A TEST OF THE HALF-LIFE OF Rb^{87}

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ABSTRACT

Title: A Test of the Half-life of Rb^{87}

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Sr/Rb analyses employing stable isotope dilution techniques were made on five mica and microcline samples from the Spinelli and Strickland quarry pegmatites, and on three mica samples from the wall rocks associated with these pegmatites. Nier, Rodgers, and Wasserburg and Hayden have obtained concordant ages for the Spinelli and Strickland quarry pegmatites using radiogenic lead methods. By assuming the average concordant age for each pegmatite as the true age of its minerals, a resultant half-life of Rb^{87} was calculated for each mineral.

The average half-life based on the published Pb^{206}/U^{238}, Pb^{207}/U^{235}, and Pb^{208}/Th^{232} ages is $4.9(\pm 0.3) \times 10^{10}$ years; the average half-life based on the published Pb^{206}/U^{238}, Pb^{207}/U^{235}, Pb^{208}/Th^{232}, and Pb^{206}/Pb^{207} ages is $4.9(\pm 0.3) \times 10^{10}$ years.

Analysis of biotite from a sample of Monson gneiss collected at the Spinelli quarry pegmatite-wall rock contact yielded a Sr/Rb age of 288×10^6 years. Similar analyses of biotite and muscovite from a sample of Bolton schist collected at the Strickland quarry pegmatite - wall rock contact yielded an average Sr/Rb age of 235×10^6 years.

It is concluded that the correct value for the half-life of Rb^{87} is $4.9 (\pm 0.3) \times 10^{10}$ years. This conclusion is in excellent agreement with the latest published values of this half-life, determined both by the indirect method and the direct-counting technique. No conclusions are made concerning the absolute ages of the wall rocks analyzed. Field structural evidence reported by the U.S.G.S. indicated an age relationship of the Monson gneiss and Bolton schist opposite to the one suggested by the Sr/Rb ages. However, it is pointed out that recrystallization at the time of pegmatite emplacement has taken place in the mica from the Bolton schist, and probably also in the mica from the Monson gneiss.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Many naturally radioactive nuclides are known to exist, but only comparatively few have been found useful in the determination of geologic age. These few are U^{238}, U^{235}, Th^{232}, Rb^{87}, K^{40}, and C^{14}. The disintegration rates of these active nuclides are fast enough to produce measurable amounts of their decay products, yet slow enough to prevent complete disappearance of the parent nuclide. Furthermore, their occurrence in geologic materials, both geographically and stratigraphically, is sufficiently common to make radioactive age measurement a valuable tool to the earth sciences.

The beta decay of Rb^{87} to Sr^{87} was first suggested as a possible means of measuring age by Goldschmidt (1937). Hahn, Strassman, and Walling (1937) extracted the strontium from a lepidolite from the Silver Leaf mine in the Winnipeg River area of Manitoba. The strontium was isotopically analyzed by Mattauch (1937), who reported that 97% of the strontium was of mass 87, an enrichment presumably due to the decay of Rb^{87} in the mineral. Thus, the method showed itself readily suited to age measurements on lepidolite; unfortunately, lepidolite is a relatively rare mineral. In an effort to broaden the scope of the Rb/Sr age method, Hahn, Mattauch, and Ewald (1943), and Mattauch (1947), reported at least 45% enrichment of radiogenic Sr^{87} in pegmatitic microcline and pollucite. However, the method was still restricted to one type of igneous rock, the pegmatite.

Whiting (1951) and Holyk (1952) investigated the possible extension of Rb/Sr age measurement to the common rock-forming minerals, biotite and feldspar, using optical spectrographic techniques. The

introduction of refined analytical techniques, such as isotope dilution and the use of ion exchange columns (Aldrich, Doak, and Davis; 1953), coupled with mass spectrometric analysis, made it possible to measure much smaller concentrations of rubidium and radiogenic strontium. Herzog et al (1953) and Tomlinson and Das Gupta (1953) found it possible to determine the rubidium-strontium ages of biotite, phlogopite, and muscovite, and of feldspars which possessed a SrO/Rb_2O ratio less than .1.

Investigators today routinely determine Rb/Sr ages on the pegmatite minerals already mentioned as well as biotite, muscovite, and feldspar from such varied igneous and metamorphic rocks as granite, diorite, diabase, gneiss, syenite, rhyolite, gabbro, and norite (Fairbairn, 1957; Herzog et al, 1956). Recently, an attempt has been made at this laboratory to apply the Rb/Sr method to hornblende extracted from three igneous rocks (Pinson, 1957a). As in feldspars, a large variation in the ratio Sr/Rb (.14 to 11) made analysis possible for one sample, barely possible for another, and impossible for the third. However, the results are encouraging enough to justify further investigation.

All Rb/Sr age measurements thus far mentioned have been on igneous or metamorphic rocks. Cormier (1956) applied the Rb/Sr method to sedimentary glauconites in an effort to establish an absolute post-Precambrian time scale, with considerable success.

Thus, the Rb/Sr method has assumed a very important role in geochronometry. Its wide range of applicability to common rock-forming minerals, and its extension into the sedimentary column, has made it a valuable tool of the modern geologist. Further, when used in conjunction with the versatile and increasingly reliable K/A method, close agreement of results has been obtained.

Despite the success of Rb/Sr dating, absolute ages determined by this method have been unreliable. This is due to the uncertainty in the half-life of Rb^{87}; obviously, it is essential in any radioactive age method to know accurately the rate of decay of the active nuclide. Usually, a known amount of the radioactive element is placed in a suitable detection chamber and its specific activity measured. From this can be calculated the disintegration rate and half-life. This measurement has been made on rubidium by a number of people. Their results are presented in Table I.

