Rubidium-Strontium Age Determinations

In The Bird River Area, Southeastern Manitoba

A Thesis

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By

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ABSTRACT

Rubidium — strontium whole — rock ages have been obtained
from greenstones and adjacent granitic intrusions in the Bird River–
Winnipeg River area of southeastern Manitoba. A grey quartz diorite
unit occurring north of the greenstone belt and intrusive into it
gave an age of 2640 $\pm$ 135 m.y. (λ Rb^{87} = 1.39 x 10^{-11} yr.$^{-1}$). The
Lac du Bonnet quartz monzonite lies south of the greenstone belt
and is intrusive into the quartz diorite and the rocks of the green-
stone belt. This unit gave an isochron age of 2495 $\pm$ 130 m.y. The
volcanic rocks of the greenstone belt were dated at 2650 $\pm$ 35 m.y.
The initial Sr^{87}/Sr^{86} ratios for the quartz diorite, the Lac du
Bonnet quartz monzonite, and the volcanics are 0.7014 $\pm$ 0.0021, 0.7088
$\pm$ 0.0068, and 0.7015 $\pm$ 0.0014, respectively. These results are
compatible with geologic interpretations of the area.

Initial results on feldspars from the Bernic Lake pegmatite
suggest extensive post-intrusive redistribution of radiogenic
strontium. A lithium muscovite from this pegmatite gives an age
of 2760 m.y.

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I INTRODUCTION

a) Geological Setting

The area considered in this study is situated near the western edge of the Canadian Shield in the Superior Province. It was involved in the Kenoran orogeny and yields ages which are generally older than those obtained for the Kenoran orogeny in the eastern part of the Superior Province. The occurrence of narrow bands of volcanic and metasedimentary rocks, which predate the granitic rocks of the Canadian Shield, is typical of this province. The present study is an attempt to establish the absolute age of the metamorphosed volcanic and sedimentary rocks (similar to the Rice Lake Group) and associated granitic rocks, and to obtain the sequence of events in the Bird River area. The occurrence of discordant ages from a Li–Cs–rich pegmatite body in the area is also noted, and an attempt is made to show how these might be the result of redistribution of radiogenic Sr. The Rb–Sr method of age determination on total rocks and minerals is used throughout the investigation.

b) Acknowledgements.

II General Geology of the Bird River Area

The area under study is located in south-eastern Manitoba (Fig.1), around Bird River (Fig.2). The rocks consist of granitic rocks (quartz monzonite and quartz diorite) which intrude a greenstone belt (metamorphosed volcanic and sedimentary rocks). The area is noted for the occurrence of a large Li-Cs-rich pegmatite body at Bernic Lake (variously referred to as the Montgary, Chemalloy and Tanco pegmatite)..

The general geology of this area has been discussed by Springer (1950), and Davies (1952), (1955), (1962). Preliminary reconnaissance work has been done by McRitchie (1969). The oldest rocks are volcanic rocks, mainly pillowed andesites and basalts, which are overlain by a series of greywacke, impure quartzite, and arkose, with some conglomerate, slate, and chert. These units were intruded by the Bird River Sill while in a horizontal position and then folded into a large anticline - the north limb of which surrounds Cat Lake. The south limb, which lies parallel to Bird River, appears to have been folded into a syncline with sedimentary rocks within the fold and therefore overlying the volcanics.

A widespread intrusion of granitic rocks followed. Two types of granitic rocks are recognized by Davies (1952, p. 16), " a course, white to grey, rock ranging from quartz diorite to oligoclase granite, often containing inclusions of older basic rock in the form of irregular blocks, bands, or ribbons", and a "fresh massive pink intrusive rock, sometimes porphyritic, but mostly equigranular". He concluded, on the basis of intrusive relationships, that the pink granite was younger than the grey granite, but that the age difference need not be large.
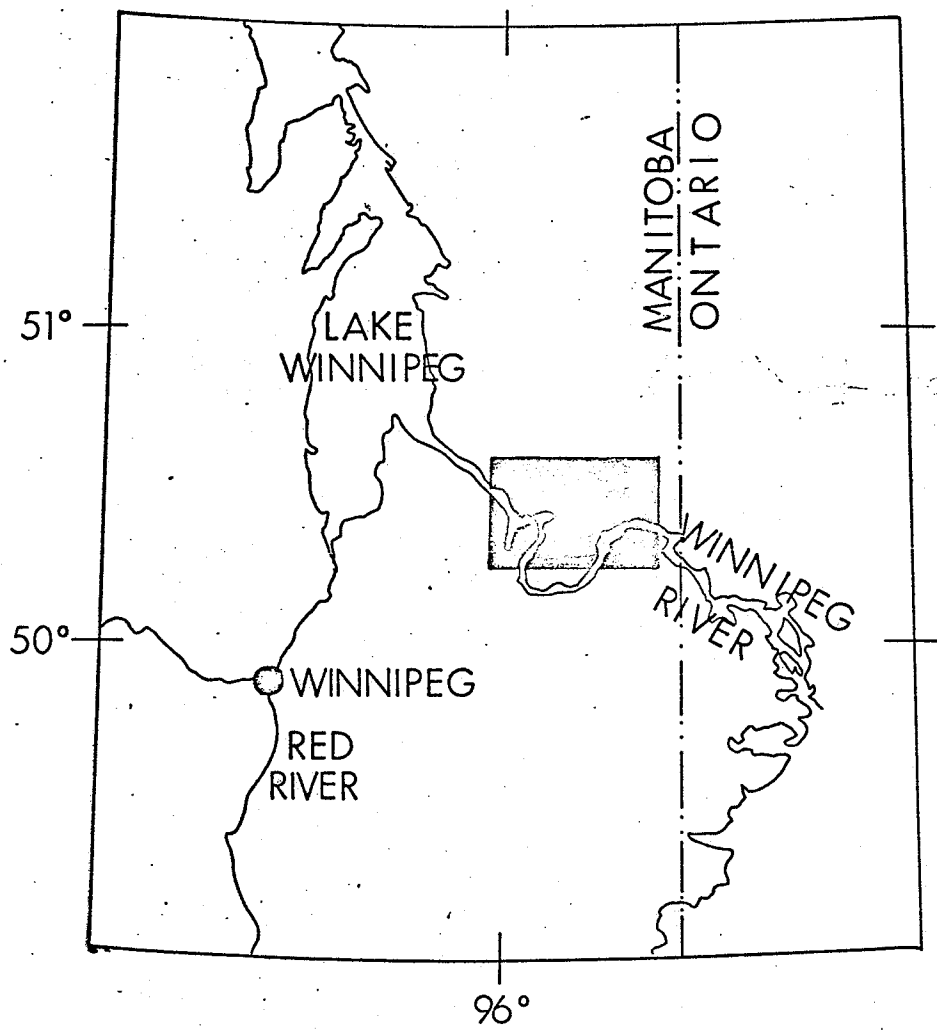
Figure 1. Location of the Bird River Area.
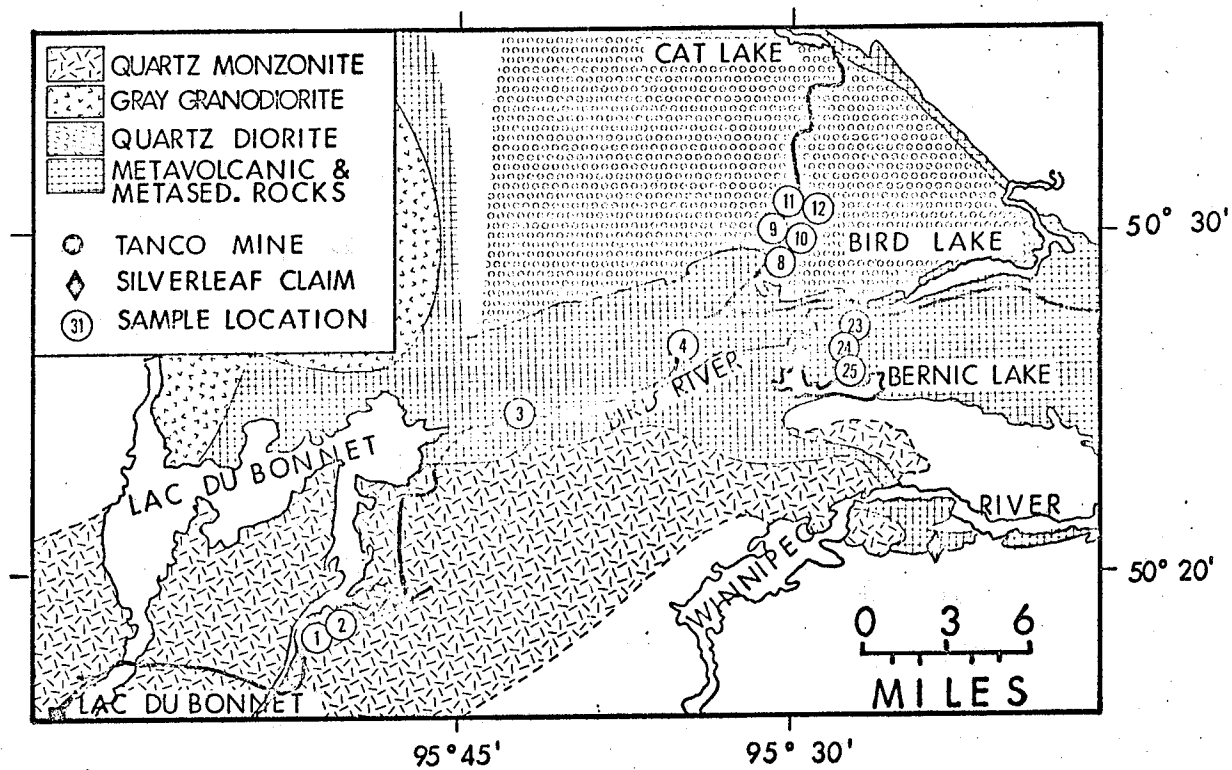
Figure 2. Geology of the Bird River –Lac du Bonnet Area with sample
locations. (from Davies, et al, 1962 and McRitchie, 1969).

