

THE DISTRIBUTION OF RUBIDIUM  
IN  
CERTAIN IRON FORMATIONS

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CERTAIN IRON FORMATIONS

BY

MATI RAUDSEPP

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This study was proposed by Professor D.M. Shaw and was completed under his able guidance. His sage counsel was well appreciated. F.G. Alcock rendered valuable assistance with the spectrographic analyses and is responsible for some of the data where indicated. The author's samples were collected during his period of employment with the Ontario Department of Mines in the summer of 1970. Time for this was kindly provided by Dr. L.D. Ayres of the Geological Branch. Data for seven of the samples were due to D. Goodale, who was concurrently engaged in a similar study of lithium on the same samples. These additional samples broadened the scope of this work considerably.

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## INTRODUCTION

The determination of the trace alkali metal, rubidium, has always been of importance geochemically. Data concerning its abundance relative to other elements in the earth's crust have relevance to problems concerning fractionation in the earth's crust. In this study, the distribution of rubidium in certain iron formations from the Superior and Churchill Provinces of the Canadian shield was studied. An attempt was made to determine the site and history of this element in these rocks by examining its abundance and behaviour relative to other elements and by inference from known geological processes.

## SAMPLES

### Location

Seven Archean iron formations were sampled by the author in the Superior province of Northwestern Ontario. Their locations are shown in Figure 1. An additional seven samples were collected by D. Goodale from the Melville Peninsula. Locational and geological data pertaining to these samples appear in Figure 2.

Each of the author's samples was collected from a different iron formation, well within the boundaries of its respective metasedimentary-metavolcanic "greenstone" belt. The samples were, therefore, well insulated from the surrounding granitic rocks and should not have experienced extensive contact phenomena. Sample MR-I-1 is from the contact aureole of a gabbro.

The Melville samples, however, have likely experienced effects due to the proximity of the granitic contact and migmatite unit as shown in Figure 2. Possible effects of the above environments are discussed in later sections.

### Petrography

Due to the extremely fine grain size of the samples (0.05-1.0 mm), petrographic work was difficult and was not done