TABLE I

Investigator	Half-Life ($\times 10^{10}$ years)	d/min/mg Rb	Method
Strassman and Walling (1938)	6.3	----	Geological
Haxel, Houtermans, and Kemmerich (1948)	5.95	43.5	4π G-M counter
Kemmerich (1949)	4.10	63.1	Screen-wall G-m counter
Curran, Dixon, and Wilson (1951)	6.41	40.4	Screen-wall proportional counter
MacGregor and Wiedenbeck (1952)	6.37	40.6	4π G-M Counter
Lewis (1952)	5.93	43.7	Scintillation spectrometer
Geese-Bähnische and Huster (1954)	4.30	60.1	4π G-m counter

The values obtained for the half-life in Table I range from 4.1 to 6.41×10^{10} years. The wide spread of values indicates difficulty in directly counting the activity of Rb^{87}. This is due to the unusual energy distribution of the emitted beta particles, as shown in Figure 1. The rather large proportion of low energy betas places the average particle energy at about 45 Kev, although the maximum energy is 275 Kev. Source and foil absorption make the shape of the lower energy end of the spectrum, where a large portion of the activity is located, very uncertain; thus, extrapolation to zero source and foil thickness is necessary in a rather critical region of the spectrum. The uncertainty in extrapolation is carried through to produce an uncertainty in the half-life of the isotope.

An indirect method of testing the half-life of rubidium^{87} is available when minerals favorable to Rb/Sr age determination occur in geologic units which have concordant ages by two or more of the U-Pb, Th-Pb, and Pb-Pb methods. By assuming the concordant ages to be the true age of the rock unit, and the uranium and rubidium minerals to be cogenetic, one can calculate the necessary half-life of Rb^{87} by measuring the ratio of radiogenic Sr^{87} to Rb^{87} in the favorable minerals.

A recent attempt to measure the half-life by this method has been reported by Aldrich et al (1956). They measured the Pb^{206}/U^{238} and Pb^{207}/U^{235} ages of a monazite and five uraninites from six pegmatites ranging in age from 375 to 2680 million years. The ages thus obtained were in all cases concordant. They then analyzed rubidium rich minerals from the same rock units for their Rb-Sr contents and for each case calculated the half-life necessary to make the Rb-Sr age agree with the

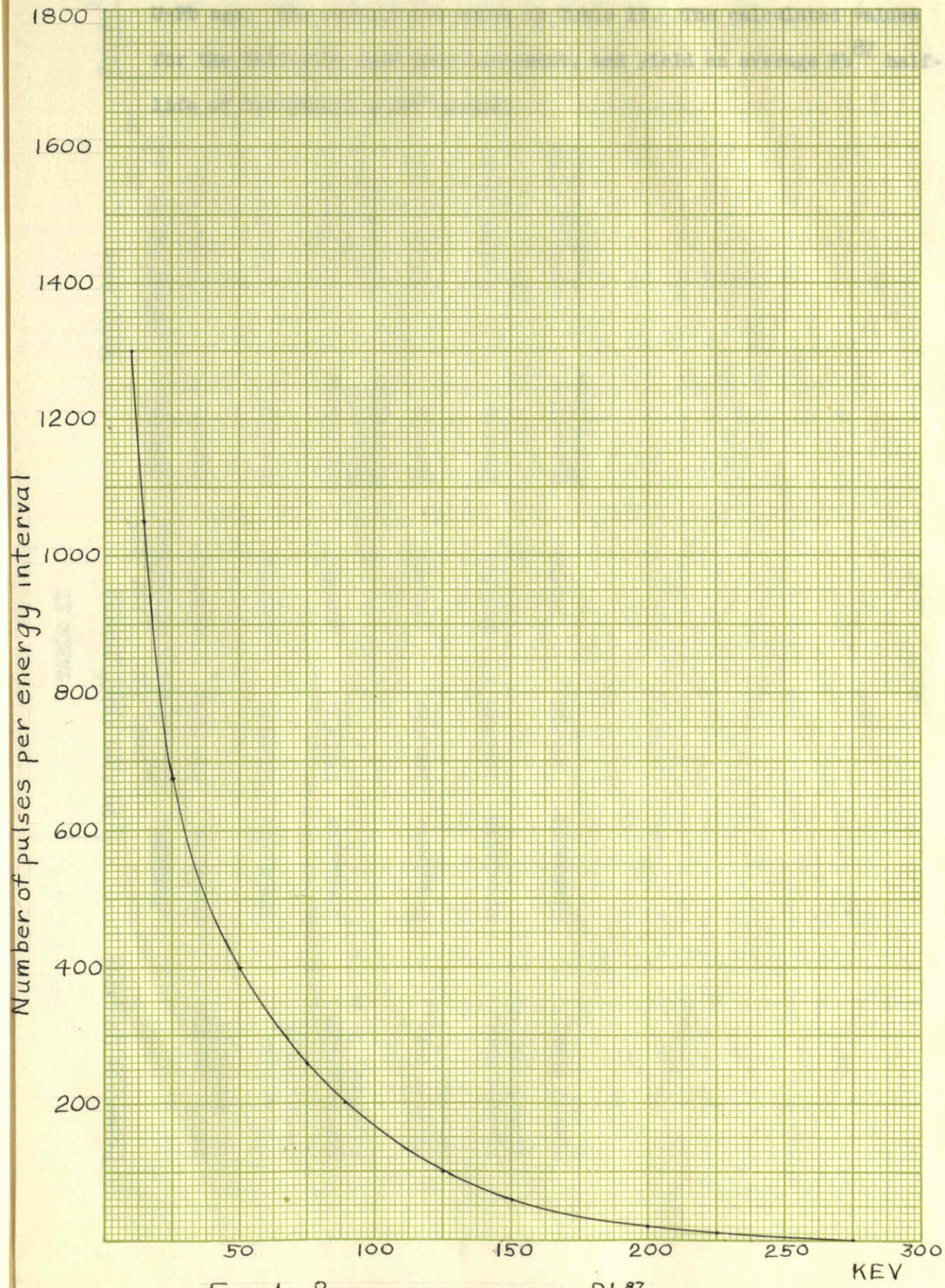

FIG. 1. BETA-SPECTRUM OF Rb^{87}

U-Pb age. The results are shown in Table II. The calculated values for the half-life show good agreement, and yield an average Rb^{87} half-life of 5.0 ($\pm$0.2) x 10^{10} years.