The map used here (Fig.2) recognizes two distinct granitic bodies. The Lac du Bonnet quartz monzonite located south of Bird River corresponds roughly to Davies' pink granite, and the quartz diorite, north of Bird River, corresponds to Davies' grey granite. The quartz diorite has been found to contain numerous greenstone inclusions.

The geology of the Bernic Lake Pegmatite has been discussed by Hutchinson (1959) and Wright (1963). Both authors proposed that the pegmatite body formed by crystallization within a closed, flat-lying system with very little interaction between the pegmatitic fluid and the wall rock. This resulted in the pronounced mineral zoning observed within the pegmatite. A later stage generation of solutions which led to the formation of some new mineral assemblages by replacement was also postulated.

III Previous Isotopic Ages

A general survey of K-Ar dates in the Superior Province has been carried out by the Geological Survey of Canada, and the results have been tabulated by Stockwell (1964), and Wanless et al. (1967). Results are also presented in Lowdon (1960), (1961). The K-Ar method (used in these investigations) yields minimum ages which will reflect any later metamorphism and/or loss of argon through diffusion processes. All Rb-Sr ages reported in this thesis are calculated using a decay constant for Rb^{87} of 1.39×10^{-11} $yr.^{-1}$

Both K-Ar and Rb-Sr ages have been reported on samples of pegmatite from the Silverleaf Property just south of the Winnipeg River(see Fig. 2). Lowdon (1960) reported a K - Ar age on a lepidolite (sample G.S.C. 59-41) of 2480 m.y. Gast, Kulp and Long (1958) reported K-Ar age of 2440 ± 60 m.y. , and a Rb-Sr age of 2680 ± 90 m.y., on a lepidolite from the same property. Lowdon (1961) obtained a K - Ar age of 2670 m.y. on a biotite sample from a small granodiorite batholith at Faraway Lake, north of Cat Lake (50° 55' N., 95° 26' W., sample G.S.C. 60 - 89). He interpreted this as being a minimum age for the Rice Lake Group. An anomalous age of 1700 m.y. was obtained on a biotite sample from a paragneiss at Black Lake, north of Cat Lake. (50° 39' N., 95° 18' W., sample G.S.C. 60 - 90). This was interpreted as being the result of a second, distinct, period of metamorphism and granitization. Laughlin (1969) obtained K - Ar ages of 2450 m.y. and 2340 m.y. from a lepidolite and an albite, respectively from the Bernic Lake pegmatite body.

Whole-rock Rb-Sr age dating has been done by Turek and Peterman (1968) in the Rice Lake - Beresford Lake area. An isochron age of 2550 ± 80 m.y. was obtained from eight samples of granite north of the Rice Lake Group. An age of 2630 m.y. was obtained from a single sample of micropegmatite from the south edge of the Rice Lake Group. This was interpreted as a minimum age for the gneisses and granites in that area. An age of 2490 ± 90 m.y. was obtained from 5 samples of phyllite from the Rice Lake Group. This anomalously low age was interpreted as being the result of a low-grade retrogressive metamorphism of the Rice Lake Group accompanying the emplacement of the northern granite.

The general picture presented by past work is that the granites in the Bird River area are probably about 2600 m.y. old, and that the greenstone ages may reflect simply the regional metamorphism accompanying the intrusion of granite. A second metamorphic event, 1700 m.y. ago, is indicated by Lowdon (1961) , but is rejected by Turek and Peterman. A period of remobilization of fluids in the Tanco pegmatite is suggested by Hutchinson (1959), with no indication as to when this might have occurred.

IV. Experimental Techniques

a) Collection and Preparation of Samples

The majority of the samples were collected in June, 1969, from exposures located close to Lac du Bonnet, along the Cat Lake Road, the Bird Lake Road, and a lumber road just north of Bernic Lake (Fig.2). The pegmatite minerals were collected by Dr. G. S. Clark at the Tanco Mine at Bernic Lake, on an earlier trip.

While collecting, particular attention was given to outcrops of blast rubble, being the least weathered, and to obtaining samples large enough so that approximately one half inch of weathered surface could be removed. About 80 samples were collected, their weathered surfaces removed, and approximately one half pound of sample ground in a jaw crusher and reduced to a fine powder in a Bleuler grinder. X-ray fluorescence analyses for Rb and Sr were made on an ARL X-ray fluorescence spectrometer to obtain preliminary estimates of the Rb/Sr ratios. The choice of samples to be analyzed was made on the basis of weathering, X-ray fluorescence results, and the amount of shearing or possible contamination by nearby rocks. The granite samples along the Cat Lake Road were especially susceptible to contamination by greenstone inclusions. All the samples analyzed were whole-rock except for the pegmatite minerals.

b) Rubidium and Strontium Chemistry.

A detailed account of the chemical procedure used is given in Appendix II. Briefly, the chemical procedure for rubidium and strontium is designed to make it possible to measure the Sr^{87}/Sr^{86} ratio and the

absolute concentration of Rb and Sr in the sample. The measurements
are performed on a mass spectrometer, with Rb and Sr samples treated
separately. Since the mass spectrometer measures isotopic composition
the measurement of absolute concentrations is made possible through
the use of spike solutions in which the isotopic composition of Rb
or Sr has been artificially altered.

The samples are initially dissolved in hydrofluoric and perchloric
acid. The appropriate amount of spike solution is then added and the
mixture of spike and sample is equilibrated. The Rb or Sr fraction
is isolated using ion - exchange columns. The final step in the
chemical procedure is the conversion of Sr samples to perchlorates
and Rb samples to sulfates.

c) Isotopic Measurement

1) Description of Mass Spectrometer

The mass spectrometer used for this work is a single focusing
instrument, with a 10 inch radius of curvature, and 90° deflection
angle. The source is a triple filament thermal ionization source of
the type described by Craig (1959). The three rhenium filaments (0.030"
x 0.001") were mounted on Picker nuclear beads (style # 297157). A
mechanical pump, oil diffusion pump at the source end, and a 50 l/s
VacIon pump at the collector end were used to maintain the required
pressure. The source can be isolated by CVC 2-inch gate valves to
facilitate fast pumpdown after venting.

Amplification of the signal was obtained using a Cary vibrating
reed electrometer and the signal was recorded on a L&N strip chart

recorder (Model W/L). The filament currents and the vibrating reed are stabilized with a Sola transformer and a Sorensen voltage regulator. A block diagram of the mass spectrometer is presented in Fig. 3.

2) Operating Procedure

The operating procedure during a Sr run was to first dissolve the sample in two or three drops of triple distilled water. Approximately half of this was then drawn up into a glass pipette, which was discarded after mounting the sample. One drop of sample was deposited on each sample filament. Using a separate power supply about 1.4 amp. were passed through the filament until the water was evaporated. Then the sample was baked by raising the current to about 1.8 amp. The sample bead was then mounted in the source block which was later mounted on the source. The source region of the mass spectrometer was vented with dry nitrogen while both the collector end and the diffusion pump at the source remained under high vacuum. (see Appendix II). After the source was mounted a pressure of 50 microns of mercury was obtained by a mechanical roughing pump (Pump 3, fig. 3), within five minutes. Valve 3 was then shut and Valve 1, leading to the oil diffusion pump, was opened. Within five minutes a pressure of less than 1×10^{-6} mm. Hg was normally obtained in the source region. Fifteen minutes were sufficient to obtain a pressure of less than 2×10^{-7} mm. Hg., except for occasional, brief surges of pressure due to outgassing of the source.

