NATURAL VARIATIONS IN STRONTIUM ISOTOPE ABUNDANCES
IN MINERALS: A POSSIBLE GEOLGIC AGE METHOD

by

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(1948)

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(1945)

SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
(1952)

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Department of Geology, May 9, 1952

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Mass spectrometric analyses of the relative abundances of the isotopes of strontium in the minerals biotite, phlogopite, muscovite, feldspar, and celestite show variations of as much as 5 per cent in the ratio of the stable isotopes, Sr$^{86}$ and Sr$^{88}$. These variations are not correlatable with the age of the mineral or with any other known parameter at present. They indicate proportional, smaller variations in the ratio of Sr$^{87}$ to Sr$^{86}$ or Sr$^{88}$. Such fractionation effects must be taken into account in determining the proportion of Sr$^{87}$ in a mineral which is radiogenic.

Much larger variations, up to 300 per cent, are found in the relative abundance of Sr$^{87}$ to Sr$^{86}$ or Sr$^{88}$ in the minerals examined, in particular, biotite in which the ratio of Rb to Sr is large, of the order of 10:1. These variations in the relative abundance of Sr$^{87}$ are approximately proportional to the Sr$^{87}$/Rb ratio and the time of formation of the mineral. It appears that a method of geologic age determination employing the Rb - Sr transmutation may be useable for a large number of biotites and other minerals, since the calculated ages for over half the biotites analyzed fall within the large limits of error of the optical spectrographic determinations of SrO and Rb$_2$O, within the ranges of possible ages inferred for particular samples on the basis of previous age determinations or field geologic evidence. More precise Sr$^{87}$/Rb ratios are needed to make this evaluation of the method conclusive.

The feldspar samples analyzed had, in general, much higher Sr/Rb ratios than the biotites, and in some cases the amount of Rb was so small that only negligible amounts of Sr$^{87}$ could have been added to the Sr in these minerals since their formation. Two of these favorable samples of calculated and inferred age greater than 1500 million years showed a depletion in Sr$^{87}$ relative to Sr$^{88}$ of less than 2 per cent compared to the 10 per cent depletion expected for minerals formed at that time on the basis of published abundances of Sr and Rb in the earth's crust.

An assemblage of celestites of various ages from presumably pre-Cambrian to Tertiary shows an even smaller decrease in Sr$^{87}$ relative abundance, confirming the feldspar indications if the celestites analyzed are actually derived from large, well-mixed bodies of water such as the oceans, for oceanic Sr should reflect in its composition the variation in rock strontium composition due to the slow buildup of radiogenic Sr$^{87}$. Both sets of data indicate that the geochronal cycles and average abundance models for Rb and Sr should be reviewed.

The isotopic composition of a.p. reagent grade SrCO$_3$ was determined to be almost precisely the same as that published by Vier for Sr metal.
While Nier used electron impact on a gas for ion formation in his measurement, thermal ionization was used in this work.

A Nier-type 60° sector-shaped magnetic field, 15 cm radius mass spectrometer was used, employing a source assembly modified for the analysis of solid samples and a null-method double-collection system of comparing ion current intensities.

Strontium samples were prepared by rough chemical concentration followed by resin column ion exchange separation of strontium from the complex biotite or feldspar assemblage of elements. Twenty-nine biotites, one phlogopite, two muscovites, fifteen feldspars, and eleven celestites were analyzed by the mass spectrometer in this work.

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The author's interest in the Rb-Sr and K-Ca, A radioactivities as possible age determination methods dates from 1950. While F. B. Whiting and L. H. Ahrens were exploring for a suitable mineral for such work, the author, starting with a design by R. E. Honig (Hn-1), was assembling a mass spectrometer in the Geology Department at M.I.T. However, in June of 1951 he learned that L. T. Aldrich at the Department of Terrestrial Magnetism of the Carnegie Institution of Washington was preparing to investigate similar problems. It was arranged, through the efforts of P. M. Hurley at M.I.T. and M. A. Tuve of the Washington laboratory, for the author to spend the summer of 1951 working with Aldrich, testing the method and standardizing techniques. He returned to D.T.M. during the early months of 1952 to make the measurements reported in this paper.

For each year's scientific advances the workers of previous years are directly responsible. The program described in this thesis could not have been attempted a score of years ago; quantitative results only became possible after the Second World War, since the precision tools needed for the investigation were not previously available.

This research is a synthesis. The problem first attacked is essentially geological — but the results obtained are also of significance in chemistry and physics. A great number of workers in
diverse fields made the measurements possible: the mass spectrometer for precision isotope analysis had to be developed; it, itself, depends on a long chain of development in the science of physical electronics. Classical chemical methods proved to be inadequate to make the separations necessary; fortunately, resin ion-exchange technology was just at the point where it offered a solution of the difficulty; this was worked out. But this solution itself was only possible because of the just developed methodology of radiotracers.

For the measurement of total rubidium and strontium in the sample, it was necessary for geochemical trace-element methods, particularly diffraction grating spectroscopy, to have attained a high degree of refinement and accuracy; these methods require impurity-free electrodes, extremely sensitive and highly specific photographic emulsions, and a densitometry, which is the art of measuring the relative blackness of lines on a photographic plate, capable of giving reliable quantitative results.

The overall processing of samples must avoid introducing measurable impurity Sr or Rb, that is, less than 0.1 microgram. Some of the more unfavorable samples were themselves below 10 micrograms. Reagents, including water, that would fulfill this requirement only became possible with the advent of resin ion exchange column technique.

Acknowledgments

The program of research described in this paper was costly
and intricate. Fortunately, three men and two organizations stood ready to support the work with funds and knowledge.

Prof. Patrick M. Hurley of the M.I.T. Geology Department is the man most responsible for the author's entry into this field, for it was at his suggestion that I spent several weeks perusing the literature of mass spectrometry, as a result agreeing to try to put together a mass spectrometer for research in geology.

This instrument will soon be joined by another and better one, thanks to the generous gift of a metal spectrometer tube from the Department of Terrestrial Magnetism of the Carnegie Institution of Washington through its Director, Merle A. Tuve.

It is difficult to disentangle the personality of an organization, if it is of manageable size, from the character of the man who directs it. In this identity, the Department of Terrestrial Magnetism is particularly fortunate. The organization is one of independent thought and action, of pertinent, incisive, and pioneering experimentation in several scientific disciplines, of warm friendliness and an atmosphere in which independent minds meet easily, and above all, of a contagious, pervasive enthusiasm that inescapably infects even the casual visitor.

Dr. Tuve and D. T. M. provided the facilities and a considerable portion of the funds necessary for the well being of this work and its author. However, the sine qua non role in the actual accomplishment of the research was played by L. Thomas Aldrich of D. T. M. His knowledge of mass spectrometric technique and theory was absolutely
indispensable to the work. He brought to these problems the necessary solid foundation of basic physics theory, a tested experimental approach and a valuable physical intuition. The author looks forward to continuing this extremely pleasant association.

It was, however, Dr. Hurley who arranged, with Drs. Tuve and Aldrich, for the author's trips to D.T.M. In spite of his numerous duties, he always kept himself available for consultation; he was ready with well-conceived suggestions, and actively interested in the work. His knowledge was of great assistance in interpreting the geological age data. In addition, he secured the Office of Naval Research sponsored research assistantship which was my personal major source of support during the last graduate year. The O.N.R. project, DIC 6617, also furnished the funds necessary to complete the M.I.T. spectrometer.

Many others went out of their way to promote this research. Noteworthy contributions were made by Mr. John B. Doak, whose electronic circuits for the D.T.M. spectrometer were given a severe test in this research and performed far beyond reasonable expectations; Drs. Phillip H. Abelson and Ellis T. Bolton, whose advice helped make the ion exchange experimentation successful, and Miss Elaine Aldous, research assistant in biophysics at D.T.M., who assisted in the tedious jobs of computation and proofing the manuscript that required several evening watches.

Stimulating discussions were had at M.I.T. with Dr. Louis H. Ahrens and Mr. Walter Holyk, both of the Cabot Spectrographic
Laboratory, regarding their work on the SrO and Rb₂O values given hereinbelow, and on geochemical matters. The members of the D. T. M. staff Luncheon Club and Gordon Davis, Louis Nicolaysen, Felix Chayes and E. G. Zeis, of the Geophysical Laboratory, also contributed ideas incorporated in this work. Davis also actively took part in the column technique development and prepared the reagents used in processing samples.

Support and training during the first graduate year was furnished the author by A. E. C. - DIC project 6620 at M.I.T.; Professors A. M. Gaudin, H. Rush Spedden, and P. M. de Bruyn of this mineral engineering project also provided stimulus and friendly criticism which influenced the present research.

The author gratefully acknowledges his debt to Mr. W. C. Hendrix for the excellent illustrations included here and to Miss Irene Debber, Mrs. Elsie Walck and Mr. W. N. Dove, all of D. T. M., for a well-typed manuscript on a very tight time schedule.

My thanks to Drs. Hurley and Aldrich for reading through this report and supplying constructive suggestions and criticism where needed.

The association with the people mentioned above made this research experience as enjoyable as it was interesting.
ISOTOPE DISTRIBUTION OF STRONTIUM FROM 'NORMAL' AND MINERAL SOURCES
PART I: INTRODUCTION

The question of the age of the earth and the rocks at its surface has kindled man's imagination since his earliest attempts to assess his place in nature.

The impressive phenomena associated with seismic and volcanic activity must have been his first clues that the serenity of the face of the earth was only seeming; as his perception sharpened, he recognized that wind, rain, cold and heat also altered earth features - that the hills only seemed everlasting because his time-scale of a man's lifetime was so short.

From this realization resulted the idea that the rocks themselves might contain records of their own history - if only one knew what to look for.

Fossils entombed in sedimentary rock, early recognized as puzzling clues to rock history, provided the first usable history of geologic events, but only after the concept of evolution had furnished pagination for the volume. The evidence of paleontology was to prove extremely valuable, for those sedimentary series in which index fossils occur, for determining the relative order of earth events. However, by itself, it yields no absolute time values, and it cannot be used at all for the four-fifths of earth history that had elapsed before living things with parts capable of preservation by natural processes became common.

Consequently, geological organizations were among the earliest and most vigorous explorers of the phenomena of radioactivity, for they recognized that from among these a method of absolute time measurement for rocks of all ages might be developed. Indeed, many of the foremost nuclear
scientists of today, as well as geologists, received support from such organisations as the Geological Society of America and the American Petroleum Institute while working for their graduate degrees.

In spite of this intensive search, no single age determination method has yet been found which is not somewhat erratic or limited to rocks or minerals which are relatively rare. There is as yet no method that can be used with confidence for age determinations of common rocks, like granite and basalt.

A major part of the research reported in this paper is a test of an age determination method which may be applicable to a variety of minerals in common igneous and sedimentary rocks.

In an igneous rock, the method requires the measurement of rubidium and the radiogenic strontium it produces, in minerals such as biotite in which the ratio of rubidium to non-radiogenic strontium is high. This measurement requires a knowledge of the isotopic abundances of common strontium in the environment from which the rock crystallised - which can be determined by analysis of strontium from minerals containing large amounts of common strontium and only traces of rubidium, in the same rock.

The strontium in such a mineral will have been out of contact with rubidium since the mineral formed and hence may be expected to show unaltered the isotopic composition of common strontium at the time of formation of the mineral, a composition in which the relative abundance of Sr$^{87}$ should be lower than that for present-day Sr by an amount depending on the mineral's age.

The changing isotopic composition of strontium in the earth as a whole should be responsible for a progressive enrichment of oceanic strontium in Sr$^{87}$
throughout time. Sediments of divers ages, containing large amounts of strontium and only traces of rubidium should reflect this changing Sr\textsuperscript{97} abundance in well-mixed ocean water.

The dating of a mineral by radioactivity requires the measurement of the amounts of parent and daughter isotope in the mineral and a knowledge of the rate at which the parent species transmutes into its daughter isotope. The calculated age will be valid if the decay rate has not changed during the lifetime of the mineral and if the system has been closed to the addition or subtraction of parent or daughter. It has not yet been possible to alter any decay rate (except extremely low energy (\textless 9KeV) K-capture processes) in the laboratory by altering the physico-chemical environment of the radioactive element within the range of conditions supposed to exist on or within the earth. However many of the methods of age determination already in use have been shown to be subject to error because of the addition or subtraction of material. As a consequence the group of age determinations at present accepted as accurate have been selected from a much larger number of highly inconsistent results. It was hoped that rubidium and strontium were similar enough geochemically that separation or leakage effects might not be serious. The present results lend qualitative confirmation to this view.

Both rubidium and strontium are common trace elements in rocks, present to an average extent of several hundredths of a percent in the rock assemblage exposed at the earth's surface. Preliminary optical spectrographic work by F. B. Whiting and L.N. Ahrens indicated that most biotites contained several hundredths of a percent of rubidium but only
thousandths of a percent of strontium, so that the fraction of Sr\(^{87}\) formed by radioactive decay of rubidium \(^{87}\) in biotites might be appreciable, approaching 100 per cent for certain samples if their assumed ancient ages were correct.

The research reported in this thesis consists of the mass spectrometric isotope analyses of strontium necessary to make Sr\(^{87}\)/Rb\(^{87}\) ratios for minerals, determined spectrochemically, usable for age determination. Thirty-two micas, fifteen feldspars and eleven celestites were analyzed in this work.

For these determinations, the Sr in from one to five grams of biotite, as little as .01 milligrams, was extracted by W.K. Helyk at M.I.T. using a process in which the Sr yield was sometimes as low as 5 per cent, and the Sr concentrate also contained Ca, Ba, Mg, Fe, Al, Li, the rare earths, and small amounts of Rb, K, Na and Cs. It was necessary to separate the Sr from this sample preparatory to mass spectrometric analysis; resin ion-exchange techniques were developed at the Department of Terrestrial Magnetism for this separation. The samples finally analyzed in the spectrometer contained from a few to 100 micrograms of Sr, and contamination Sr was kept below .5 \(\mu g\) Sr, the limit of measurement.

The mass spectrometric analyses show that biotites do, in general, contain radiogenic strontium, the amount varying from zero for quite recent material to 12 per cent for a pre-Cambrian specimen. Preliminary age calculations made using spectrochemical Rb and Sr determinations of large probable error indicate that the Rb–Sr biotite age method may be useable in a large number of cases; however more precise Sr/Rb ratio
measurements are needed to adequately evaluate the method.

The analyses of ancient feldspars and celestites indicate that the amount of variation in the relative abundance of Sr$^{87}$ to that of Sr in geologic time may be much smaller than the 20 per cent expected on the basis of geochemical evidence as to the ratio of Sr to Rb in the earth's crust. The actual variation in three billion years appears to be less than 5 per cent from the data so far obtained. Variations in the ratio of the stable isotopes, Sr$^{86}$ and Sr$^{88}$, to each other were also found in this research. All the minerals studied showed variations in this ratio of about 4 per cent maximum difference, and the distributions of ratios were different for each mineral. These variations cannot be correlated with age and their cause is not known at present; however, they may result from chemical and/or thermal gradients, in common with isotope fractionation effects already described for elements of smaller mass. These variations make impossible accurate estimates of radiogenic strontium on the basis of the ratio Sr$^{87}$/Sr$^{86}$ or Sr$^{87}$/Sr$^{88}$ alone for samples containing less than about 5 per cent radiogenic strontium. There is hope however that they are systematic and that the ratio of Sr$^{87}$ to total Sr may be useable for age determinations even for low-radiogenic Sr samples, when these variations are better understood. Their effect on the estimation of large amounts of radiogenic strontium is negligibly small.
PART II: BACKGROUND OF THE PRESENT RESEARCH

Geochemistry of Rubidium and Strontium

The geochemistry of rubidium and strontium has been treated by Ahrens (Ab-1,2,3,4) and Rankama and Sahama, (R-1) among others, in published work. An understanding of the factors governing the occurrence of these elements will be helpful in understanding the research reported in this paper; however, a complete treatment cannot be attempted here. The author hopes that the following paragraphs will serve the purpose of introducing the reader who may not be an expert in this field to the subject, and that experts in the field will pardon the omissions and simplifications, both necessary and inadvertent.

The geochemistry of the minor elements is a field in which concepts are, at present, in a state of constant revision as the results of new research become available. Part of the information given below is speculative, and therefore subject to such revision as future research indicates.

