SOME GEOCHEMICAL ASPECTS
OF
PRECAMBRIAN IRON FORMATION

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By

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SCOPE AND CONTENTS:

Rock samples of "Algoma-type" iron formation and associated Archean volcanics were collected from the Kirkland-Larder Lakes area of Ontario.

Whole rock chemical compositions were determined in the chemical laboratory. Two groups of minor elements were analyzed by spectrochemical methods - (1) the abundances and distribution of the rare alkalis (Li, Rb and Cs) were determined in the whole rock whereas, (2) the same elements plus the trace ferrides, Ga, Cu, Al and Mg were analyzed in some purified magnetite fractions. To compare the geochemistry of iron formation in the Precambrian, data were also used from occurrences in Northwestern Ontario, Melville Peninsula and the iron ores of Sweden. The K/Rb, K/Cs and K/Na ratios were used to study facies relationships and modes of formation. The range of trace elements in the magnetites resembles those of volcanic-sedimentary iron deposits of the world.

Volcanic emanations and the physico-chemical conditions of the depositional environment were of prime importance in the development of the iron formation at Kirkland Lake.

ABSTRACT

Spectrochemical analyses of rock samples of iron formation from the Archean of Ontario and Melville Peninsula reveal the generally low abundances of (1) the alkali metals (Li, Rb, Cs) in the whole rock; (2) the trace ferrides, Ga, Cu, Al and Mg in the magnetite fractions.

In the oxide facies of iron formation there is a slight enrichment of Rb and a significant enrichment of Cs, with respect to K. Much of the Rb and Cs is trapped or adsorbed in the magnetite fraction. Lithium is concentrated in the silicate and clay fractions of the iron formation giving a positive correlation between Li and Al, reflecting the variation in physico-chemical conditions of deposition. Correlation of K/Na ratio with stratigraphic height agrees with the development of iron formation, in the Kirkland Lake area, as a late stage of an Archean volcanic cycle.

The trace ferrides (Ti, V, Cr, Mn, Co, Ni) and Ga, Cu, Al and Mg are extremely depleted in the magnetite fraction, their ranges of abundances resembling those of volcanic-sedimentary iron deposits.

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M. Raudsepp and D. Goodale are responsible for some of the data where indicated.

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CHAPTER 1

INTRODUCTION

Layered ferruginous rocks are present throughout the geologic column, but the origin and depositional chemistry of the banded iron formations of the Precambrian have captured the interest of geologists for decades; their studies and diverse opinions are well documented in the literature.

In his classical paper on sedimentary facies of iron formation, James defined "iron formation" as follows:

> ".... a chemical sediment, typically thin bedded or laminated, containing 15 per cent or more iron of sedimentary origin, commonly but not necessarily containing layers of chert ... the term is extended to include rock that normally would not be called iron formation, such as graphitic slate, because of facies relationships to more typical varieties of iron formation." (H.L. James, 1954; pp.239-240).

The purpose of this thesis is to study the geochemistry of selected groups of minor elements in "Algoma type" iron formations of the Canadian Precambrian Shield. Goodale (1971), Raudsepp (1971) have briefly described the mineralogy, major element geochemistry, and lithium and rubidium distribution within sequences of "Algoma type" iron formations from Melville Peninsula and N.W. Ontario, respectively. Much of this thesis concerns the major and minor element geochemistry of the iron formations in the Kirkland-Larder Lake area of Northern Ontario, supplemented by analytical data from other Canadian and world iron formations (Goodale, 1971; Raudsepp, 1971; Landergren, 1948; Freitsch, 1970).

Iron formations are ubiquitous, but often minor members, of the various fold belts of the Canadian Shield. Although not always recognized as iron formation, the various facies are commonly associated with mineralized zones in metavolcanic sequences. Their use as marker beds, for correlation purposes in areas with complex structural and stratigraphic relationships is generally of great economic importance.

The more recent concepts of the tectonic and stratigraphic framework for the Kirkland-Larder Lake area have led to a better understanding of the position of the Boston iron formation and its correlatives in the early Precambrian (Ridler, 1969). In addition, the association of localized potash-rich volcanic tuffs with the iron formation have raised the following points of question:

1. What is the distribution of the alkalis (K, Na, Rb, Li, Cs) in the iron formation and its correlatives?
2. Can the alkali metal abundances and their ratios (K/Rb,

K/Cs, K/Na) in the iron formation, be used for genetical considerations?

3. Iron formations occur at various stratigraphic positions in the Archean. The Boston iron formation occurs intercalated with volcanic tuffs and pyroclastics. Does iron formation then develop as a closing stage of a highly differentiated volcanic cycle?

Samples were collected by the author in the summer of 1970, from a detailed cross-section of the oxide facies of iron formation at the Adams Mine near Kirkland Lake, and from the other sedimentary facies and associated rocks in the surrounding area. These samples and their magnetite fractions were subjected to spectrographic analysis to determine trace element contents. The alkali metals were determined in the whole rock and ferride elements were determined in the magnetite fractions. As well, the bulk chemistry of the various facies and associated rocks was determined by classical wet chemical and atomic absorption methods in the analytical laboratory under the expertise of John Muysson.

The minor element content of banded iron formations occurring in Canada, and elsewhere in the world, have not been studied in great detail, with the exception of Landergren's excellent work on the geochemistry of Swedish iron ores (Landergren, 1948) and a geochemical project presently being carried out on Canadian iron formations by G.A. Gross of the Geological Survey in Ottawa (personal communication, 1970). As concerns the study undertaken in this thesis, careful consideration was given to the study of two groups of minor elements rather than try to extend the study over several groups of elements.

In addition to the geochemical study of the iron formations and correlatives in the Kirkland-Larder Lake area, samples of trachytes, syenites and basic volcanics also collected, were analyzed for major elements and trace alkali elements, to assess the criteria for the strong fractionation in the igneous rocks of the area (e.g. low K/Rb, K/Cs ratios, etc.).

The data presented will be finally discussed in light of the possible origin of the iron formations, and the results have implications which will be qualitatively consistent with the recently proposed ideas on the volcanic-metallogenic model (Ridler, 1970).

A. Sample Locations

The samples were collected from three main areas: first, and most important in terms of detailed study was the Boston iron formation of Kirkland-Larder Lake area; secondly, samples from Melville Peninsula, District of Franklin, N.W.T. (collected by D. Goodale); finally, seven samples obtained from individual iron formation members within the Setting Net-North Spirit-Birch Lake metavolcanic sequences of Northwestern Ontario (collected by M. Raudsepp). The general geology and sample locations from N.W. Ontario and Melville Peninsula iron formations are shown in

Figure 1, 2A and 2B, respectively. The sample locations and general geology for the Kirkland-Larder Lake area are presented in Figure 3 (inside back cover), a generalized geological map modified from Hewitt (1963), Cooke and Moorehouse (1969) and Ridler (1969).

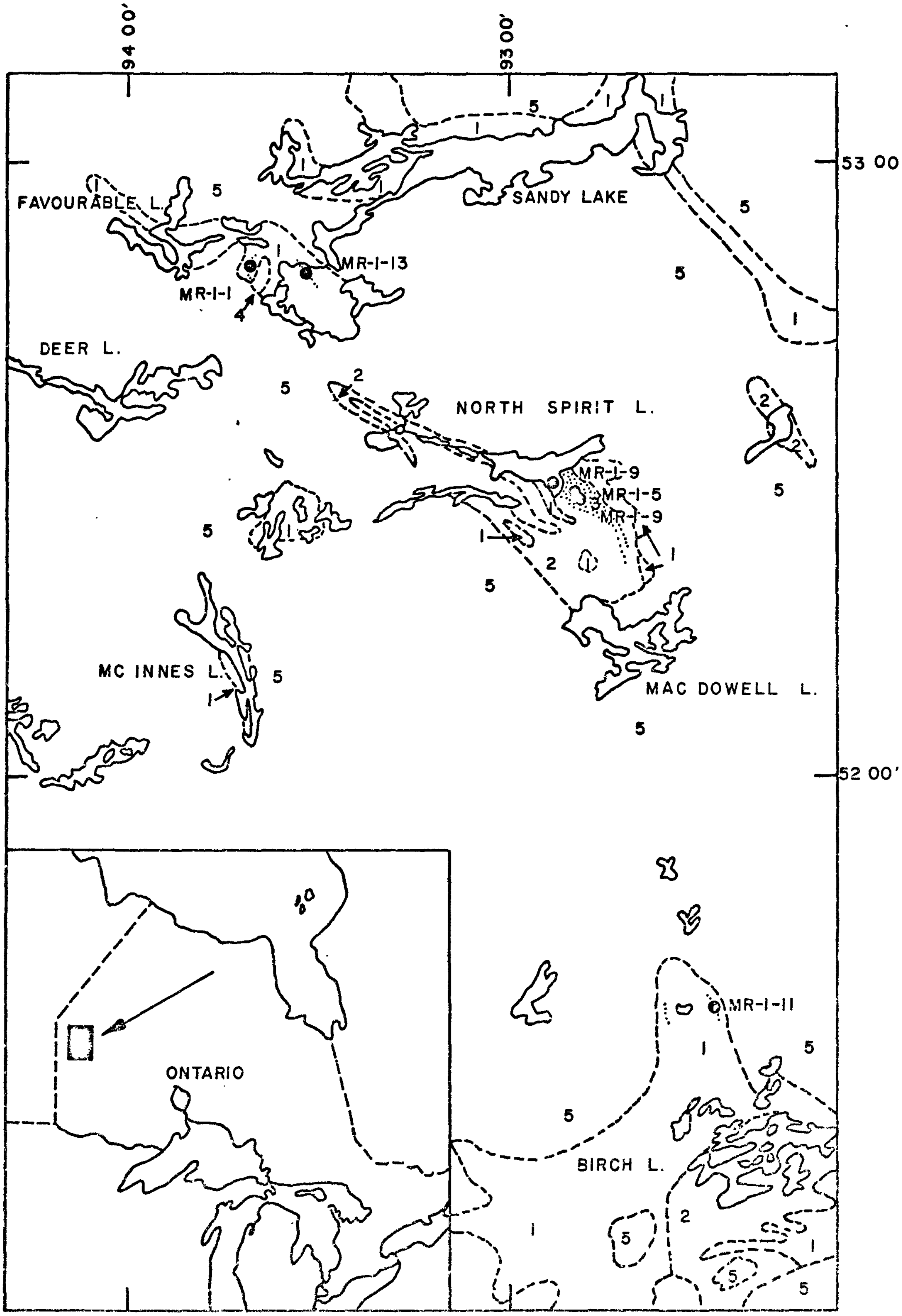


FIGURE I. N.W. ONTARIO IRON FORMATIONS, SAMPLE LOCATIONS - M. RAUDSEPP. (Legend follows)