Fig. 3

Top View of Mass Spectrometer
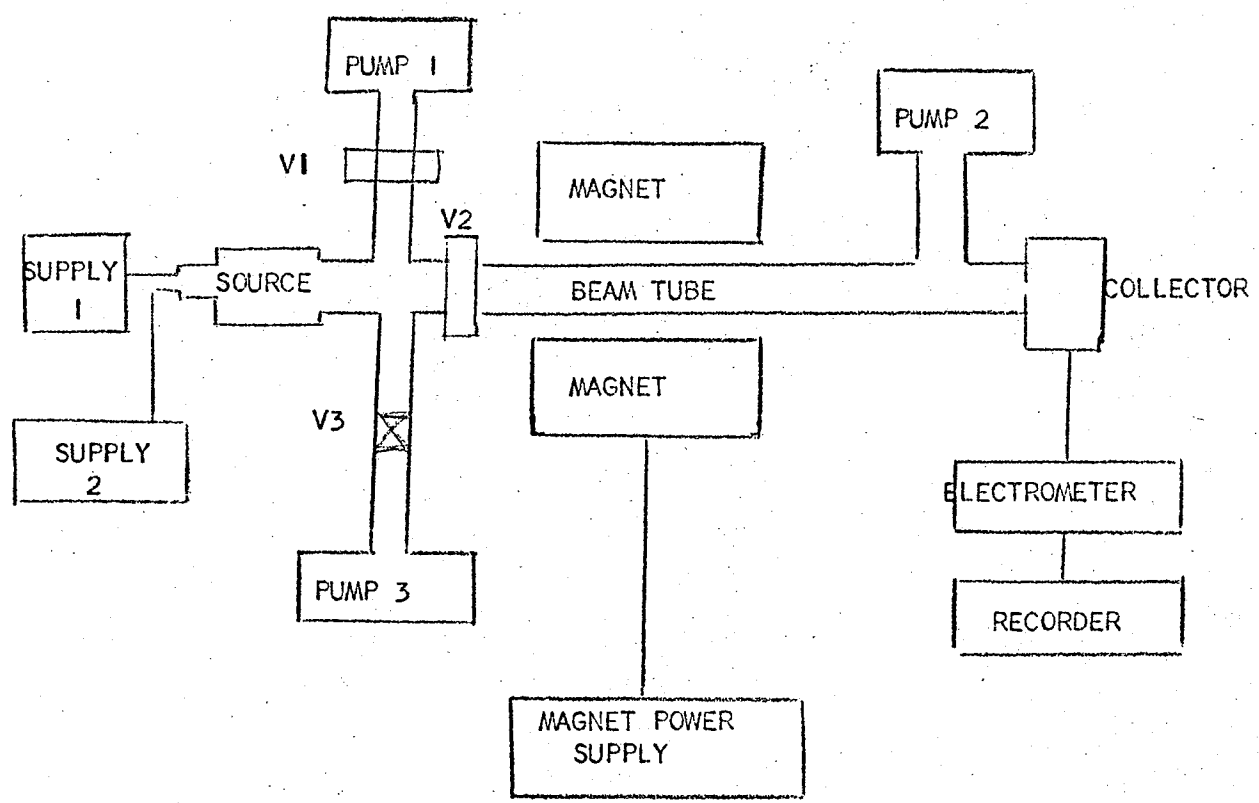
PUMP 1 — mechanical fore pump, oil diffusion

pump, Veeco Type RG – 31 X ionization gauge

VI, V2 — C V C   2 inch gate valves

PUMP 2 — Varian Assoc. Vac Ion Pump Model 921 – 0012

V3   —   Veeco screw valve

PUMP 3 — mechanical roughing pump.

Electrometer — Cary Model 401 Vibrating Reed Electrometer
Recorder — Leeds and Northrup Model W / L

Supply 1 — Filament
Current Supply

Supply 2 — Fluke High
Volt. Supply Model
410 B

A current of 0.3 amp. and 3.0 amp. was passed through the side and
centre filaments respectively, to obtain preliminary degassing. During
the run the side filaments were normally kept at 0.4 to 0.5 amp. current
and occasionally as high as 1.1 to 1.3 amp. when the sensitivity was
low. The centre filament current was kept between 3.5 and 4.5 amp.
in general. An accelerating voltage of 3.8 kv. was used in order to
obtain as good resolution as possible without inducing constant arcing.
During the run each of the three Sr isotopic ratios (88/86, 87/86,
84/86) were measured separately, with eight measurements of each ratio.
The Sr^{88}/Sr^{86} ratio was measured twice, at the beginning and the end,
to check for variations due to fractionation.

The Rb samples were treated similarly except that more care was
required in the mounting of the sample, since there were often a lot
of impurities present, which made the sample form a brittle cake.
Also, the sample filament currents were usually kept between 0.5 and
0.7 amp., and the centre filament current was kept as low as possible
(about 2.5 to 3.0 amp.). No attempts were made to estimate fraction-
ation of Rb isotopes on the mass spectrometer.

3) Error in Mass Spectrometry

The errors in the measurement of the three Sr isotopic ratios
during the run are approximately the same. Errors due to sample
instability and graphical measurement of peak heights will affect
all four isotopes equally. The Sr^{88} peak will be somewhat more re-
liable since base line errors, resolution errors and electronic noise
won't effect it as strongly. Sr^{87} was the major concern since there

was some difficulty resolving this mass completely from Sr^{88},
although this should not show up in the precision of the measure-
ment, but in the accuracy. The correction made in the Sr^{87} peak
height due to poor resolution was generally less than 0.25%,
although more than one attempt to run was often made before such
resolution was obtained. The error in a single ratio measurement
during a Sr run was approximately 0.15% (1σ), and since eight scans
were normally taken, the error in the value used for calculations
(the mean value) was 0.05%. The error in a single measurement during
a Rb run was slightly higher at 0.20% (1σ).

Calculations performed on an isochron for samples 1a, 1e, 2a
and 2c seem to indicate that errors in mass spectrometery are capable
of explaining approximately one-half of the total error observed on
the isochron.

b) Isotope Dilution Calculations

For the majority of samples one spiked Rb analysis was performed
to obtain the Rb concentration in micromoles /gm. The Sr concentration
and Sr^{87}/Sr^{86} ratio were obtained on a single spiked run. For the
pegmatite minerals an unspiked Sr analysis was also performed to
obtain Sr^{87}/Sr^{86} directly. Spike solutions of Rb Cl enriched in Rb^{87}
and $Sr(NO_3)_2$ enriched in Sr^{84} were used. The concentration of the Rb
spike was 0.05889 umoles/ml. with the isotopic composition: 87/85= 111.37.
The concentration of the Sr spike was 0.01111 umoles/ml. with the isotopic
composition: 88/86 = 3.3915, 87/86 = 0.4235, 84/86 = 22.509. The
preparation of the spikes is described in Appendix II.

All Sr^{87}/Sr^{86} ratios were corrected by normalizing the sample Sr^{88}/Sr^{86} ratio to 8.375. Also a correction in sample Sr isotopic composition due to variations in Sr^{87}/Sr^{86} was made. The notation and equations required for the isotope dilution calculations are given below.

Notation: m = mixture of sample and tracer

s = sample

t = tracer (spike)

$(84/86)_m = Sr^{84}/Sr^{86}$ atomic ratio in the mixture of tracer and sample

$(85/87)_s = Rb^{85}/Rb^{87}$ atomic ratio in the sample.

The Rb calculations employ the equation:

$$(85/87)_m = \frac{(85)_s + (85)_t}{(87)_s + (87)_t}$$

From the natural composition of Rb:

$$(85)_s = 0.722A$$

$$(87)_s = 0.278A$$

where A is the number of micromoles of sample. Using the isotopic composition, concentration, and the volume of the Rb tracer, both $(85)_t$ and $(87)_t$ are known. Therefore A is uniquely determined in terms of $(85/87)_m$ which is measured on the mass spectrometer. Given A, the concentration of Rb^{87} is calculated using the natural composition of Rb and the sample weight.