TABLE II

Pegmatite Location	U/Pb Ages ($\times 10^6$ years)			Rb/Sr Data		$T_{\frac{1}{2}}$ ($\times 10^{10}$ years)
	Mineral	Pb^{206}/U^{238}	Pb^{207}/U^{235}	Mineral	Radiogenic Sr^{87}/Rb^{87}	
Bikita Quarry, So. Rhodesia	Monazite	2640±100	2680±100	Lepidolite	0.0380±.001	5.0
Viking Lake, Saskatchewan	Uraninite	1790±50	1830±50	Biotite	0.0270±.001	4.8
Bob Ingersoll, Keystone, S. D.	Uraninite	1580±30	1600±30	Lepidolite Muscovite Microcline	0.0239±.001 0.0244±.001 0.0224±.001	4.8
Cardiff Twsp., Ontario	Uraninite	1020±20	1020±20	Biotite	0.0140±.0007	5.1
Fission Mine, Wiberforce, Ont.	Uraninite	1040±20	1050±20	Biotite	0.0140±.0007	5.2
Spruce Pine, N. C.	Uraninite	375±10	380±10	Muscovite Microcline	0.00515±.0002 0.00535±.0002	5.0

It was the object of the research reported here to investigate further the question of the true half-life of Rb^{87}, using the indirect method as described in the preceding paragraphs.

CHAPTER I - BASIC CONSIDERATIONS

A. U-Pb, Th-Pb, and Pb-Pb age methods

The following three nuclear processes:

$$U^{238} \longrightarrow Pb^{206} + 8\ {}_2He^4 ,$$

$$U^{235} \longrightarrow Pb^{207} + 7\ {}_2He^4 ,$$

$$\text{and } Th^{232} \longrightarrow Pb^{208} + 6\ {}_2He^4 ,$$

can each be used to determine the geologic age of a mineral, provided the parent and its daughter products have been part of a closed system, and a correction is made for original lead in the minerals analyzed. Each of the three processes above involves a long decay scheme consisting of many unstable nuclides. An age may also be calculated from the ratio Pb^{206}/Pb^{207}, based on the difference between the half-lives of the two parent isotopes, U^{238} and U^{235}.

When two or more of these radiogenic lead ages are found to agree, they are termed "concordant". It has generally been accepted among workers in the field that concordant ages represent the most reliable determinations of geologic age currently available. They have been used to calibrate constants of the newer age methods, such as in this work. Some of the most crucial dates in the geologic time scale rest on concordant radiogenic lead ages.

In many cases, striking discordancy between the ages is shown. This may be the result of preferential leaching of uranium (Collins et al, 1954), radon leaks (Kulp et al, 1954), or daughter isotope diffusion (Nicolaysen, 1957). The cause of discordancy in these ages is not well known and constitutes a major phase of current geochemical research (Tilton, 1956; Ahrens, 1955).

B. Rb-Sr method

After Thompson (1905) first reported the evidence of beta activity in rubidium, Rb^{87} was shown to be the parent isotope and Sr^{87} the daughter by Hemmendinger and Smythe (1937) and Hahn, Strassman, and Walling (1937). As mentioned previously, the majority of the betas emitted by Rb^{87} are of rather low energy; hence, the nuclide has a long half-life, on the order of ten times the latest estimates of the age of the Earth. As a result of this longevity, in order for a mineral to yield a reliable Rb/Sr age, it must be rich in rubidium and/or older than about 60 million years. In addition, samples younger than Precambrian should have a ratio of common strontium to total rubidium less than 1/3. This is due to the fact that nearly all the common rock-forming minerals contain original strontium, about 7% of which is Sr^{87}, and which will, in rubidium poor environments, completely overshadow any radiogenic Sr^{87} added to the mineral since its crystallization. As with all radioactive age methods, the mineral must meet the requirement of having been a closed system with respect to the parent and daughter isotopes. Also, the isotopic composition of both the daughter element originally included in the mineral and the parent element must be known.

C. Mathematical basis

The decay of a radioactive nuclide can be represented by the equation:

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

where

N_o = number of atoms of the nuclide originally present,

N = number of atoms of the nuclide left after a time t, and

λ = decay constant.

The decay constant is the fraction of the radioactive atoms which disintegrates per unit time.

In the decay of the Rb^{87} to Sr^{87}, both parent and daughter have the same mass. In this case, it can be shown that

$$N_o = N + R \qquad (2)$$

where

R = concentration of radiogenic Sr^{87},

N_o = concentration of Rb^{87} originally present, and

N = concentration of Rb^{87} present after time t.

Substituting in (1),

$$N = (N + R)\, e^{-\lambda t} \qquad (3)$$

$$\text{or } \frac{N}{N\ R} = e^{-\lambda t}$$

$$\text{or } 1 + R/N = e^{\lambda t} \qquad (4)$$

Taking the natural logarithm of (4),

$$\lambda t = \ln (1 + R/N)$$

or

$$\lambda = \frac{1}{t} \ln (1 + R/N) \qquad (5)$$

Equation (5) enables one to calculate the decay constant of Rb^{87} if the age of the mineral and its concentrations of radiogenic Sr^{87} and Rb^{87} are known.