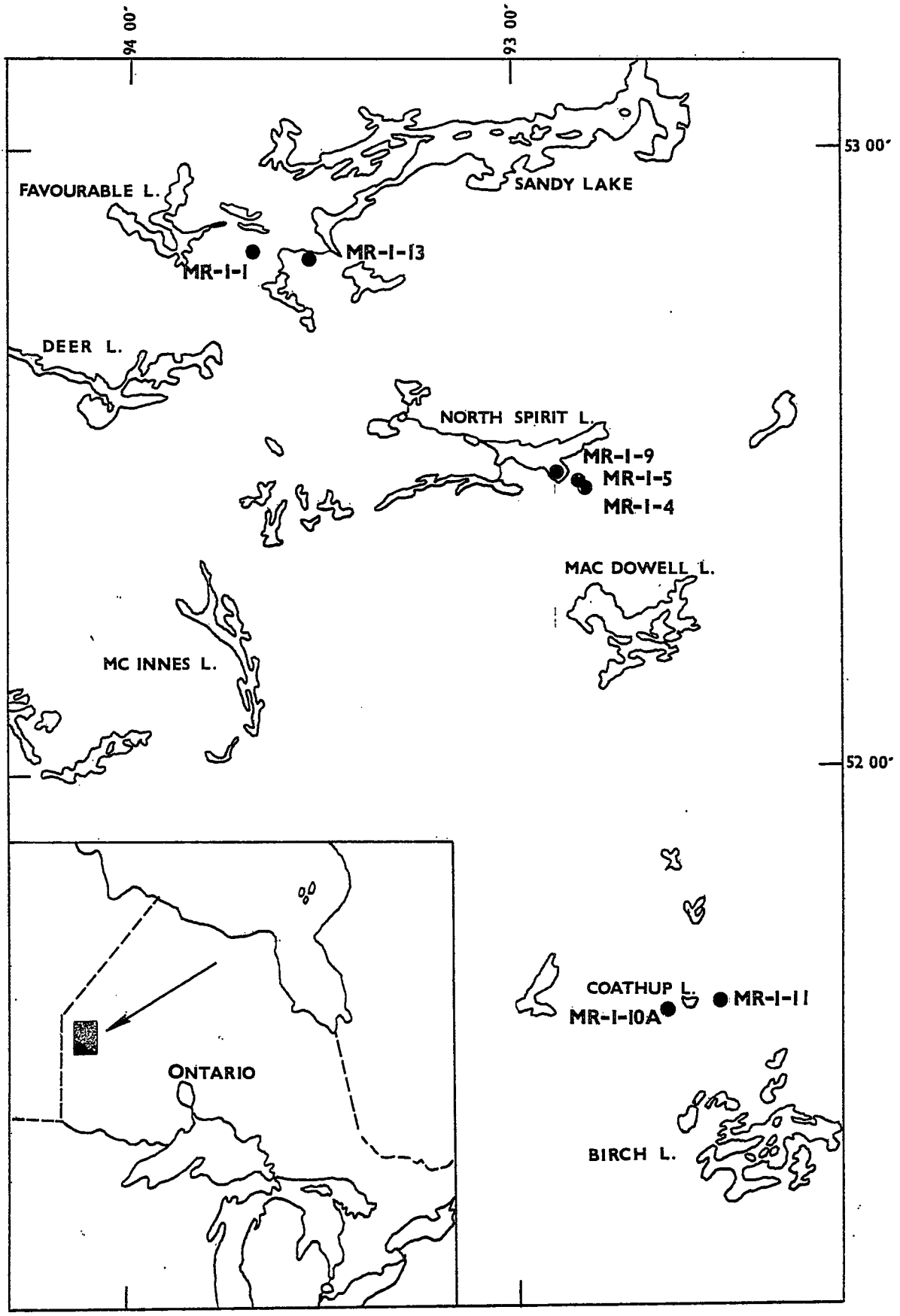


FIG. 1. SAMPLE LOCATIONS. M. RAUDSEPP, 1 INCH TO 16 MILES.

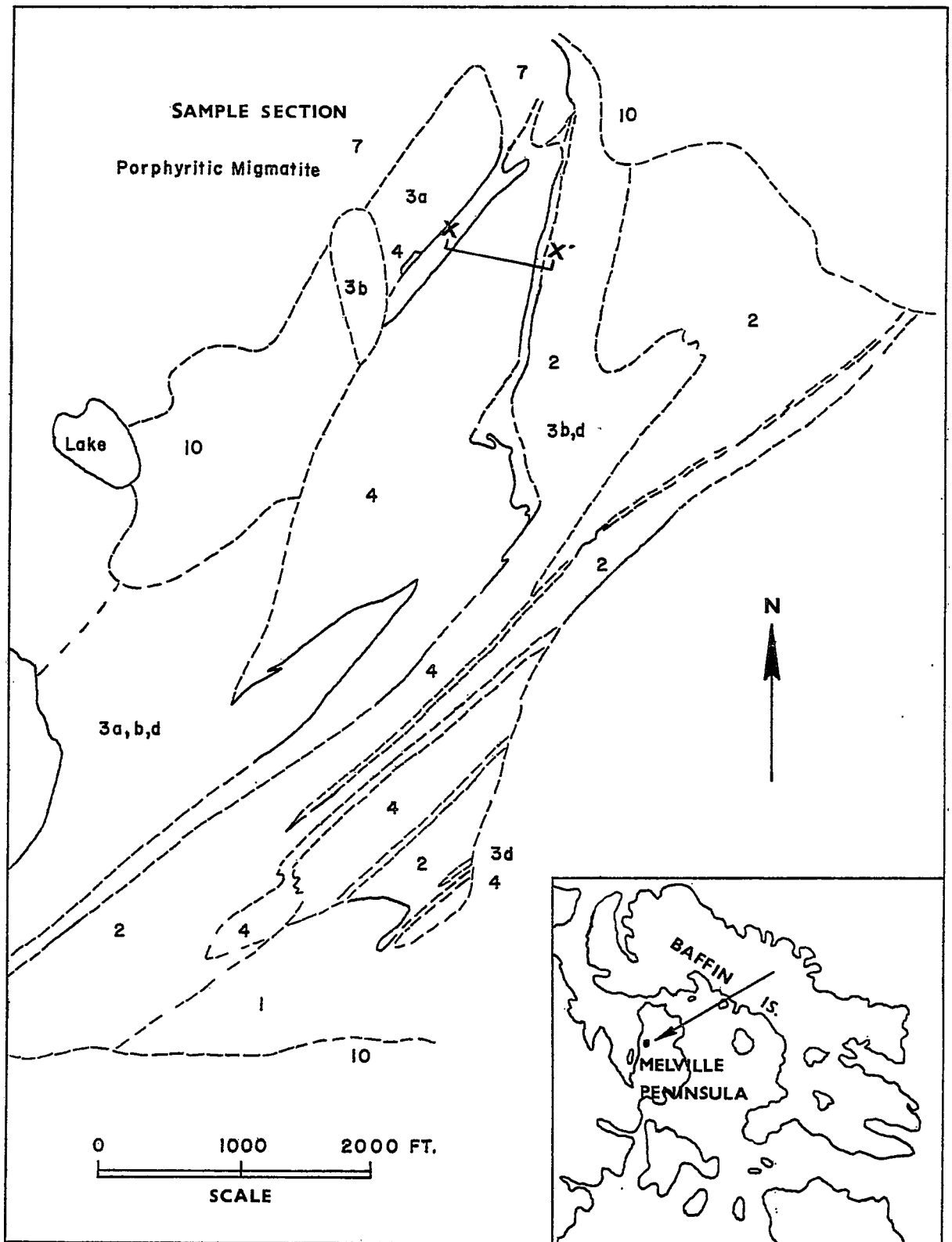
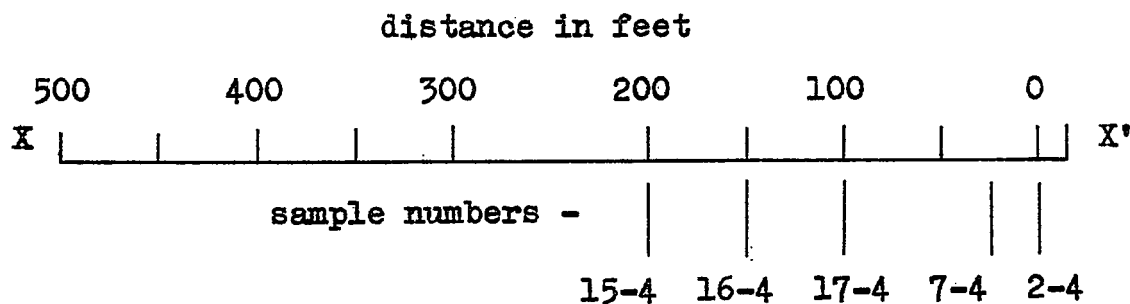