There are no rubidium minerals, in the sense that there are calcium and potassium minerals. The ionic radius of Rb⁺, 1.49A, is within 15 per cent of that of K⁺, 1.33A, and hence Rb can compete with, and form isomorphous series with, potassium in minerals since according to Goldschmidt's rule, such isomorphous replacement is possible when the radii concerned are less than 15 per cent different.

But, because its charge/radius ratio is smaller than that of K⁺, Rb⁺ competes at a disadvantage during crystallization and thus becomes enriched relative to K, in minerals formed towards the end of crystallization. The K/Rb ratio is approximately constant and equal to about 100 for bulk rocks.
ranging from gabbro to granite. The late stage enrichment of Rb relative to K only shows itself in the hydrothermal stage of pegmatites and in similar small, late forming accumulations. Lepidolite, hydrothermal microcline and pollucite are especially rich sources of Rb.

Strontium has two types of geochemical behavior. The radius of Sr\(^{++}\) has been calculated by Cohen (Ge-1) to be 1.27 Angstroms, only a bit smaller than that of K\(^+\) but well over 15 per cent larger than Ca, which, however is the closest-in-size abundant element of the same charge. Strontium therefore competes with both K\(^+\) and Ca\(^+\) for crystal sites. Its charge/radius ratio is much greater than that of K\(^+\), so that it is favored in the competition between the two, provided that its excess charge can be balanced by another substitution somewhere in the growing crystal. Such substitution appears, by and large, to be possible in complex silicates but not in simple salts such as KCl, where no negative doubly charged ion of the proper size is generally available to proxy for Cl\(^-\).

On the other hand, Sr\(^{++}\) is at a great disadvantage in competition with Ca\(^{++}\). Here its charge/radius ratio is much less than that of Ca\(^{++}\), and in addition it cannot form stable isomorphous series because its radius is more than 15 per cent greater than that of Ca. At high temperatures, it does enter some such compounds, but the Sr-member normally ex-solves upon cooling.

Strontium competes so unfavorably with calcium that it becomes concentrated enough to form its own minerals in the later stages of igneous activity: the celestite, SrSO\(_4\), and strontianite, SrCO\(_3\), of mineral deposits.

Because of these differences, Sr and Rb are somewhat separated during crystallization: Ca minerals containing the bulk of the Sr form for the
most part before K minerals, and also, the Sr in K minerals is concentrated in those that form earliest because of the favorable charge/radius ratio of \( \text{Sr}^{++} \) compared to \( \text{K}^+ \). Thus certain minerals become enriched in Sr and depleted in Rb, while others become Rb-rich and Sr-poor. The Rb-rich mineral group, which includes biotite, may be expected to be useful for age measurements dependent on measuring the radiogenic strontium\(^{87} \) produced by rubidium decay, while the Sr-rich minerals, such as calcic feldspar, should be useful for age determinations depending on the variation in abundance of "normal" Sr\(^{87} \) as it has been added to throughout time by radiogenic Sr, and for helping to determine the Rb/Sr ratio in the rock forming part of the earth. Geochemical evidence indicates that this ratio should be about 1.4, with Rb 0.035 per cent and Sr 0.025 per cent of the earth's crust (Ahrens, personal communication).

Francis Whiting (Mb-1) investigated a number of minerals and concluded that biotite offered the most favorable Sr/Rb ratio for age determination. The replacement of \( \text{Rb}^+ \) by \( \text{Sr}^{++} \) to a limited extent in biotite should not be too disruptive to the crystal lattice; the daughter ion, \( \text{Sr}^{++} \), is not greatly different from the parent \( \text{Rb}^+ \) in size and actually closer in size to \( \text{K}^+ \), the element \( \text{Rb}^+ \) is presumably substituting for, than \( \text{Rb}^+ \) is itself; and if the electron emitted in the transmutation is captured by the crystal, as is probable, charge balance will be maintained.

It is thus not to be expected that daughter Sr would be lost preferentially from crystalline biotite, certainly no more so than the other, normal strontium which already forms by far the greatest part of the total strontium in the biotites analyzed.

On the other hand, it does seem possible that throughout time, Rb might be forced out of the crystal structure if there were a reservoir
of K atoms adjacent to the crystal and exchanging with it, because K+ has a higher charge/mass ratio than Rb+. If this process took place, the measured age would be higher than the true age; this research may be an indication that it does not.

In potassic feldspar, the behaviour of rubidium and strontium with respect to potassium should follow the same principles as in the case of biotite, taking into consideration the somewhat earlier formation of the feldspar. In calcic feldspar, on the other hand, strontium proxies for calcium, and it appears that, on cooling, there should be a tendency for Sr to be forced out of the structure to form local units of strontian feldspar. But this tendency should have no influence on the isotopic composition of the Sr from these feldspars as analysed today.

Celestite is a simple salt of strontium itself; only processes in which strontium in the celestite is exchanged with strontium in its environment, such as ground water percolation, should have any effect on its isotopic composition once the mineral has been formed.
Radioactivity of Rubidium$^{87}$

In the Philosophical Magazine of 1905, J.J. Thomson (T-1) reported his finding that compounds of the alkali metals give off streams of negatively-charged corpuscles; the next year N.R. Campbell and A. Wood, investigating this phenomenon, proved that both potassium and rubidium exhibited beta activity, and that this activity was not correlatable with any of the previously known natural decay series. (Cs-1, 2).

That the beta activity of rubidium was due to the 87 isotope was demonstrated in a conclusive way by two very different investigations in 1937. A. Heemendinger and W. R. Smythe, using the high-intensity mass spectrometer devised at Caltech by Smythe, took a direct route: they placed a rubidium sample in the spectrometer and then collected, separately, mass fractions from 84 to 90. They found that the activities of all the other fractions as measured by a geiger tube were negligible compared to that of the 87 fraction. Meanwhile, Hahn, Strassman and Walling had obtained a rubidium-rich mica from Manitoba and separated from it a strontium concentrate; this was analyzed by J. Mattauch using the high-resolution double-focusing mass spectrograph, and compared with a normal strontium salt. The mica strontium produced a strong line at mass 87 on the photographic plate, and no other strontium lines, while the normal strontium sample showed the characteristically preponderant 88 isotope and much fainter lines at 86 and 87. (Na-1, K-1).

Because a certain amount of background activity can never be completely eliminated, high precision laboratory determinations of the decay constants of very long-lived radioactive elements are extremely difficult. The
The decay constant used in this thesis is $1.18 \times 10^{-11}$/year, as determined by Curran, Dixon and Wilson (C-1) and is possibly the best value currently available. Other determinations, given in terms of half life, are $6.3 \times 10^{10}$ years, by Strassman and E. Walling (S-1) in 1937; $1.2 \times 10^{11}$ years, by W. Mühlpoff (Mu-1) in 1950), a recalculation of his 1930 value based on new data from Nier (N-3) and Kovarik and Adams (Ko-1); and $5.8 \times 10^{10}$ years, by Ekblund in 1946, a theoretical calculation.

The decay constant used in this work corresponds to a $5.87 \times 10^{10}$ year half life. (Half life values including those given here are summarized by G.T. Seaborg and I. Perlman in their 1949 "Table of Isotopes" (Se-1).

The final word has obviously not yet been said on this value; however, the value used is very probably within 10 per cent of the correct figure. An error here will introduce a systematic error into the absolute ages calculated in this paper, but will not change relative ages at all.

The comparison of the ages determined by the rubidium-strontium method with ages determined by other radioactivity methods, for the same rocks, should provide a correlation between the various decay constants used.
The Minerals Selected for Analysis:
Biotite, Feldspar and Celestite

To test the possible age method depending on the measurement of
daughter Sr$^{87}$ produced by Rb$^{87}$ activity, a mineral in which the Sr to
Rb ratio was less than 1:100 was desired. Whiting's work (Wh-1) showed
that most biotites fulfilled this requirement.

To determine the variation in the isotopic composition of normal
strontium in igneous rock throughout time, a mineral in which the Sr/Rb
ratio was greater than 10, so that the radiogenic Sr$^{87}$ contribution would
be negligible, or at least small, was desired. Whiting and Holyk's
(Ho-1) work showed that plagioclase feldspar often had the desired Sr
content.

A common sedimentary strontium mineral was required to test the
suggestion by Wickman (Wi-1), among others, that the change in Sr$^{87}$ in well
mixed Sr during geologic time could be used to date sediments. Celestites
are found associated with igneous and volcanic activity but by far the
largest accumulations are sedimentary. An attempt to obtain representative
sedimentary celestites of various ages was therefore made to test this
third age-determination possibility.

Biotite is a rather complex potassium aluminosilicate, K(Na, Fe)$_3$
$\text{AlSi}_{3}\text{O}_{10}$(OH)$_2$; it occurs both as a primary and secondary mineral, forming
the familiar shiny, dark plates, flakes and books of mica common in
both igneous and metamorphic rock. It is rather stable both chemically
and physically. It does not alter as easily as olivine, augite, hornblende
or calcic plagioclase, among the common rock forming minerals. Only zircon,
tourmaline, monazite and garnet are more stable than biotite during the
weathering cycle. However whether, while remaining intact, it exchanges cations with other minerals, grain boundary material, or interstitial solutions is not known.

Muscovite, KAl\textsubscript{2}Si\textsubscript{3}O\textsubscript{10}(OH)\textsubscript{2}, contains on the average ten times the amount of Sr contained by biotite. Nevertheless, the present work, in which two muscovites were analysed, indicates that it may be useable for age determination work in spite of its necessarily smaller per cent radiogenic Sr content.

One specimen of phlogopite, K\textsubscript{2}Fe\textsubscript{3}Al\textsubscript{2}Si\textsubscript{3}O\textsubscript{10}(OH)\textsubscript{2} was also analyzed, with very encouraging results. Its Sr/Rb ratio, 0.05 as determined by Holyk, is well within the favorable, biotite, range for age determination purposes.

The micas have a distinct sheet-like structure based on the Si\textsubscript{2}O\textsubscript{5} group. The potassium atoms lie between the (Al, Fe) Al\textsubscript{2}O\textsubscript{3}Al\textsubscript{2}O\textsubscript{3} silicate sheets, bound but feebly to 12 oxygen neighbors. One-fourth of the electrically neutral clay sheet structure Si\textsuperscript{4+} ions have been replaced by Al\textsuperscript{3+} in phlogopite and muscovite, demanding the addition of K\textsuperscript{+} or other large unipositive ions between the sheets to neutralize the structure. In the brittle micas, further substitution of Al for Si requires that large alkaline-earth ions be inserted between the sheets to neutralize the structure; the difference in charge accounts for the more brittle nature of these micas.

The weakness of the K-bending of the clay-like sheets of the micas accounts for the excellent cleavability they exhibit. But, because the K\textsuperscript{+} ion is only weakly bound and the site it occupies is a large one, the structure of the micas is relatively insensitive to replacement of K\textsuperscript{+} by
Rb⁺ or Cs⁺, or even a divalent atom.

In the feldspars, however, the cations are much more firmly bound. A unipositive ion is necessary in orthoclase and albite, to neutralize the excess negative charge produced by the replacement of one out of four Si⁺⁺⁺ ions by Al³⁺. In the divalent-cation feldspars, celsian (BaAl₂Si₂O₈) and anorthite (CaAl₂Si₂O₈), two out of four Si atoms are replaced by aluminum. The possibilities of cation exchange with the environment would seem to be much greater for the micas than for the feldspars, but Ahrens' work, coupled with mass spectrometric work, has shown that the mica lepidolite, K₂Li₂Al₅Si₆O₂₄, does not undergo such change (s.b: Ab-3).

The feldspars include a large variety of the aluminosilicates of K, Na, Ca and Mg and the less abundant Mg, Ba, Sr and Rb. Of these, it may be possible to use orthoclase, KAlSi₃O₈, like biotite, for age determination. The calcic plagioclase anorthite offers promise as a mineral from which the variation of the isotopic abundances of Sr during geologic time may be learned. As noted above, it is rather more easily altered by chemical weathering than biotite, being more unstable in the chemical and physical environment existing at the earth's surface, but proper selection of samples should circumvent this difficulty.

It is difficult to separate fine-grained feldspar into pure orthoclase and plagioclase fractions. The suite of feldspars analyzed in this work suffered from this difficulty; though calcic plagioclase was sought, Sr/Rb ratios in the feldspars separated by Whiting indicate that in some cases the samples may have been quite high in potassium feldspar.

Celestite, SrSO₄, was shown in this work to be a rather pure salt, containing only very minor amounts of alkali metal ions. Its simple com-
position made it possible to run this mineral on the mass spectrometer without any previous chemical processing.

Some of the celestites analyzed may have had a volcanic or hydrothermal origin, although sedimentary samples were requested from Ward's, the suppliers. Most sedimentary celestites, however, are themselves thought to have been formed by the re-working of strontium-bearing gypsum (CaSO₄) deposits by percolating water. Such reworking should not alter the isotope ratio in the salt produced unless the amount of Sr in the percolating water were large compared to the amount in the gypsum; such conditions are thought to be very rare. Hence sedimentary celestite, even if re-worked should show the strontium isotope abundances characteristic of sea strontium at the time the deposit was formed.
Mass Spectrometry

Rays of positive electrical charge, or "canalstrahlen," were first observed by Goldstein (G-1) in 1886 in low pressure electrical discharge; in 1898 Wien (We-1) showed that these rays, in common with the negative cathode rays, could be deflected by magnetic fields.

In a series of brilliant investigations, Sir J.J. Thomson described many of the intricate phenomena connected with these rays — however to this day many other features of low pressure discharge still await explanation.

Earliest investigations of the rays were made by actually observing the glow produced by their passage through a rarefied gas. Later, screens of powdered willemite, which glows a faint green when struck by the rays, were used for more accurate observation. Dechend and Hamner (D-1) improved on this technique by photographing the impact of the rays on the screens from outside the tube, but in 1910 first Koenigsberger and Kutschewski (K-1) and later, independently, Thomson made a major advance by recording the impact of the rays directly on photographic plates placed inside the tube.

Thomson's method for his investigations of positive rays consisted in collimating them by means of a fine tube and then analyzing the beam produced with crossed magnetic and electrical fields. The fact that the parabolas produced on the photographic plate by Thomson's device were sharp streaks and not blurs was the first experimental proof that atoms of the same element had even approximately the same mass. (T-2)

Although Thomson's method was powerful, others soon set out to improve on it. If the positive ray beam can, in some way, be made monoenergetic,
only a magnetic field is required to separate ions of different mass. This was the basis of a device built, in 1918, by A. J. Dempster of the Ryerson Laboratory, Chicago. (De-l). The method is essentially that used by Classen in his 1907 determination of the ratio e/m for electrons.

Meanwhile, at the Cavendish, Thomson was joined by Frederick Aston, and in 1912 they completed an improved parabola apparatus capable of distinguishing between masses differing by 10 per cent. In his 1913 address to the Royal Institution Thomson announced the discovery of a parabola at mass 22 which could not be attributed to any known element or compound; the intensity of this parabola varied in the same manner as that of neon. At this time, Thomson was not prepared to definitely claim that a new kind of neon, of weight 22, had been discovered (and, it must be confessed, throughout his remaining years Thomson continued to take a dim view of Soddy's "isotopes," perhaps especially because of his erroneous parabola-method demonstration that chlorine was a simple element), but when later work by Aston and Watson (As-1) ruled out the improbable compound, NaH₂, it appeared very probable that a single revolutionary interpretation of the data remained: that neon exists in two forms of different mass, in exactly the same way that Soddy had postulated that the chemically inseparable "radioelements" must be atoms of the same element, of different weight.

Although these experiments were indicative, they were not conclusive. This led Aston to undertake two distinct investigations of neon, the first aimed at separating the two kinds, if they existed, and the second, analysis by positive rays. The first line of attack proved to be tedious and Aston was the victim of an unfortunate accident in which his "lightest"
fraction was lost. Nevertheless, he achieved (1913) what would today be recognized as a significant separation, the weights of his remaining end fractions being 20.28 and 20.15 ($0 = 16.00$). On the other front, his parabola work indicated that the "light" isotope of Ne had a weight less than 20.2 and hence if the chemical weight assigned to neon was correct a heavier kind had to exist.

At this promising stage of the research, world war intervened. When the work was resumed, the actual existence of isotopes had already been proved unequivocally by the atomic weight work of Soddy, Richards and others on uranium-leads and thorium-leads — actually, the pioneer work in the field of the present thesis for of course U — and Th — mineral samples were used.