LEGEND FIGURE 1

PRECAMBRIAN

5 - Massive leucocratic granite, syenite, quartz diorite

4 - Gabbro, diorite

3 - Iron formation, interbedded with 1 and 2

2 - Sedimentary rocks; derived schists and gneisses

1 - Volcanic rocks, amphibolite

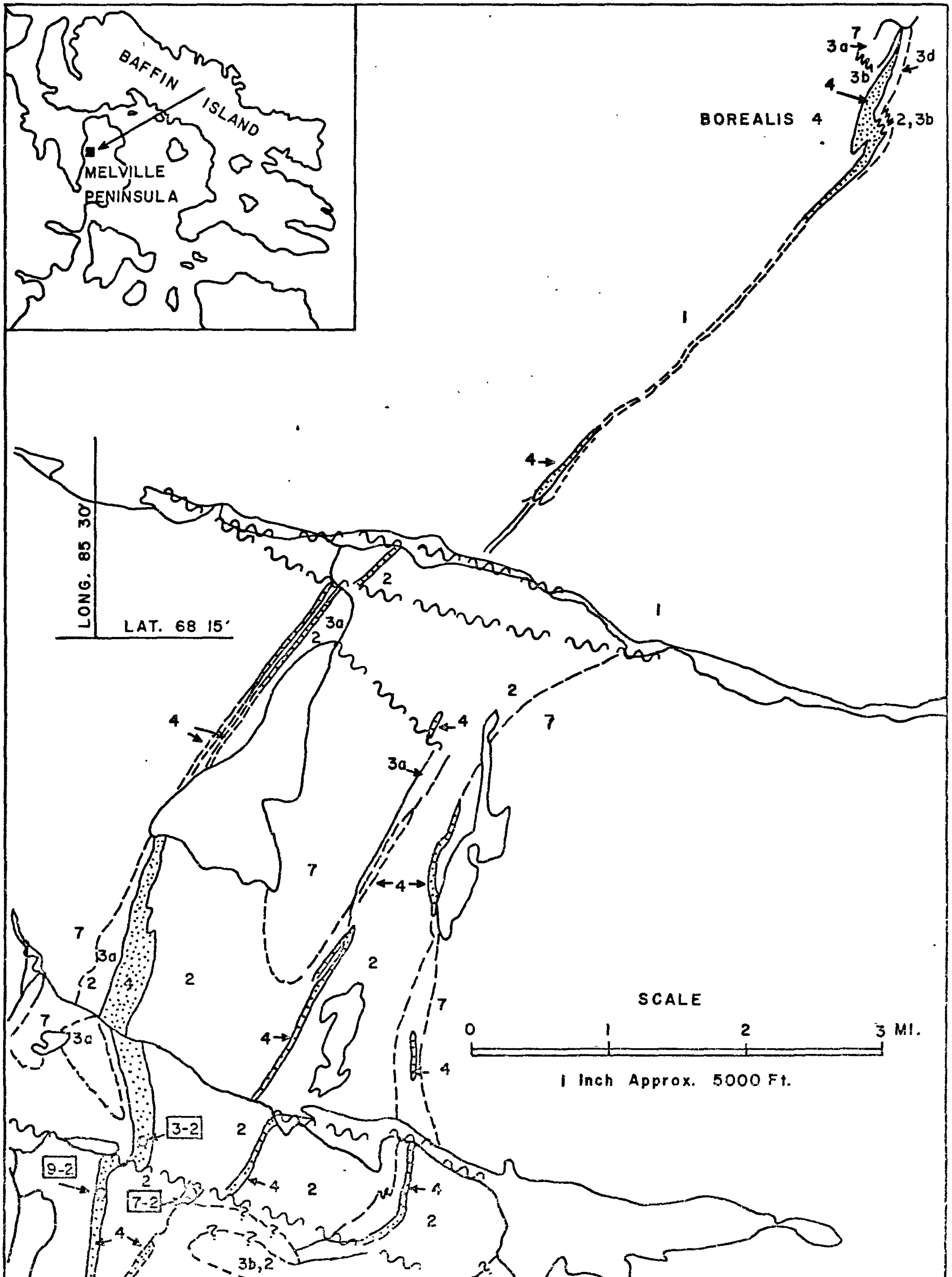


FIGURE 2A. MELVILLE IRON FORMATION, SAMPLE LOCATIONS-D. GOODALE
(Legend follows)

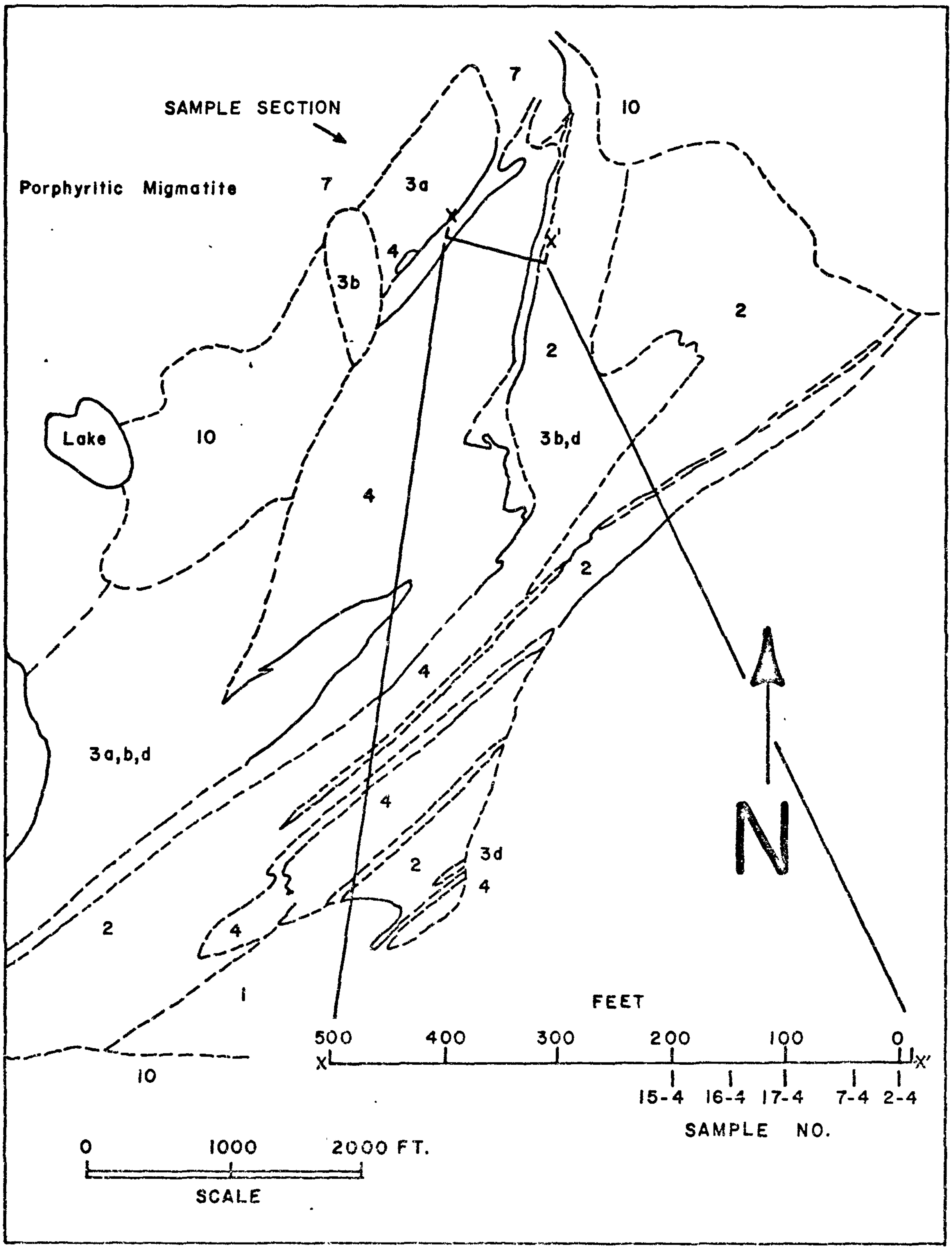


FIGURE 2B. SAMPLE LOCATIONS, BOREALIS 4 IRON FORMATION, D. GOODALE.

LEGEND FIGURE 2

CENOZOIC

10 - Glacial Drift

PRECAMBRIAN

9 - Diabase, primarily dikes

8 - a. Basal quartzite, includes pebble conglomerate, magnetite and hematite lenses

b. Quartzite or feldspathic quartzite

UNCONFORMITY

7 - Intrusive granite, migmatite

6 - Peridotite, serpentinized peridotite, talc lenses

5 - Metagabbro

4 - Iron formation

3 - Metasediments
  - a. Quartzite
  - b. Quartz-biotite schist
  - c. Garnet-biotite schist

2 - Greenstone and/or amphibolite

1 - Granite gneiss, granitic migmatite

CHAPTER 2

GENERAL GEOLOGY OF THE KIRKLAND-LARDER LAKE AREA

All exposed bedrock in the Kirkland-Larder Lake area is Precambrian, consisting of Archean age formations except on the extreme east and west of the map area (Figure 3), where Proterozoic rocks (Cobalt Series) overlie the older Keewatin and Timiskaming rocks.

The Kirkland Lake area, once a leading Canadian gold producer, has been mapped in great detail using stratigraphic and structural methods that are so important in unravelling the stratigraphy of the Archean.

A purely lithologic subdivision into the Keewatin volcanic series and the Timiskaming sedimentary series, accepted for many years, no longer applies. In the Kirkland Lake area the Timiskaming complex consists of an east-west trending belt of sediments and volcanics that overlies extensive Keewatin volcanics on the north and the south. Both these series were intruded by granite batholiths and syenitic stocks of varying ages, the youngest being the Otto Stock (1.73 b.y., Purdy and York, 1968). The whole complex is a south facing homocline bounded on the north by a pronounced unconformity and on the south by a shear zone known as the Kirkland-Larder Lake Break

(Thomson, 1946).

Ridler (1969) re-interpreted the Kirkland-Larder Lake Break as carbonate facies iron formation rather than a massive hydrothermal replacement body as previously thought. His conclusions were the consequence of a study of the lateral variation of the Boston iron formation - the oxide facies were found on and south of the axis of the fold-belt towards the shelf, whereas the carbonate facies were found north of the main axis towards the basin (Ridler, op.cit.). He was able to trace the carbonate facies for some distance as a structurally concordant unit.

D.F. Hewitt (1963) has defined the Kirkland Lake area as the type area for the Timiskaming Series, and has presented a detailed description of the structure, lithology and stratigraphy of the eugeosynclinal sediments in the area. Cooke and Moorehouse (1969) have elucidated the volcanic evolution of the Timiskaming lavas; the initial phases were calc-alkaline, evolving to late differentiates of potassic trachytes and leucitic lavas, heretofore unknown in the Archean of the Canadian Shield. Fairbairn et al (1965) have presented Rb-Sr whole rock isochrons for the Timiskaming and Keewatin volcanics (2368 and 2343 m.y., respectively), which are essentially equivalent. This evidence would seem to be in disagreement with the pronounced unconformity, but the experimental error of ±40-50 m.y. could allow for this (Fairbairn et al, 1966).

The volcanic-sedimentary cycle model for Archean greenstone belts of the Canadian Shield as proposed by Goodwin (1968) has been applied to the rocks in the Kirkland-Larder Lake area to study the volcanic stratigraphy (Ridler, 1969). Generally, a simple volcanic pile was constructed, progressing from mafic to felsic constituents as the volcanism proceeded in the area. Throughout the Archean there is a broad areal distribution of the lower mafic parts of an assemblage, with indications of linear fissure eruptions, and a clustering distribution of the upper felsic parts to central volcano vent eruptions. It is the upper felsic layer of volcanic rocks with which the regional distribution of iron formation and sulphide mineral occurrences are related in the Kirkland-Larder Lake area. In fact, this type of volcanic complex at Kirkland Lake is repeated at Noranda and Porcupine, other areas of regional distribution of mineralization.