FIG. 2. SAMPLE LOCATIONS, BOREALIS 4 IRON FORMATION, D. GOODALE.

## LEGEND FIGURE 2

10	Glacial Drift
9	Diabase, primarily dikes
8	a Basal quartzite, includes pebble conglomerate, magnetite and hematite lenses b Quartzite or felspathic quartzite
UNCONFORMITY	
7	Intrusive granite, migmatite
6	Peridotite, serpentized peridotite, talc lenses
5	Metagabbro
4	Iron formation
3	Metasediments a Quartzite b Quartz-biotite schist d Garnet-biotite schist
2	Greenstone and/or amphibolite
1	Granite gneiss, granitic migmatite

## SAMPLE LOCATIONS ALONG SECTION X—X'



extensively. The samples may be considered as essentially three-phase rocks: chert (microcrystalline quartz), magnetite and silicates. X-ray diffraction studies demonstrated that the silicate fraction is primarily amphibole of the cummingtonite - grunerite series. Very minor amounts of calcite and sphene were observed in some of the specimens. The rocks are characteristically well-banded and are extremely contorted and folded on the outcrop scale. Banding is of the order of one to ten millimeters. According to Gross (1965), the rocks are Algoma type iron formation. Modal analyses are given in Table 4.

#### Preparation

Since this type of iron formation is quite susceptible to weathering, the samples were chosen carefully from fresh rock. Any remaining weathered material was removed before crushing. One quarter inch slabs were cut across laminations in the hand specimens and crushed to 2-5 mm pieces in a Bico-Braun jaw crusher, or in a steel mortar and pestle. A suitable portion was separated by quartering and reduced to less than one hundred mesh in a Spex Shatterbox. This sample was further quartered to yield approximately one hundred grams for spectrographic analysis and the remainder for chemical analysis. Thin sections were made for all samples. Figure 3 summarizes the sample preparation method.