The Sr concentration is calculated using the equation:

$$(84/86)_m = \frac{(84)_s + (84)_t}{(86)_s + (86)_t} \qquad (1)$$

Using the natural composition of Sr:

$$(84)_s = 0.0056 \ A \qquad\qquad (2)$$

$$(86)_s = 0.0986 \ A \qquad\qquad (3)$$

where A = No. of umoles of Sr in sample. This allows for the calculation of the Sr^{86} concentration directly. The calculated sample concentration (A) is then added to the known concentration of spike (in umoles) to obtain the number of umoles in the mixture. The ratios measured during the mass spectrometer run allow us to calculate the concentration of each Sr isotope 84, 86, 87, 88 — in the mixture. The known concentration of spike is subtracted from these four values to obtain the concentration of each isotope in the sample. This yields $(88/86)_s$, $(87/86)_s$, $(84/86)_s$ directly.

If the correction due to high $(87/86)_s$ ratio is to be made, it should be made at this point. Equations 2 and 3 must be rewritten to read:

$$(84)_s = 0.0056 \, \alpha \, A$$

$$(86)_s = 0.0986 \, \alpha \, A$$

$$\text{where } \alpha = \frac{(84/86)_s + (87/86)_s + (88/86)_s + 1}{(84/86)_s + (87/86)_o + (88/86)_s + 1} \qquad (4)$$

$$(84/86)_s = 0.0568$$

$$(88/86)_s = 8.375$$

$$(87/86)_o = 0.706$$

$$(87/86)_s = \text{initial estimate obtained above.}$$

This initial estimate of α allows us to recalculate everything above and obtain a new set of sample ratios. The value $(87/86)_o = 0.706$ was also used to obtain equations 2 and 3. It is an initial estimate of $(87/86)_s$. If the factor α is being used then the final answers will not depend on this value (0.706), and any number could be used instead.

It should be noted that the use of the factor α will increase the calculated total Sr concentration but will not affect the calculated Sr^{86} concentration at all, and will only affect $(87/86)_s$ very slightly. What it will do, however, is to significantly improve the calculated $(84/86)_s$ ratio, which is very sensitive to this correction. In the case of pegmatites with very high $(87/86)_s$, the factor α or some equivalent method must be used. Here an iteration may be required until two successive estimates of $(87/86)_s$ are appropriately close together.

The correction for isotopic fractionation is made in the usual way. The value of $B = 1 - (88/86)_s / 8.375$ is calculated. $(88/86)_m$ is multiplied by $(1 + B)$, $(87/86)_m$ is multiplied by $(1 + B / 2)$, and $(84/86)_m$ is multiplied by $(1 - B)$. The above calculations for sample composition and concentration are again performed, using the same value of α and the corrected values of $(88/86)_m$, $(87/86)_m$.

Only in the case of a high value of B and very high $(87/86)_s$, might α have to be revised once more, after the fractionation correction. For the fractionation correction one iteration is usually sufficient to obtain $(88/86)_s = 8.375$. A sample calculation is shown in Appendix III.

$\underline{V}$ Analytical Results

A) Rubidium and Strontium Standards

The results of two types of standards are tabulated here. Eimer and Amend (E&A) standard $SrCO_3$ has been analyzed to obtain the precision in the measurement of Sr^{87}/Sr^{86} in a spiked run. Whole-rock standards have also been analyzed to obtain the precision in the measurement of Rb and Sr concentrations. Both these standards can be used as interlaboratory checks on systematic errors although the whole-rock standards are subject to inhomogeneity which makes them unreliable.

The results of E + A Sr CO_3 analyses are presented in Table I. The average value of these results is 0.7086 $\pm$ 0.00065 (2σ). The standard deviation on a single determination is 0.11% (1σ).

Data on whole-rock standards is presented in Table 2. The results of similar analyses performed by other workers can be found in Flanagan (1969). He tabulated a value of 48.6 ppm. Rb for BCR -1, and 240 ppm. Sr for GSP - 1, using the isotope dilution technique. The results of three Rb determinations for BCR - 1 (Table 2) show large errors. The first determination is unreliable since part of the sample was lost immediately after spiking the sample. If the equilibration was not complete then this would lead to error. All three aliquots of BCR - 1 had large amounts of impurity, probably Fe, present after one passage through the ion-exchange columns. The third sample was passed through the ion exchange columns twice resulting in a clean sample, with, however very little Rb present. Contamination by natural Rb during the spectrometer run may account for the high value of 50.0 ppm. since the sensitivity was very low. These three

Table I — Eimer and Amend Sr CO_3 DATA[1]

DATE	(Sr^{87}/Sr^{86}) meas.	(Sr^{87}/Sr^{86}) Norm.[2]	ANALYST
1/26/70	0.7088	0.7095	A. Penner
6/23/70	0.7083	0.7090	A. Penner
		0.7088	R.B.Farquharson
		0.7090	" "
		0.7075	" "
		0.7077	" "

1. Lot no. 492 327

2. normalized to $Sr^{88}/Sr^{86} = 8.375$

TABLE 2:   Rb — Sr   Data on Whole — Rock
Standards.

SAMPLE	Rb ppm.	Sr ppm.	Sr^{87}/Sr^{86} meas.	Sr^{87}/Sr^{86} norm.
BCR — 1	43.2			
	46.3			
	50.0			
GSP — 1		237.0	0.7651	0.7680
		231.6	0.7655	0.7697

values are not used in any error estimates. The results of strontium determinations for GSP - I are somewhat more consistent. The values obtained for the Sr concentration disagree by 2.4% and the results on the Sr^{87}/Sr^{86} ratio disagree by 0.22%.

The possibility of sample inhomogeneity has been noted by Compston et al. (1969), who propose the use of a standard such as NBS 70a K - feldspar[1]. Data on this standard is presented in Tables 3 and 4. The results of five Rb analyses (Table 3) yield a precision on the mean value of 0.24% (2σ). The five total Sr concentrations (Table 4) yield a precision on the mean value of 0.66% (2σ), and the precision on the mean value of the spiked analyses of Sr^{87}/Sr^{86} is 0.070% (2σ). The accuracy of these results must await the comparison with results from other laboratories.

b) Results from the Bird River - Lac du Bonnet Area

I) Quartz Diorite (Cat Lake Road)

Five samples of quartz diorite collected along the Cat Lake Road were analyzed and one sample (12b) was duplicated. The results are shown in Table 5. Figure 4 shows an isochron plot of these samples. All isochrons in this work are calculated using the least - squares regression analysis of York (1966). The weighting factors required for the program were obtained using errors of 0.15% and 1.4% for the Sr^{87}/Sr^{86} and Rb^{87}/Sr^{86} ratios respectively. The exact values used as weighting factors were found to have very little effect on

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[1] Distributed by the National Bureau of Standards, Wash., D.C.

Table 3: Rb Concentrations for NBS 70(a) K – Feldspar

Rb(ppm)	Analyst	Date
532.5	R. B.Farquharson	3/18/70
529.4	A. Penner	5/28/70
532.6	G. S. Clark	6/1/70
532.9	G. S. Clark	12/4/69
531.7	G. S. Clark	6/24/70

Table 4. Sr Data for N.B.S. 70(a) K-feldspar

$Sr^{86} \times 10^{-11}$ m/gm	Sr^{87}/Sr^{86} [1] (normalized)	Radiogenic Sr (ppm)	Total Sr (ppm)	Date	Analyst
7083	1.1985	3.010	66.0	6/5/70	G. S.Clark
7058	1.1982	2.998	65.7	6/2/70	G. S. Clark
6983	1.1987	2.969	65.0	6/24/70	G. S. Clark
6988	1.2003	2.981	64.9	6/16/70	A. Penner
6987	1.2019*	2.990	65.1	3/18/70	R.B.Farquharson

[1] obtained from Sr^{84} spiked run except for sample indicated.

* unspiked run.