A. The Boston Iron Formation

The Boston township iron range was first discovered in 1902, and has since been of great importance both geologically and economically. It is typically "Algoma-type" iron formation (Gross, 1965), occurring as thin banded chert and iron oxides up to 2000 feet thick in places. As shown in Figure 4 the Adams Mine property of the Jones and Laughlin Steel Corporation encompasses most of the larger occurrences. The iron range consists of several horizons of iron formation, cherty quartzite and volcanic rocks; the sequence of deposition is illustrated in Figure 4. Not all of the three horizons of iron formation are

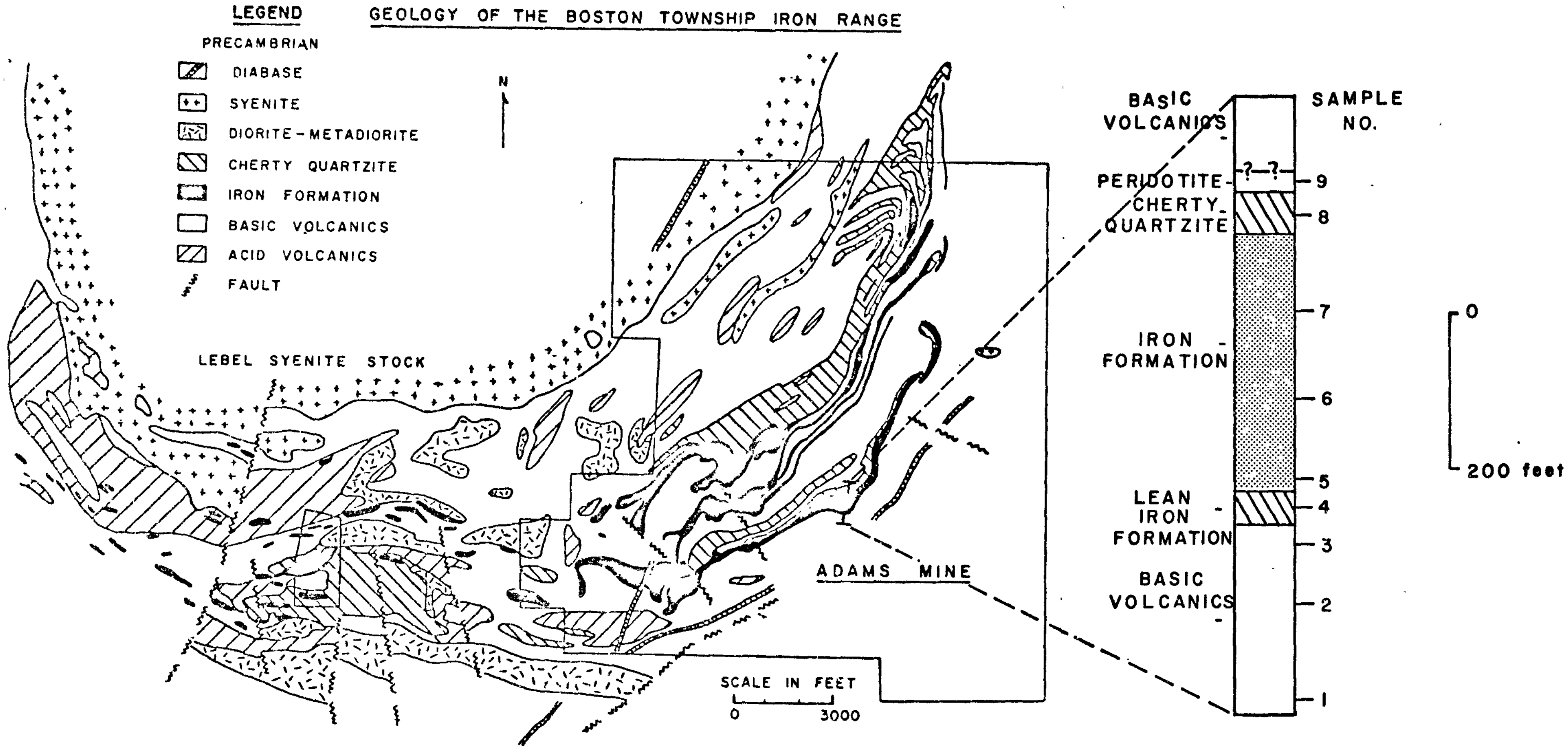


FIGURE 4. GEOLOGICAL PROFILE (VERTICAL SECTION) THROUGH BOSTON IRON FORMATION AND LOCATION OF ANALYSED SAMPLES (MODIFIED FROM DUBUC, 1966)

necessarily always present as the cycle of deposition varied greatly in the sedimentary basin.

The carbonate facies of iron formation (shown in Figure 3) is found adjacent to the Lebel Stock on the north and extends east to the Quebec border following the "Kirkland-Larder Lake Break". A sulphide facies is less well developed, but occurs locally and cannot be shown in Figure 3 and 4.

B. Sampling Technique in the Kirkland-Larder Lake Area

Field sampling was carried out with a sledge hammer, so that 1-2 lb. samples were obtained, free from obvious surface weathering and shears. The total spread of sampling was about 20-25 miles, mainly in an east-west direction. A composite sample of the iron ore was supplied by courtesy of the Adams Mine.

CHAPTER 3

DETERMINATION OF LITHIUM, RUBIDIUM AND CESIUM IN IRON FORMATIONS AND ASSOCIATED ROCKS

A comprehensive investigation was carried out by Gurney and Erlank (1966) to develop a DC arc spectrographic technique for the estimate of the trace alkali metals in basalts and ultra-basics. Their method, using a calcium fluoride carrier, provided a detection limit of 0.1 ppm for each element with satisfactory accuracy and precision. Other advantages to this method were that no pre-enrichment techniques were required, and that all the elements could be determined simultaneously and directly from the rock powder. The author modified Gurney and Erlank's method for the particular problem of analyzing iron-rich rocks, but without loss of accuracy and precision. The method used employs a spark ignited unidirectional (DC) pulsed arc excitation which combines the high precision of the spark discharge with the high sensitivity of the DC arc to provide optimum excitation. This source is used for extremely low concentration of various elements. The Stallwood Jet was not utilized since the argon in the A/O_2 supply normally used, has a spectrum line coincident with Cs 8521. Tests with other gas mixtures were not pursued. The various stages of the analytical method are now described.

A. Details of Analytical Procedure

Figure 5 illustrates sample preparation procedure. Particular attention was given to cleaning all apparatus before crushing samples and also between samples. Obtaining a proper "sample" from the banded ores was important, so large samples were crushed to -60 mesh in the Bico pulverizer and then quartered until a convenient sample size was obtained (about 50 gm). These samples were then ground to 200 mesh using the tungsten carbide shatterbox.

Because of a lack of satisfactory natural rock standards at the concentration levels required, synthetic standards were prepared. The composition of the synthetic standards approximates that of an oxide iron ore, consisting of one part "Specpure" SiO_2 to one part "Specpure" Fe_2O_3. The base was thoroughly mixed and standards were prepared by adding "Spex Mix" (containing 1.27% of 49 elements) to this base to give a standard containing 1000 ppm of Li, Rb and Cs. Subsequent dilutions of this standard with the base produced standards to cover the range down to 0.5 ppm.

It was also necessary to analyse some of the silicate rocks associated with the iron formations (trachytes, syenites, graywackes, basalts, etc.). A set of standards consisting of U.S.G.S. rock standards (BCR-1, GSP-1, G-1, but excluding W-1) and silicate samples, analyzed by J. Muysson, were utilized.

It is well known that synthetic standards prepared from chemicals do not behave in a similar way to natural materials in the arc. One sample of the banded ore (#6), was therefore

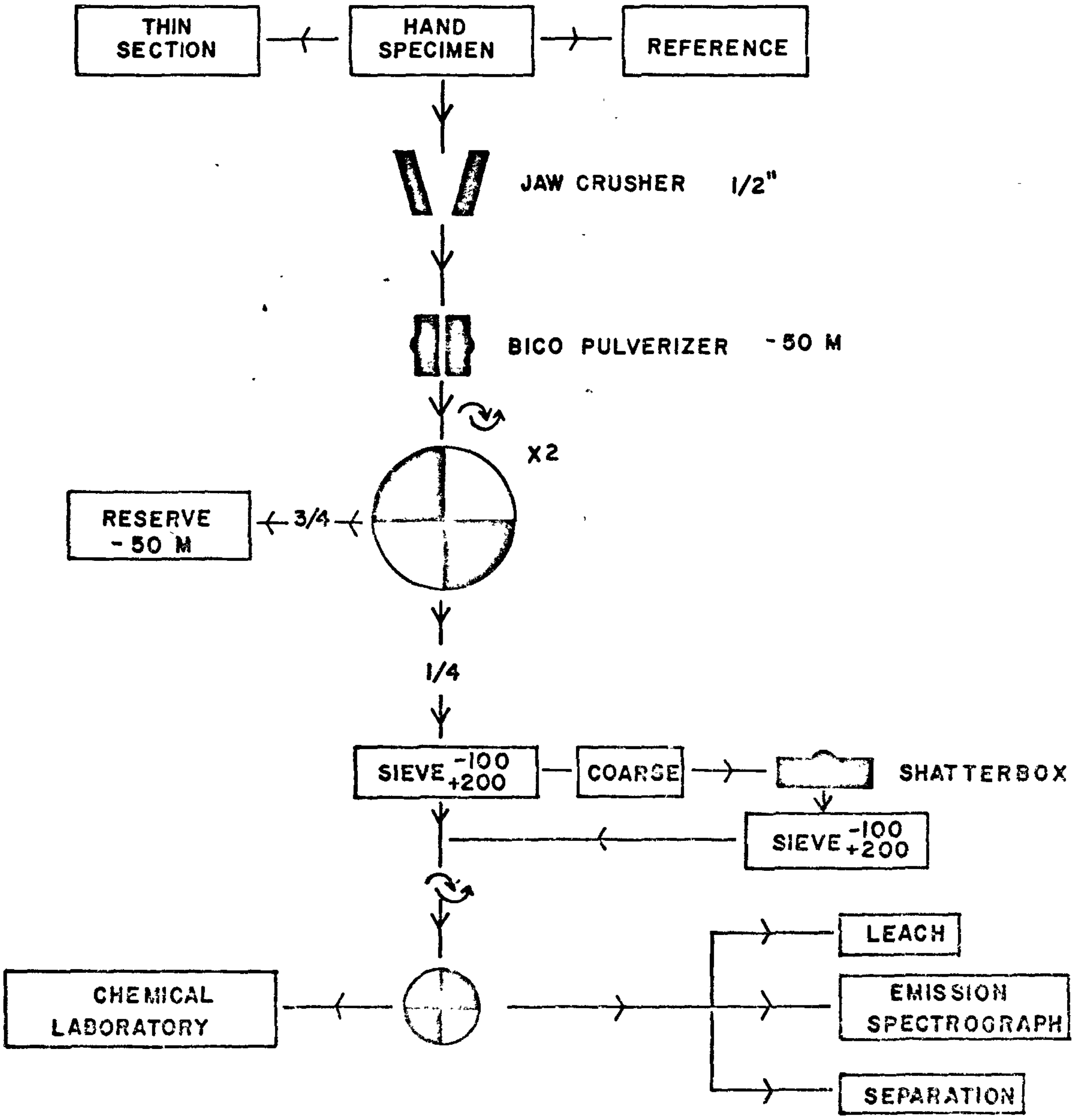


FIGURE 5. FLOW CHART OF SAMPLE PREPARATION

analyzed several times to obtain a reliable analysis of Li, Rb and Cs by comparison with synthetic standards and by the "addition method" of Ahrens and Taylor (1961, pp.158-159). The U.S.G.S. basalt standard (BCR-1) was then diluted in successive steps using #6 as a base to produce a set of natural standards. Analyses using these standards verified the presence of a matrix affect, not between synthetic versus natural samples as expected, but instead between silicate rocks and iron-rich rocks. The presence of large amounts of iron may have a suppressing affect on the excitation of the alkali metals, since the calibration curves for silicate rocks are displaced parallel to the calibration curve for the iron-rich rocks. (See analytical curves in Appendix C).