The half-life ($T_{\frac{1}{2}}$) of a radioactive substance is defined as the time required for the substance to decay to one-half of its initial activity. Expressed in the terms of equation (1),

$$N \equiv \frac{N_o}{2} \text{ at time } T_{\frac{1}{2}} = t.$$

Substituting in equation (1),

$$N_o/2 = N_o\, e^{-\lambda T_{\frac{1}{2}}} \qquad (6)$$

Again using the relationship (2),

$$\frac{N+R}{2} = (N+R)\, e^{-\lambda T_{1/2}}$$

or

$$2 = e^{\lambda T_{1/2}} \qquad (7)$$

Taking the natural logarithm of (7),

$$\lambda T_{\frac{1}{2}} = \ln 2 = 0.69315$$

or

$$T_{\frac{1}{2}} = \frac{0.69315}{\lambda} \qquad (8)$$

Substituting (5) in (8),

$$T_{\frac{1}{2}} = \frac{0.69315\ t}{\ln (1+R/N)} \qquad (9)$$

Equation (9) enables one to calculate the half-life of Rb^{87} if the age of the mineral and its concentrations of radiogenic Sr^{87} and Rb^{87} are known.

The process of decay is a statistical one; thus, when using a decay rate or half-life, the number of events must be sufficiently large so that statistical methods are valid. In this work, as is usually the case, this requirement is satisfied. A full treatment of the theory of radioactive decay may be found in Lapp and Andrews (1956).

Equations (5) and (9) have been used to calculate the results presented in Chapter III.

CHAPTER II - SAMPLE SELECTION AND ANALYTICAL TECHNIQUES

A. Sample selection

During the fall of 1956, a field trip was made to the Spinelli and Strickland quarries near Middletown, Connecticut, for the purpose of collecting suitable samples for this investigation. Participating in the trip were Prof. J. W. Winchester, Prof. H. W. Fairbairn, Prof. W. H. Pinson, Jr., Dr. R. F. Cormier, and the writer, all of the M.I.T. Department of Geology and Geophysics. Samples of biotite, muscovite, feldspar, and lepidolite were collected.

The muscovite and feldspar samples were in the form of books and crystals disseminated throughout the pegmatites; the lepidolite sample was finely crystalline and was found on the north waste pile of the Strickland quarry. The wall rock samples were obtained within five feet of the pegmatite-wall rock contact at both quarries.

A detailed description of the Strickland and Spinelli quarries can be found in Cameron et al (1954).

B. Sample preparation

When possible, preliminary hand-picking was used to eliminate obvious impurities in the feldspar and muscovite samples. Then the following procedure was employed:

(1) Samples were crushed and ground, either by mechanical jaw crusher and wheel grinder or by mortar and pestle. All equipment was thoroughly cleaned and precontaminated before using.

(2) Samples were screened and separated into 100 mesh, 140 mesh, and 200 mesh size fractions, then washed in acetone.

(3) Lepidolite, muscovite, and biotite samples were concentrated by processing on a Frantz magnetic separator.

(4) Feldspar samples were concentrated by processing in heavy liquids.

C. Chemical separation of Rb and Sr

The method employed throughout this work for the extraction of Rb and Sr is a standard technique used by this laboratory. It was described in detail recently by Pinson (1957b), and only the general procedure is indicated below:

A known weight of sample is placed in a platinum dish and known quantities of Sr^{84} and Rb^{87} spike solutions are added. The sample is dissolved in the analytical grade reagents, HF and $HClO_4$, and the resulting solution is evaporated to dryness. The residue is dissolved in a small volume of 2N HCl. Approximately 10 ml of radioactive Sr^{85} tracer is added, and the solution is added by pipette to an ion exchange column. The separation of Rb and Sr is effected by eluting with 2N and 3N HCl. There is an enrichment of rubidium as the last trace of potassium leaves the column; this fraction is located and collected by monitoring for potassium by the flame test. The strontium-enriched fraction is located and collected by monitoring for the Sr^{85} tracer with a Geiger counter.

The Rb fraction is converted to nitrates and about 1 mg. or less is applied to the tantalum ribbon filament of the mass spectrometer; the Sr fraction is converted to oxalate and about 1 mg is applied to the filament.

D. Mass spectrometers

The mass spectrometers used in this investigation were the Nier type, 60° sector, 6 inch radius, direct-focussing instruments. Positive ions were produced by thermionic emission, accelerated by a 2500 volt negative potential, and passed through a sectored magnetic field of 6 inch radius and about 4000 gauss. This split the ion beam into a number

of beams, each having a characteristic mass/charge ratio. The split and deflected beams were then automatically swept back and forth over the collector slit by varying the intensity of the magnetic field. The resulting ion current, proportional to the intensity of the ion beam, was amplified by a vibrating reed electrometer and fed to a Weston or Brown strip chart recording potentiometer.

A complete description of the mass spectrometers used in this research has been written by Cormier (1956); for a discussion of mass spectrometers in general, see Nier (1947), Barnard (1953), and Inghram and Hayden (1954).

E. Isotopic abundances

To obtain the accuracy inherent in the method of stable isotope dilution, one must accurately know:

(1) The weight of sample used.
(2) The weight of spike added.
(3) The relative isotopic abundances of the spikes.
(4) The relative isotopic abundances of normal Rb and Sr.

The isotopic abundances of the Rb and Sr spikes supplied by the A.E.C. have been determined a number of times by this laboratory within the past four years. The determination is made by mass spectrometrically analyzing the pure spike; the isotopic abundances of the Rb and Sr spikes used in this research are shown in Table III.

TABLE III

Spike Batch	ISOTOPES			
	85	87		
Rb^{87} Spike I, II	.1018	.8982		
	84	86	87	88
Sr^{84} Spike I	.4607	.1438	.0881	.3075
Sr^{84} Spike II	.543	.137	.038	.282

The relative isotopic abundances listed for Sr spike II are as determined by the A.E.C.; this spike batch was just recently received by this laboratory and we have not yet verified the A.E.C. isotopic analysis. Only two samples in this report were spiked with this new Sr spike, the Spinelli quarry wall rock biotite (B3372) and the second isotope dilution analysis of the Strickland lepidolite (L3375).