Aston realized that the parabola apparatus had several serious shortcomings. Chiefly, these stemmed from the use of a fine tube, which easily became clogged with dirt, and the excessive gas pressures, which meant that a large number of beam ions were not reaching the plate because of collisions en route. In his first mass spectrograph, constructed in 1919, Aston successfully reduced these difficulties: so much so that in November of that year he was able to publish definite proof of the existence of the two isotopes of neon, an element of which there was then less than a gram in purified form in existence. 

Then, in a very few weeks, Aston demonstrated the isotopic complexity of chlorine and mercury, and formulated the "whole number rule," taking

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1/ The story of the development of this spectrometer, as well as a summary of the advances in the field of mass spectrometry until 1941, is given in a very lively fashion in Aston's book, "Mass Spectra and Isotopes" (As-2).
as his standard integers, oxygen 16 and carbon 12. Progress was now rapid: twenty elements yielded to this analyst in 1920. In December of that year he was joined by Dempster, who announced his discovery of the isotopes of magnesium. During 1921, Aston, in quick succession, completed analyses for all the group I elements — among them, Rubidium. Strontium, the other element essential to the present investigation, did not defer to his spectrograph until 1923, after he had worked out the method of accelerated anode rays.

Aston's irreplaceable Gaede mercury pump kept on revolving throughout the vigorous research years of the twenties and thirties, for 19 years, driven all this time in its repetitive rounds by its even more historic electric motor, which had been taken out by Scott on his final polar expedition. It was never necessary to dismantle or clean this remarkable pump. However as the science of the mass spectrograph grew the investigator found it necessary to replace his original mass spectrograph tube (which, with the Gaede pump, Scott's motor, and the magnet and other venerable accessories now rests in the Science Museum, South Kensington) twice by tubes of improved design.

In all Aston analyzed 76 elements. For his pioneering work, he was awarded a Nobel prize.

Meanwhile, research on this new technique was rapidly expanding elsewhere, particularly in Germany and the United States. In Germany the development was led by J. Mattauch, his students and co-workers. It was Mattauch's analysis (N-1) of the strontium extracted by Hahn, Strassman and Walling (Ha-1) from an ancient mica from Manitoba that first definitely proved that there was a radiogenic Sr isotope and that it could
become concentrated in certain minerals. In this work Mattauch used his extremely accurate double-focusing mass spectrograph. The complete theory of all configurations of a homogeneous magnetic field and radial electric field for which direction and velocity focusing can be achieved had previously been published (1934) by Mattauch and R. Herszog (Hs-1) and Herszog (Hs-2).

Since this time, however, the European school has more and more devoted its efforts to more accurate mass measurement rather than abundance determinations; in the United States, such names as Dempster, Bainbridge, and Jordan are associated with a parallel development. The photographic method of abundance determination used by Aston and the European school almost exclusively suffers from the inherent inaccuracies of all methods depending on quantitative measurement of the blackening of photographic plates, plus some distinctive difficulties due to mass-variation of line width. But in the United States under the concerted efforts of such men as Blackney, Tate, Brewer, Bluett and Sampson, electrical methods of measuring these abundances developed rapidly and soon demonstrated their superiority to the photographic method.

The early spectrometer designed by A.O.G. Nier (N-2), a student of Tate, was especially outstanding. This instrument, incorporating the theory of Blackney (B-1), could detect abundances as low as 1 in 100,000. By 1941 when the United States entered World War II, Nier had provided data of unequaled accuracy for over 20 elements. The beautifully simple, sensitive, accurate analytical instrument for gas analysis developed by Nier, which formed the basis for the spectrometer used in this research, is described in an article in the Review of Scientific Instruments for 1947 (N-3).
Nier's interest in the geological problems amenable to his technique is evidenced by many published measurements, especially lead isotope analyses for geologic age determination purposes. Unfortunately for geological research however his time, together with that of most mass spectrometrists has, since the war, been monopolized by the pressing and interesting problems of nuclear research.

Fortunately, a valued co-worker and student of Nier has decided to devote his knowledge to the problems of interest in geology. At Minnesota, L. T. Aldrich had investigated the abundance of helium and argon from mineral sources (A-2, 3), while working with Nier. At the Department of Terrestrial Magnetism of the Carnegie Institution of Washington, he set up a program along similar lines, to investigate isotope abundance differences caused by other radioactive transmutations. For this work, Aldrich proposed to use thermal ionisation, a method of ion production first used by Gehrke and Reichenheim (Ba-1, page 3), in order to eliminate the background peak effects which are troublesome sources of error in conventional gas-bombardment analyses.

It was at this stage that the author joined Aldrich at the Department of Terrestrial Magnetism for the work described in this paper. He had become interested, early in 1950, in mass spectrometric methods of age determination in conversations with P. M. Hurley, his teacher in radioactivity as applied to geology, at M.I.T. There was at this time extant in the Geology Department a gas-analysis spectrometer built by R. E. Honig (Hn-1) in 1944, but since unused. This instrument was rebuilt by the author and redesigned for thermal ionization and greater efficiency when used for gas analysis. The spectrometer had been tested on neon,
argon and CO₂ by June of 1951, at which time the writer learned of the project at the Department of Terrestrial Magnetism.

Through the joint efforts of Professor Hurley and M. A. Tuve, Director of the Terrestrial Magnetism laboratory, it was arranged for the author to spend the summer of 1951 at the Department of Terrestrial Magnetism with Aldrich working out and standardizing techniques for their similar programs. This collaboration, essentially an apprenticeship in mass spectrometry for the author, proved valuable and productive, and he was permitted to continue it in the early months of 1952 for the research reported in this paper. Between the periods at the Department of Terrestrial Magnetism he continued work on the M.I.T. spectrometer and it successfully underwent tests, using the thermal ionization source to resolve and analyze the peaks of potassium and rubidium.

At the present time mass spectrometric research on strontium continues at M.I.T., at Terrestrial Magnetism, and, in addition, at the Lamont Laboratories of Columbia University.
Isotopic Abundances of Rubidium and Strontium

In order to use total strontium determinations to calculate geologic ages, it is necessary to know the proportion of strontium which is radiogenic.

The isotopic composition of an element does not show local differences, at a given time, because of the radioactivity of one of its isotopes. It may show such differences, however, if isotope fractionation has taken place for any other reason.

The isotopic composition of rubidium was first examined by Aston in 1922. In 1932, an improved anode ray analysis by him reported two isotopes, 87 and 85, with the heavier making up 25 per cent of the total. In 1934, Brewer and Skeck refined this measurement by using thermionic emission. They reported 72.1 ± 4 per cent and 27.9 ± 4 per cent as the abundances of 85 and 87. Brewer in 1938 re-analyzed rubidium and obtained 72.2 and 27.8 per cent. In 1936 Nier had obtained somewhat different values, 72.8 per cent and 27.2 per cent, but his 1950 electron-impact vapor analysis confirmed Brewer's results. Aldrich and the writer in 1951 obtained a value not measurably different from Nier's using reagent RbCl and thermionic emission. The Nier and Aldrich-Herzog values are:

\[
\text{Rb}^{85}/\text{Rb}^{87} = 2.591 \pm .003 \quad \text{Rb}^{85} = .7215 \pm .0003 \quad \text{Rb}^{87} = .2785 \pm .0003
\]

In his 1938 paper, Brewer reported that the ratio of the two isotopes varied slightly, from 2.59 to 2.61 in the samples tested. The value he gives is for an "artificial spodumene" prepared from rubidium metal. (Nier also used Rb metal for his 1936 analysis). Five California lepidolites gave Rb 85/87 values for 2.61, as did a Virginia Zinnwaldite and
rubber tree seeds from Hali and apple seeds from the United States. While such variations will make only a negligible difference in any age calculations, they should be followed up as perhaps another case of isotope fractionation in the medium mass range.

Aston was also first to investigate Strontium (1923). In 1932 he reported three isotopes: 86, 87 and 88, with percent abundances of 10.0, 6.6 and 83.3. In 1936 Bluet and Sampson discovered another isotope, at 84, with an abundance of 0.5 per cent.

The 1936 analysis by Sampson and Bleakney, the 1938 analysis by Nier which has been adopted as a standard and a recent analysis by White and Cameron are tabulated below, together with that obtained in the course of this work by Aldrich and the author:

<table>
<thead>
<tr>
<th>Investigators</th>
<th>Fractional Abundance of Isotopes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampson and Bleakney (1936)</td>
<td>0.5 9.6 7.5 82.4</td>
</tr>
<tr>
<td>Nier (1938)</td>
<td>0.56 9.86 7.02 82.56</td>
</tr>
<tr>
<td>White and Cameron (1948)</td>
<td>0.55 9.75 6.96 82.74</td>
</tr>
<tr>
<td>Aldrich and Hersog (1952)</td>
<td>0.58 9.87 7.03 82.52</td>
</tr>
</tbody>
</table>

Nier and White and Cameron used electron-impact on Sr vapor for ion production; Sampson and Bleakney and Aldrich and Hersog used thermionic emission.

The present investigation shows that a statement as to the source of the element analyzed should always be given with isotopic analyses. In the present investigation, values quite similar to all the above have been recorded; the table value is for reagent-grade c.p. strontium carbonate from Eimer and Amend, batch No. 492327, the source of which is
being investigated. At present it is presumed to have come from
celestite of Mesozoic or Tertiary age, but this is merely a conjecture
from the data. Nier's reagent may have a generally similar origin.
White and Cameron used commercial metallic Sr as a source of ions, as
did Nier; Sampson and Bleakney do not give their source of Sr.

All the values given above are contained in Preliminary Report No.
9 of the Nuclear Science Series of the National Research Council (Ba-1),
by Bainbridge and Nier, which also lists in a comprehensive bibliography
the publications from which the values were taken.
PART III: SAMPLE SELECTION AND PROCESSING

Selection of samples

The samples analyzed in this research were chosen by Francis B. Whiting (Wh-1) and used by him in his thesis research in spectrochemistry at M. I. T. This was the study which indicated that biotites were worth investigating as possible Sr-age determination source materials.

Some of the samples were obtained from the collections of the M. I. T. Geology Department, while others were donated by interested individuals. Whiting made a particular effort to obtain specimens in which the biotite appeared to be unaltered and primary; coarse-grained samples were preferred because impurities in the biotite fraction could be removed by hand picking.

The feldspar fractions analyzed were obtained from the same rocks as the biotites. Plagioclase feldspar was sought but, considerable amounts of potash feldspar were often included in the samples taken. From one to five grams of biotite were concentrated by Whiting and later chemically treated by Walter Holyk (Ho-1) at M. I. T. to obtain Sr concentrates.

The rocks chosen were predominantly granites. Of these, over half were from intrusives thought to be pre-Cambrian in age.

A list of the samples upon which mass spectrometric work was done is presented in part VII.

Suitability of Samples:

In retrospect, it is only too easy to say that the selection of samples made by Whiting was unfortunate for a test of the biotite-Sr method of age determination.
The samples were not collected in the field by any of the analysts. The locations from which many of them were taken are not known with the precision necessary for an unequivocal estimate of age, on geologic grounds, to be made.

Many samples from Canada were called "early Archean" or "late Archean" largely because they are from the shield. Certainly this order of age can be inferred, but actual evidence for these specimens is missing. It is not known, at present, whether the "Red Granite" or the "Grey Granite" was the source of the specimen called "St. Cloud Granite." Furthermore, some of the samples chosen are from highly controversial areas. This is particularly true of the samples from the mountains of the southeastern U. S., such as Mt. Airy, N. C. and Stone Mtn., Ga. Any of these may be either pre-Cambrian or late Paleozoic as the evidence now stands.

The biotite from a "Pegmatite from Southern Rhodesia" is probably not from the same pegmatite from which Ahrens has dated a lepidolite at 2000 million years, and therefore is not necessarily of the same age.

Of the samples selected, two are especially suitable for testing a new age method: the specimens of Llano, Tex., granite and a Canadian granite from the Grenville, and of these, the second loses considerable value because its exact location is unknown. The Llano age is well known: the value 1050 million years has been obtained by several age methods. The Grenville age is well known for certain facies, with values of 970 to 1030 million years for different minerals obtained. But the field relations in this area are not simple, with abutting rocks thought to be of a very different age and hence the field location of this sample is very important.

From another standpoint, however, the selection made by Whiting is admirable. It provides an almost random cross section of rocks for which
a biotite age method would be eminently suitable, and for his preliminary grating spectrographic work, this is, of course, what he wanted.

The writer's current ideas on critical samples for future work are given in part XI of this thesis.
Physical Separation of Minerals

The necessary separation of biotite and feldspar from rock hand specimens was performed by Whiting as a part of his thesis research. The following description of his procedures is quoted from his thesis (Wh-1):

"1. Separation of Biotite and Plagioclase Feldspar.

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

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

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

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

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


"Where absolutely pure samples of the minerals in one rock were required ... cleavage flakes were chipped from large crystals of each of the types . . . . . .

"4. Technique for sheet mica.

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

"A notable feature of the strontium method is the lack of importance of any contamination of the sample by the rock splitter, screens, trays, jaw crusher, separator, or mortars. Any elements which might be introduced occur naturally in the samples in considerable amount and, in any event, were not to be determined."
Chemical Processing of Samples at M.I.T.

At M.I.T., Walter Holyk undertook to concentrate the Sr in the biotites selected by Whiting and to send these concentrates to D.T.N. for mass spectrometric analysis. The method of concentration used is essentially that given by Ahrens (Ah-4); his exact procedures are given by Holyk (Ho-1) in his thesis. This perchloric acid separation is summarized here in detail.

The silicate sample is treated with the mixture hydrofluoric-perchloric acid (HF-HClO₄), which decomposes it, and evaporated to dryness. The silicon goes off as SiF₄ vapor; the residue consists of perchlorates of the cations in the mineral.

The residue is ignited at 550°C in a muffle furnace. The alkali metals are thus converted to chlorides. The alkaline earth metals, including the desired Ca and Sr, are expected to convert mostly to chlorides, but partly to oxides. Mg, Fe, and Al perchlorates are expected to convert mostly to the oxides.

The chlorides are dissolved in warm water and removed from the insoluble oxide residue. Iron which was not left behind as oxide may be precipitated by NH₄OH at this point; excess ammonia is removed by ignition.

Perchloric acid is now added to the chloride fraction and the mixture taken to dryness, forming perchlorates. These are treated with anhydrous ethanol. Rb, K, and Cs perchlorates are sparingly soluble, while Ca, Sr, Na and Li are highly soluble in ethanol. The soluble fraction is evaporated and ignited, again converting the perchlorates to chlorides.

The final M.I.T. chemical concentrate consists mainly of chlorides of Sr, Ca, Ba, Na and Li. However small but important amounts of K, Rb, Fe,
Al and the rare earths are also not removed by the processing. This necessitates the further processing developed at D. T. M. and described below.

**Advantages of the procedure:**

The perchloric acid separation is far from perfect as a means of concentrating Sr. However, it had already been developed at the time Helyk started his research, was the best method then known for this concentration, was relatively fast, and had been already used at MIT by Ahrens and others so that a body of experience had built up. Furthermore, its main disadvantages did not appear until a large number of samples had been run mass spectrometrically, by which time all the available samples had been perchloric acid-treated by Helyk.

**Disadvantages of the procedure:**

The major disadvantage of the perchloric acid separation is the highly erratic yield of Sr it gives. The yield seems to be intimately dependent upon the composition, even to minor constituents, of the individual biotites, and on the impurity minerals that are retained in the biotite fraction.

While the yield for some of the smallest Sr samples (notably No. 26) must have been very nearly 100 per cent, for others it was unquestionably below 10 per cent, so that mass spectrometric runs were not successful. Now that this shortcoming of the perchlorate separation is known, other separation procedures are being developed which should have the advantage of high, consistent yield and a considerably decreased time requirement.

Perchloric acid is extremely hazardous, and this is a major disadvantage of the perchlorate separation. Helyk mentions in his thesis that extreme care must be taken to be sure that all the ammonia is removed.
before the second addition of HClO₄ in his procedure, for any ammonia left will form ammonium perchlorate, which is unstable and decomposes explosively later in the treatment when the perchlorates are ignited. Several samples were completely lost, in spite of precautionary measures, because of this reaction.

Perchloric introduces a hazard in the very use of a fume hood. Grease from the blower lubricant can catalyze its decomposition under suitable conditions, causing an explosion.

For these reasons, perchloric acid as a reagent is to be shunned except where it cannot be replaced. New methods of treatment designed with this as well as the desire for better or yield in mind are described in part X below.
Contamination in M. I. T. Sample Processing

The chances of contamination of the sample by other Sr during the treatment of the sample at M. I. T. are considerably greater than those during the D. T. M. processing because more operations and more reagents are involved.