B. Spectrographic Carrier/Buffer

Gurney and Erlank (1966) found that the presence of CaF_2 in the arc enhanced the intensity of all the alkali metals, particularly lithium. Adding 20% CaF_2 to each sample for optimum enhancement shortens the period of distillation appreciably (Figure 6). This carrier was adopted but a further addition of 10% "Specpure" NaCl suppressed the cyanogen interference that occurred with using CaF_2 only (Gurney and Erlank, op.cit., p.1837). In addition the CaF_2 and NaCl added to the sample acted as a conventional buffer too.

The excitation and apparatus data are given in Table 1.

Table 1. Spectrographic Parameters and Conditions

Spectrograph	Jarrell-Ash 21 foot grating, Wadsworth mount, first order dispersion 5A/mm.
Condensing Optics	25 cm focal length cylindrical lens (horizontal axis) 16 cm from slit; diaphragm with 3 mm aperture 28 cm from slit; 10 cm focal length spherical lens 58 cm from slit; arc located 73 cm from slit.
Arc Stand	Spex Industries
Slit Width	30 microns
Slit Length	10 mm; accommodate 7 steps
Step Sector	7 step sector at slit, log intensity ratio = 0.2
Filter	yellow; removes second order interferences
Analytical Gap	4 1/2 mm
Electrodes	Ultra Carbon; sample (anode), preformed electrode 223402 (#1671) U-2 grade; counter electrode, 3/16 in rod 721202 (u45-2), U-2 grade - pencil point
Emulsion and Range	Kodak 1-N plate, backed 6100-8600 Å
Processing	4 min development in Kodak D-19 at 20C; 15 sec stop-bath; 3 min in Kodak Rapidfix; 20 min wash

Spectrographic Conditions (continued)

Excitation Source...........Spark Ignited Unidirectional Pulsed Arc (Full Wave Uni-Arc), Jarrell-Ash Custom Varisource, Model 40-650

Voltage.................280 v. DC

Inductance..............625 μh

Resistance..............residual

Capacitance.............0.0025 μf

Discharges/half cycle....20

AC arc..................9.6 amps RF

Full Wave Rectification

Exposure................60 sec (see Figure 6)

Sample......................7 parts sample (200 mesh), 2 parts CaF_2 (B.D.H. extra pure), 1 part Specpure NaCl

Electrode Packing...........manually; 80 mg sample, 36 mg buffer/carrier in 2 electrodes

No. of Superimposings........2, except for high concentrations where single exposure adequate

Densitometry................Jarrell-Ash Microphotometer

Calibration..................3 step plate calibration

Spectral Analysis Lines......K 6939A
Rb 7800A
Li 6103, 6707, 8126A
Cs 8521A
no internal standard - total energy method

Working curves are presented in Appendix C 1-6

All analytical curves were corrected for background

NOTE: Traces of Li were present in the buffer/carrier and necessitated a blank correction

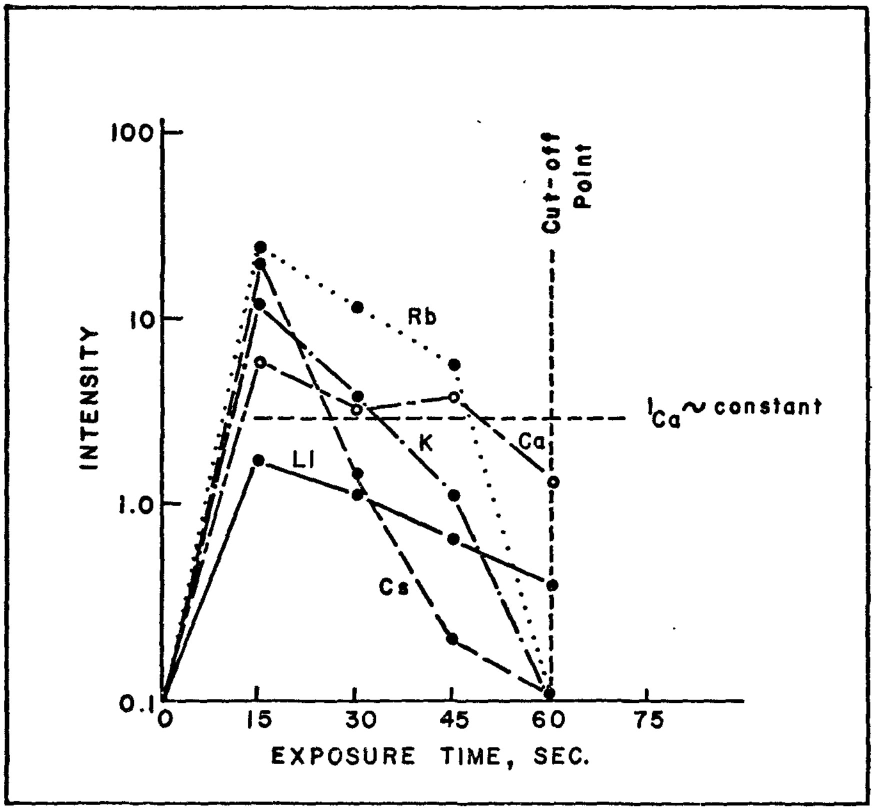


Figure 6. Distillation time of alkali metals with 20% CaF_2 carrier

(Analyst, F.G. Alcock)

C. Precision and Accuracy

Precision data are listed in Table 2, expressed as the relative standard deviation, derived by arcing one sample several times and by arcing a series of samples in triplicate, collected on various days and from various rock types.

To assess the accuracy of the method the diabase standard, W-1, was run as an unknown; the data is presented in Table 3 as a comparison of spectrochemical values and chemical, or accepted values.

Table 2. Analytical Precision

	Rb			Li			Cs		
Rock type	a all	b I.F.	c W-1	a all	b I.F.	c W-1	a all	b I.F	c W-1
Range, ppm	0.5-60	1-3	23	1-40	0.5-1	14	1-60	<1	1
Coefficient of Variation,%	8.3	32.1	10.6	7.8	28.5	8.6	10.7	-	-

a - series of 38 samples arced in triplicate; results pooled for precision calculation

b - 4 replicates each of oxide iron formation (#5, #6); results pooled for precision calculation

c - 4 replicates of silicate standard, W-1

Table 3

Comparison of Chemical and Spectrochemical Results on Various Rocks

		Rb	Li	Cs
Basalt	chem*	23	-	-
(#1)	spec	26	20	1.0
Iron Formation	chem*	12	-	-
(#7)	spec	9.8	0.6	<1
Mafic Trachyte	chem*	60	-	-
(#26)	spec	51	20	<1
W-1	**	22	12	1.0
	spec	23	14	1.0

* - determined as Rb_2O (Appendix A)

** - recommended values (Fleischer, 1969)

CHAPTER 4

THE DISTRIBUTION OF THE ALKALIS IN SOME PRECAMBRIAN IRON FORMATIONS AND ASSOCIATED ROCKS OF THE CANADIAN SHIELD

A. Oxide Facies of Iron Formation

S. Landergren investigated the distribution of K, Rb and Li in Swedish iron ores, but to the best of the author's knowledge no analyses of Rb, Li and Cs have been reported for the iron formations of the Canadian Shield, with the exception of a few Rb determinations in iron formation from Schefferville (Fryer, 1970). The availability of samples from several localities in the Canadian Shield makes possible the study of the distribution of the alkali metals in iron formations in general, and more specifically, elucidation of the geochemical character of the individual iron formations.

The analyses of Li, Rb and Cs are listed in Appendix A along with the bulk chemical analyses. Sodium and K were determined by atomic absorption (except for K in leach residues - determined by emission spectroscopy), as also was Rb when the abundances exceeded the spectrographic range.

1. Frequency distributions

To preserve as much of the original data as possible, the results are summarized in histograms and scatter diagrams. The histograms have been prepared with the abscissa in ppm and the ordinate in per cent frequency to demonstrate most effectively the dispersion of the alkalis in the iron formations. Equal intervals are used, given by a power factor of 1.58 (each log cycle contains exactly 5 intervals) (Ahrens, 1954).

Examination of the histograms in Figures 7 and 8 indicate that Rb and Li abundances in the oxide facies show strong positive skewness. This is because many of the samples have abundances near the limit of detection. Almost 65% of the Rb occurs in the range of 0.4-2.5 ppm (Figure 7) while nearly 75% of the Li occurs in the same interval range (Figure 8). Cesium is not represented, since its abundance in the oxide facies is generally below the lower limit of calibration (1 ppm), except for a few samples from N.W. Ontario and Melville Peninsula groups. It is to be noted that no geographical weighting has been introduced to these distributions, also that a substantial number of the Melville Peninsula samples (Appendix A-1) have quite high Rb, Li and Cs abundances. As concentrations conform better to a lognormal than a normal law, it will be convenient to deal with geometric means rather than the arithmetic means (Ahrens, 1954), but for sake of comparison both means have been indicated in the histograms.

Examination of K and Na frequency diagrams in Figures 9 and 10, suggests the lognormal distribution agrees better with the behaviour of these two elements in the oxide facies, than in the case of Li and Rb.