The spike solutions are calibrated for spike concentration by mixing a known amount of normal element solution with a known amount of spike solution and analyzing the mixture mass spectrometrically. Replicate analyses are made, and the average of the results is used as the spike solution concentration. Cormier (1956) discusses the spike calibration procedure in detail.

The concentrations of the spike solutions, and the samples in which they were used, are shown in Table IV.

TABLE IV

Spike Solution	Concentration	Samples Spiked
Rb^{87} I	61.6 µg/ml	L3375(I.D.I), F3371, F3374, M3370, M3373
Rb^{87} II	49.3 µg/ml	B3372, L3375(I.D.II), B3376, M3376
Sr^{84} I	20.4 µg/ml	B3376, M3376, L3375(I.D.I), F3371, F3374, M3373, M3370
Sr^{84} II	19.8 µg/ml	B3372, L3375(I.D.II)

The isotopic abundance of normal rubidium has been determined by a number of investigators, among them being Brewer (1938), Nier (1950), and Herzog et al (1953); the isotopic abundance values used in this work are shown in Table V.

In the case of the isotopes of strontium, 84, 86, and 88 are non-radiogenic, whereas 87 is partly derived from the beta decay of Rb^{87} and partly derived from the original distribution of the elements. As time increases, therefore, there is a corresponding increase in the universal abundance of Sr^{87}, increasing the relative isotopic abundance of Sr^{87} which is incorporated into recent minerals over the Sr^{87} abundance that was incorporated into very old minerals. This time dependency of original Sr^{87} abundance in minerals will have a negligible effect in rubidium rich environments, since the original Sr^{87} fraction will be completely overshadowed by the post-crystallization radiogenic Sr^{87}. However, in environments with a high Sr/Rb ratio, such as some meteorites and tektites, the time variation of original Sr^{87} has a decided effect upon the measured age of geologically old materials. Herzog and Pinson (1956) have calculated that the relative Sr^{87} abundance in bulk terrestrial strontium 4.7×10^9 years ago was .0683 ± .0010.

The present relative abundance of Sr^{87} in terrestrial strontium has been measured as .0702 by Nier (1938), and values closely similar to that have resulted from measurements by Aldrich and Herzog (1952; .0703), and a series of analyses on celestite, sea water, etc., made at this laboratory (Cormier, 1956; .0701).

Since all the strontium analyzed in this work was from rather rubidium rich environments, and since the minerals are too young to show any appreciable depletion in original Sr^{87}, the relative abundance of .0702 for non-radiogenic Sr^{87} has been assumed in this report.

All relative isotope abundance values used in this research are listed in Table V.

TABLE V

Element	Isotopes			
		85		87
Rubidium		.7215		.2785
	84	86	87	88
Strontium	.0056	.0986	.0702	.8256

F. Treatment of data

The ion currents were recorded by sweeping the separated ion beams, each of characteristic mass to charge ratio, back and forth over the collector slit. The range of sweep was variable so as to include the ion beams of masses 84, 86, 87 and 88 for strontium runs, and masses 85 and 87 for rubidium runs. Each sweep over the mass range is referred to as a set. The ion peaks were continuously recorded by a Brown or Weston strip chart potentiometer.

The peaks were then measured using an engineering scale of 60 divisions to the inch. The average peak height for every ten consecutive sets was then computed for each isotope. From this data, the ratios $^{84}/_{88}$, $^{86}/_{88}$, and $^{87}/_{88}$ for strontium, and $^{85}/_{87}$ for rubidium, were computed. After this, a grand average of each of the ratios was taken. This procedure was found to retain a sufficiently close check on the possibility of fractionation during a run, while considerable shortening the task of computation. The previous method employed by this laboratory was to compute the ratios for every pair of sets instead of every ten sets. The length of runs reported here varied from 60 to 140 sets

for rubidium analyses, and from 80 to 160 sets for strontium analyses.

Fractionation of strontium isotopes during thermionic emission within the mass spectrometer has been reported by a number of workers (Herzog et al, 1954; Cormier, 1956). Due to the physical process of evaporating ions off the filament, an overabundance of the lighter isotope should occur near the beginning of an analysis, while the reverse should hold true near the end of the run. The maximum degree of fractionation observed at this laboratory has been 3%, occurring in the ratio Sr^{84}/Sr^{88}. When fractionation does occur, a correction must be made or erroneous ratios will result. However, in the analyses reported, no fractionation of isotopes has been noted.

The concentrations of normal rubidium, normal strontium, and radiogenic strontium were calculated from the ratios Rb^{85}/Rb^{87}, Sr^{84}/Sr^{88}, and Sr^{87}/Sr^{88} in the standard procedure used at this laboratory (Pinson, 1957b; Cormier, 1956). The errors attached to these calculations are in all cases, except the isotope dilution analysis of the Spinelli microcline, assumed to be no greater than ± 5%. This "standard" error has been arrived at through replicate analyses, contamination experiments, and standard deviation calculations on many analyses made at this laboratory, using procedures similar to those in this work.

In the case of the Spinelli microcline, a rather low ratio of normal strontium to spike strontium admitted the possibility of an error as large as ±20%. An isotope ratio analysis, in which the strontium is isotopically analyzed spike-free, was made on this sample, lowering the error to the "standard" ± 5%.

CHAPTER III - RESULTS

Results of analyses of five pegmatite minerals from the Spinelli and Strickland quarries are shown in Table VI. The Rb^{87} decay constants and half-lives calculated from this data are based on the concordant lead ages shown in Table VII. Results of analyses and calculated ages of three Spinelli and Strickland quarry wall rock minerals are shown in Table VIII.