Table 5.   Rb-Sr Data for the Quartz Diorite
(Cat Lake Road)

Sample	Rb (ppm)	Sr (ppm)	Rb^{87}/Sr^{86} (atomic)	Sr^{87}/Sr^{86} meas.	Sr^{87}/Sr^{86} norm.
8a	46.0	236.0	0.5632	0.7203	0.7234
10	40.2	178.0	0.6525	0.7243	0.7247
11a	43.3	151.0	0.8329	0.7311	0.7331
12a	70.3	155.0	1.3133	0.7489	0.7497
12b	60.4	83.7	2.0994	0.7785	0.7827
12b	60.3	83.0	2.1148	0.7800	0.7807
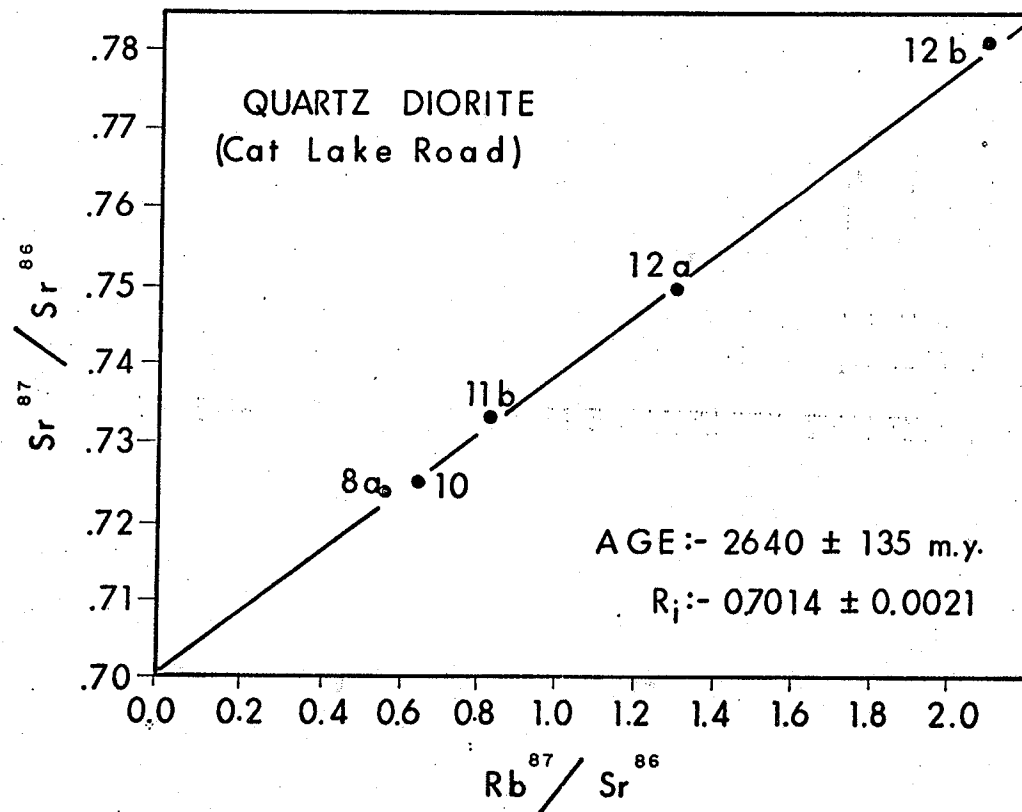
Figure 4. Whole-rock isochron for the quartz diorite.

the age and intercept so the same values were used for all isochron
fits. The whole-rock age found for the quartz diorite is 2640 ± 135
m.y., with an initial Sr^{87}/Sr^{86} ratio of 0.7014 ± 0.0021. The errors
quoted on all ages and intercepts are 2σ limits. These can be converted
to 95% confidence limits using Student's t-distribution with n - 2
degrees of freedom, where n is the number of samples.

2) Lac du Bonnet Quartz Monzonite

Five samples of the Lac du Bonnet quartz monzonite were analyzed
and one sample (2a) was duplicated. The data are presented in Table
6 with an isochron plot in Figure 5. The calculated age of the Lac
du Bonnet quartz monzonite is 2495 ± 130 m.y., with an initial inter-
cept of 0.7088 ± 0.0068.

3) Bird Lake Volcanics

The data on the Bird Lake volcanics is given in Table 7 and
the isochron in Figure 6. The age found for the volcanics is 2650 ±
35 m.y. with an intercept of 0.7015 ± 0.0015. The isochron fit does
not include samples 3a, which is a metamorphosed sedimentary rock,
and 9a, which is a greenstone inclusion in the Cat Lake Road granite.
Examination of the isochrons of the Cat Lake Road granite and the
volcanics shows that sample 9a could easily be included with either
set of data without significantly changing the results.

4) Bernic Lake Pegmatite

The data on six pegmatite samples from the Bernic Lake pegmatite
is shown in Table 8. Two spiked runs and one unspiked Sr run were
performed on each of samples T -1, T - 3, and T - 4, to check for

systematic errors in the method of calculation. All samples are

feldspar, except for T - 5, which is lithium - muscovite.

Table 6. Rb—Sr Data for the Lac du Bonnet Quartz Monzonite

SAMPLE	Rb (ppm)	Sr (ppm)	Rb^{87}/Sr^{86} (atomic)	Sr^{87}/Sr^{86} meas.	Sr^{87}/Sr^{86} norm.
2 c	154.3	162.0	2.771	0.8045	0.8053
2	170.4	164.4	3.028	0.8160	0.8176
1 a	226.3	180.0	3.674	0.8342	0.8374
2 a	193.8	153.0	3.708	0.8398	0.8409
	191.9	148.8	3.777	0.8445	0.8424
1 e	328.4	175.0	5.514	0.8990	0.9031
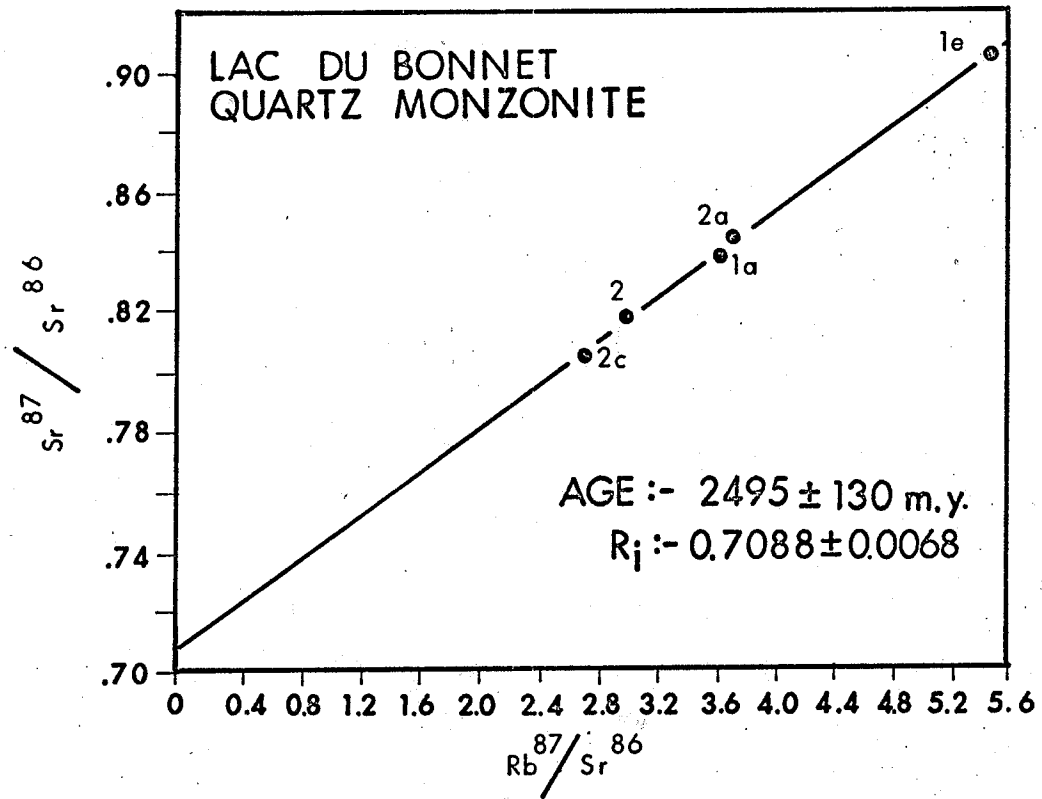
Figure 5. Whole-rock isochron for the Lac du Bonnet quartz
          monzonite.

Table 7.   Rb-Sr Data for the Metavolcanics.