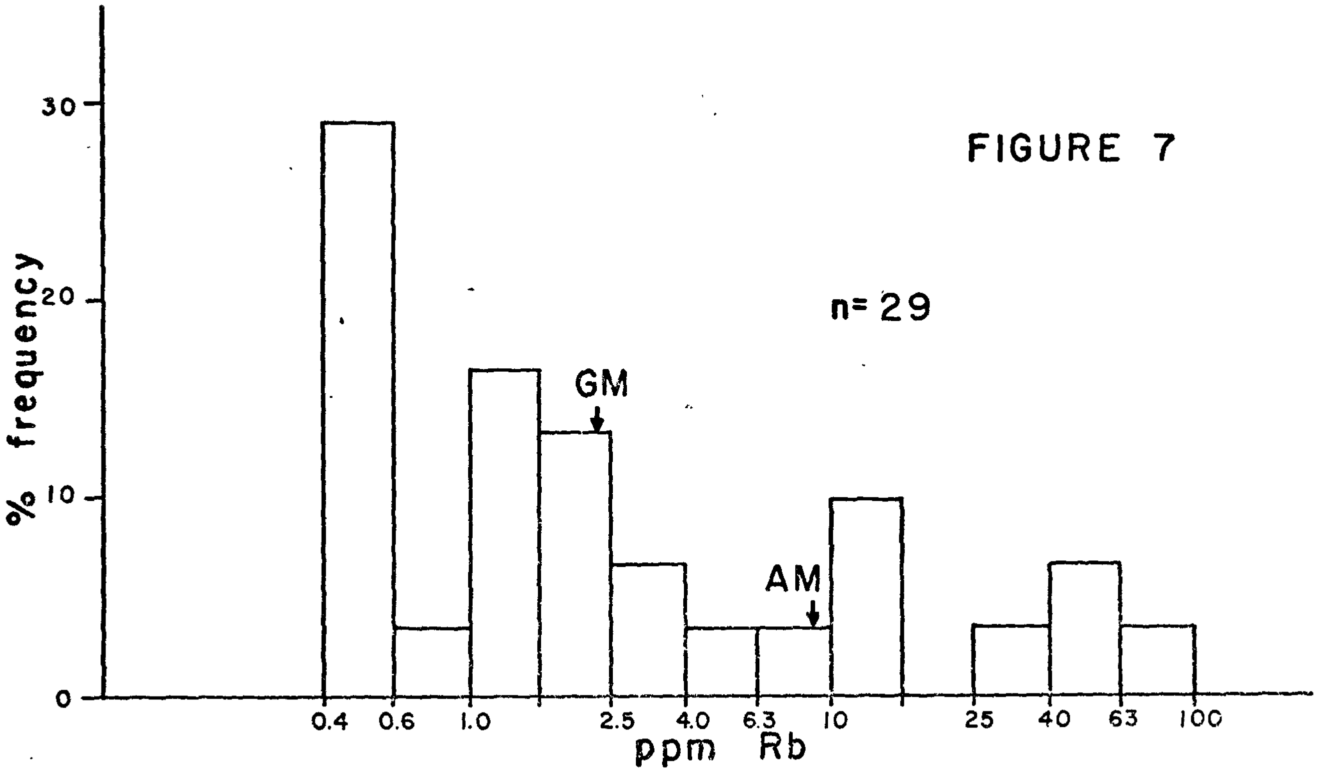


FIGURE 7

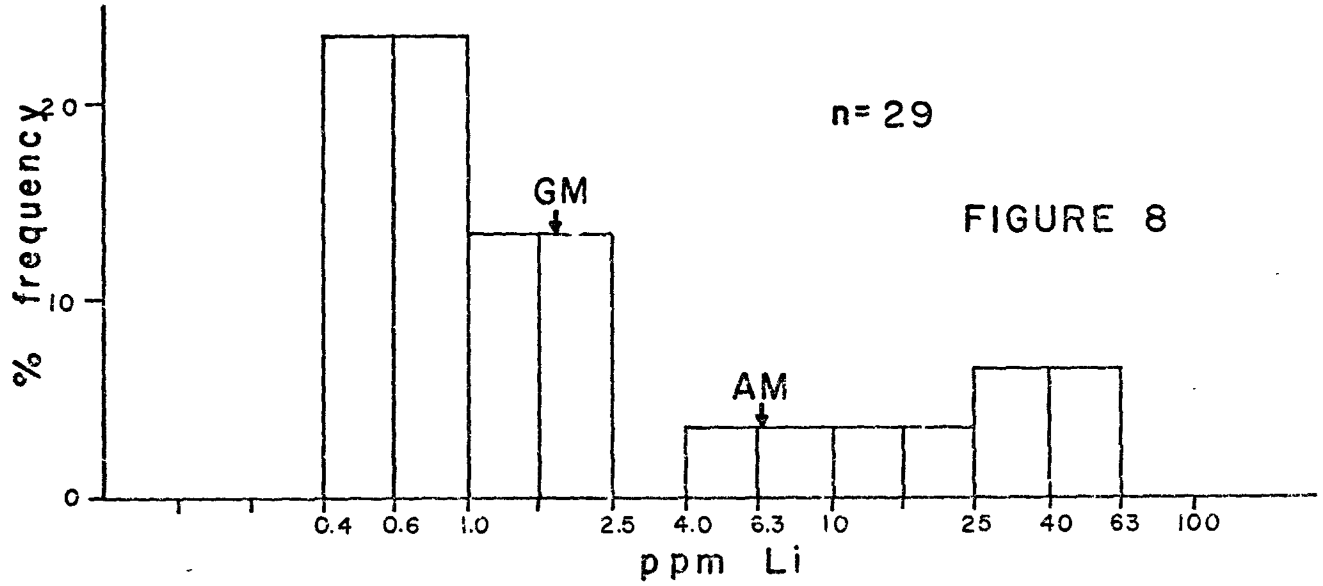


FIGURE 8

Figures 7 and 8. Distribution of Rb and Li in Oxide Facies of Iron Formation (Kirkland Lake, N.W. Ontario and Melville Pen. - see Table 4).

FIGURE 9

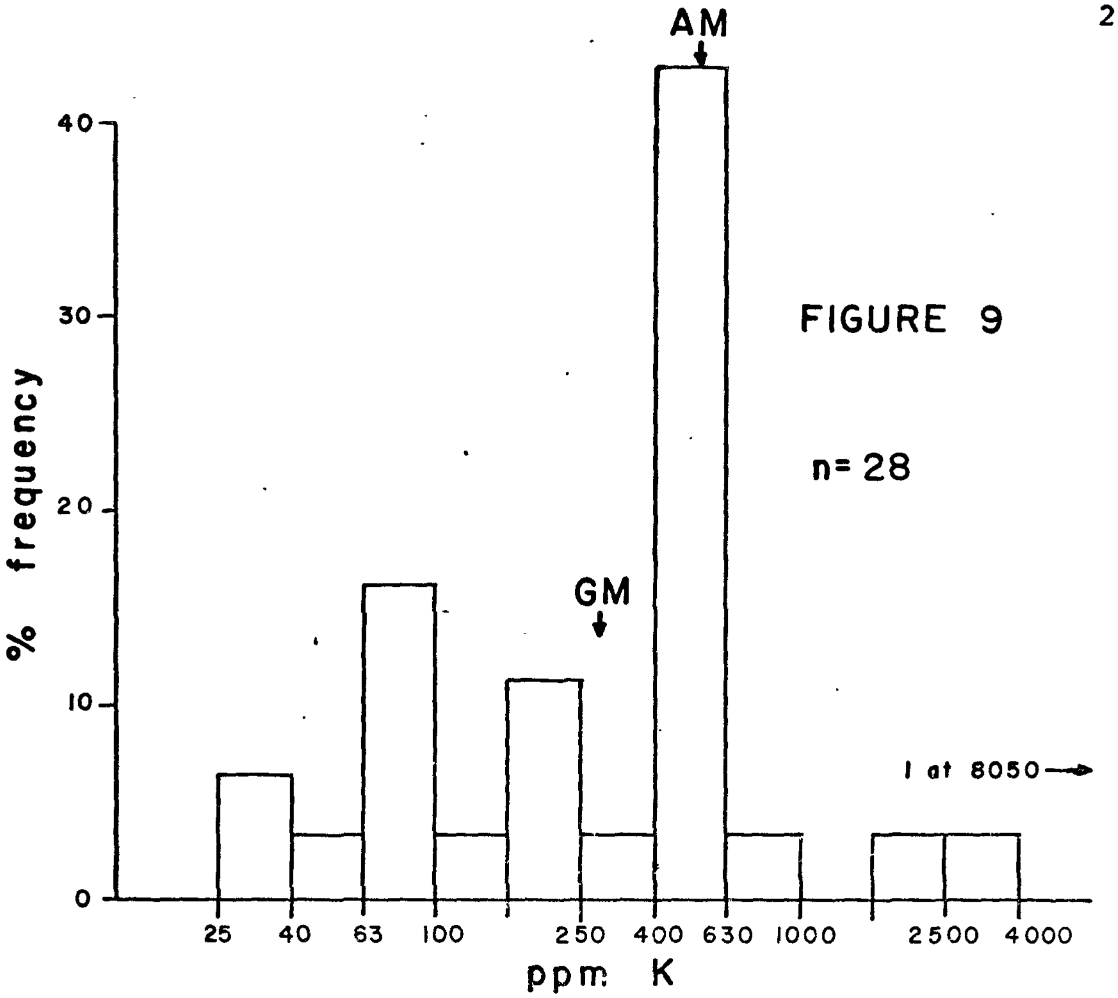
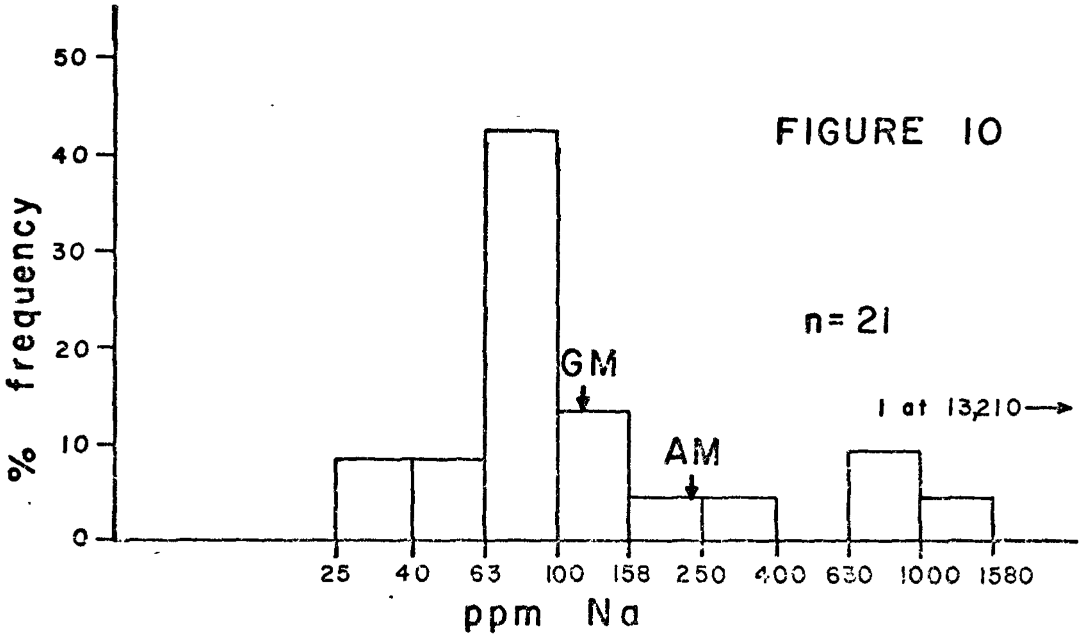


FIGURE 10



Figures 9 and 10. Distribution of K and Na in Oxide Facies of Iron Formation (Kirkland Lake, N.W. Ontario, and Melville Pen. - see Table 4).

2. Alkali metal abundances

Table 4 summarizes the abundances for the alkali elements in the oxide iron formations, including data from the iron ores of Central Sweden. The distribution in the less well-developed facies of iron formation and in the silicate rocks will be dealt with separately. Comparison reveals that the Kirkland Lake and N.W. Ontario iron formations are quite similar in their Rb, Li and Cs content, but Na and K contents are higher at Kirkland Lake. Melville Peninsula samples are relatively enriched in alkali metals, with the exception of Na, in comparison with the other two Ontario occurrences: this will require a special explanation.