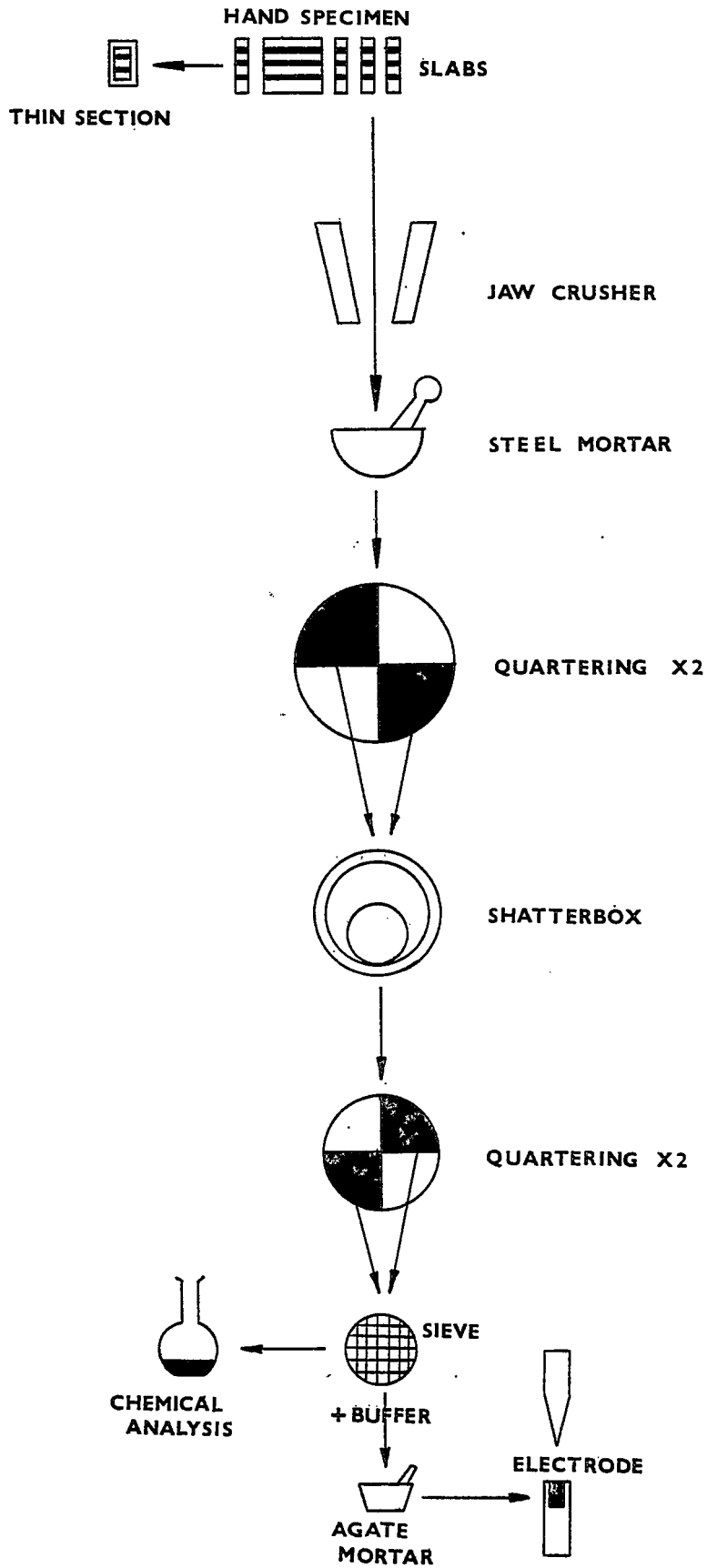


FIG. 3 SAMPLE PREPARATION

## SPECTROGRAPHIC METHOD

The spectrographic method employed was one modified by F.G. Alcock from the method of Gurney and Erlank (1966). Each sample was mixed with a buffer and double exposures were taken. The buffer was prepared from Specpure NaCl and CaF<sub>2</sub> in the ratio 1 to 2. Using a precision torsion balance, the buffer was mixed with the sample in the ratio 3 to 7, giving a total of 116 mg of mixture for arcing. This mixture was mixed with acetone and ground in an agate mortar. Two type 1671 electrodes were packed with the mixed and ground material and dried in an oven at 110°C before arcing. The electrodes were stored in a dessicator prior to arcing. Instead of using an internal standard, a standard sample was arced adjacent to each sample on the plate. This standard sample was prepared from appropriate proportions of Specpure SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and Spex Mix to yield reference Rb concentrations of 0.5, 2.5, 5.0, 10.0 and 25.0 ppm.

To allow for variations in plate emulsion, the position of each spectrum on the photographic plates was staggered as shown in Figure 4. Thus each sample analysis was repeated three times. This scheme was followed exactly for samples MR-I-1, MR-I-4 and MR-I-5. A slightly modified scheme was used for samples MR-I-9, MR-I-10A, MR-I-11 and MR-I-13, each sample analysis being repeated six times. A summary of arcing conditions

is given in Table 1.

<u>Plate 1</u>	<u>Plate 2</u>	<u>Plate 3</u>
Sample X	5.0 ppm std.	Sample Y
0.5 ppm std.	Sample Z	0.5 ppm std.
Sample Y	10.0 ppm std.	Sample X
2.5 ppm std.	Sample X	10.0 ppm std.
Sample Z	2.5 ppm std.	25.0 ppm std.
5.0 ppm std.	Sample Y	Sample Z

Figure 4. Representative analysis scheme

A three-step method calibration was used to give a working curve of log (intensity) versus concentration. This curve was found to correspond favourably with F.G. Alcock's working curve. The latter curve was used since it was based on a least squares fit of considerably more analyses of similar rocks. It was shifted parallel to itself to correspond to various arcing conditions during each run.

Table 1. ARCING CONDITIONS

---

Spectrograph	JACO 3.4-meter concave grating spectrograph. Dispersion 5.2 Å/mm
Filter	Yellow
Wavelength	6100 to 8600 Å
Source	JACO Varisource
Source parameters	
Power	Uni-arc 2, high range full wave rectification
Current	9.5 amperes
Slit	30 microns
Plate	Kodak 1-N plate, backed
Electrodes	Anode: Ultra Carbon Corp. type 1671 Cathode: Ultra Carbon Corp. type U45-2
No. of superimposings	Two
Sectoring	Seven step with 0.2 ratio
Buffer	NaCl:CaF <sub>2</sub> = 1:2, Buffer: sample=3:7
Analysis lines	Rb 7800, 7947 Å
Developer	Kodak D-19 (4 min.)
Fixer	Kodak Rapidfixer (3 min.)
Calibration	Three step method
Exposure	60 sec./superimposing
Analytical gap	4.5 mm

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### Leaching experiment

Although these rocks are predominantly non-detrital, that is they were deposited from solution, the possibility of a significant detrital phase exists. In thin section, a brown amorphous material is present interstitially which may represent this detrital portion and presumably contains Rb that is not tightly held in crystal lattices. In order to explore this possibility, samples MR-I-9, DG-15-4 and DG-16-4 were leached in 25 percent (by volume) acetic acid for 24 hours by F.G. Alcock and analysed spectrographically in the same way as the other samples. The results are listed in Table 5.