Sample	Rb (ppm)	Sr (ppm)	Rb^{87}/Sr^{86} (atomic)	Sr^{87}/Sr^{86} meas.	Sr^{87}/Sr^{86} norms.
9 a	1.4	452.0	0.009	0.7022	0.7024
24 a	65.5	314.7	0.6021	0.7229	0.7228
25 a	63.4	169.7	1.0836	0.7423	0.7435
23 a	71.6	81.1	2.574	0.7972	0.7987
25 b	89.2	78.7	3.314	0.8252	0.8264
3 a	133.6	93.9	4.171	0.8467	0.8507
4 b	140.8	42.4	9.953	1.0730	1.0768
4 c	119.8	31.7	11.359	1.1189	1.1231
	118.4				
4 a	138.2	33.3	12.543	1.1752	1.1706
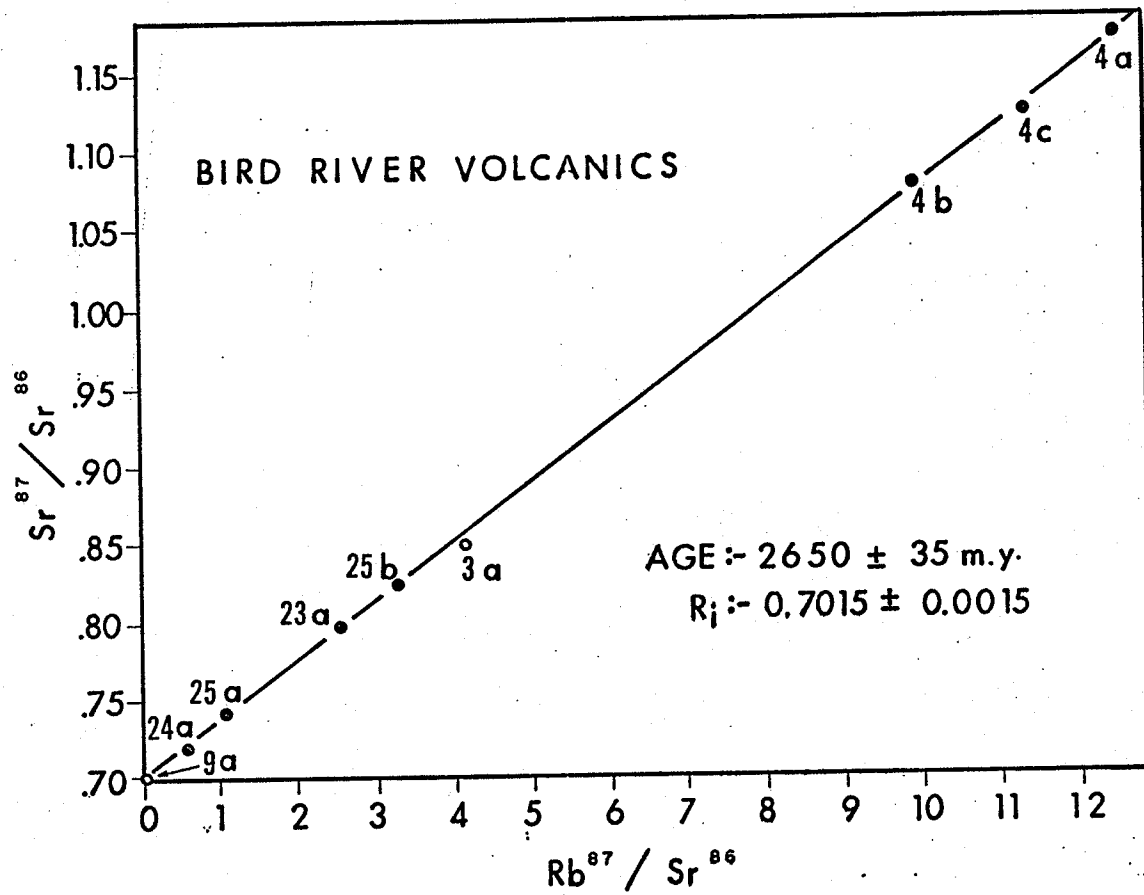
Figure 6. Whole—rock isochron for the Bird River Volcanics. Samples 3a and 9a were not used in the age calculation (see text).

Table 8. Rb — Sr Data for the Bernic Lake Pegmatite

Sample number	Mineral	Rb ppm.	Common Sr ppm.	Radiogenic Sr ppm	Rb^{87}/Sr^{86} (atomic)	Sr^{87}/Sr^{86} Meas.	Sr^{87}/Sr^{86} Norm.
T — 1	Microcline	19810	46.8	166.6	1222.5	36.752	36.781
		19040	45.3	163.6	1214.3	37.387	37.324
						36.891	36.858
T — 3	Orthoclase	5381	26.7	54.4	581.5	21.391	21.326
		5306	26.6	56.3	576.0	22.226	22.149
						22.28	22.36
T — 4	Albite	1197	24.9	14.5	139.0	6.611	6.631
		1207	24.4	14.3	143.1	6.673	6.680
						7.079	7.085
T — 5	Li—muscovite	26750	1.1	298.7	67209.0	2633.7	
T — 9	Microcline	21240	12.0	225.7	5111.0	191.20	191.26
T — 10	Microcline	26252	34.2	221.1	2161.0	66.06	66.17

VI. Interpretation of Data

a) Discussion of Errors.

Replicate analyses yield a standard deviation of 0.55% and 1.28% for a single analysis of Rb and Sr concentrations respectively. The standard deviation of Sr^{87}/Sr^{86} is 0.153%. These errors have been obtained on rocks from the Bird River area. The difference between the errors in the Rb and Sr concentrations may be the result of random variations which would be eliminated if more replicate analyses were performed. From the Rb and Sr concentration errors a standard deviation of 1.4% (1σ) in the measurement of Rb^{87}/Sr^{86} is obtained. All the isochron fits performed (using errors of 1.4% and 0.15% in Rb^{87}/Sr^{86} and Sr^{87}/Sr^{86} respectively) indicate that there are no observable external sources of error. That is, the errors observed between replicate analyses are capable of accounting for all the errors observed in the isochron.

The errors observed in the pegmatite analyses are notably higher that those in the whole-rock samples, for three reasons. First of all, the unspiked Sr analyses performed on samples T – 3 and T – 4 are unreliable since the samples were not completely dissolved during the chemical procedure. This could lead to the error observed in T – 4 unspiked Sr. The results from the unspiked analyses of T – 3 and T – 4 were not used in any calculations. Secondly, because of the low common Sr and high Rb content it was difficult to spike these samples properly unless a different procedure were used.

Especially in the Rb analyses this meant that any small errors in
mass spectrometry would lead to high errors in the Rb concentration.
The error magnification factor, defined as the ratio of percentage
error in Rb concentration to percentage error in the $(Rb^{85}/Rb^{87})m$
ratio, was as high as 7.0 compared to the usual values of 1.2 - 1.5.
Thirdly, because of the high Sr^{87}/Sr^{86} ratios, resolution of the
Sr^{87} and Sr^{86} peaks became difficult. This meant that the base line
of the Sr^{86} peak was ambiguous, which would affect all 3 measured
isotopic ratios.

b) Discussion of Age Relations

Previous geological interpretations have concluded that the
Bird River volcanics are the oldest rocks in the area, followed by
the northern quartz diorite and the Lac du Bonnet quartz monzonite.
The ages reported here support those findings although the ages are
not statistically separable. The ages of the northern quartz diorite
and the Lac du Bonnet quartz monzonite agree with previous data
obtained by the Geological Survey of Canada, and by Turek and Peterman
(1968). The age of 2650 ± 35 m.y. reported here for the volcanic
rocks agrees with the minimum K - Ar age of 2670 m.y. obtained for
the Rice Lake Group by Lowdon (1961). It is lower than the age of
2720 ± 185 m.y. obtained by Turek and Peterman (1968) from gold-
quartz veins in the Rice Lake Area. (This age was considered to be
a minimum age for the Rice Lake Group). This seems to indicate that
the age of the Bird River volcanics has been partially affected by
metamorphism accompanying the granitic intrusion, a possibility already
mentioned by Turek and Peterman.

The initial Sr^{87}/Sr^{86} ratios of the volcanics and the quartz

diorite are 0.7015 ± 0.0015 and 0.7014 ± 0.0021. Both of these

ratios are typical of rocks of this age, if they represent primary

mantle or deep crustal material and have not undergone extensive

remobilization at a later date or suffered from contamination by pre-

existing crustal rocks. The initial Sr^{87}/Sr^{86} ratio of the Lac du

Bonnet quartz monzonite is 0.7088 ± 0.0068, which is considerably

higher than the other two values. The error on this ratio is also

high, so that the differences between the ratios may be the result

of experimental error. If this is not the case then the difference

between the ratios may be the result of contamination by pre-existing

crustal rocks, or it may reflect the time that elapsed between the

inital separation of the granitic material from its parent body and

the final crystallization; that is, the time spent as a Rb – rich phase.

(The emplacement of these two granitic bodies in the area has been

interpreted (Davies, 1952) as occurring during two stages of the same

metamorphic event). The average Rb^{87}/Sr^{86} ratio for the samples of

Lac du Bonnet quartz monzonite analyzed (from Table 6) is about 3.5.

If we assume that the initial Sr^{87}/Sr^{86} ratio of this body was the

same as that of the quartz diorite (0.7014), and that it grew homo-

geneously within a fluid system with $Rb^{87}/Sr^{86} = 3.5$, then it can be

calculated how long it would take to reach a value of 0.7088, at

which time the fluid crystallized and the ratio was fixed. The

amount of time required is about 150 m.y. This can be regarded as

a time of cooling or length of duration of the metamorphism. It is

close to the difference between the two ages (144 m.y.). The error

(2 σ) on both these numbers is as high as the numbers themselves, but

they have been obtained completely independently and may indicate the

duration of the metamorphic event.

c) Anomalous Pegmatite Results

It is not possible to obtain anything approaching a true isochron

from the pegmatite data and so the true age and initial Sr^{87}/Sr^{86}

value remain unknown. It is, however, possible to calculate an

apparent age for each sample by assuming an initial Sr^{87}/Sr^{86} value

of 0.710. The calculated age is quite insensitive to the exact

value of the initial value chosen due to the high enrichment of

radiogenic Sr in each of the samples.