It is well known that K, Rb and Cs behave similarly in the geochemical cycle; the latter two elements following K closely in most rock-forming processes. Lithium, on the other hand, behaves quite differently in the weathering cycle, in that its active migration under surface conditions is quite limited (Horstman, 1957; Ronov, 1970). Because of this Li will be discussed from a different perspective.

Generally for the alkali metals which have been released through agencies of chemical weathering, and exist as ions in an aqueous medium, the reason for their relative separation must be explained by differences in the adsorptive capacity of these elements (Heier and Adams, 1963). This is certainly the case in argillaceous sediments where adsorption to colloids and clays is most important. This involves electrostatic attraction and Welby (1958) has stated that the hydrated radius of the alkali

Table 4. Ranges and Geometric Means (G.M.) of Alkali Metal Content (ppm) in Precambrian Oxide Iron Formation

Element	Kirkland Lake		N.W. Ontario		Melville Peninsula		Central Sweden**	
	Range*	G.M.	Range*	G.M.	Range*	G.M.	Range*	G.M.
Na	<74-13210 (9)	320	37-130 (6)	59	<74-740 (7)	130	-	-
K	<100-8050 (16)	340	33-980 (6)	140	<50-3900 (7)	480	<70-20000 (33)	2200
Rb	<0.5-49 (16)	2.0	<0.4-11 (6)	1.0	<0.4->60 (7)	8.4	<3-600 (50)	12
Li	<0.5-44 (16)	1.5	<0.4-5.3 (6)	0.8	1.0-58 (7)	7.5	3-200 (51)	8
Cs	<1.0-4.8 (16)	<1	<1.0-3.7 (6)	<1	<1.0-50 (7)	3.6	-	-

* From Appendices A-1, A-2

** Data from Landergren (1948)

() No. of sample analyses

ion controls its behaviour in the sedimentary cycle to a certain extent. Heier and Billings (1969) have summarized the above relationships as shown in Figure 11.

Table 5. Field Function = Ionization Potential/ Hydrated Radius of Alkali Element

(from Heier and Adams, 1963)

Cation	I/R
Li^{+1}	1.47
Na^{+1}	1.83
K^{+1}	2.27
Rb^{+1}	2.31
Cs^{+1}	2.33

The field functions (Table 5) also indicate that the alkali elements are adsorbed on colloidal material from their aqueous solution in the following order: Cs>Rb>K>Na>Li.

In igneous rock series the distribution of Li has been interpreted in accordance with the classical distribution rules of Goldschmidt (1954) which explain why Li will not substitute for Na and K in minerals, but will for Mg and Fe^{+2}. Consequently the geochemistry of Li differs from that of the other alkalis in that

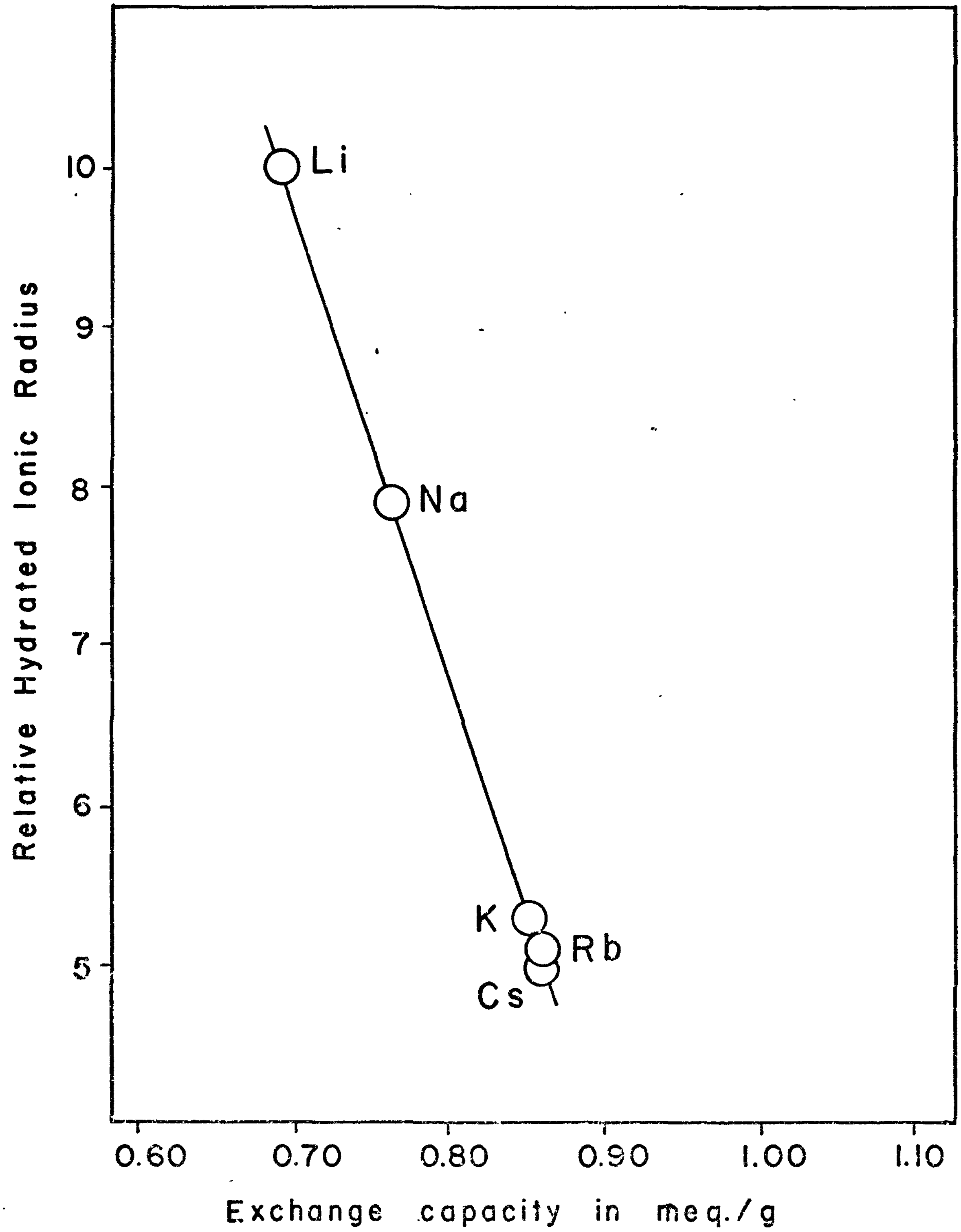


FIGURE 11. Behaviour of Alkalis in Sedimentary Cycle - Based on Hydrated Ionic Radii (after Heier and Billings, 1969).

it tends to accumulate in the mafic silicates. The increase in Li/Mg ratio with differentiation is also a common feature in many magmatic rocks. Another less important type of Li substitution is for Al in the various aluminum silicates (muscovite, plagioclase, etc.). The distribution of Li in igneous rocks is determined by chemical equilibrium processes that are reasonably well understood, but in sediments Li follows a less predictable pattern since non-equilibrium processes prevail.

During weathering and sedimentation the alkalis (Na, K, Rb, Cs) are released from the rock forming minerals, but Li, with its smaller ionic radius, is held more tightly in the mineral structures and consequently is retained. Horstman (1957), in his study of the behaviour of the alkalis in the weathering cycle, found that the absolute amount of alkalis present in rocks is generally reduced by weathering, however Li show no such trend; the Li content remains essentially constant for any one rock type. This is in agreement with conclusions by Ronov et al (1970), in their extensive studies of the geochemistry of Li during weathering and deposition in the Russian Platform. They established that the commonest type of Li distribution in sedimentation involves proportional deposition with Al^{+3} in the alumino-silicate structures of clay minerals as seen in Figure 12. In their mineralogic and chemical examination of over 21,000 specimens, Ronov et al concluded that the lithium distributed in the various weathering crusts is not dependent on the type of parent rock, initial Li content or the geological age of the crust but instead

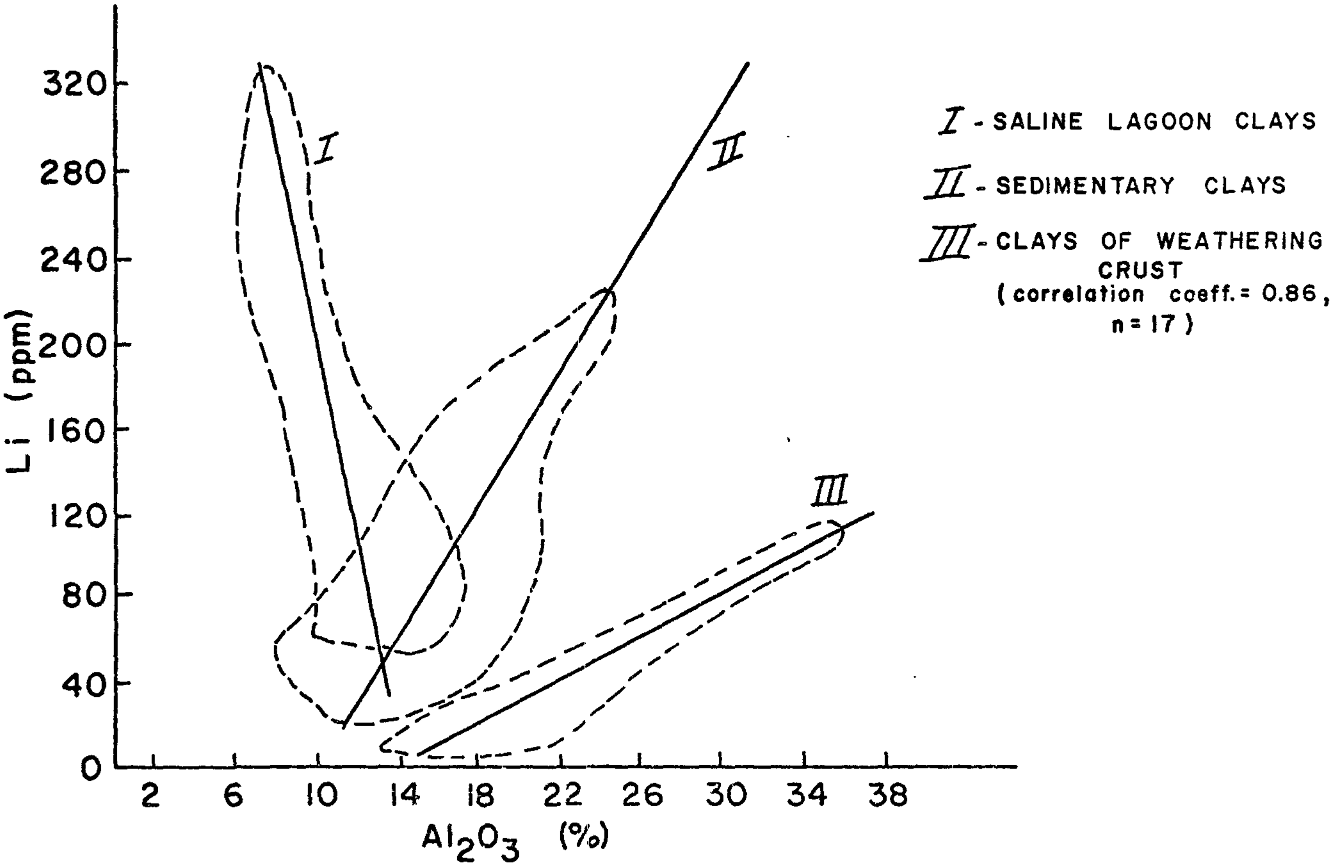


Figure 12. Relation of Li to Al_2O_3 in clay horizons

(Adapted from Ronov et al, 1970)

bears a direct relation to the extent of weathering in the erosion zone and area of sedimentation. The stages and zones of weathering can be summarized as follows: (from Ronov et al, op.cit.)