### Magnetite separation

Magnetite was mechanically separated from sample MR-I-9 by F.G. Alcock and analysed for Rb. The result is listed in Table 6 along with the total Rb contribution of magnetite to the sample.

### U.S. Geological Survey standard - W-1

The U.S.G.S. standard rock, W-1 (diabase), was analysed for Rb using the same method to check the reliability of the other analyses. A value of 40 ppm was obtained. The accepted value is 22 ppm (Fleischer, 1969). The observed discrepancy is due to the effects of an iron-rich matrix during the arcing of predominantly silicate material. A correction factor of 0.68 was determined by F.G. Alcock using a silicate analysis

Table 2. Spectrographic Results - Analysis line  
Rb 7800 Å  
(Rb concentrations in ppm)

Sample No.	Concentration Rb	Range	Concentration K (ppm)	K/Rb
MR-I-1	2.1	1.5-3.0	572	273
MR-I-4	0.40	0.38-0.68	124	311
MR-I-5	0.55	0.22-1.1	83	151
MR-I-9	12	8.2-16	979	82
MR-I-10A	2.1	1.7-2.5	232	111
MR-I-11	too low	-	33	-
MR-I-13	too low	-	33	-
DG-2-4	0.64	n.a.	166	259
DG-7-4	9.0	n.a.	498	55
DG-15-4	29	n.a.	581	20
DG-16-4	55	n.a.	2490	45
DG-17-4	too high	-	3901	-
DG-3-2	14	n.a.	249	18
DG-9-2	too high	-	-	-
W-1	40	0*		

\* two analyses of W-1 gave 40 ppm for both

n.a. - not available

Table 3. CHEMICAL ANALYSES

	MR-I-1	MR-I-4	MR-I-5	MR-I-9	MR-I-10A	MR-I-11	MR-I-13
SiO <sub>2</sub>	45.19	35.27	44.78	46.17	35.54	53.25	42.82
TiO <sub>2</sub>	0.03	0.0	0.01	0.03	0.05	0.01	0.01
Al <sub>2</sub> O <sub>3</sub>	1.07	1.00	0.75	1.32	1.47	0.64	0.55
Fe <sub>2</sub> O <sub>3</sub>	18.17	32.54	29.41	18.92	38.82	23.24	23.98
FeO	22.22	25.21	19.19	26.80	21.43	18.51	23.33
MnO	0.35	0.36	0.48	0.07	0.05	0.02	0.80
MgO	2.81	4.73	3.73	4.33	2.21	2.12	4.15
CaO	5.06	0.93	1.34	0.48	0.97	1.99	3.29
Na <sub>2</sub> O	0.006	0.005	0.005	0.017	0.039	0.012	0.008
K <sub>2</sub> O	0.069	0.015	0.010	0.118	0.028	0.004	0.004
P <sub>2</sub> O <sub>5</sub>	0.11	0.45	0.30	0.29	0.08	0.10	0.21
CO <sub>2</sub>	4.37	0.00	0.00	0.07	0.00	0.00	0.00
Rb <sub>2</sub> O	n.d.	n.d.	n.d.	0.0012	n.d.	n.d.	n.d.
C				0.90			
TOTAL	99.46	100.51	100.01	99.52	100.68	99.90	99.55
Fe as Fe <sub>2</sub> O <sub>3</sub>	42.87	60.56	50.74	48.71	62.64	43.81	50.35

Table 3. continued.

	DG-2-4	DG-7-4	DG-15-4	DG-16-4	DG-17-4	DG-3-2	DG-9-2
SiO <sub>2</sub>	46.70	71.09	48.12	59.78	6.61	41.27	38.47
TiO <sub>2</sub>	0.03	0.03	0.02	0.04	0.03	0.01	0.01
Al <sub>2</sub> O <sub>3</sub>	2.20	1.33	1.25	1.91	1.99	1.11	1.18
Fe <sub>2</sub> O <sub>3</sub>	31.61	17.81	34.16	26.01	60.13	57.27	57.50
FeO	16.56	9.22	15.13	11.87	27.75	18.67	1.02
MnO	0.14	0.12	0.05	0.08	0.06	0.02	0.0
MgO	1.52	0.85	0.60	0.83	1.45	0.90	0.13
CaO	2.03	0.08	0.92	0.07	0.44	1.48	0.12
Na <sub>2</sub> O	0.10	0.01	0.0	0.01	0.01	0.04	0.0
K <sub>2</sub> O	0.02	0.06	0.07	0.30	0.47	0.03	0.0
Total	100.92	100.60	100.32	100.90	99.04	99.80	98.43
Fe as Fe <sub>2</sub> O <sub>3</sub>	50.03	28.06	50.98	39.20	90.97	58.02	58.63