Helyk attempted to assess the maximum amount of contamination that could occur in his processing by testing reagents in the same way he ran his samples. He tested the carbon electrodes, and hydrofluoric acid, perchloric acid, and ammonium hydroxide by immersing a carbon electrode in them and arcing in the usual way. He saw no Sr lines on his plates for any of these reagents, and believes that for them, contamination of over 1 microgram (0.0001 per cent) is therefore not possible.

At the time of writing of this thesis, he had not completed tests on the water and ethanol used. M. I. T. tap distilled water, which is of very poor quality, was used. However, very little was required. Ethanol is capable of easy purification, but because of the high solubility of SrCl₂ in it, it cannot be ruled out either, as yet, as a source of contamination.
Chemical Processing of Samples at D. T. M.

It was discovered that the samples obtained from Holyk were unsuitable for analysis. Too much potassium and rubidium remained in the small strontium-calcium sample and these impurities made high precision mass spectrometric analysis impossible. (See section on m. s. analysis technique.)

Work on other samples revealed that the alkali metals lithium, sodium, potassium, rubidium and cesium could each be troublesome in certain samples, and, in addition to these, the alkaline earths calcium and barium, yttrium and the rare earths, and aluminum could interfere with rapid, accurate analysis.

Resin ion exchange chemical separation:

A method which would separate these elements from the strontium sample was needed. At D. T. M. the biophysics group was using ion-exchange chemistry and chromatography for chemical separations, especially of organic compounds. Even before the author arrived at D. T. M., Aldrich had become interested in these techniques and with the cooperation of Phillip H. Abelson and Ellis T. Bolton, had begun preliminary experiments using radiotracer techniques on a method of separating the elements of groups I and II of the periodic table from each other. This research program was stepped up during the summer of 1951 when the author was at D. T. M., and by the time he returned to D. T. M. in January 1952 a workable scheme for separating all the Sr from all the Li, Na, K, and Cs, and as much of the Ca as was desired, had been worked out.

The particulars of the ion exchange process used are given in a paper now in preparation, by the D. T. M. group. (A-1) The accompanying illustration (III.-1) shows the separation attained for the samples treated in this research.
SEPARATION OF Rb, Ca, AND Sr, WITH AMBERLITE IR 120, 50 MESH RESIN

COLUMN VOLUME = 2 mL
COLUMN LENGTH = 19 CM
FLOW RATE = 4 COLUMN VOLUMES/HOUR
The ion exchange resin used was Amberlite IR-120, sized to pass the 50-mesh sieve. The capacity of this resin is two milliequivalents per milliliter. The volume of the columns used, which were constructed of 1 mm bore capillary tubing, was 2 ml and the resin length about 20 cm.

IR-120 is a cation exchanger, furnished in the "sodium form" by Rohm and Haas Co. Essentially, the resin is a highly inert substance which contains in its rather open structure sites at which a structural hydrogen ion, $H^+$, can be replaced by other cations. The extent of such replacement depends on the ionic properties of the different elements such as ionic size and charge. Variations within the individual groups of the periodic table are systematic and are the basis for chemical separations by ion exchange. Such phenomena as complex ion formation complicate the picture and can work against good separations, but when properly understood can oftentimes be used to better separate certain groups of ions.

The theory of ion exchange is at present incomplete and lags far behind the technology of resin separation, which is expanding on an empirical basis at a rapid rate. This expansion is a direct result of the number of new things such resins can accomplish; they make routine separations that are difficult, at best, by standard chemical means, and do it with near-100 per cent yields and complete separation of elements as inseparable as the rare earths and the homologous twins, zirconium-hafnium. In the present case, the separation of Ca and Sr from a complex group of elements is achieved in a short time by a procedure that requires little attention from the analyst and makes use of only two reagents, constant boiling (6.2 normal) HCl and pure water, $H_2O$, which itself is prepared to conductivity water standards by trickling distilled or tap
water through a cation and an anion exchanger in series.

**Actual operation of exchange columns:**

The process of washing the column with a solvent is known as elution. The new resin material, as mentioned, is in the "sodium form". The column is converted to the "hydrogen form" by washing it in 6.2 N HCl, making use of the mass action principle. Then excess HCl is removed by washing the column with impurity-free water, first in the forward (gravity flow) direction, then in the reverse direction. This process, in which the resin particles are drawn upwards in the column by the water current and then settle down again when suction ceases, is called resettling.

(In the following discussion "HCl" refers to the constant boiling (6.2 N) acid referred to above, which was prepared for this work by Gordon Davis of the Geophysical Laboratory, and by "water" is meant the conductivity-grade reagent prepared from distilled water by demineralization on the series cation-anion exchangers, Dowex 2 and Dowex 50.)

**Biottite:** The Helyx biotite samples were put in solution in hot water plus a few drops of HCl. The sample was then placed on the column, usually in about 30 ml of water. The water slowly, about 1 ml per minute, passed through the column, leaving its cation load bound to the topmost resin particle exchange sites. Now 50 ml of 0.9 N HCl was passed through the column. The concentration of H⁺ ions in this weak acid is sufficient to displace Li, Na, K, Rb, Cs and most of the Ca from the column and they appear successively and discretely in the effluent.

The concentration of H⁺ was then increased by passing 10 ml of 1.6 N HCl through the column. Any Cs and Ca left is removed immediately, followed by a little Sr.
Fig. III-2

ELUTRIANT

2 ml RESIN

ELUATE

RESIN COLUMN
6 ml of 6.2 N acid removed the desired Sr, together with some Fe and Al, if present, as complex ions and, towards the last, the first of the Ba and a small amount of rare earths. Elution with an additional 30 ml of 6.2 N HCl removes the rest of the Ba, rare earths, Sr, Fe, and Al quickly and leaves the column in the mineral-free hydrogen form ready for water washing and resettling.

Various fractions are collected as desired by replacing the effluent receptacle with another one at suitable times during elution. For most of the samples treated in this work, only Sr was desired and hence only the first 6 ml 6.2 N fraction was saved.

Operation of the columns was checked by collecting the effluent in small portions with an automatic fraction collector using a standard made up to resemble the mineral samples but including radiotracers for Na, K, Rb, Ca and Sr as desired. Over the entire period of operation no variation in properties of the resin columns appeared.

All glassware used was kept scrupulously clean by extensive detergent washing, next allowing a mixture of HCl and HNO₃ with a few drops of HF to stand a few minutes in the ware, then several conductivity water rinsings and a final steam cleaning using mineral-free water as the source of steam.

The Sr fraction was dried down at reduced (water aspirator) pressure and the evaporite taken up in 2 drops of water in a capillary glass dropper. The sample was now ready to be placed on the filament for mass spectrometric analysis.

If storage of the sample was necessary, the two ends of the capillary dropper were wrapped in "parafilm," which gave an air-tight seal. When amounts of sample were left after a sufficient amount of sample had been applied to the filament, they were saved similarly.
**Feldspars:** The amount of Sr in the feldspar samples was an order of magnitude greater, on the average, than that in the biotites. It was thought that Sr might be preponderant enough to allow these samples to be run without prior column treatment, but this was not the case. The amounts of Ba, Rb, K, Na and Ca present were still too great. Ba was especially high and so most of it was removed prior to putting the sample on the columns by utilizing the high insolubility of BaCl₂ in HCl. After this separation, the soluble part of the sample was columnized and treated in the same way as the biotites.

**Celestites:** A preliminary run on one celestite (sample C-1) was made with material converted by Gordon Davis to the chloride form. However, repeat runs on this sample and all the runs on other samples used celestite itself. A powder of SrSO₄ was scraped off a clean surface of the hand specimen with a clean knife onto filter paper. The powder was put in a clean test tube and a few drops of water added. The colloidal range particles were then taken up in a capillary dropper and applied to the filament much as the feldspars and biotites were.

**Fluorite and apatite:** The preliminary Ca and Sr measurements on fluorite (CaF₂) and apatite (Ca₅Sr₂FPO₄O₁₂) were performed on powdered mineral prepared in the same manner as the celestites.
Applying Samples to the Filament

Placing the sample on the ribbon filament was the most delicate part of the sample preparation procedure. The sample was placed on the center portion of the filament using the very finely-drawn capillary droppers mentioned above, by drying down the deposit between small drop additions of solution or suspension. A separate small filament transformer and variable resistance assembly was used to supply heat for drying. The final drying was done under the heat lamp so that the coldest part of the filament was at the center and sample distribution and binding to the filament would be optimum.

Any amounts of sample not required were stored as already described and are available for further analysis. Such residual samples are available for most of the samples run.

When the sample was dry, the source was reassembled and its alignment was checked by placing a pocket flashlight source above the last slit and observing whether the ribbon filament was illuminated.

Cleaning the source: Between samples, the used filament was removed with tweezers and the filament support posts and the shield box were cleaned by immersion in a mixture of HNO₃ and HF, after which they were rinsed in pure water and dried under a heat lamp. This cleaning procedure is quite effective for tantalum. A clean filament was then spotwelded onto the support posts, the source assembly having been inverted on a workbench to facilitate this operation and the subsequent application of the sample to the filament.
Contamination in D. T. M. Sample Processing

The procedures to which the samples were subjected after their arrival at D. T. M. were subject to rigorous test to determine the amount of contaminant Sr that might have been introduced in this handling.

The filaments used were tested by heating representative bare filaments in the spectrometer. No Sr was ever seen, although the omnipresent K and Na were detected in small amounts, and traces of Rb occasionally appeared.

The sample processing was checked by subjecting a 100 μg sample of spike strontium, that is, Sr with an entirely different isotopic composition from normal Sr, to the entire procedure, taking care to use less than normal care in handling. Even so, no normal Sr was detected. This experiment fixed the amount of Sr that could have been introduced in the D. T. M. processing at less than 0.5 μg (0.000 000 5 grams), the limit of accuracy for a 100 microgram sample. There is no positive evidence, that even this much Sr was ever introduced in the D. T. M. processing.
PART IV: OPTICAL SPECTROGRAPHIC ANALYSIS
FOR RbO AND Rb₂O

In order to make the geologic age computations reported in part I, it was necessary that the amounts of Rb and Sr in the sample, as well as the amount of Sr which was radiogenic, be determined. This work was done in the Cabot Spectrographic Laboratory of the Department of Geology at the Massachusetts Institute of Technology, under the direction of L. H. Ahrens, by F. W. Whiting (Wh-1) and W. K. Holyk (Ho-1).

Two methods of optical spectrographic analysis can be used to determine the Sr/Rb ratio in a sample. The more direct method is to compare the intensities of selected spectral lines of the two elements with each other on the same photographic plate and to link the observed intensities to actual Sr/Rb ratios by means of a "working curve" prepared from a series of standards. In the other method, Rb and Sr can be measured separately against other standards and the ratio Sr/Rb computed.

Both Whiting and Holyk used the second method since the values of Rb₂O and SrO in minerals it yields are themselves of geochemical interest.

The instrument used was a Hilger prism spectrograph equipped with interchangeable glass and quartz prisms. The glass prism was used, giving a dispersion of 30 A/mm at 7000 Angstroms. The wavelength range from 4900 A to 10,000 A can be recorded on a single ten inch plate. Eastman Kodak I-L type film, on glass, was used; this film gives a satisfactory medium intensity for wavelengths between 3000 and 10,000 A.

Rubidium analysis:

Arcing was by anode excitation with a d. c. current of 3 amperes. Line voltage was about 225 volts. A rotating step sector with adjacent steps increasing the exposure by a factor of two was used to provide six
steps, from $1/4$ to $1/128$. Five spectra were recorded on each plate. No intermittency effects were expected, since the sector rotated in excess of 500 rpm.

Pure carbon electrodes $1/8''$ in diameter were used, with a cavity $1/16'' \times 1/4''$ in one end. Most analyses were made in triplicate.

Sodium was used as an internal standard for Rb measurement by both analysts. The normal Na$_2$O content of biotites ranges from 0.30 to 1.78 per cent according to Whiting. To assure that all the samples contained essentially the same content of sodium, two parts of Bureau of Standards standard albite were added to each. This albite contains 10.73 per cent Na$_2$O. Hence, with one part of biotite, the content of Na$_2$O in the diluted sample should range between $21.8$ and $23.3$ per cent. The mean of these values was used and assumed invariable for purposes of calculation of Rb$_2$O.

Considerable systematic error may be introduced in spectrographic analyses if the material used as a "base" for preparing standards and the working curve is very different from that being analyzed. For this reason, biotite sample No. 9 was selected as the base. Rb 7947 was the line used in the analyses; it was compared to Na 5668.2, about 3-1/2 inches away on the photographic plate.

Whiting considered that self absorption only began to be significant when the Rb$_2$O content of his samples exceeded 0.05 per cent. He considers values obtained in excess of this figure to be "less accurate."

Reagent grade RbCl was used as an additive in preparing the standard samples for the working curve determination.

**Strontium analysis**

The first method of Sr analysis adopted by both Whiting and Holyk made use of Sr as an internal standard. The two elements volatalize
together. Ba 4726 is 1-1/2 inches from Sr 4607, to which it was compared, on Whiting's plates.

According to Whiting, "the barium content of biotites is low, ranging between 0.1 and 0.8 per cent ... For analysis arcings, all samples were mixed with two parts of pure carbon powder that carried 3 per cent BaSO₄. This procedure introduced an excess of barium, reducing the probable range of Ba content in the arcod mixture to between 2.1 and 2.5 per cent. This variation is negligible."

This assumption is examined in part VI.

For the Sr analysis, the plate holder was set to record wavelengths from 4500 to 8000 Angstroms. Six ampere current d. c. anode excitation was employed. The albite technique could not be used because the standard albite contains more Sr than the biotites to be analyzed. Undiluted biotite does not arc well, so carbon powder was added, but sputtering troubles persisted. Whiting considered water to be responsible for this difficulty. He was able to minimize it by heating the sample to 750-800°C in a muffle furnace for three minutes before arcing. He considers that no preferential loss of any constituent occurred in this treatment, or in the slight loss of material due to sputtering that still occurred.

Various proportions of SrO and BaSO₄ mixed with amounts of pure carbon and biotite No. 50 were used to determine the working curve. The reproducibility obtained was excellent — about ±3 per cent, between the triplicate analyses.

Self absorption of the analysis line starts at 0.020 per cent SrO and "increases strongly" as the SrO content increases to 0.05 per cent. This effect occurs eminently above 0.03 per cent SrO and so Whiting did not consider his working curve valid above this value.
Holyk felt that Whiting's assumption that variations in the Ba content of the biotites analyzed could be neglected was not justified. He therefore used the "total energy method" for his determinations of Sr in feldspar and made independent determinations of the Sr in the biotites arced by Whiting. He also rechecked Whiting's Ba-standard and Na-standard biotite values, using Whiting's plates and his own, different working curves. The three determinations yield the widely different SrO/Rb₂O ratios given in part IX. In the total energy method, no standard is used, except a working curve for the analysis line.

A Hilger non-recording microphotometer was used to measure the densities of the analysis line and standard line for Sr. A Jarrell-Ash microphotometer was used for the Rb measurements. Line densities were recorded for as many of the sector steps as possible for each line; each density was divided into the reading for the clear plate and the results plotted on semilog paper. Comparisons between lines could then be made graphically.
PART V: MASS SPECTROMETRIC ANALYSIS

Introduction

The mass spectrometer used in this work is based on a design by Nier (N-4). This design has been modified for thermal ionization of solid samples instead of electron bombardment of a gas, and to allow speedy sample changing and cleaning, the source and collector assemblies have been made easily dismountable. Certain changes in the electronic circuitry given in Nier's paper have been made in the spectrometer circuits used at the Department of Terrestrial Magnetism by Dr. John B. Deak, who designed and built them. These modifications are discussed in a paper by L. T. Aldrich and the author (A-4) and those most pertinent to this research are treated in detail below.

The mass spectrometer is a device for sorting out ions according to their mass to charge ratios.

Ions (atoms, originally electrically neutral, which have gained or lost orbital electrons) are formed in a "source area" by methods such as electron bombardment, gas discharge, or thermal ionization. The source area is usually partly enclosed and the gas pressure in it is somewhat greater than that in the rest of the mass spectrometer tube.