TABLE VI

Pegmatite Location	Mineral		Normal Sr (ppm)	* Sr^{87} (ppm)	Total Rb (ppm)	* Sr^{87}/Rb^{87}	($\times 10^{-11}$ $yr.^{-1}$) $\lambda(1)$	$\lambda(2)$	($\times 10^{10}$ yr.) $T_{\frac{1}{2}}(1)$	$T_{\frac{1}{2}}(2)$
Spinelli quarry	Muscovite		9.36	2.79	2730	.00361	1.39	1.36	5.0 ± 0.3	5.1 ± 0.3
	Microcline	I.D.	11.2	.255	219	.00411	1.59	1.55	4.4 ± 0.9	4.5 ± 0.9
		I.R.		.246		.00397	1.53	1.50	4.5 ± 0.2	4.6 ± 0.2
Strickland quarry	Muscovite		3.64	1.31	1260	.00367	1.42		4.9 ± 0.2	
	Lepidolite	I.D.I.	9.71	7.12	7540	.00334	1.29		5.4 ± 0.3	
		I.D.II (3)	12.8	8.43	16700	.00179	.694		10.0 ± 0.5	
	Microcline		29.8	1.05	992	.00373	1.44		4.8 ± 0.3	

(1) = Based on average of Pb^{206}/U^{238}, Pb^{207}/U^{235}, and Pb^{208}/Th^{232} ages.

(2) = Based on average of Pb^{206}/U^{238}, Pb^{207}/U^{235}, Pb^{208}/Th^{232}, and Pb^{206}/Pb^{207} ages.

(3) = Results rejected.

* = Radiogenic Sr^{87}.

TABLE VII

Concordant Ages[1] ($\times 10^6$ yr.)

Pegmatite Location	Mineral	Pb^{206}/U^{238}	Pb^{207}/U^{235}	Pb^{208}/Th^{232}	Pb^{206}/Pb^{207}
Spinelli quarry	Samarskite	253	255	266	280
Strickland quarry	Uraninite	268	266	239	---

1 - From Faul (1954) and Wasserburg and Hayden (1955)

Since the U-Pb, Th-Pb and Pb-Pb ages play the role of keystone in this indirect method of testing the half-life of Rb^{87}, an evaluation of their reliability is in order at this point.

A. Concordant ages

Several people have calculated radiogenic lead ages for the Spinelli quarry pegmatite. Chemical analysis of samarskite from Spinelli was made by Wells (1937). Nier et al (1941) determined the isotopic constitution of the lead content by means of a mass spectrograph and calculated the following ages: Pb^{206}/U^{238}: 253×10^6 years; Pb^{208}/Th^{232}: 266×10^6 years; Pb^{207}/Pb^{206}: $280(\pm 60) \times 10^6$ years, using the decay rate of thorium determined by Kovarik and Adams (1938), and a decay rate of uranium^{238} calculated by Nier et al (1941, reference 6) using measurements of Kovarik and Adams (1941).

Rodgers (1952) calculated four lead ages for the Spinelli quarry pegmatite using the chemical and isotopic analyses of Wells and Nier. He assumed with Nier that common lead has the composition 1: 18.5: 15.4: 38.2. After subtracting the common lead fraction from each isotope, Rodgers calculated the following U-Pb and Th-Pb ages: Pb^{206}/U^{238}: 251×10^6 years; Pb^{207}/U^{235}: 255×10^6 years; and Pb^{208}/Th^{232}: 264×10^6 years. The formulas which Rodgers used for his calculations were developed by Keevil (1939), but modified to make use of the decay rates of U^{238}, U^{235}, and Th^{232} as determined by Nier et al (1941), Fleming, Ghiorso, and Cunningham (1951), and Kovarik and Adams (1938), respectively. Rodgers also calculated $^{a}Pb^{207}/Pb^{206}$ age of 280×10^6 years, using a graph of Wickman's (1939).

Previously, Holmes (1947) had also calculated U-Pb and Th-Pb ages for the Spinelli quarry samarskite. He assumed a slightly different isotopic composition for common lead; however, the average of those ages calculated by Rodgers differs from the average of Holmes' ages by only 0.7%. Since Holmes apparently used an incorrect set of coefficients in calculating his ages (see Rodgers, p. 413, footnote 3), and since Rodgers' ages are based on more recent data (see same footnote), Holmes' lead ages were not used in this work.

Faul (1954, p. 267) presents a set of concordant ages for the Spinelli quarry which is a mixture of the ages determined by Nier and Rodgers. The Pb^{206}/U^{238} and Pb^{208}/Th^{232} ages listed by Faul are those of Nier; the Pb^{207}/U^{235} age is that of Rodgers; the Pb^{207}/Pb^{206} ages determined by both investigators were identical. Since the maximum difference between the two sets of ages as calculated by Rodgers and Nier is only 0.8%, the set of concordant ages as listed by Faul was used in this work.

The general pattern exhibited by these ages, i.e. $Pb^{207}/Pb^{206} > Pb^{207}/U^{235} > Pb^{206}/U^{238}$ is frequently found, in a more pronounced manner, among age measurements made on U- and Th- bearing minerals. Aldrich et al (1955) have discussed the possibility of radon leakage and recent "catastrophic" loss of lead. Nicolaysen (1957) has dealt quantitatively with the theory of daughter isotope diffusion in connection with this problem. Many other workers have also investigated the problem of discrepant radiogenic lead ages, but as yet no one really knows the true cause of the discrepancies. Since the agreement between the Spinelli lead ages is considered good, they have been used as concordant ages in this work, and as such, have been taken to

represent the true age of the Spinelli quarry pegmatite.