Table 4. MODAL COMPOSITION  
(volume percent)

Sample	Magnetite	Quartz	Silicates
MR-I-1	50	31	19
MR-I-4	58	10	32
MR-I-5	44	27	27
MR-I-9	37	25	38
MR-I-10A	55	15	30
MR-I-11	37	34	29
MR-I-13	32	26	42
DG-2-4	-	-	-
DG-7-4	30	66	4
DG-15-4	44	54	2
DG-16-4	31	64	5
DG-17-4	68	7	25
DG-3-2	-	-	-
DG-9-2	-	-	-

working curve. The Rb concentration of W-1 is, therefore, 27 ppm, as determined by this analysis.

Table 5. Leaching results  
(after Alcock)

Sample	Rb (ppm) before leaching	Rb (ppm) after leaching	Rb (ppm) detrital
MR-I-9	16	7.3	8.7 (54.5%)
DG-16-4	58	45	13 (22.5%)
DG-15-4	17	7.7	9.3 (54.7%)

Table 6. Rb abundance in magnetite  
(after Alcock)

Sample	Rb (ppm)	Volume Percent in sample	Rb (ppm) contribution in sample by magnetite
MR-I-9	17	37	6.3 (39.4%)

## RESULTS

### Spectrographic analysis

The abundance of Rb was determined from the analysis line Rb 7800Å. The other Rb line did not yield satisfactory results due to greatly varying intensity. The log (intensity) values for each sample were averaged and the corresponding concentration of Rb was determined from the working curve. Table 2 lists the results. The comments "too low/high" in this table indicate that the Rb line was either too weak or too intense to measure respectively. "Range" of Rb concentration indicates the value determined from the lowest log (intensity) and the value determined from the highest log (intensity) for the replicate analyses of each sample.

### Chemical analysis

The samples were analysed for major element oxides by J. Muysson. These data appear in Table 3. Complete analysis of the author's samples was not available at the time of this writing (April, 1971).

## DISCUSSION

Abundance of Rubidium

Rb concentrations determined in this study fall in the range 0.40 to 55 ppm, with two values above this range and two values below (Table 2). In general, the Rb content of the author's samples (Northwestern Ontario) is lower than the Rb content of the Borealis 4 iron formation (Melville Peninsula). Table 7 lists the Rb content of several rock types. It is evident that the values from this study correspond with the values for sedimentary rocks, especially the siliceous and chemical sediments. The author's results compare favourably with those of Fryer (1970), while the Melville values are generally much higher. The observed split in Rb concentrations between the two groups suggests different controls of Rb concentration.

Since quartz is not receptive to Rb, the latter may reside in the silicate fraction, in the magnetite or in interstitial detritus. Leaching experiments indicated that 22.5 to 54.7 percent of the Rb content was contained in a presumably detrital fraction (Table 5). This value may be too low, however, since some of this material may have been made inaccessible by being trapped between quartz crystals during recrystallisation of the original chert. One analysis demonstrated that 39.4



percent of the Rb was contained in magnetite (Table 6). For sample MR-I-9, therefore, the Rb distribution was as follows: magnetite 39.4 percent, detritus 54.5 percent, silicates 6.1 percent. Since this distribution is based on one exploratory analysis, the values are not absolutely definitive and serve only to demonstrate that the Rb distribution in these rocks is complex and its interpretation is largely beyond the scope of this work. Some speculations, however, may be forwarded.

Figure 4 illustrates the dependence of Rb concentration on K concentration. Since the slope is not unity, the K/Rb ratio varies with absolute concentration. The data exhibit considerable scatter but the increase of Rb with K is evident. This lends support to the supposition that a portion of the Rb is bound in crystal lattices replacing K, presumably in silicates. Inspection of the modal data in Table 4 with respect to Rb concentration does not reveal any strong trends with the possible exception of quartz (Figure 6). As the volume percent of quartz in the rocks increases, the concentration of Rb increases. This may be due to increasing quartz producing increased grain surface area and increased interstitial space providing additional volume for detrital and/or adsorbed material containing Rb.