A schematic diagram of a Nier-type mass spectrometer is given in figure V-1. The spectrometer tube used in this research is of copper and Inconel metal, with silver soldered joints. It is symmetrically oriented about a constricted central portion placed between the poles of an electromagnet designed to provide a uniform sector-shaped 60° field. The tube makes a 120° bend in the magnet section and is perpendicular
Schematic drawing showing mass spectrometer tube, magnet, pressure gauge, and pumping system.
to the edges of the magnet pole pieces at its points of entry and exit, to give first order, but not second order, focusing of ion beams when the effective source point and collection point and the vertex of the sector-shaped field, whose dimensions = the magnet pole piece itself plus a fringing field approximately equal to the pole gap width, lie on the same line.

Ion beams are in focus along the same line at the collection end of the tube; this is the basis of the mass spectrograph, in which a photographic film plate placed along this line records a spectrum of ion beams. In the mass spectrometer ion currents are recorded electronically. A collector placed at the point where the line of center of the tube crosses the "focus" line picks up the current due to a single peak and transmits it to a preamplifier and amplifier; the output is transmitted to a moving strip chart recorder (Brown Electronik) for visual reproduction.

Ions formed in the source are drawn into the slit system by a "drawing out" field. The heterogeneous ion beam is focused by a pair of deflecting plates, accelerated by a potential difference usually of the order of kilovolts, and collimated by a pair of finely-slit plates.

If the energy imparted to the ions in the process of their formation is negligible compared to that added by acceleration, each ion in the beam entering the magnetic field has a kinetic energy,

\[ (K.E. = \frac{1}{2}mv^2 = eV) \]  

where \( V \) is the potential difference of the accelerating plates, \( e \) is the charge of the ion, \( m \) is its mass, and \( v \) is its velocity.

The uniform magnetic field perpendicular to the direction of travel of the ions acts as a momentum filter, separating the heterogeneous ion
beam into bundles of radius

\[ r = \frac{mv}{Be} \]  

(2)

where \( r \) is the radius of the path of a particular ion beam in the magnetic field, \( B \) is the magnetic field intensity in webers/meter\(^2\), \( m \) is in kilograms, and \( e \) is in coulombs.

By adjustment of either the magnetic field or the accelerating potential, particular ionic species may be brought to the collector by making \( r \), the radius of curvature of the path of the given ion species, equal to \( R \), the radius of curvature of the center of the tube, in this case, 15 cm.

The equation given above can be rewritten for purposes of calculation, as

\[ \frac{mv}{e} = 4.82 \times 10^7 B^2 r^2 \]  

(3)

where \( e \) is in electronic charges (e\(^-\) = 1) and \( m \) is in atomic mass units (\( 0.16 = 16,000 \) amu.)

For constant magnetic field and accelerating field, the resolving power of the instrument is found by differentiating (3):

\[ \frac{dm}{m} = 4.82 \times 10^7 B^2 (2r \, dr) \]  

(4)

Combining (3) with (4) one obtains

\[ \frac{dm}{m} = 2 \, \frac{dr}{r} \]  

(5)

This equation assumes a well-collimated beam. It shows the dependence of the resolution of the instrument on the magnet pole pieces used, for their size fixes the maximum dimension that \( r \) can have. Resolv-
ing power is independent of the angle of deflection of the beam but depends upon the widths of the final source collimating (object) slit and the collector (image) slit.

The slit widths chosen depend upon the mass numbers one wishes to separate, since the higher adjacent masses are, the smaller their separation on the collector plate. It can be shown (for example, see Eqn-1) that the separation between ideal peaks at the collector, \( x_c = 2d\alpha \). Hence, from (5)

\[
x = r \frac{dm}{m}
\]

Where \( r \) is 15 cm and the masses chosen are 99 and 100, the separation \( x_s \) is 1.5 mm.

But real peaks spread out over a "base width" equal to the width of the object slit plus some broadening caused by such factors as mutual repulsion of the like-charged ions of the beam and aberrations in the ion lens system. In order that flat-topped peaks may be recorded it is necessary both that the beam being recorded be able to travel a short distance completely within the slit, and that no adjacent mass beam enter the slit during this travel. In order for peaks to be completely resolved at the base, adjacent peaks must be separated by a distance greater than one base width. For ideal peaks the maximum permissible collector slit width equals half the peak separation; that is, 0.75 mm for masses 99 and 100 in the 15-cm radius spectrometer. But for the ideal peaks of the actual spectrometer, which have a 99 per cent base width of about .25 and are produced from an object slit of width .20, a slit of .50 is used in the collector plate for resolving masses
A range of masses can be scanned by varying either the accelerating voltage or the magnetic field; however, changing the electrical field in the source area introduces a "mass discrimination" effect and the spectrometer must be calibrated to correct for this. While it is more difficult to reproduce a magnetic field than an electrical one, varying the magnetic field is the method of peak selection generally used since no mass discrimination is introduced. Magnetic field mass selection was used in this work. A resistor, in series with the magnet coil and driven by a slow clock motor reversible by toggle switch, was used to vary the current through the magnet coils. Voltage sweeping, accomplished by slowly discharging a large capacitor through a high resistance, was used only for complete spectrum scanning for impurities or tuning in on peaks.

Chart records of magnet-scanned peaks are reproduced in this thesis as the frontispiece. Complete resolution and the flat-topped condition signifying accurate recording of maximum mass current were achieved, together with low noise level and elimination of background.

A typical fast spectrum sweep by voltage change is shown in figure V-2 in the section on thermal ionisation.

The spectrometer used gave very little trouble; it operated continuously over one three-month period daily, seven days a week, with from one to four samples being run per day. Only the normal outgassing of the tube by baking was necessary except during the celestite runs, when it became necessary to torch the constricted portion of the tube between the magnet poles (which is not wound with heater coils) on a few
SPECTRUM OF MASSES ABOVE 80 AT HIGH TEMPERATURE
Two source assemblies were available for this spectrometer so that a new sample could be prepared in advance and placed in the spectrometer as soon as the used source was removed. After breaking vacuum, the spectrometer pumped down to working pressure in about two hours.

Certain points mentioned in the summary above, especially where the spectrometer used departs from Hier's design, are treated more fully in the following sections.
The Vacuum System

For clean resolution of peaks, the mean free path of the particles in the mass spectrometer tube except in a small region within the source must be kept an order of magnitude or more greater than the length of path actually traversed by an ion in the system. Modern vacuum technique makes the low pressures necessary, $10^{-5}$ mm. of Hg or below, readily attainable. The Department of Terrestrial Magnetism spectrometers are of non-magnetic copper and Inconel, which are not gassy, around which heater coils are wound for outgassing. A fast glass mercury diffusion pump is backed by a Welch Duo-Seal rougher pump. Mercury vapor is kept from back diffusing into the tube by a cold trap. A dry ice-alcohol mixture or liquid air-dry ice can be used as refrigerant. The former takes a temperature of $-78^\circ$ C and the latter $-195^\circ$ C. The higher temperature dry ice mixture is more convenient and was used in this work.

After the tube was opened and a new source installed, both pumps were turned on and the tube was baked an hour or more. The spectrometer was usually ready after another half hour for cooling, to run with a pressure of less than $2 \times 10^{-6}$ mm Hg. The tube was filled with helium gas when breaking vacuum as a further aid in speeding sample changing time.

The vacuum seal was effected by the bearing of a machined ring on the source on an aluminum gasket resting on the plane-machined surface of the tube flange. The aluminum gaskets were re-usable for an average of 10 runs and completely satisfactory.

Six allen-head bolts through the source and tube flanges exerted the pressure necessary for making the seal.
Nickel-plated Wolfram Filaments

The filaments used were of NaOH cleaned wolfram which had been plated with a thin layer of nickel in order to prevent chemical reaction between W and the alkali earth oxides at elevated temperatures from taking place. This composite filament was adopted when experience had shown that platinum, rhodium, molybdenum, tantalum and wolfram were unsuitable because of too low melting points or too great reactivities with SrO.

The filaments were rectangular in cross section, 0.001 inch in thickness, .020 inches in width, and 1/2 inch in length. They were heated, in the spectrometer, by a Variac coupled to the filament through a high-voltage insulated, 6.2 volt filament transformer. Line voltage for the entire spectrometer was moderated by a large Sola voltage stabilizer.

The only detectable impurities on the bare filament were Na and K, and in the filament, Nb and Mo.
Thermal Ionisation

Ions are formed at the source filament by thermal ionisation, a process in which heat energy delivered to the filament is used to boil off a vapor cloud of atoms and to ionize a portion of them by breaking the bond between a valence electron and the atom. The efficiency of thermal ionisation varies with the atomic species, its chemical state of combination on the ribbon, the chemical environment of the atom (that is, what other substances are also on the filament), the material of the filament and temperature.

Thermal ionisation is inefficient for all elements, but there are tremendous differences in efficiency between species of atoms and, within a species, between the various chemical combinations in which it can be placed on the filament. The efficiency of thermal ionisation is highest for the alkali metals and barium and probably radium. It is appreciable for strontium and calcium but at least two orders of magnitude less than that for Rb, Na, K, Ca, and Ba. The tendency towards lesser efficiency in group II is exemplified by Mg, which is not appreciably ionizable by this method, even at the temperature at which wolfram melts.

Quantitative statements of these efficiencies are not possible at this time. The basic work that must be done has so far only reached the stage of determining the comparative rates at which atoms of the different group II elements are vaporized from filaments in vacuum systems (Mo-1).

However, our research indicates that the efficiency of thermal ionisation for the rare earths and yttrium (as oxides), and especially for aluminum is high relative to that for Sr or Ca at the temperatures of Sr emission.
At somewhat higher temperatures, ions of Sr and Mo, Nb, and W from the Ni-plated W filaments, are readily produced. If a Pt ribbon is used, ions of the lower-melting members of the noble metal group are obtained at Sr-ionization temperatures, while if Ir is the ribbon material, the higher melting noble metals can also be ionized.

Among the cation-forming elements that may be expected to have been present on the filament in the various samples, only Fe, Ni, and Si were never seen as ions.

As mentioned, thermal ionization as a method of ion production for Sr suffers from its low efficiency relative to that for other elements usually present as impurities, and also on an absolute basis. However, this is not too serious a disadvantage and in any case it is considerably outweighed by two factors: first, only unipositive ions (H+) are formed; second, background peaks, in particular those due to hydrocarbons, are completely eliminated. Hence no troublesome subtraction for a background of unknown and variable size and distribution is necessary.

Theoretically, thermal ionization efficiencies should differ with mass for different isotopes of the same element. But all other methods of ion formation are also discriminatory to some extent. It is the size of the effect that is important. It is reasonable to ask: does thermal ionization give reproducible results, and how do they agree with those obtained by other methods?

In answer: reproducibility is excellent, apparently limited only by the accuracy of the measuring device. For Sr, isotope ratio values obtained show no variation with time if the sample is left on the filament, emitting ions at a useable rate, for several days. Our results for all
the elements analyzed from mass 39 up, have agreed to within one-half per cent with results obtained by other investigators using other methods, such as electron bombardment of a gaseous sample. Indeed we feel that thermal ionization results may even be more free from error than those given by electron bombardment, because of the lack of background and the fact that only unipositive ions are formed.

Choice of compound for filament emission:

The compounds used in this work with Sr were the chloride, carbonate, sulfate and oxalate. Ca was run once as a fluoride, and once as a fluorophosphosphate. In each case, conversion of the sample to the oxide took place at a temperature below ion formation. The carbonate and oxalate provided the greatest number of ions, but were not greatly superior to the other compounds so whichever compound was most convenient for a particular sample was used. The biotites were in general analyzed as chlorides, as were the feldspars. Oxalate was used only on the first few biotites and abandoned because the amounts of sample were in most cases too small to form precipitates with oxalic acid. The celestites were run in their native form as sulfates, and as chlorides. Reagent SrCO₃ was run as carbonate, chloride, oxalate, and sulfate.

Impurity-free Strontium Emission:

The temperatures necessary for Sr and Ca runs are quite high: the conversion point of SrSO₄ to SrO, 1500° C, marks the start of Sr emission. On the other hand, the alkali metals ionise at much lower temperatures, from 500–1000°. However, as there is a steep temperature gradient along the ribbon from the central hot spot to the relatively cool posts, it
is possible to have Rb and Sr, and K and Ca emission at the same time, from different parts of the ribbon.

Vaporized material collects on the shield box and in particular near the slit. This local area also becomes quite hot, being nearest the filament, and at some point during the increasing of the temperature of the filament, revaporation of alkali metal atoms from the shield becomes appreciable. Some of these atoms strike the filament, where they are ionized with a very high efficiency. Rb and K from this source may appear on the record during the Sr emission period.

Rb and Sr have a common mass number, 87, and this is the isotope of greatest interest since it is the "daughter" Sr isotope; to measure variations in its abundance accurately it is desirable to keep Rb emission zero or as low as possible. This was accomplished by

1) minimizing Rb in the original sample as described in the section on ion exchange techniques;

2) keeping the sample in the center of the ribbon to minimize emission area and heat production necessary;

3) using ribbon filaments of such a size that Sr is emitted below the point where enough power was being pumped into the system to heat up the shield enough to vaporize appreciable Rb; and

4) keeping alkali metals in the ribbon itself as low as possible (it is almost impossible to get rid of Na and K completely), and alkali earth metals at zero.

These precautions succeeded so well that in a few runs (feldspars and celestites where Sr was relatively high) no Rb ion current ever appeared.
At the other extreme, in only one or two cases when Sr was extremely low, was the Rb\textsuperscript{85} peak even 1/10 as large as Sr\textsuperscript{88}. In one case breaking the vacuum in order to clean the shield when Rb started to back-evaporate enabled a critical run to be made.

Other impurities are less serious because they do not have mass numbers which conflict with the Sr analysis, however it is still desirable to minimize them since experience has shown that when the total ion current being produced by the source becomes very large, a mass-sensitive discrimination effect can be introduced. Voltage sweeping of the entire mass spectrum made it possible to quickly determine whether seriously high amounts of impurities were present for a given sample; if so, appropriate steps, such as waiting for the objectionable element to substantially complete its emission, were taken.

Barium and aluminum start to be emitted slightly before Sr, and Ca at about the same time. Moore (No:1) has found that for each atom of platinum evaporated from a Pt filament, one Ca atom, 30 Sr atoms, and \(10^5\) Ba atoms are vaporized. These figures demonstrate that it is important to keep Ba as low as possible. How this was done is described in the section on column technique.

Yttrium 89 was seen rarely. Yttrium ordinarily was emitted as \(Y_6^{105}\) together with the rare earth oxides (mass 155 and up), starting towards the end of Sr emission. Zr was present in quantity only in one sample; it ionizes at a slightly higher temperature still. If a noble metal filament is used, Pt, Rh and Pd ionize in the Sr-Zr range. But if Ni-plated W is used, no filament ions are seen until the filament heat-controlling Variac reading is about double that for the Sr run. Then Mo and Nb, filament impurities, appear, followed soon by W itself. Just
before the burnout occurs, Hg appears. Ni is evaporated from the filament without ionizing.

At the high heats near burnout, all the alkali metals and some other elements are being vaporized from the shield and posts, and a sweep spectrum taken at this time is rather complete. Such a spectrum is shown in figure V-1.
The Source Assembly

Figure V-3 shows, diagramatically, the source assembly used. The electron gun, electron beam, and electron collector of Nier's design have been replaced by the ribbon filament described above, mounted on two tantalum posts within a large tantalum "shield box" which serves as an electrostatic shield and as a surface for the radiative loss of heat produced by the filament as well.

The filament is placed about 1 mm below the slit in the shield box and is at the same potential, about 2000 volts. Actually the shield is connected to the center tap of the 6.2 volt isolated filament transformer; and no point on the filament is more than 2 volts in potential compared to the shield, and if the sample is kept to the center of the filament for the ions formed this difference is only about 0.5 volts.

Positive ions formed at the filament are drawn to the slit by a weak potential gradient "valley" which is set up by the drawing out field, part of which protrudes into the shield box through its slit.

A drawing out field, variable from 0 to 500 volts, can be set up between the shield and the split pair of plates next. Either of these plates can be made to take a potential from 0 to 50 volts higher than the other. This combination of variable drawing out field and split pair deflecting field constitutes the focusing mechanism for the spectrometer; optimum focusing is attained by "building up" a suitable peak to the maximum height obtainable by trying different positions of the drawing out and deflection focusing controls.

The final pair of slit plates are collimating system and both are at ground potential, so that at least 3/4 of the acceleration of
SOLID SAMPLE ION SOURCE
ions takes place between the split pair and the first collimator. The slit in the final plate, the object slit, is designed to give base-width separation of peaks at the collector as described above, and is 0.20 mm wide. All plates are of non-magnetic Advance metal.