Two half-lives have been calculated for each mineral from Spinelli; one is based on an average of the Pb^{206}/U^{238}, Pb^{207}/U^{235}, and Pb^{208}/Th^{232} ages, and the other is based on an average of all four lead ages shown in Table VII. This was done for two reasons: one, to make possible a strict comparison with the results of the Strickland quarry minerals, where only Pb^{206}/U^{238}, Pb^{207}/U^{235}, and Pb^{208}/Th^{232} ages were used; two, the lead-lead ratio age is 8% higher than the average of the other three ages, which agree very closely. Although many physicists consider the Pb^{207}/Pb^{206} age to be the best of the lead age methods, it is subject to several errors. Holmes (1937) recognized that a rather large error may be introduced by the uncertainty in the composition of the original lead, especially in younger rocks. Loss of radon^{222} tends to raise the lead ratio age, while lowering the Pb^{206}/U^{238} age and leaving the Pb^{207}/U^{235} age unchanged (Rankama, 1954). Presence of old radiogenic lead may also cause a large error (Faul, 1954).

The concordant ages for the Strickland quarry uraninite were measured by Wasserburg and Hayden (1955), using the following decay constants:

$$\lambda Th^{232} = 4.99 \times 10^{-11} \text{ year}^{-1},$$
$$\lambda U^{238} = 1.54 \times 10^{-10} \text{ year}^{-1}, \text{ and}$$
$$\lambda U^{235} = 9.72 \times 10^{-10} \text{ year}^{-1}.$$

The U^{238}/U^{235} ratio was assumed to be 137.7. The good agreement obtained betweem the ages suggests that they represent the true age of the pegmatite, and have been used as such in this report.

B. Evaluation of pegmatite analyses

Of the seven analyses made for the purpose of testing the half-life of Rb^{87}, only one is so seriously anomalous that it must be rejected.

This is the second isotope dilution analysis of the Strickland lepidolite. A second analysis was made on this sample in an effort to decide whether the rather low radiogenic Sr^{87} to Rb^{87} ratio resulting from the first analysis was real or simply an analytical mistake. Contamination of sample or a mistake in analysis has obviously occurred in the second isotope dilution run of this lepidolite, since the results show an increase of 33% in normal strontium and over 100% in rubidium. Normally, results of analyses made at this laboratory can be reproduced with an accuracy of at least 2% for rubidium and 3% for strontium. When such a complete lack of agreement occurs in a replicate analysis, one can either perform a third analysis or accept one or the other of the first two. Since time did not permit a third analysis to be made, and since the first analysis was the more reasonable of the two, it was retained and the second isotope dilution analysis of the Strickland leipdolite was rejected. Actually, lepidolite is the most favorable of all minerals to Rb/Sr age measurements because of its very low ratio of common strontium to rubidium.

Two strontium analyses were made on the Spinelli microcline. The first was a standard isotope dilution run (indicated by I.D. in Table VI). The large error (±20%) associated with this analysis was due to a combination of rather low total rubidium content and very unfavorable ratio radiogenic Sr^{87}/spike Sr^{87}. For this reason, a second run was made (indicated by I.R. in Table VI) using the pure unspiked strontium concentrated from the microcline. The isotope ratios of strontium were measured and the radiogenic Sr^{87} computed. Although the concentrations of radiogenic Sr^{87} calculated from the isotope dilution and isotope ratio runs do not differ greatly (4%), the error was reduced from ±20%

to ±5%. In computing the average Rb^{87} half-life reported in the next section of this chapter, the isotope ratio data have been issued.

Although the normal strontium concentration vary from 3.64 ppm to 29.8 ppm, and although the total rubidium concentrations vary from 219 ppm to 7540 ppm, the ratios radiogenic Sr^{87}/Rb^{87} show little deviation, not only for each pegmatite, but for both rock units as a whole. This indicates that both the Spinelli and Strickland quarry pegmatites formed at approximately the same time, and the mica-feldspar minerals within each pegmatite crystallized contemporaneously. There is a slight indication in the data that the feldspars give higher radiogenic Sr^{87}/Rb^{87} ratios than the muscovites and lepidolite. This would correspond to an older age, if true, but the evidence here is too inconclusive to prove or disprove a trend of that sort.

The Strickland quarry microcline, because of its relatively high ratio normal Sr/total Rb, have an associated error of ±7%; all other errors have been conservatively estimated at ±5%, with the exception of the isotope dilution analysis of the Spinelli microcline. In this case, an isotope ratio strontium run has reduced the error to ±5%.

The estimate of at least 5% accuracy in these analyses is based on results of interlaboratory comparison determinations, made on the same samples. Many comparison analyses made in collaboration with the Lamont Geological Observatory, the Carnegie Institution of Washington, and the Institute for Nuclear Studies at the University of Chicago, have shown that measurements made at this laboratory, using the standard procedures employed in this report, have an absolute accuracy of at least ±5%.

The computed values for the half-life of Rb^{87} range from 4.5×10^{10}

years to 5.4×10^{10} years. All values agree within experimental error, except the isotope dilution analysis of the Strickland lepidolite. As explained in the preceding paragraphs, a second isotope dilution run was made on this sample, but gave results so seriously anomalous that it had to be rejected. No reason has been found at this time for the slightly high half-life value computed from the data of this lepidolite.

It is significant that none of the values reported here for the half-life of Rb^{87} compare with the higher values obtained by many previous direct-counting experiments. Thus, the higher range of values reported for the half-life (5.9--6.4×10^{10} years) by Strassman and Walling (1938), Curran, Dixon, and Wilson (1951), Lewis (1952), etc., is most doubtful when viewed in the light of recent "indirect" determinations, such as this work, and the direct-counting experiment of Geese-Bäfnisch and Huster (1954). (Huster, in a private communication to Aldrich, amended the published result of 4.3×10^{10} years to 4.9--5.0×10^{10} years.)

C. Evaluation of wall rock analyses

As an interesting sideline to the main problem of this thesis, it was decided to collect and analyze samples of the wall rocks associated with the Spinelli and Strickland quarry pegmatites. This was done for the following reasons:

(1) Excellent opportunity to collect samples during field trips to the quarries.