Examination of variation in chemistry across the Borealis iron formation from east to west does not reveal any meaningful information, other than the correlation between Rb and K established in Figure 4. This is either due to the small number of samples or to the disturbing influence of the granite

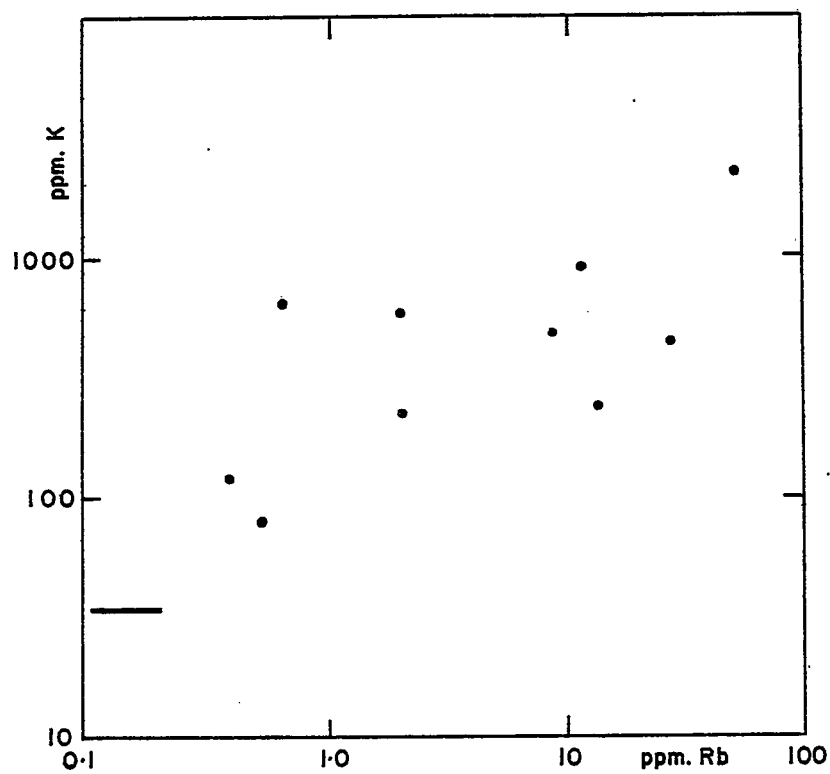


FIG. 4. K-Rb RELATIONSHIP.

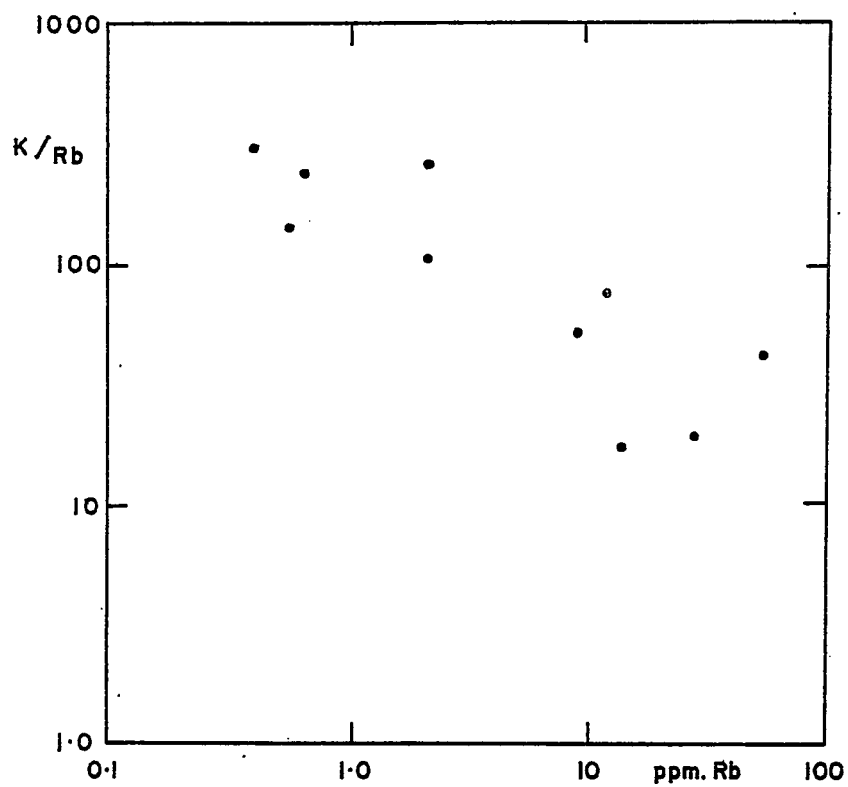


FIG. 5. K/Rb - Rb RELATIONSHIP.