The source assemblies used were designed for ease of assembly and disassembly. About three minutes was required for assembly, the longer operation of the two.

The source is the very heart of the spectrometer. Its function is to produce a sufficient supply of essentially monoenergetic ions in a steady manner, and to focus, accelerate and collimate this beam and project it down the center of the mass spectrometer tube to the magnetic analyzer. The monoenergetic condition can only be approximated; any deviation adds to the image peak width at collection. In this spectrometer, the total acceleration used was about 2000 volts. Ions deviated from this figure about 0.5 volts as already mentioned because the filament was not all at the same potential, and from 0 to 0.5 volts additionally due to the unavoidably different energies imparted to the ions in thermal ionization. However the beam was still monoenergetic to 0.1 per cent, which is quite adequate.
Collection of Magnetically Analyzed Ion Beams

The essentially monoenergetic ion beam produced in the source is split into bundles of ions having the same m/e ratio in the magnetic analyzer. No major design changes were made in the analyzer described by Nier.

The collector system used consists of two plates and a Faraday cup. The assembly is shown in figure V-4. The first plate sighted by ions which have not already deviated enough to hit the sides of the spectrometer tube has a large rectangular opening, 8 x 20 mm, allowing all beams within this spread to pass through and rejecting the rest. It is set at a potential 45 volts more negative than the next, or collector, plate in order to force secondary electrons formed by ion beam bombardment of the collector plate to return to it. This is necessary since a negative electron leaving the plate gives the same pulse as a positive ion arriving.

The slit in the collector plate is 0.50 mm wide, this dimension having been selected, as described in the introductory section, to give flat-topped, resolved peaks. The slit is off center on the collector plate, so that if mass 86 falls through the slit into the cup, 87, 88 and 89 only will hit the plate on the high mass side but masses down to 77 will be collected on the low mass side. This arrangement was designed for the collection of Ca, so that when the rather rare isotope at mass 44 passed through the slit the abundant mass 40 isotope would hit the plate. It works quite adequately for Sr, as well.

The single-mass beam passing through the collector slit is collected in the Faraday cup shown. The current it sets up passes through a pre-
DOUBLE COLLECTOR FOR ION CURRENT RATIO DETERMINATION
amplifier stage to the "A" amplifier and meter; current hitting the collector plate after preamplification goes to the "B" amplifier and meter. The ion currents to the collector used in this work were in the $10^{-14}$ to $10^{-10}$ ampere range. For accurate results on samples where only the lower of these values was possible, an extremely quiet amplification system was required, and had been achieved, as already described, by J.B. Doak in his design.
Methods of Data Taking

The different bundles of ions of the same m/e ratio separated by the magnetic analyser can be brought to the collector slit one by one by varying the accelerating voltage or the magnetic field.

Voltage sweeping:

In this research, selection of masses by varying the voltage was used only for rapid peak scanning of a wide range of masses, as in the estimation of impurities in the sample. Figure V-2 shows such a record.

Magnet sweeping:

Scanning of a small range of masses by varying the magnetic field was used for all samples to determine the ratio $\text{Rb}^{85}/\text{Sr}^{86}$, to see whether any peaks other than Sr or Rb were present in the range mass 75-90 and if so to estimate their abundances relative to $\text{Sr}^{86}$, and for the actual determination of Sr isotope ratios when the amount of sample was too small or the amount of Rb too high to provide sufficient sensitivity or accuracy in the ratio measurements.

For several samples, ratio measurements were checked against scanned sets to be sure that the two methods gave the same result. For those samples where ratio measurements were possible, magnet sweep sets were still taken and serve as a permanent record, insurance against "human error".

Where it was necessary to use the sweep method to measure Sr isotope abundances, a large number of sweeps were made back and forth across the Sr mass range: ten to twenty sets, where possible. For those samples where it was possible to obtain this much information, the results are
considered to be within 1/2 per cent of the correct value. Occasionally, when the sample was very small or Rb very high, this number of sets was not attainable, and the accuracy, as noted, is therefore less.

Sets of magnet sweeps for normal and biotite Sr are given in the frontispiece.

Ratio measurements:

The premier method of isotopic abundance analysis consists of comparing the currents representing two masses, amplified, by a well calibrated decade resistance box.

This method was approximated in this research by comparing the current received at the collector Faraday cup with that falling on the collector plate. When mass 86 passed through the slit, all the other masses between and including 77 and 89 hit the plate. When 88 was in the slit, all masses between 79 and 91 hit the plate. Ideally, only the peaks of Sr, at 84, 86, 87 and 88 were present, but in many cases small amounts of Rb, which has isotopes at 85 and 87, were also collected on the plate. On one or two occasions, \(^{89}\)Sr appeared fleetingly. A peak of unknown origin at mass 83 occasionally gave trouble: Its possible source is discussed in part X. Sweep peaks served as a check on the values taken in these cases, which could also be checked internally by a method described under "computations".

Reproducibility:

Values obtained for a given sample on a given source could be reproduced on the other source at a different time to within the limits of accuracy, 1/2 per cent, claimed for the values. In one case the value 0.6 per cent radiogenic Sr was reproduced to better than this accuracy two months after the original run.
There was no discernable time-variation of the values determined due to any mass discrimination effects present or other causes for periods of Sr-emission as long as three days. Most runs were completed in a much shorter time, averaging about 4 hours Sr-emission.

Reproducibility was equally good whether magnet-sweep peak data or ratio data were taken, and the two methods gave the same values when compared, within the error of measurement. For the measurement of masses 86 and 87 to 88, however, the ratio method is superior because "base line drift" which is present to a small extent in the sweep data, and variations in ion current have no influence on the ratio values determined.

Isotopic abundances determined by us for materials which had been analyzed by other workers in other laboratories, who, in general used methods other than thermal ionization for ion production, agree quite well with the previous determinations. The values for a Sr$^{84}$ enriched stable isotope tracer obtained from the Atomic Energy Commission are within 1/3 per cent of those measured at Oak Ridge. Agreement with Nier for reagent Sr and White and Cameron (but not Nier) for reagent Ca is similarly good.
Computation

Strontium abundances:

Calculation of Sr abundances from sweep data is straightforward except when Rb is present. Ratios between the measured heights of the flat-topped peaks for the different isotopes are computed directly, then the results are converted into percent-of-total-Sr abundances.

Rubidium has isotopes at 85 and 87; the latter alone coincides in mass number with a Sr isotope. Since we are especially interested in the relative abundance of the partly radiogenic Sr$^{87}$, the Rb$^{87}$ correction is quite important. Today as nearly as we know, all Rb$^{87} = 0.386 \times$ Rb$^{85}$, neglecting for the present any isotopic fractionation effects. Hence the desired correction can be made by measuring the Rb$^{85}$ peak and subtracting .386 of this amount from the measured 87 (Sr + Rb) peak.

The ratio-method measurements are somewhat more complex because more than one peak falls on the collector plate.

If we let $E$, designating "everything," stand for all masses -- Sr, Rb, Y, and "mass 83" -- that appeared at any time in the ratio work in the range of masses that can hit the collector plate when mass 86, 87 or 88 is passing through the slit, then the ratios

$$A = \frac{E-86}{86}, \quad B = \frac{87}{E-87}, \quad C = \frac{86}{E-86} \quad \text{(1)}$$

denote the currents compared in the three cases. The resistance box is set up to compare a smaller to a larger current, hence the inversion of the expression for $A$. 

From the above
\[
\frac{37}{36} = \frac{B(1 + C)}{C(1 + B)} \quad \frac{37}{36} = \frac{B(1 + A)}{(1 + B)} \quad \frac{36}{35} = \frac{C(1 + A)}{(1 + C)} \quad \ldots \ldots \ldots (2)
\]

Also, if only Sr is present and "Sr" is used to designate total strontium,
\[
\frac{\text{Sr}^{88}}{\text{Sr}^{87}} = \frac{1}{1 + A} \quad \frac{\text{Sr}^{87}}{\text{Sr}^{86}} = \frac{B}{1 + B} \quad \frac{\text{Sr}^{86}}{\text{Sr}^{85}} = \frac{C}{1 + C} \quad \ldots \ldots \ldots (3)
\]

With Rb or other impurities present, corrections are necessary and the procedure is more complex.

The Rb\(^{87}\) correction is easiest applied to the ratio 37/36, since Rb\(^{85}/\text{Sr}^{36}\) is the measure of Rb recorded in this work.
\[
\frac{\text{Sr}^{37}}{\text{Sr}^{36}} = \frac{37}{36} - \frac{386 \text{ Rb}^{85}}{\text{Sr}^{36}} \quad \ldots \ldots \ldots (4)
\]

Then Sr\(^{37}/\text{Sr}^{36}\) can be computed:
\[
\frac{\text{Sr}^{37}}{\text{Sr}^{36}} = \frac{\text{Sr}^{37} \times \text{Sr}^{36}}{\text{Sr}^{36} \times \text{Sr}^{36}} \quad \ldots \ldots \ldots (5)
\]

These equations are valid even if impurities other than Rb are present, since E cancels out. However, the equations for Sr\(^{36}/\text{Sr}\), etc. given above are not valid if ions other than Sr are present since they yield in this case Sr\(^{36}/E\) instead of Sr\(^{36}/\text{Sr}\), etc. Sr\(^{36}/\text{Sr}\) can be found as follows:

Let D = Rb\(^{85}/\text{Sr}^{36}\) and F = "mass 83"/Sr\(^{36}\). Then
\[
\frac{\text{Rb}^{85}}{E} = \frac{D \times \text{Sr}^{36}}{E} = \frac{CD}{1 + C} \quad \text{and} \quad \frac{83}{E} = \frac{CF}{1 + C}
\]

Now
\[
\frac{\text{Sr}^{37}}{E} = \frac{37}{E} - \text{Rb}^{37} \quad \text{and so} \quad \frac{\text{Sr}^{37}}{E} = \frac{37}{E} - \frac{\text{Rb}^{37}}{E}
\]
while Sr = E - Rb - 83, so that $\frac{Sr}{E} = 1 - \frac{1.366 \text{ Rb}^{85}}{E} = \frac{83}{E}$.

Substituting,

$$\frac{Sr^{87}}{Sr} = \frac{B}{1 + B} - \frac{0.366CD}{1 + C}$$

$$ \ldots \ldots \ldots (6b)$$

and similarly,

$$\frac{Sr^{86}}{Sr} = \frac{C}{1 + C}$$

$$ \ldots \ldots \ldots (6a)$$

$$\frac{Sr^{86}}{Sr} = \frac{1}{1 + A}$$

$$ \ldots \ldots \ldots (6a)$$

$$\frac{Sr^{88}}{Sr} = \frac{1}{1 + A} - \frac{0.366CD}{1 + C}$$

If there is no "mass 83" present, the term containing F is zero;

if no Rb is present, the D terms are zero, and we are left with the equation already derived for the case of Sr only.

The ratio equations that can be derived from the above general equations are also the same as those already given, but such derivation shows that the ratio $\frac{Sr^{86}}{Sr^{88}}$, is independent of any impurities present as long as they fall on the collector plate when both A and C are taken. Similarly, the 87/88 ratio is independent of all impurities except Rb$^{87}$.

$$\frac{Sr^{86}}{Sr^{88}} = \frac{C(1+A)}{1+C} \quad \frac{Sr^{87}}{Sr^{88}} = \frac{B(1+A)}{1+B} - \frac{C(1+A)(0.366D)}{1+C} \ldots \ldots \ldots (7)$$

Two sets of abundances can now be calculated, the first depending on the estimates made of any impurities present; the second unaffected by impurities, requiring the statement $Sr^{87}/Sr^{88} = 1$, for purposes of calculation.
In the ratio work done both methods of calculation were used. To compare the results an additional assumption as to the abundance of Sr$^{84}$ and its constancy must be made. Since no significant error would be introduced in the other values if this isotope did vary by as much as 10 per cent in abundance, we used Nier's (op. cit.) published value, Sr$^{84}$/Sr = 0.0056; that is, Sr$^{84}$/Sr$^{88}$ = 0.007, in our calculations.

Where a small amount of Rb was the only impurity, the correlation between the two sets of results if remarkably good. However, in three cases "mass 83" apparently started to be emitted during the run so that there is a discrepancy between the 83-sensitive and 83-independent abundances. When the sweep peaks for these two runs were examined the presence of "83" was confirmed. Nevertheless, an error in recording D, the Rb$^{85}$/Sr$^{86}$ ratio, remains a possible source of the error for these three cases.

Geologic age computations:

The ratio of Sr$^{87}$/Sr in c.p. reagent grade SrCO$_3$ (Nier and Amend) today is 0.0702. This is the normal Sr$^{87}$ abundance reported by Nier (N-1) and others, and also as found by us. Whether this strontium deserves to be called "normal" present day Sr or not is discussed in the results below. However, if we assume that it is normal, and that, for normal Sr, it has not changed during the, say, 3500 million years of earth history (not correct), and that normal abundances are the same in, for example, biotite, feldspar and celestite (also incorrect: all these points are taken up in the results section), we need only subtract 0.0702 from the Sr$^{87}$ abundance found by us to determine the amount of radiogenic Sr in the sample. Call this amount, the excess Sr$^{87}$, "x," when it is expressed as
a fraction of total Sr. To calculate an age, we need then to know only
Y, the Sr/Rb ratio in the mineral and the decay constant of Rb$^{87}$.

The decay constant, $\lambda$, for Rb$^{87}$ used in this research is
$1.18 \times 10^{-11}$/yr., and so in 3500 million years only $(3.5 \times 10^9 \times 1.18 \times 10^{-11})$ or about 4 per cent of the original Rb$^{87}$ will have become Sr$^{87}$. If we assume that no loss in parent Rb has taken place, we shall intro-
duce no appreciable error except for very old samples and for these the
error introduced is at present tolerable, since it is small compared to
the other uncertainties involved in sampling and spectrochemical work.

Thus the age calculation becomes

$$\text{Age (mill. yrs.)} = \text{fraction "excess" } 87 \times \frac{\text{Sr}}{\text{Rb}} \times \frac{10^4}{\lambda \times 10^6}, \text{ or}$$

$$\text{Age (m.y.)} = 2.81 \times 10^5 \times Y \times \text{Sr}^4/\text{Rb}^20 \quad \ldots \ldots \ldots \ldots \ldots (8)$$

since $\text{Sr}/\text{Rb}^{87} = 3.320 \text{ Sr}^0/\text{Rb}^20$, using the following atomic weights:
Rb = 85.43; Sr = 87.63; 0 = 16.00, and taking $\text{Rb}^{87}/\text{Rb} = 0.2785$.

This equation was used to compute the results presented in this report.

It was recognised that the assumption that "normal" Sr$^{87}$/Sr was con-
stant and equal to .0702 throughout geologic time cannot be true. But in
order to correct this error, the actual variation of Sr$^{87}$ with time must
be known. It was hoped that the feldspars might, because some of them
were almost Rb-free, provide a clue as to this variation. Those which
contained appreciable Rb could be corrected by subtracting a radiogenic
Sr contribution calculated using the Rb$^{20}$ value obtained by Holyk, from
that actually observed. This is done in the results using (where Sr$^{4}$
stands for radiogenic 87),
(correction to)

\[
\frac{\text{Sr}^{87}}{\text{Sr}} = \frac{\text{Sr}^\Delta}{\text{Sr}} \times \frac{\text{Sr}^{80}}{\text{Sr}^0} = 0.00035 \frac{T}{\text{Sr}/\text{Rb}_20}
\]\n
where \( T \) is in 100 million years units and the factor 0.00035 is derived as follows:

\[
\text{Rb}_2/\text{Rb}_20 = 0.914; \quad \text{Rb}^{87}/\text{Rb}_20 = 0.2725 \times 0.914; \quad \text{Sr}_0/\text{Sr} = 1.18.
\]

Hence, \( \text{Sr}^\Delta = \text{Rb}^{87} \times 0.914 \times 1.18 \times 10^{-11} T \times \text{Rb}_20 \)

\[\text{Sr}^\Delta = 0.3003 \frac{\text{Rb}_20}{T} \times 10^{-11} \quad \text{and} \]

\[
\frac{\text{Sr}^0}{100 \text{ mill. yrs.}} = 0.00035 \frac{\text{Rb}_20}{T}.
\]

Two sets of values were used for \( T \): one set for the age estimated on geological grounds, the other, for the ages determined in this work using Whiting and Holyk's \( \text{Sr}_0/\text{Rb}_20 \) ratios, and the author's excess-87 values.