(2) Uncertainty as to the effects of metamorphism or nearby magmatic activity on rubidium and strontium in host minerals.

(3) Uncertainty as to the absolute and relative ages of the wall rocks associated with these pegmatites.

The general structural picture of the Middletown area of Connecticut is extremely complicated. Cameron and others (1954) have given a detailed description of the structure and lithology of the region. There are a total of six metamorphic formations outcropping in an area 14 miles long and 9 miles wide; however, only two, the Bolton schist and Monson gneiss, are of interest in this report.

The Bolton schist crops out in a pattern resembling the letter "H"; the Monson gneiss crops out in the north opening of the "H" and along the east side. The Spinelli pegmatite is located in the northern portion of the Monson gneiss, and the Strickland quarry pegmatite occurs about 3.3 miles further south, in the Bolton schist. The composition of this latter formation was described by Cameron et al as ".....quartz-mica schists, mica gneiss, lenses of amphibole schist, and beds of quartzite and marble". The Monson gneiss varies considerably in composition from place to place. The same authors describe its composition as ".....a medium-grained biotite granite gneiss, composed of microcline, orthoclose, quartz, oligoclase or oligoclase-andesine, biotite, and muscovite".

The only known ages in the area are those that were determined by radiogenic lead methods on four pegmatites: the Spinelli quarry, Strickland quarry, Hale quarry, and Rock Landing quarry. All of these ages are concordant in the 260 - 280 million year range, tentatively placing them in Late Devonian in the geologic time scale. Also, field evidence indicates that the Monson granite gneiss has intruded the Bolton schist (Cameron et al, 1954). Thus, all that is known about the ages of the two wall rocks reported on here is that they are probably pre-Late Devonian, with the Bolton schist being the older of the two.

TABLE VIII

Location	Mineral	Normal Sr(ppm)	* Sr^{87}(ppm)	Total Rb(ppm)	Age ($x10^6$ yr.)
Spinelli quarry (Monson gneiss)	Biotite	10.6	1.44	1270	288 ± 14
Strickland quarry (Bolton Schist)	Biotite	23.9	.906	929	247 ± 17
	Muscovite	9.87	1.81	2050	223 ± 13

Table VIII lists the results of rubidium-strontium analyses of micas from the Monson gneiss and Bolton schist. The data presented seems to suggest an opposite age relationship than the one proposed in the foregoing paragraph; however, it is important to remember that these samples were collected at the pegmatite-wall rock contact. Sharpness of contact and minor folds in adjacent wall rocks indicate an intrusive emplacement of the pegmatites; one would expect the contact wall rock to be appreciably affected by such an intrusion.

In the case of the Strickland quarry, the concordant U-Pb and Th-Pb age for the pegmatite is 258 million years, whereas the Rb/Sr analysis of the wall rock yields 235 (±15) million year age. This evidence suggests a complete recrystallization of the mica in the Bolton schist, in the immediate region of the pegmatite, at the time of emplacement of the pegmatite.

The concordant radiogenic lead age for the Spinelli quarry pegmatite is approximately 260 million years, but here Rb/Sr analysis of biotite from the Monson gneiss wall rock has given an age of 288 million years. The relative age relationship in this case is plausible, but here again one must remember the proximity of the wall rock sample to the intrusive pegmatite. If this is the true age of the Monson gneiss, then the Bolton schist must be older than 288 million years, if the structural interpretation is correct. However, this one analysis of the Monson gneiss at the pegmatite-wall rock contact is insufficient to support any definite statement regarding the wall rock age relationships in this area.

D. Conclusions

1. The average half-life of Rb^{87} based on the Pb^{206}/U^{238}, Pb^{207}/U^{235}, and Pb^{208}/Th^{232} ages of both pegmatites is 4.9 (±0.3) x 10^{10} years; the average half-life of Rb^{87} based on the Pb^{206}/U^{238}, Pb^{207}/U^{235}, Pb^{208}/Th^{232}, and Pb^{206}/Pb^{207} ages of the Spinelli quarry pegmatites is 4.9 (±0.3) x 10^{10} years. Thus it is concluded from the evidence presented here that the correct value for the half-life of Rb^{87} is 4.9 (±0.3) x 10^{10} years. This conclusion is in excellent agreement with the recent results of Aldrich et al (1956; 5.0(±0.2) x 10^{10} years), and Geese-Bahnisch and Huster (1954), as recently amended by Huster (4.9--5.0 x 10^{10} years).

E. Recommendations for future research

1. Additional corroborative determinations of the half-life of Rb^{87} are needed, especially by more refined direct-counting techniques. Several indirect determinations similar to this one have been made recently, with excellent agreement on a value of the half-life of 4.9--5.0 x 10^{10} years. Two of these have compared K-A and Rb-Sr measurements on the same sample (Pinson, 1957c; Wasserburg, 1956); this is not really an unequivocal test due to the slight uncertainty in the branching ratio of K^{40}. One other recent indirect test of the Rb^{87} half-life was made by Aldrich et al (1956), using concordant radiogenic lead ages of pegmatites, similar to the work reported here but of much wider scope. Although these four recent tests show excellent agreement, they are not really absolute determinations of the decay rate and half-life, since they are based on other natural decay schemes. Thus, additional direct-counting experiments are needed, such as the recent one by Geese-Bahnisch and Huster (1954). This experiment, as

amended by Huster, also gave a Rb^{87} half-life of $4.9--5.0 \times 10^{10}$ years.

2. Samples of the Monson gneiss and Bolton schist should be collected at regularly increasing distances from the pegmatite-wall rock contact. By analyzing the suitable minerals in these samples for Rb-Sr concentrations, knowledge of the mobility of these two elements in large rock units would be gained. Also, the true age relationships of these formations might be learned, provided the metamorphism of the formations has not been too intensive.

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