The "ages" of the feldspar samples from the Bernic Lake pegmatite

are listed in Table 9. A plot of apparent age versus Rb concentration

is shown in Figure 7. The range over which these ages vary is incom-

patible with the experimental errors. Therefore a geological mechanism

must be postulated in order to explain them. The simplest explanation

is that the pegmatite body is the same age as the granites in the area

and that it has been affected by a later metamorphism approximately

2000 m.y. ago. This explanation, however, must include the possibility

of a sample gaining excess radiogenic Sr, as well as losing radio-

genic Sr, during the metamorphism. The redistribution of radiogenic

Sr within pegmatites from the Middletown Area, Connecticut has been

noted by Brookins et al. (1969). Riley (1970)

Table 9 – Calculated ages for the Bernic Lake Pegmatite Feldspars.

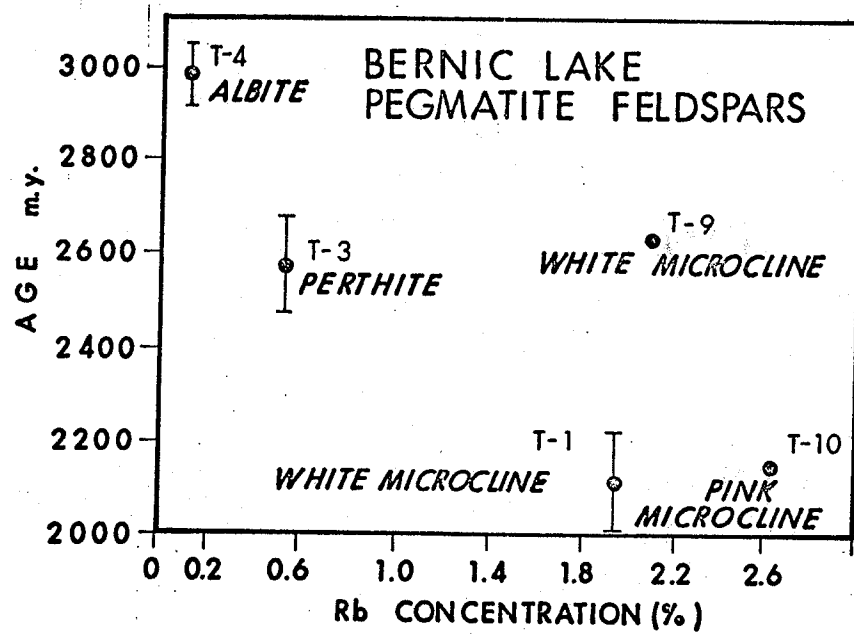| Mineral	Sample	Rb (ppm)	Common Sr ppm.	Age m.y. (2σ)
Microcline	T – 1	19425	46.0	2111 ± 110
Orthoclase (Perthite)	T – 3	5343	26.6	2568 ± 103
Albite	T – 4	1202	24.6	2973 ± 68
Microcline	T – 9	21240	12.0	2632
Microcline	T – 10	26250	34.2	2147

Figure 7. Plot of apparent age versus Rb concentration for
the Bernic Lake Pegmatite feldspars (Assumed initial
ratio of Sr^{87}/Sr^{86} is 0.710).

has also observed anomalous ages (from 1170 m.y. for lepidolite to 1730 m.y. for muscovite) in various pegmatite minerals from Black Hills, South Dakota. A nearby granitic body (Harney Granite) yielded a whole-rock isochron age of 1744 ± 24 m.y. He presented data on five samples of muscovite which show a consistent negative correlation between apparent age and Rb concentration.

The ages of the feldspars analyzed similarly show a negative correlation with Rb concentration. The direction of this correlation seems to exclude the possibility that redistribution of Rb has occurred. The main question is whether this redistribution occurred in response to a short-term metamorphic event, or as a result of continuous diffusion through all time. Wright (1963) has stated that alkali replacement has taken place late in the history of the Bernic Lake Pegmatite. More recently, Dr. P. Cerny (personal communication) has noted evidence of metasomatic alteration in this pegmatite. Dr. Cerny has also found evidence to suggest that the lithium-muscovite in the pegmatite is a product of later metasomatism. A single analysis of Li - muscovite during the present study gave an age of 2760 m.y.

The results for the pegmatite minerals reported here must be considered preliminary. Any attempt to further resolve the reasons for the anomalous ages will have to await analyses on mineral samples collected with more control on the mineralogy in this complexly zoned pegmatite.

VII Summary and Conclusions

Data obtained from the pegmatite body at Bernic Lake suggests that a post-crystallization metamorphism has taken place, although the nature and length of duration of the event has not been established.

Rubidium - strontium whole-rock ages have been obtained for two granitic units and a volcanic sequence in the Bird River area. The Lac du Bonnet quartz monzonite is considered the youngest unit dated since numerous dikes of this body penetrate the greenstones and the quartz diorite to the north. The age obtained is 2495 ± 130 m.y. with an initial Sr^{87}/Sr^{86} ratio of 0.7088 ± 0.0068. This is the youngest age obtained, although it cannot be statistically separated from the other two ages. The apparently high initial Sr^{87}/Sr^{86} ratio suggests that the Lac du Bonnet quartz monzonite represents remobilized crustal material, or, that it has incorporated radiogenic Sr from the assimilation of pre-existing rocks.

The gray quartz diorite to the north gives a whole-rock age of 2640 ± 135 m.y. with an initial Sr^{87}/Sr^{86} ratio of 0.7004 ± 0.0021. This unit appears to be intruded by the Lac du Bonnet quartz monzonite and contains inclusions of the adjacent greenstones. The initial Sr^{87}/Sr^{86} ratio suggests a primary igneous origin.

The volcanics analyzed range in composition from andesitic to rhyolitic and yield an isochron age of 2650 ± 35 m.y. with an initial Sr^{87}/Sr^{86} value of 0.7015 ± 0.0015. The volcanics have been metamorphosed and therefore the age obtained should be considered a minimum age for the metamorphosed volcanic and sedimentary rocks of the Bird River greenstone belt since it is quite possible that these fine-grained volcanics have been isotopically rehomogenized during the granitic intrusion and the accompanying deformation. The ages reported here show that the Kenoran orogeny occurred 2650 m.y. ago in this region.

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Appendix I : Description of Samples

I a — medium grained pink granitic rock near the contact with a grey

   granite.

I e — Pink, orthoclase — rich pegmatitic segregation at the same

   location as I a. Diameter of feldspar crystals is approximately

   one half inch.

2 —   pink pegmatitic granite

2 a — pink pegmatitic granite associated with black banding in the

   granite.

2 c — pink granite of same appearance as I a but coarser grained.

8 a — sheared grey quartz diorite with biotite along shear planes.

10 — grey granite with a small amount of pink orthoclase.

II b — intermediate grey to pink granite at contact of pink and

   grey phases.

12 a — fine grained grey granite at contact with fine grained pink

   granite, with a nearby greenstone inclusion.

12 b — fine grained pink granite at same location as 12a.

3 a — fine grained sedimentary rock, schistose.

4 a — grey metarhyolite with quartz phenocrysts.

4 b — same as 4 a.

4 c — same as 4a, but this sample has a distinct foliation.

9 a — fine grained greenstone inclusion in granite.

23 a — fine grained silicified rhyolite

24 a — intermediate metavolcanic, slightly schistose.

25 a — foliated metavolcanic.

25 b — same as 25 a.

Bernic Lake Pegmatite Minerals

T – 1   White microcline

T – 3   orthoclase with approximately 5% albite, (perthitic).

T – 4   fine – grained albite.

