B., (1951) Use of biotite for strontium age measurements, M. I. T. Dissertation.

BIOGRAPHICAL SKETCH

The writer was born in Revelstoke, British Columbia, Canada on March 1, 1921. He received his early education in the Greenslide Public School and the Revelstoke High School where he completed his senior matriculation in 1939.

After several years of varied employment he enlisted in the Royal Canadian Air Force in 1942 and served as a navigator and navigation instructor in England during World War II.

He entered the University of British Columbia in 1945 and obtained a Bachelor of Applied Science degree in Geological Engineering in 1949. This was followed by one year of graduate work at the same university. Further post graduate work was started at the Massachusetts Institute of Technology in 1950. He held a teaching fellowship at M. I. T. from 1950 to 1951 and a research assistantship until 1952.

The writer married Helen Duncan in 1950.

His professional experience consists mainly of summer employment and includes three summers with the British Columbia Department of Mines and one with the Raindor Gold Mines, Toronto. Non-professional experience is varied and includes farming, logging, railroad work, and mining, amongst others.