This method should if all the assumptions mentioned in the introduction are correct yield correct values both for the "primitive strontium 87" variation throughout geologic time and for the ages of individual specimens, after a series of approximations.

That it did not show that one or more of the assumptions made was not always correct.
PART VI: POSSIBLE SOURCES OF ERROR

An appraisal of the possible sources of error in any scientific investigation is in order.

In this work contamination could be introduced either in the standard chemical techniques or in the ion exchange column processing; errors could be introduced in addition either by incorrect isotope ratio determinations with the mass spectrometer, or in the optical spectrographic determination of SrO and Rb₂O. If no appreciable error were introduced by any of these sources, the results themselves should provide a check on the tentative assumption that no addition or subtraction of daughter or parent material has taken place during the lifetime of the sample and on the half-life value used for Rb³⁷. These matters and the assumption that the ratio Rb³⁷/Rb³⁵ is constant are discussed in part X.

Certain checks on procedure have already been mentioned, but will be summarized here briefly. Contamination in the ion exchange chemistry and mass spectrometric analysis was fixed (part III) at less than 0.5 µg. If this much contamination did exist, it would be negligible, compared to other sources of error, for a 50 µg sample. All samples in which ratio measurements were possible exceeded this size. An uncertainty of 10 percent exists for samples of 5 µg; it is possible that some of the samples for which only preliminary measurements by magnet sweeping could be made were this small. Such cases are noted in the results.

W. L. Helyk has not as yet tested the tap distilled water or the ethanol used in his processing. These reagents remain possible sources of contamination. However, arcings of his other reagents indicate no Sr impurity. A mass spectrometer analysis of a 100 µg spike Sr²⁴ tracer
subjected to the entire chemical procedure used in both laboratories would be most instructive.

It is felt that the mass spectrometric determinations reported are valid to $\pm 1/2$ per cent except where otherwise noted. Reproducibility of repeat runs on the same sample and checks with independent measurements of certain samples by analysts at other laboratories were all within the stated experimental error. Any systematic error would have to be common to the determinations of others as well.

Grating spectrographic analyses show the largest spread in results, though individual determinations in triplicate on the same sample by the same analyst using the same method generally have a very small scatter, about 10 per cent. The determinations of $\text{Rb}_2\text{O}$ and $\text{SrO}$ by the two investigators using different methods, or the same method, however, differ in a large number of cases by a factor of two or more. When these values are converted to ratios, the spread is even greater. Differences of as much as a factor of 5.2 exist in the lowest and highest ratios of $\text{SrO}$ to $\text{Rb}_2\text{O}$ that can be computed from the data. Such variation is intolerable for accurate age determination.

It appears that the values for $\text{SrO}$ determined by using $\text{Ba}$ as an internal standard are the most subject to systematic error, since Whiting's assumption that the amount of $\text{Ba}$ in the samples would be negligible compared to the 3 per cent of $\text{BaO}$ he added for comparison purposes is not valid. The situation is even worse for feldspar analyses, where unknown amounts of the barium feldspar celsian were intergrown with the plagioclase and potassic feldspar. In the feldspars $\text{BaO}$ may have reached 10 per cent for some samples.
Helyk recognized this large source of error and therefore substituted the total energy method for the determination of SrO in feldspar, and used both methods as a check on the biotite determinations. The total energy method values are used in this report to calculate ages except where only Ba-standard analyses were available. The amount of error in these determinations is difficult to assess; they may be very accurate. But the spread between individual determinations is much higher than for the Ba-standard method, so that the small number of determinations for each sample is not sufficient, statistically, to reduce the probable error to a desirably small level. In this sense these values must be considered preliminary.

To summarize: The errors introduced into the Sr isotope analysis of the sample by resin column treatment and mass spectrometric isotope abundance measurements appear to be negligible compared to other sources of error. The amount of contamination in the tap distilled water and ethyl alcohol used by Helyk should be investigated by stable Sr tracer technique. Large errors, exceeding 200 per cent in some cases, are possibly present in the optical spectrographic determinations of Rb2O and SrO. These could be minimized by improvements in technique and repeated analysis of samples, or by the substitution of another, more accurate method of obtaining this information such as the Sr94 spike technique suggested in part XI of this thesis.
PART VII: DESCRIPTIONS OF SAMPLES


8. Oliverian syenite. A series of domes of this rock outcrop along a belt running from New Hampshire to southern Connecticut. Age: Probably late Devonian.

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

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


15. Syenite from Salem Willows, Massachusetts. The rock is considerably altered. Age: As this is Beverly syenite, part of White Mountain
Magna Series, the age is considered to be Mississippian. Biotite fraction contains 5 per cent feldspar.


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

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


21. Pascolet granite from South Carolina. Age: Late Palaeozoic or Precambrian. Biotite fraction contains 1 per cent feldspar.


26. Stone Mountain granite, from Georgia. Age: Disputed, but possibly late Palaeozoic. Biotite fraction contains 1 per cent muscovite, 1 per cent feldspar. May be Precambrian.

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

30. Baserachite, a fine-grained gabbro from Sudbury, Ontario. The biotite seems to be concentrated near pyrrhotite in this rock. Age: Precambrian.

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


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

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

52. Pegmatite close to No. 51. Age: Presumably early Archean. The biotite is slightly altered to sericite, etc.

53. Granite from Nova Scotia. No. 1722 A in Helium-Age Record system. Age: Late Devonian. Biotite fraction contains 3 per cent chlorite, quartz, feldspar.

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

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


63. Anorthosite, New York state. Age: Possibly 1000, 1500 or 600 million years. In dispute.

64. Biotite from pegmatite, Southern Rhodesia. Age: Probably 2000 million years.


C-2. Celestite from Travis County, Texas.

C-3. Celestite from Calabogie, Ontario, Age: possibly Precambrian.


C-6. Celestite from Lansdowne township, Ontario, Age: May be Precambrian.

C-7. Celestite from Girgenti, Sicily. Appears to be a vug filling. Age: Called Upper Miocene.


C-11. Celestite from Brown County, Texas.
PART VIII: RESULTS OF MASS SPECTROMETRIC ANALYSES OF STRONTIUM

Strontium Reagent Standard

Five determinations of the isotopic abundances of strontium from batch No. 492327 of c. p. reagent \( \text{SrCO}_3 \) prepared by Riner and Amend Chemicals division of the Fisher Scientific Co. were made, using the double collection technique. These determinations, valid to \( \pm 1/2 \) per cent individually, were in good agreement with each other. The isotopic abundances for this sample, called "standard strontium" or "normal strontium" in this paper, are

\[
\begin{align*}
\text{Sr}^{88} & = 0.8252 \pm 0.0005 \\
\text{Sr}^{87} & = 0.0703 \pm 0.0002 \\
\text{Sr}^{86} & = 0.0967 \pm 0.0002 \\
\text{Sr}^{84} & = 0.0058 \\
\end{align*}
\]

The value for \( \text{Sr}^{84} \) was calculated from the other values.

The values for various isotope ratios for this standard strontium are:

\[
\begin{align*}
\text{Sr}^{87}/\text{Sr}^{88} & = 0.712 \\
\text{Sr}^{87}/\text{Sr}^{86} & = 0.0852 \\
\text{Sr}^{86}/\text{Sr}^{88} & = 0.1196
\end{align*}
\]

These values are in almost exact agreement with those published by Nier (N-1) and given in part II.

The Fisher Scientific Company is at present cooperating with our group in an attempt to determine the mineral deposit from which batch No. 492327 was obtained, however this information had not been received at the time this thesis was written.

The analyses of standard Sr are included in the table of celestite data, table VIII-J, because preponderant evidence indicates that the standard strontium came from a celestite deposit.
Biotite

The mass spectrometric investigations of strontium from biotites show that this mineral contains both radiogenic Sr and "normal" strontium. Radiogenic strontium varied from 0 to 12 per cent of total Sr in these samples. The distribution of radiogenic Sr is shown in figure VIII-1, in terms of the ratio, Sr$^{87}$/Sr$^{88}$. This histogram shows that there is no marked concentration of samples about any value, for the samples analyzed. Only Tertiary samples show no measurable enrichment in Sr$^{87}$ due to the rubidium$^{87}$ decay process, as compared to standard strontium. There is a tendency towards increased radiogenic content with assumed geologic age, however, with marked exceptions. (Figure VIII-3) The highest concentration of Sr$^{87}$ was found in a specimen (Stone Mtn., Ga; see frontispiece) thought to be either late Paleozoic or very late preCambrian; the age determined supported the latter interpretation. On the other hand some samples assumed to have ages in excess of 1,000 million years showed Sr$^{87}$ enrichments of less than 1 per cent.

The geologic ages calculated on the basis of these figures are presented in part I of this thesis.

Biotite also showed the largest variation in the ratio of the presumably stable isotopes, Sr$^{86}$ and Sr$^{88}$. The exceptionally low values for samples No. 7 and No. 9 should be rechecked since only one ratio measurement was taken, but even excluding these values a spread of 4 per cent in the ratio as determined remains. There is a possibly significant concentration of samples about the ratio 86/88 = 0.1180; there does not seem to be any correlation of ratio with geologic age. These ratios are presented in figure VIII-2.
Phlogopite

One phlogopite sample (18F) was analyzed using the double collection method. It contained over 6 per cent radiogenic Sr and its $\text{Sr}^{86}/\text{Sr}^{88}$ ratio would have been quite normal for a biotite.

Muscovite

Two muscovites were analyzed (29M, 66M). One of these showed a $\text{SrO}/\text{K}_2\text{O}$ ratio in the low feldspar range, the other, in the biotite range.

These samples contained, respectively, 0.2 and 0.4 per cent more $\text{Sr}^{87}$ than the standard strontium.

Their $86/88$ ratios differed by 3 per cent; both values are in the biotite range but one is greater than that obtained for any feldspar.

The muscovite and phlogopite data is presented with the biotite analyses.
**Fig. VIII-3**

**Measurements**
- ■ = Double Collector
- ◦ = Magnet Sweep

**Variation in \( \text{Sr}^{87} / \text{Total Sr} \) in Biotites with Inferred Geologic Age**

**Y-Axis:** Ratio of \( \text{Sr}^{87} \) to Total Sr

**X-Axis:** Inferred Geologic Age in \( 10^6 \) Yr. Units

- Data points labeled with numbers corresponding to specific samples or measurements.
Feldspar

As was expected, there is considerably less spread in the feldspar Sr$^{87}$/Sr$^{88}$ ratios than in those for biotite. Wherever the SrO/Rb$_2$O ratio obtained by Holyk is greater than 10, the $^{87}/^{88}$ ratio is less than that for the strontium standard. However the maximum amount the $^{87}/^{88}$ ratio is reduced, relative to normal Sr, in any sample is only 2.3 per cent.

Where the feldspar was rich in rubidium, as evidenced by a SrO/Rb$_2$O ratio in the biotite range, there is a definite excess of Rb$^{87}$ above that in the standard, exactly as in the case of the biotites. The other samples, with SrO/Rb$_2$O ratios between 0.1 and 10.0, fall in intermediate positions. There is, however, considerable overlap between groups. These findings are presented graphically in figure VIII-1.

No feldspar analyzed had a Sr$^{86}$/Sr$^{88}$ ratio as great as that of the strontium standard, while five biotite analyses exceeded this value, 0.1196. Feldspar analyses showed $^{86}/^{88}$ ratios from 0.1164 to 0.1194, with a suggestion of two groupings, one below 0.1176 and the other about 0.1190. These apparent groupings may be merely due to a statistically inadequate sample. The feldspar $^{86}/^{88}$ ratios are shown in figure VIII-2.

Thirteen feldspar concentrates were analyzed using the double collector. Magnet sweep measurements were tried three times on an important sample, 62F, where a high radiogenic content (ca. 6 per cent) may have been present. Unfortunately, the sample was too small to make an accurate estimate. This sample had a Sr/Rb ratio far in the biotite range.
Table VIII-1A -- Sr Isotope Analyses for Biotite and Feldspar

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<th>87/Sr</th>
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n = No analysis possible

Error: Limits of error for 87 measurements are given in (87/Sr) - .0702 column as they most seriously influence this value. Limits of error for 86 measurements are given in 86/88 ratio, that is, in the value measured.
Table VIII-3

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Celestite

The Sr$^{87}$/Sr$^{88}$ ratios for the celestites analyzed are quite well grouped about 0.0852, the value found for the standard, or normal, strontium. This grouping, in which as many determinations are greater than that for "normal" Sr as are less than this value, many indicate that for celestite, a higher present-day $87/88$ ratio must be adopted. A decision on this point awaits further information as to the geologic settings and ages of the celestite samples and in particular, the so-called normal strontium, which appears to be a celestite. Figure VIII-1 contains a histogram of celestite $87/88$ values.

The range of values found for Sr$^{86}$/Sr$^{88}$ for celestites is definitely higher than that for either feldspar or biotite. Four of the eleven samples analyzed lie within ±0.0002 of the value, 0.1196, obtained for standard strontium. Two Canadian celestites show distinctly lower values, near 0.1162; a Texas sample had the highest ratio, 0.1220. The Sr$^{86}$/Sr$^{88}$ values for celestite are presented diagramatically in figure VIII-2.

The results of this investigation are summarized in tables VIII-1 to VIII-3 in this section. Table VIII-1 is a summary of the double collection method data for biotites and feldspars. Table VIII-2 summarizes magnet-sweep biotite data; table VIII-3 presents double collection data for celestite and standard strontium. These tables include the isotope ratios computed as well as abundances.
PART IX: RESULTS OF OPTICAL SPECTROGRAPHIC ANALYSES FOR SrO AND RB₂O

Table IX-1 lists the values for RB₂O and SrO obtained by Holyk and Whiting using the methods described in part IV. In computing ages, in the next section, Holyk's RB₂O values and his SrO values by the total energy method were used. Holyk believes these are the most reliable analyses. The few cases where such analyses were not available are noted in the table.

The SrO/RB₂O ratios from Whiting's analyses and Holyk's Ba-standard SrO determinations are also computed. These ratios make up table IX-2. For each sample for which more than one kind of analysis was made, the maximum and minimum ratios that could be computed from any of the figures, and the ratio of these values has also been computed as an indication of the possible errors involved in the determinations. As will be seen, spreads of a factor of two are common and the maximum spread noted between such ratios is 5.2.
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### Table IX-2A -- SrO/Rb₂O for Biotites and Feldspars

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**Explanation:**

1. Ratio on Holyk's plates of SrO, using total energy method, to Holyk's Rb₂O values on his plates using Na-standard.
2. Ratio of values determined by Ba-standard method by Holyk from Whiting's plates, using Holyk's working curve, to Holyk's values, using his Rb working curve, for Whiting's Na-standard Rb₂O plates.
3. Whiting's original data. Ratio of Ba-standard SrO on Whiting's plates using Whiting's working curve, to Na-standard Rb₂O determined by Whiting on his plates using his working curve.

B = Biotite  P = Phlogopite  M = Muscovite  F = Feldspar
PART X: AGES AND AGES

Biotite

Thirty-two biotite ages have been calculated from the analyses summarized in the preceding sections. The results are presented in this section in tabular form and graphically.

It is of interest to compare these calculated ages with those that can be inferred on the basis of geological evidence; however it is possible to link only two samples with rock units whose ages are accurately known as the result of several consistent analyses by two or more other methods of geologic age determination. For the other samples, only estimates on the basis of geologic relations in the area or previous age determinations in the same geological province were possible. Many of these estimates may be grossly in error, a major contributing reason being the highly generalized locations of some samples in regions of more than one known orogeny.

In spite of this, the two sets of data, calculated age and inferred age, show a promising correlation. For ten samples out of thirty-two, the age calculated using the SrO and Rb₂O analyses preferred by Holyk lies within the range of values inferred from geological evidence and/or previous radioactivity-method age determinations. Eleven more analyses would have fallen within their respective permitted ranges if another SrO/Rb₂O ratio within the range of values determined in the three optical spectrographic analyses had been chosen. The eleven remaining calculated ages cannot be brought into agreement with their inferred ages by the substitution of any SrO/Rb₂O ratio derivable from the Whiting-Holyk data.
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Note: M = Muscovite    P = Phlogopite    S = Sweep

"Within limits" column—If answer is yes, an age within limits of calculated maximum and minimum lies within inferred age range.

Where inferred ages are highly controversial, both possible ranges are listed.
However, as has been previously mentioned, many inferred age ranges are no doubt incorrect.