T – 5   Li – rich muscovite intergrown with albite
(purple color, –80 + 140 mesh, density = 2.85 – 2.89)

T – 9   white microcline

T – 10 pink microcline

Appendix II

Detailed Rubidium — Strontium Chemical Procedure

Using the X-ray fluorescence results the amount of sample required to produce a Sr^{84}/Sr^{86} ratio of at least 0.5 (and Rb^{85}/Rb^{87} ratio of 0.5) in the mixture of spike and sample was calculated. These ratios represent the optimum spiked ratios for the compositions of spikes used (see page 13 for data on spikes.) This amount was weighed in aluminum foil boats and transferred to a 100 ml teflon beaker. Twenty ml. of 40% HF (manufactured by E. Merckag: Suprapur) were added to the samples; they were covered with a teflon disk and heated for one half hour at approximately 250F. About 3 ml. of 70% $HClO_4$ (G. Frederick Smith, double distilled) were added at this point to convert the sample to perchlorates, they were covered again and allowed to digest at 250F. for at least 8 hours. Generally there was very little or no undissolved portion at this time. Then the covers were removed and the samples were evaporated to a perchlorate mush. Care was taken to try to evaporate all free liquids completely, with out actually burning the sample brown. Twenty ml. of doubly distilled water were added and the sample was again evaporated to a mush to eliminate any remaining HF. The appropriate amount of each spike was then added to the Rb and Sr samples, using a pipette. Generally, two ml. were added to Sr samples and five or ten ml. to Rb samples. Twenty ml. of vycor distilled 6.2N HCl (constant boiling) were added to all samples, they were covered and heated for one half hour to

equilibrate sample and spike.

After equilibration of sample and spike the covers were removed and all samples were evaporated to a mush, until most of the perchlorate fumes were driven off. After this point the Rb and Sr samples were treated separately. Five ml. of methanol were then added to the Sr samples to leach out the alkaline earths. They were transferred to a 5 ml. centrifuge tube and centrifuged until the supernate was clear. (usually less than 5 min.) The supernate was poured into a 30 ml. beaker, 10 ml. of 6.2 N HCl were added, and the solution was evaporated to a volume of 4 ml. The 4 ml. of solution, which should be 6.2 N, were diluted with water to 10 ml to yield about a 2.5 N HCl solution, and added to the ion exchange columns. The ion — exchange columns (cation-exchange resin AG 50 W — X 8, 200 — 400 mesh) had been previously calibrated using an atomic absorption spectro-photometer to determine when the Sr fraction came out. Also, a 2.5 N HCl solution was found to give a good separation of Sr and Ca on the columns. Once the samples were absorbed on the columns, four 10 ml. portions and one 65 ml. portion of 2.5 NHCl were added, allowing each portion to be completely absorbed, before adding the next. The sample was collected in the next 40 ml. and evaporated to dryness as perchlorate. The Sr columns were cleaned with 100 ml. of 6.2 NHCl, and kept moist with 2.5 N HCl periodically.

The Rb samples, after spiking, equilibration, and evaporation to a perchlorate mush, had 10 ml. of IN HCl added to them. They were then evaporated to complete dryness and 2 to 3 ml. of IN HCl were added.

The samples were centrifuged until the supernate was clear and then added to the Rb columns. Once the samples were completely absorbed three ml. portions of In HCl were added separately to each column and then 100 ml. of 1N HCl were added. The samples were collected in the next 30 ml. of 1N HCl and evaporated to dryness as sulfates by adding a drop of 10% H_2SO_4 during evaporation. The Rb columns were first cleaned with 100 ml. of 6.2 N HCl, then 50 ml. of double distilled water, and 50 ml. of 1N HCl.

The spikes were obtained from Oak Ridge National Laboratory as Sr $(NO_3)_2$ and Rb Cl, and were prepared by Dr. G. S. Clark. They were dried at 120°C. overnight and allowed to cool in a dessicator. The spike salts were then carefully weighed and transferred to 200 ml. volumetric flasks and diluted to volume in 0.5 N HCl. A ten ml. aliquot of the Sr^{84} spike was diluted to 1000 ml. in a weak HCl solution. A 15 ml. aliquot of the Rb^{87} spike was similarly diluted to 1000 ml. to obtain the appropriate concentration. The isotopic composition of the stontium spike was measured in a mass spectrometer run. Accurate values of the spike concentration were obtained by calibration against Sr CO_3 (J. T. Baker Chemical Co., 99.2% pure) and Matheson Coleman and Bell Rb Cl (99% pure). These standards were previously prepared gravimetrically.

APPENDIX III

Isotope Dilution — Calculation Example

A program was written for use on an Olivetti — Underwood
Programma 101, to simplify the Sr isotope dilution calculations. The
program is shown below.

Left column:

```
        V
      d ↓
      C X
      c -
      f ↕
      d ↓
     .B X
        ↕
      b ↓
        -
      f ↕
      A ◊
S/ —  S
        •
      A ◊
      / ◊
      f ↕
      A ↕
      d •
      D •
      e •
      A ↕
        ↕
      E ↕
      E ◊
      E ↓
      f X
```

Right column:

```
      B -
      A ◊
      / ◊
      E ↓
      d X
      A ◊
      f X
      b -
      A ◊
      / ◊
      E ↓
      D X
      A ◊
      f X
Sz —  S
        -
      A ◊
      / ◊
      E ↓
      e X
      A ◊
      f X
S3 —  S
        -
      A ◊
      / ◊
        S
```

Input data required:

b = # umoles Sr^{84} in tracer

B = # umoles Sr^{86} in tracer

c = % Sr^{84} in sample

C = % Sr^{86} in sample

d = (84/86) measured

D = (87/86) m

e = (88/86) m

Data required at intermediate steps:

    S1 : total # umoles of Sr in tracer

    S2 :   # umoles Sr87 in tracer

    S3 :   # umoles Sr88 in tracer

Sample 4 c has been chosen for this calculation because of its

high radiogenic Sr content, and because the final $(84/86)_s$ agrees

very well with the accepted value.

    Output number 1, shown below, was obtained with the initial estimate

α_o = 1. The program first solves equation (1) for αA, stops at S 1,

then division by α is done manually to obtain A, and the program is

re-started at S1.

	$\underline{1}$		$\underline{2}$		$\underline{3}$	
	0·018304	b↑			0·018304	b↑
	0·0008132	B↑			0·0008132	B↑
	0·0056	c↑			0·0056	c↑
	0·0986	C↑			0·0986	C↑
$(84/86)_m$ ——	1·1460	d↑			1·1375	d↑
$(87/86)_m$ ——	1·0853	D↑			1·0894	D↑
$(88/86)_m$ ——	8·075	e↑			8·136	e↑
		V		V		V
α A =	0·161757772	A◊	0·161757772	A◊	0·163094901	A◊
Divide by α ——	1·0	÷	0·9608	÷	0·9608	÷
A =	0·161757772	A◊	0·168357381	A◊	0·169749064	A◊
S1 ——	0·02222	S	0·02222	S	0·02222	S
A+Tracer=	0·183977772	A◊	0·190577381	A◊	0·191969064	A◊
$(\%86)_m$ =	0·088446264	E◊	0·088446264	E◊	0·088005702	E◊
$(86)_s$ =	0·015458946	A◊	0·016042657	A◊	0·016081172	A◊
$(\%84)_m$ =	0·101359418	A◊	0·101359418	A◊	0·100106486	A◊
$(84)_s$ =	0·000343879	A◊	0·001012812	A◊	0·000913348	A◊
$(\%87)_m$ =	0·095990730	A◊	0·095990730	A◊	0·095873411	A◊
S2 ——	0·0003444	S	0·0003444	S	0·0003444	S
$(87)_s$ =	0·017315760	A◊	0·017949261	A◊	0·018060328	A◊
$(\%88)_m$ =	0·714203581	A◊	0·714203581	A◊	0·716014391	A◊
S3 ——	0·002758	S	0·002758	S	0·002758	S
$(88)_s$ =	0·128639583	A◊	0·133353047	A◊	0·134694612	A◊

The first output yields:

$(88/86)_s = 8.3214$

$(87/86)_s = 1.1201$

$(84/86)_s = 0.0222$

From equation (4): $\alpha_1 = 0.9608$

Using the revised value of α the second calculation is performed

with the same input data, to obtain : $(88/86)_s = 8.3124$

$(87/86)_s = 1.1188$

$(84/86)_s = 0.0631$

Second estimate of α : $\alpha_2 = 0.9609$

This is not significantly different from α_1, and so the iteration is

stopped here. $(87/86)_s$ has been decreased by 0.12%, $(84/86)_s$ has

been increased by a factor of 3, due to the use of α. This brings

$(84/86)_s$ much closer to the desired value of 0.0568.

The fractionation correction, $B = +0.0075$, can now be calculated

(see page 16), together with the new values for the isotopic ratios

in the mixture. The third output shown above gives the results

after the fractionation correction has been made.

$(88 / 86)_s = 8.376$

$(87 / 86)_s = 1.1231$

$(84 / 86)_s = 0.0568$

$(88/ 86)_s = $ is sufficiently close to 8.375 so that the program

can be stopped here. $(84/86)_s$ agrees very well with the desired

value. In general, the final $(84/86)_s$ values fell within the range

$0.0569 \pm .0001$.