1. alkaline stage - Na, K, Mg and Ca are leached from the decomposing rock-forming minerals of parent rock.
2. metastable clay products - increase with decrease in primary aluminosilicate minerals (chlorite, montmorillonite).
3. Kaolinite - develops with concomitant changes in composition and structure of clays in a less alkaline to weakly acidic medium.
4. Laterite - may or may not form, involving the final disintegration of clays, removal of SiO_2 and formation of oxides such as goethite, hematite, bauxite, etc.

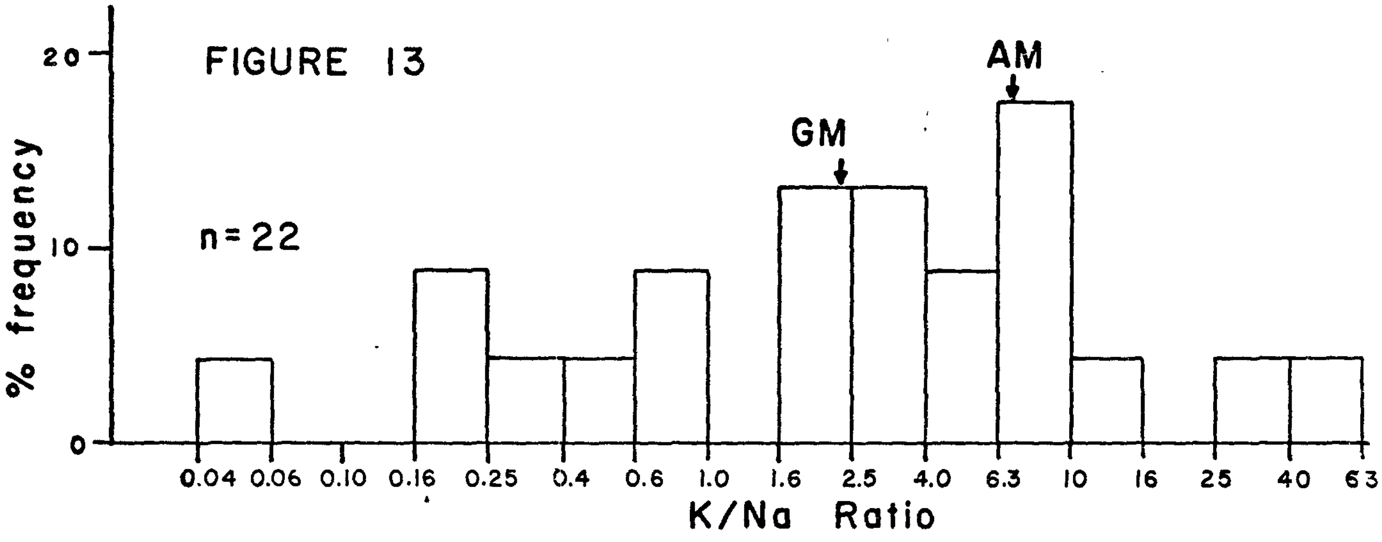
The clay products from the initial stages of weathering (area III in Figure 12) illustrate an almost functional relationship between Li and Al content. The sedimentary clays (area II in Figure 12) show an increase in Li relative to Al, compared to clays of the weathering crust. This is a result of the Li in the laterite zones of the crust being passed on by ground waters to the kaolinite zone where it is trapped by the clays.

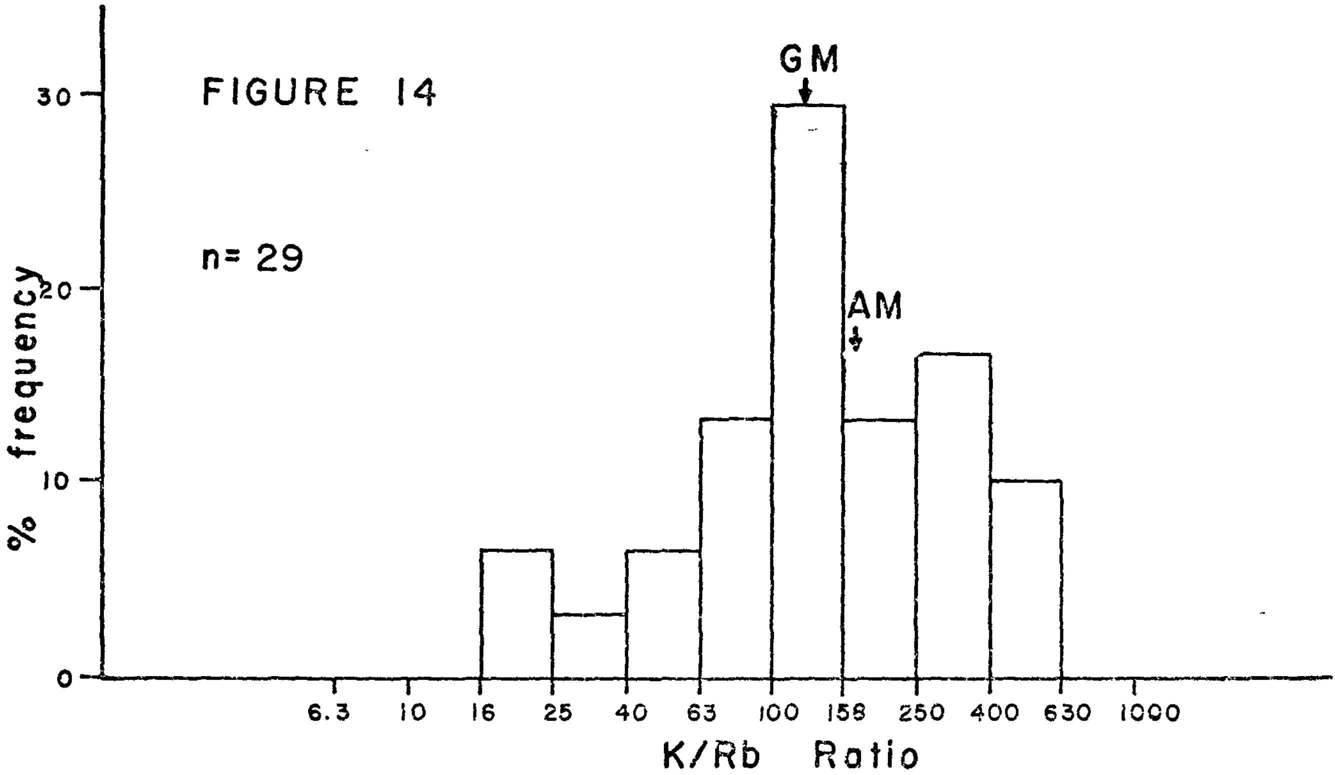
In his extensive work on the Swedish iron ores, Landergren (1948) found a strong deficiency of Li, which he considered a geochemical phenomenon, since it is expected to find Li enriched in these ores, which are high in both magnesium and iron: "The deficiency of lithium and rubidium and the magnitude of the ratios Li/Mg and (K/Rb), respectively, indicate that no magmatic residual solution can be put in relation to the formation of iron ores within this region." (Landergren, op.cit., p.164). In the iron formations discussed here the Li and Rb contents are usually very low and less than the mean compositions quoted for the iron formations of Central Sweden (Table 4). Of the Canadian occurrences the Melville Peninsula iron formation contains the highest Li contents (up to 58 ppm), however the post-depositional history of these rocks has been more severe and metasomatism could be a determinig factor. So like the Swedish Precambrian iron ores, the iron formations considered in this study show similar deficiencies in Li and Rb.

3. Alkali ratios

Table 6 indicates the low K/Rb ratio of the Melville group as a whole, compared to the other oxide iron formations, and shows the high enrichment of Rb (and probably Cs) relative to K. A converse relationship exists for the K/Na ratios, which are highest in the Melville group and show an enrichment of K relative to Na. Histograms have been prepared for K/Na, K/Rb ratios and are presented in Figures 13 and 14. The K/Na ratios show a wide dispersion but appear to be lognormally distributed, with almost 60% of the ratios occurring in the range of 1.6-10 K/Na; the geometric mean being 2.3, a factor of at least 2 greater than for the estimate of the Canadian Precambrian shield (1.0) by Shaw (1967).

It would seem that iron formations, although containing





Figures 13 and 14. Frequency Distributions of K/Na and K/Rb Ratios in Oxide Facies of Iron Formation (Kirkland Lake, N.W. Ontario and Melville Pen.).

Table 6. Ratios of Alkali Metals in Precambrian Oxide Iron Formations*

Ratio	Kirkland Lake	N.W. Ontario	Melville Peninsula	Central Sweden
K/Rb	170	140	57	160
K/Na	1.1	2.4	3.7	-
K/Cs	(>340)[1]	(>140)	130	-
Rb/Cs	(>2.0)	(>1.0)	2.3	-

* Ratios computed on basis of G.M. from Table 4

[1] Bracketed values indicate estimated ratios obtained from using a Cs abundance of 1 ppm even though the value may be <1 ppm

small abundances, show an enrichment of K relative to Na, reflecting either the higher adsorption capacity for K during deposition of the sediment, or an influx of K into the depositional basin (possibly from highly differentiated effusives). The latter would appear to be the case for the Kirkland Lake samples which are associated with potash rich volcanic rocks, and probably for the N.W. Ontario occurrences also, since they are interlayered with metavolcanics (Raudsepp, 1971). However this relationship is probably only partly true for the Melville group since the presence of introduced material is suspected due to the numerous associated granitic and migmatic intrusions (Goodale, 1971).

In the K/Rb frequency diagram of Figure 14, 75% of the K/Rb ratios are concentrated in the 63-400 range, and there is an overall geometric mean of 120 which is somewhat lower than the K/Rb ratio range of 150-300 for the continental crust (Taylor, 1966; Heier and Adams, 1963). This low ratio would indicate the concentration of Rb relative to K in the oxide facies of iron formation (see also Figure 19, discussed later). The banded ores of Central Sweden have their K/Rb ratios presented in the form of a frequency diagram (Figure 15), which conforms with a lognormal distribution (geometric mean = 160). In Table 6 it was observed that Kirkland Lake and N.W. Ontario occurrences have similar K/Rb ratios to the Swedish iron ores, with the exception of the Melville samples. It is concluded then that on the basis of K/Rb ratios, the banded iron formations of the Canadian Shield, with a few exceptions, have a close geochemical similarity to those of Central Sweden.