The biotite results are presented in table X-1/figures X-1 and X-2. An attempt has been made in these illustrations to show the effects of the measurement and age-estimate uncertainties already discussed on the results. For this purpose it would perhaps be best to represent each correlation by a rectangle, with one dimension given by the range of possible ages inferred for the sample and the other joining the highest and lowest ages calculable from the spectrochemical data. Such a plot, however, becomes very crowded and so the rectangles are each replaced in these diagrams by a vertical line showing the spread in calculated ages, and a horizontal line showing the spread in inferred age. The latter line is drawn at the level corresponding to the age calculated using the optical spectrographic data preferred by Holyk.

Samples 60B and 64b, from Southern Rhodesia, appear to be cases in which the inferred ages are very greatly in error. 2,000 million years is the age inferred for both samples on extremely broad grounds. But essentially identical ages of a widely different order were calculated: 15-20 million years. If 100 per cent of the Sr found in these samples in Holyk's analyses were radiogenic, instead of the 1 per cent shown by isotopic analysis, their calculated ages would still be considerably less than 2000 million years. And there is excellent reason to believe that the Sr in these samples has not been contaminated by "normal" Sr since they were formed, for these two samples have the lowest total SrO content of any biotites analyzed. Furthermore, the samples themselves are perhaps the most ideal-appearing biotites in the suite: large, clean, shiny sheets that would make excellent textbook illustrations of pegmatite book.
Fig. X-1

Calculated vs inferred geologic ages, 0-700 million years
Fig. A-2

Calculated vs inferred geologic ages, 500-3500 million years.
mica. It seems not improbable that these samples are actually Tertiary, as calculated, and hence should have been scored as "hits" instead of "misses" in this comparison of data. For how many other samples the case may be similar cannot be determined.

Of the two samples whose ages are well known through other work, one (18F) has a calculated age in excellent agreement with previous determinations, the other (27B), shows a factor of two errors if Helyk's data is used, but is exactly correct if Whiting's original data is used. It may be significant that 18F is a phlogopite, the only one analyzed.

These samples illustrate the basic difficulty encountered in attempting to evaluate the age determination method under test: the optical spectrographic data so far obtained do not have the necessary precision to allow a critical evaluation of the calculated ages. In the next section a possible means of by-passing this difficulty is presented. Until it has been used on a number of samples of well-authenticated age, a verdict as to the usefulness of the biotite-strontium method of age determination is not possible.
Feldspar

The feldspar analyses were undertaken in the hope that variations in the isotopic composition of strontium due to the decay of Rb$^{87}$ throughout geologic time might be systematic for igneous rocks as a whole, as would be expected if, for example, all igneous rocks separated from the same deep parent magma only a short time before solidification. The results, as is often the case, show that the actual phenomenon is not as simple as one might desire.

It was hoped that Whiting's selection procedures would yield a suite of feldspars containing only trace amounts of Rb, so that the necessity of a correction to the determined Sr$^{87}$ abundances might be avoided. Unfortunately, only three of the 15 samples analyzed met this specification. Three others had high enough SrO/Rb$_2$O ratios that only very small corrections for radiogenic Sr were necessary. However for the other samples the SrO/Rb$_2$O ratio extended from this high value down very far into the range of values favorable for age determination found for biotite. The corrections indicated for many of these samples are much larger than the anomaly sought.

The feldspar data of table X-2 have been plotted against two sets of ages: the inferred and calculated biotite ages already discussed. Neither plot shows an unambiguous systematic variation of Sr$^{87}$/Sr with time. However, all samples having reasonably high Sr/Rb ratios are depleted in Sr$^{87}$ compared to biotites and the strontium standard. Two of the corrections-free values, for 62F and 1F, show a depletion of only .0013 in Sr$^{87}$ relative abundance (compared to the standard, 0.0702) in over 1500 million years on the basis of inferred ages, or 3000 million years if the
Table X-2 -- Primitive Strontium Variation after Rb Correction

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calculated ages are correct. If the simple model of igneous rock genesis just presented were valid these values would mean that the Rb/Sr ratio for the earth determined from geochemical analyses must be quite erroneous, for it predicts that in 3000 million years an amount of Sr$^{87}$ equal to 1.4 per cent of total Sr should have been added to common strontium; this would mean, for rocks crystallized at that remote time, a Sr$^{87}$ abundance of about 0.0560 and a correction of 0.0140 to compensate for the original assumption that the abundance had not varied from that of the standard strontium in the past.

It is apparent that a great number of additional analyses must be made before the mode or modes of variation of Sr$^{87}$ relative abundance in surface rock can be determined. Suitable samples, in particular ancient low-Rb minerals, are at present being collected for such a study.

It does appear, however, that any systematic correction necessary to biotite ages because the common Sr$^{87}$ abundance, assumed constant in this work, has varied, being less for common strontium in any rock crystallized in the past, will not be nearly as great as had been expected and may even be negligible for biotites where over 1 per cent radiogenic Sr is found; however much larger specific corrections may be necessary because of variations that this research appears to indicate are present in the Rb/Sr ratios in the sources of various crystalline rocks.
Celestite

Estimates of age were available at the time of writing this section for only half the celestite samples analyzed, and some of these estimates are subject to considerable question. It is therefore impossible at this time to accurately evaluate the potential Sr isotope variation method of dating sediments containing strontium minerals. However, the celestite strontium isotope analyses made do not show a variation in the ratio Sr$^{87}$/Sr$^{88}$ of even the order of magnitude expected by Hickman and others, if they actually include representatives of geologic periods from pre-Cambrian to the present as the age estimates indicate. The feldspar data just presented supports this evidence that the Sr$^{87}$ buildup effect on the isotopic composition of ocean strontium over geologic time is much smaller than expected and will hence be more difficult to use as an age criterion, if indeed it can be distinguished from isotopic abundance variations from other natural causes.

Speculation as to the reason behind this lack of correlation between the geochemical evidence as to Sr/Rb ratios on and in the earth, and the mass spectrometric investigation results, may rightly be deferred to a later time; the author's present belief is that the seeming contradiction does not arise from gross analysis errors by either method but from the inherent difficulty one encounters, in part in weighting individual samples to obtain an average for a large unit such as the earth's crust, but even more in interpreting this average in terms of a model when the relative extent of such processes as granization of sediments as opposed to intrusion of magma from depth is unknown, and the question of the existence of a "primitive" atmosphere and ocean, and their compositions if they did exist, are still almost completely unsolved.
PART XII: SUGGESTIONS FOR FUTURE WORK

Always, when one looks back at a piece of scientific work, he sees immediately things that he would, in the light of his present knowledge, do differently. This attitude is in a large part a reflection of interim progress in the field of the investigation and the instruments and processes used, perhaps in part due to the research itself.

It may be of value if I state here my present ideas on the future course which research on the problems discussed in this thesis should take. These fall into three broad categories: improvements in selection of samples; improvements in chemical processing, and improvements in instrumentation.

Sampling:

The shortcomings of the sample suite investigated have been fully presented above. It is apparent that for an adequate test of the strontium age methods a very carefully chosen group of samples is required. As many of these as possible should be from rock units already dated by two or more radioactivity methods by reliable analysts. The other samples should approach this criterion as far as possible. However, radioactive dating itself is not sufficient. The unit from which the sample comes should also be one that is well-studied, whose relations to other units are known with a high probability. Previous petrographic and structural studies of the unit can provide important information as to whether more than one stage of mineral formation is involved, and on similar questions.

The rock should contain a variety of minerals suitable to test by the Sr method. A large enough sample should be taken to insure that repeated analysis will be possible. The rock samples should be fresh, the minerals coarse grained and with a minimal amount of fracturing. Representative thin
sections from the samples should be examined under the polarizing microscope
as an integral part of the research. Minerals such as mica should be subjected
to x-ray analysis and other suitable tests to determine their composition and
quality, so that any correlations between specific varieties and success or
failure of the age determination method may be readily recognised.

Additional problems:

The present research indicates that Whiting's estimate of which minerals
might be suited to mass spectrometric age determination work by the strontium
method was unduly sanguine. Minerals other than biotite should be investigated.
As has been mentioned, phlogopite should perhaps be the first to be tested.
The Sr/Rb ratios in some muscovite, hornblende, and potassic feldspars seem
to also be favorable for such work. No doubt other equally useable minerals
as yet have not been discovered.

The celestite selection should be augmented by many new samples and
supported by studies on other minerals such as strontianite, gypsum, fluorite,
calcite, and apatite, that contain easily concentratable amounts of strontium.
The results of such studies should be correlated with additional low-Rb
feldspar determinations.

Chemical processing:

For work in which only trace amounts of the substance of interest can
be obtained and quantitative work is essential, it is always the rule that
the least chemistry is the best chemistry.

Improved ion-exchange and chromatographic techniques now make it possible
to eliminate much of the pre-column processing used in this research. The
details of the currently used process will not be described here since the
treatment has not yet reached its final form.
Precautions against contamination and error can easily be included in this processing through the use of radiotracer and stable isotope dilution techniques. It is planned that isotope dilution will also be used for quantitative analysis of Rb and Sr. Quantities of "spike" Sr$^{84}$ and Rb$^{87}$ — that is, concentrates in which the isotope ratios are considerably different from normal — have been obtained from the A.E.C. for this purpose. The Sr$^{84}$/Sr$^{88}$ ratio in the Sr$^{84}$ spike, for example, is 3.0:1 compared to 0.0056:1 in common strontium. The stable isotope tracer can be added at the start of chemical processing; blank runs with the tracer provide estimates of contamination of unrivalled accuracy, and in actual runs, the "spike" strontium, of course, behaves in the same way as other Sr and hence losses in processing cannot influence the result of a quantitative analysis.

Although quantitative analysis by isotope dilution should be used for the age work, optical spectrographic analysis will remain very useful as a quick method of exploring samples to determine roughly their Sr and Rb content, which not only determines the size of sample that must be processed but also is necessary information for optimum use of the spike technique, since the amount of spike added depends on the amount of material to be analyzed.

**Instrumentation:**

Several improvements in the mass spectrometer and its auxiliary equipment are indicated by the present research.

Starting at the source assembly, an investigation of the suitability of metallic iridium as a filament material has been already initiated. In the collector, a variable slit-width, variable inter-slit-spacing, two-slit, two Faraday cup system would be a major improvement, and development work on such a system will soon be started.
The amplification system used was highly satisfactory except for occasional trouble with "base line" drift. The substitution, vibrating reed electrometer for amplifier, should correct this difficulty.

It would be very convenient to be able to record, simultaneously, the two currents from a double collection system such as that just described, or the one used in this thesis, on the same chart. Electronic recorders that can do this job are now available.

Basic studies of different source configurations and their possible effect on isotope ratio measurements, and of coated-cathode filament emission with the goal of determining which compound to use for optimum ionization efficiency, and what electrostatic configuration provides the most efficient use of ions formed, should be undertaken for their own intrinsic value as well as their obvious application to the problem of interest.

Improvements such as those outlined above should enable much of the necessarily qualitative information included in this thesis to be replaced by the accurate quantitative results necessary to evaluate the Sr age methods tested and to investigate the other problems brought to light by this research.
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Wi-1 Wickman, F., Jour. Geol., v 56 p 61, 1948.
The author of this thesis was born in Syracuse, New York, on
17 June, 1926, the son of Alma Jillson and Leonard Frederick Herzog.
A sister, the beautiful Jill, was born several years later. The family
went to California on vacation in 1935 and stayed permanently, settling
in Hollywood, where the elder Herzog resumed the practice of law.

Herzog attended successively Cheremoya School, Joseph Le
Conte Jr. High School, and Hollywood High School, graduating as val-
edictorian in 1943.

He matriculated at the California Institute of Technology the
same summer, but was called to Army duty in 1944, being discharged
in 1946. He was graduated from Caltech in Geology in 1948. While in
the service, he had been graduated from Oregon State College in Civil
Engineering.

He entered the Graduate School at the Massachusetts Institute
of Technology later in 1948; while attending M.I.T. he completed a
minor in Civil Engineering at Harvard University. During 1951 and
1952 he spent several months at the Department of Terrestrial Mag-
netism of the Carnegie Institution of Washington in collaborative re-
search on the subject of this thesis.

The author has been elected to the following honorary societies:
Tau Beta Pi (engineering) at Oregon State College, Sigma Xi (scientific
research), and Kappa Kappa Sigma (chemistry) at M.I.T. He was
awarded the ASCIT Honor Key two years while at Caltech. His collegiate activities are indexed in the 1947-48 edition of "Who's Who Among Students in American Colleges and Universities". He is also a member of the Ephebian Society of Los Angeles, a civic improvement honorary. Other societies and guilds in which he holds membership include the A.G.U., S.E.G., G.S.A., A.S.C.E., A.F.R.I., A.E., and S.A.G.

During his Army service he was chief of the Public Relations office, Antilles Department, headquartered in San Juan, Puerto Rico, with master sergeant rating, and staff correspondent of "Yank" and "Army Times". He has edited the Losey Field (Puerto Rico) "News" daily, and the "California Tech", two years. He has been a staff member of the Hollywood "Citizen News" since 1941. He wrote, directed, and took part in productions of the Armed Forces Radio Service while at San Juan and has broadcast over radio stations in New York, Massachusetts, and California for various periods since 1930.

At Caltech his research in geology comprised four field investigations of areal geology concerning parts of the Sunland, Red Mountain Quadrangle, and San Jose Hills areas of California and the Zuni Mountains of New Mexico, and a geophysical thesis on the resistivity method of ore location as applied to a chalcocite deposit in the Zuni uplift. Unpublished work at M.I.T. includes research on: the dissociation product of zanthic acid; synthesis and x-ray analysis of
pyrite and marcasite; ocean sedimentation rates and dating using the
ionium disequilibrium, other radioactivity studies, and the completion
of a mass spectrometer for solid sample isotope analyses of mineral
elements.

Four technical papers are in process, in collaboration with,
Holyk, E. T. Bolton and P. H. Abelson on various aspects of the re-
search described in this thesis, but references are not yet possible
for these.

The abstract of a paper delivered at the May, 1952 meeting
of the American Geophysical Union, on the research of this thesis,
is published in the A.G.U. proceedings supplement covering this
meeting.

During his M.I.T. years, the author has received support
from research assistantships on project 6629, sponsored by the
A.E.C., and project 6617, sponsored by the O.M.R., and in the
form of scholarships awarded by the Institute.
1905 Phil. Mag. 27 T alk metamp waq copper.
1906 NR Camp, A word !K, D. & " not in Kuma.
1937 87 fosters - Henneman & Smyth 54-90 - kyoar.
- H, 2%W, Manganica - I, 1470.

x) Decay constant - low wq & difficult
\lambda = 1.1 \times 10^{-11}$/yr - Corder, Dixon, Wilson, 1932

The 0.4, 2 \times 10^{-9} S & W 1937
1.2 \times 10^{-9} Mikhlov 1950 (1930)
5.8 \times 10^{-10} Ecklund 1946 Theory
5.87 \times 10^{-10} C & D Phil 1952

x) 8.5 ppm rel. ok. may be abs.

x) Numbers, check: 

1) Activity $A_x/10 < 10$ - Bristle (Whiting).
2) Normal $A_x/20 > 100$ - play. $S$ gap -> amoebic.
3) Field - Celestial, planctonite.

Bristle - IC (Mg Fe)$_3$ Al$_2$Si$_3$O$_{10}$ (OH)$_2$; aluminum.
- pres, sec, eq, meta. - very planctonic.
- Cult, hard, dry, warm, mild, not play.
- less not only $S$-gap, but, money, gap.
- does it as chance exists this? Probably yes.
1) Speculation

Rb

1) no Rb minerals
2) C/I Rb < K < so conc. fixed
3) K/Rb ≈ 100 qass. quest.
4) lepidolite, hydro micas, pollucite

ΔAB 2 behaviors - compare 1) K (Rs/Rb long) Rb+ (grid size) = 1.27 Å
2) Ca (Sr/Rb less)

1) will compete favorably w/ K+ if chq can be balanced
2) C/I Rb > 0.15 so no iso. (exc. hi T)

Own min. data - A (Cpx ortho) - calcite (poon)

1) Ca min. form largely before K min. & Li min. knowing

2) Methods -

Rb next Sr poor min.
Sr much Rb negligible min.

x) Rb/Ar ratio 1st Alvarens "crust"

9/23 many metasom I widgets 1/4
7/40 Brown, Goldschmidt I, New

x) Writing favorable min. study Rb/k

Res of Dauphiné? Improbable - maybe some Rb forced out this - by Sr or by K