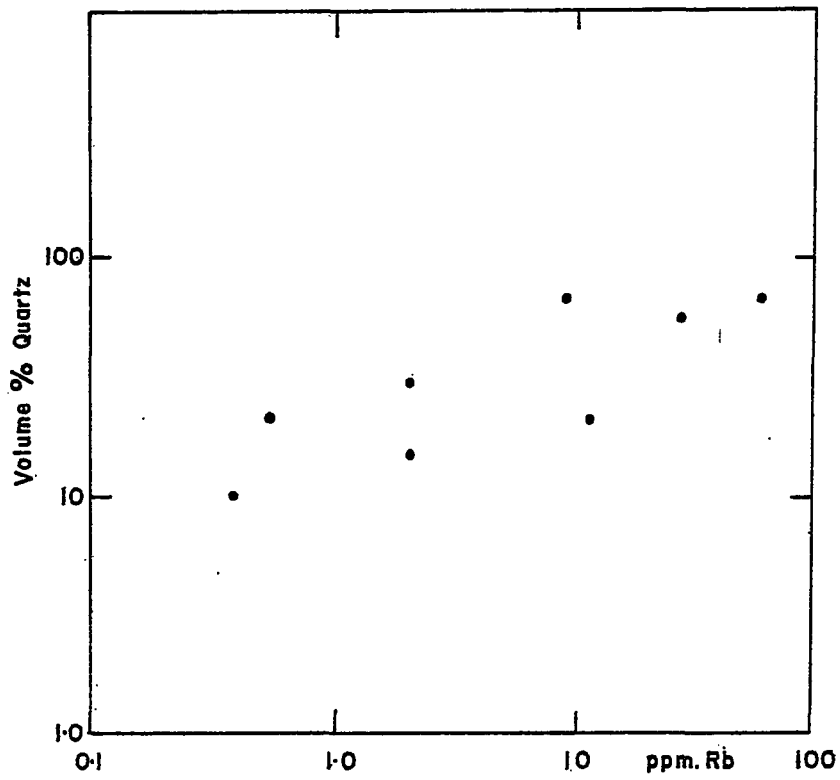


FIG. 6. QUARTZ - Rb RELATIONSHIP.

Table 7. Rb content (ppm) and K/Rb ratios  
of common rocks  
(Heier and Billings, 1970)

Rock type	Rb (ppm)	K/Rb
Granite	190-196	200-210
Gabbro and basalt	32	200-600
Olivine basalt	18	
Alkali basalt	30	
Eclogite	6.9	100-700
Dolomite	45	
Silty limestone	75	
Sand and sandstone	46	200
Shale	164	
Argillaceous sediments	128	110-150
Soil	140	
Iron formation (Fryer, 1970)	0.11-5.08	
Crustal average	11-65	160-300

intrusion which truncates the northeastern end of the formation.

### K/Rb Ratios

K/Rb ratios for these rocks are listed in Table 2. They range from 18 to 311. As for the absolute concentration of Rb, the ratios are split between the two sets of samples. In the Borealis 4 iron formation, the ratios are extremely low with one exception, while in the author's samples the ratios are consistent with siliceous sedimentary rocks, with one exception (Table 7). Absolute concentration of Rb is plotted against K/Rb ratios in Figure 5. The ratio, in general, decreases with increasing Rb, the K content of the rocks remaining relatively constant. It is evident that the Melville iron formation has undergone processes which are not consistent with Rb controlling processes in normal siliceous sedimentary rocks, while the history of the element in the author's samples appears to be relatively normal.

### Precision of Results

The standard deviation for 14 samples and W-1 was 0.145 for the log (intensity) values. Choosing an arbitrary concentration of 100 ppm and converting to parts per million, the value above, gave coefficients of variation of 20 percent and 14 percent for samples with 3 replications and 6 replications respectively. Values for W-1 were identical to two decimal places for both analyses.

## CONCLUSIONS

1. There are several likely sites for Rb in these iron formations:
  - a. replacing K in silicate crystal lattices;
  - b. unknown site in magnetite, but in the lattice since not affected by leaching;
  - c. interstitially, either in detritus or adsorbed.
2. The history of the element in the author's samples is relatively consistent with known sedimentary processes and the data compares favourably with previously published data.
3. The history of the element in the Melville iron formation is anomalous, and no known process could be invoked to explain its behaviour. It is likely that extensive contact phenomena and subsequent metasomatism have affected the partitioning of Rb in the formation.
4. The site and history of Rb in this type of rock is complex; it is found in all phases except crystalline quartz. It is therefore proposed that whole rock analysis is inadequate to elucidate the behaviour of Rb in iron formations.
5. The precision of the spectrographic method outlined in this work is good. The reproducibility of the results is excellent in most cases.

## SUGGESTIONS FOR FURTHER WORK

Perhaps one of the most significant achievements of this work has been to realize some basic inadequacies in the procedure. Several suggestions are proposed to future workers:

1. In spite of difficulties induced by the extreme fine grain of the rocks in question, a serious attempt should be made to separate the various mineral phases into three groups: magnetite, chert and silicates. Before separation by either magnetic or specific gravity methods, the minerals may be separated approximately by sawing out the appropriate laminae from the hand specimen. This separation will enable the worker to have a better understanding of where the Rb is in the sample. Chemical analysis of the separated phases is also recommended. As a result, four phases will be available for analysis: whole rock, magnetite, chert and silicate.

2. Each of the above fractions should be leached to remove detrital and adsorbed Rb, and the results compared with the non-leached portion.

3. Samples should be acquired from surrounding rock units, otherwise it is not known whether the data obtained is unique. This is especially critical for samples acquired from intrusive

environments. Data from the other samples will, in addition, enable the study of the history of the Rb through its relative abundance.

4. The detailed geological environment each sample is critical to an understanding of the history of the element.

5. Once the above data has been realized and the worker has a fair idea of where the Rb is, that particular fraction may be easily studied further.



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