As already mentioned, most of the samples contain detectable amounts of Cs but are reported as less than 1 ppm so that the K/Cs values from such data are only a rough guide to order of magnitude (Table 6). However some samples from Melville Peninsula and N.W. Ontario contain appreciable amounts of Cs (Appendix A), well within the reliable spectrographic calibration range. It is interesting to note that ratios for these rocks were still an order of magnitude less than that reported for other rocks (Table 7). It is quite evident that an enrichment of Cs has taken place relative to both K and Rb, at some time

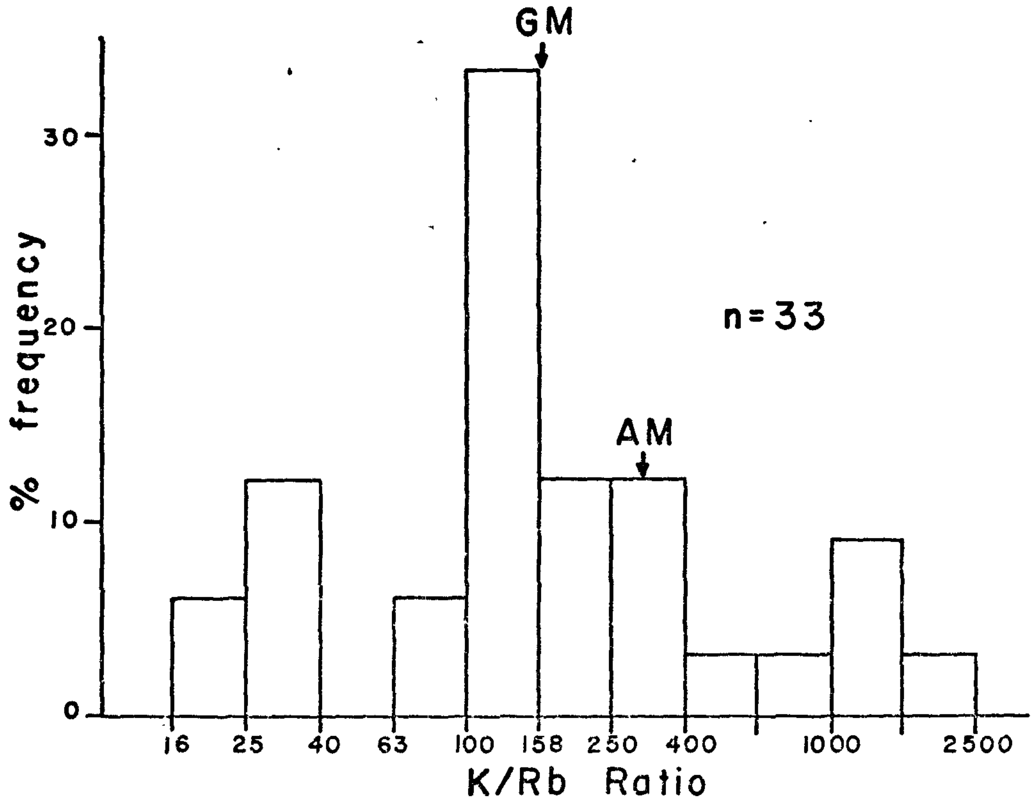


Figure 15. Frequency Distribution of K/Rb Ratio in Banded Iron Ores of Central Sweden (adapted from Landergren, 1948).

Table 7. Averages of Alkali Abundances and Ratios from literature

	Na %	K %	Rb	Li	Cs	K/Na	K/Rb	K/Cs	Rb/Cs
Average composition of Canadian Shield (Shaw, 1967)	2.57	2.57	118	22	-	1.0	220	-	-
Average for Basic Members of Archean Volcanic Belts (Noranda-Kirkland-Michipicoten) (Hart et al, 1970)	-	0.21	5.9	-	0.4	-	360	5890	16
Continental Crust (Taylor, 1964)	2.4	2.1	90	20	3	0.9	230	7000	30
Average Sediment (Horstman, 1957)	1.0	-	110	53	4	-	-	-	28

during the history of these iron formations.

B. Metamorphic Effects

Archean rocks are invariably metamorphosed, so that in discussing their geochemistry the affect of metamorphism must be considered and evaluated before one even attempts to discuss their "primary geochemistry". The problem is - were these iron formations essentially closed systems with respect to the alkali metals during their long history of metamorphism? The detailed field geology for the Melville Peninsula and N.W. Ontario occurrences is not well known and so little can be said here about these "systems". The Boston iron formation at Kirkland Lake has been studied in more detail and

> "... regional metamorphic grade is generally low, with primary microscopic and mesoscopic textures often well preserved. Immediately adjacent to stocks metamorphic rank may increase."
>
> (Ridler, 1970, p.36).

There is no indication of Rb metasomatism in the metamorphosed basalts associated with the iron formation (Table 12, Chapter 5) as the K/Rb ratios are similar to or higher than those in fresh basalts (Hart et al, 1970). In the Kirkland Lake occurrence then, these low grade metamorphosed rocks can be assumed to have behaved as closed systems and for the most part metasomatism has not been an important process in this iron formation (personal communication, Ridler, 1971). Since the N.W. Ontario occurrences, on the whole, have similar alkali abundances and ratios, they too have probably not been altered by metasomatism (with the possible exception of MR-1-9. See magnetite analyses, Chapter 6). On the other hand, the data for Melville Peninsula would indicate that this iron formation behaved as an open system during metamorphism since the K/Rb, K/Cs ratios are extremely low (Table 6). The presence of "porphyritic migmatite" associated with this iron formation (see Figure 2B) lends support to this interpretation.

This iron formation then is of little use for establishing general relationships between the alkali metals, since the alkalis, particularly K, would be mobile in such high grade metamorphism and extensive material transport could take place over moderate distances. The iron formation was probably receptive to such a phenomena; the end result being an enrichment in K, Rb, and Cs relative to Na and Li.

C. Carbonate-Sulphide Facies of Iron Formation

Samples representing the carbonate and sulphide facies of iron formation are from the Kirkland Lake area only, and the relevant data are in Table 8. Samples #15 and #16 are considered carbonate facies of iron formation following Ridler's criteria (see above), despite the fact that they contain less than 10% iron (Appendix A). According to definition (James, op.cit.), the iron content of the rocks must be at least 15% to be called an iron formation. However the Fe contents of all the iron formation samples analyzed here (including oxide facies) are highly variable demonstrating that the distribution of Fe content in such heterogenous rocks is vitally affected by the sample size used for analysis.

The abundances and certain ratios of the alkalis in these facies are significantly higher than those observed in the oxide facies (Tables 4 and 6). Most noticeable in this respect are the K/Rb and K/Cs ratios which are similar to the averages in Table 7. Clastic material makes up a large percentage of these rocks so it is expected to find the ratios similar to those of igneous and sedimentary rocks. H. James notes in his discussion of the chemistry of sulphide facies of iron formation that

Table 8. Alkalis in Carbonate-Sulphide Facies, Boston Iron Formation, Kirkland Lake, Ontario (ppm)

Sample	Na	K	Rb	Li	Cs
#14a	74	250	0.6	44	<1
#14b	9130	11870	38	2.4	1.3
#13	29310	5730	13	2.0	<1
#15	150	8470	26	10.8	1.0
#16	6750	14030	44	6.7	3.7

Sample	K/Na	K/Rb	K/Cs	Rb/Cs
#14a	3.4	400	(250)	(0.6)
#14b	1.3	310	9100	29
#13	0.2	440	(>5700)	(>13)
#15	56.5	330	8500	26
#16	2.1	320	3800	12
Average		350	6800	20

#14a - Carbonate-oxide)
) Mixed facies
#14b - Carbonate-sulphide)

#13 - Sulphide facies

#15 - Carbonate facies

#16 - Carbonate facies

> "... with a few exceptions ... the heavily pyritic rocks are black shales or their equivalents, with a large content of organic matter or carbon."
> (1966, p.W25)

The close association of dolomite, chert, clastics and variable amounts of carbon and sulphur in the rocks further demonstrates the irregularity and instability of the physico-chemical environment for the deposition of such sediments.

D. Correlation Coefficients

The principal mineral components of samples from oxide facies of iron formation are quartz (chert), magnetite/hematite, clay minerals (assumed), diagenetic/metamorphic silicate minerals and minor sulphides (modal analyses are presented in Appendix B). Modal analyses were not available for all samples analyzed but chemical analyses were, so that the principal effort was directed towards interpreting the chemical analyses.

Co-variation of the alkali metals with the major constituents is summarized by the use of correlation coefficients, as presented in Table 9. There is not a functional relationship between any of the variables, but a trend is seen for some; the degree of correlation is presented below:

Table 9. Correlation Coefficients in Sample Population from Oxide Facies (Kirkland Lake, N.W. Ontario and Melville Peninsula, 23 samples total)

	Al	Mg	K	Na	Total Fe	MnO	SiO_2	Rb	Li	Cs
Al	1.00	0.13	0.53	0.24	0.10	-0.02	-0.16	0.35	0.67	0.31
Mg		1.00	0.03	0.23	0.32	0.53	-0.16	-0.04	0.07	-0.03
K			1.00	0.27	-0.07	0.07	-0.17	0.86	0.62	0.71
Na				1.00	0.03	-0.19	0.11	0.15	0.24	-0.05
Total Fe					1.00	-0.15	-0.64	0.10	0.15	0.26
MnO						1.00	0.12	-0.06	-0.06	-0.06
SiO_2							1.00	-0.23	-0.32	-0.56
Rb								1.00	0.62	0.77
Li									1.00	0.64
Cs										1.00

It is assumed that Al is indicative of detrital silicates and clay minerals; the SiO_2 documents chert variation, and the total Fe is indicative of magnetite-hematite-ankerite.

Correlation coefficients are generally quite low (<0.5). The correlation coefficients for the alkalis (indicated in Table 9) are all positive, and it is clear that Rb, Cs and Li vary sympathetically with K content, but no trend is discernible with Na. As expected no real trends exist between the rare alkalis and the iron minerals since the spinel and carbonate structures are not conducive to substitution by alkali metals. Lithium is the only trace alkali to show a fair positive correlation with the clay and silicate mineral content, as represented by Al content, in Table 9. So any Li in the carbonate and sulphide facies of iron formation is probably contained in the clay minerals and detrital silicates present therein, agreeing with a similar conclusion reached by Weber (1964) in his study of dolomites.

Figure 16 serves to illustrate the general lack of correlation between Li and Mg in the various facies of iron formation. Ronov (1970) found that a relationship existed between Li-Mg in saline lagoons, the Li accumulated along with Mg, SO_3 and Cl of sea water rather than in the products of the weathering crust. Samples #15 and #16 of the carbonate facies iron formation contain appreciable amounts of Mg, due to the presence of ferroan dolomite (see modal compositions - Appendix B), but as seen in Figure 16 there appears to be little correlation with the Li concentrations.

The position of points in Figure 17 shows a positive trend between the Li and Al contents in the oxide facies of iron formation, confirming relations observed by Ronov (1970) that Li content is characterizing the physio-chemical conditions of accumulation. It is interesting to note that the carbonate-sulphide facies of iron formation (for Kirkland Lake only) show poor correlation between Li and Al, although there is a paucity of samples to fully illustrate this relationship. The distribution of Li, in relation to Mg and Al serves to separate the oxide facies from those (carbonate-sulphide facies) in which detrital

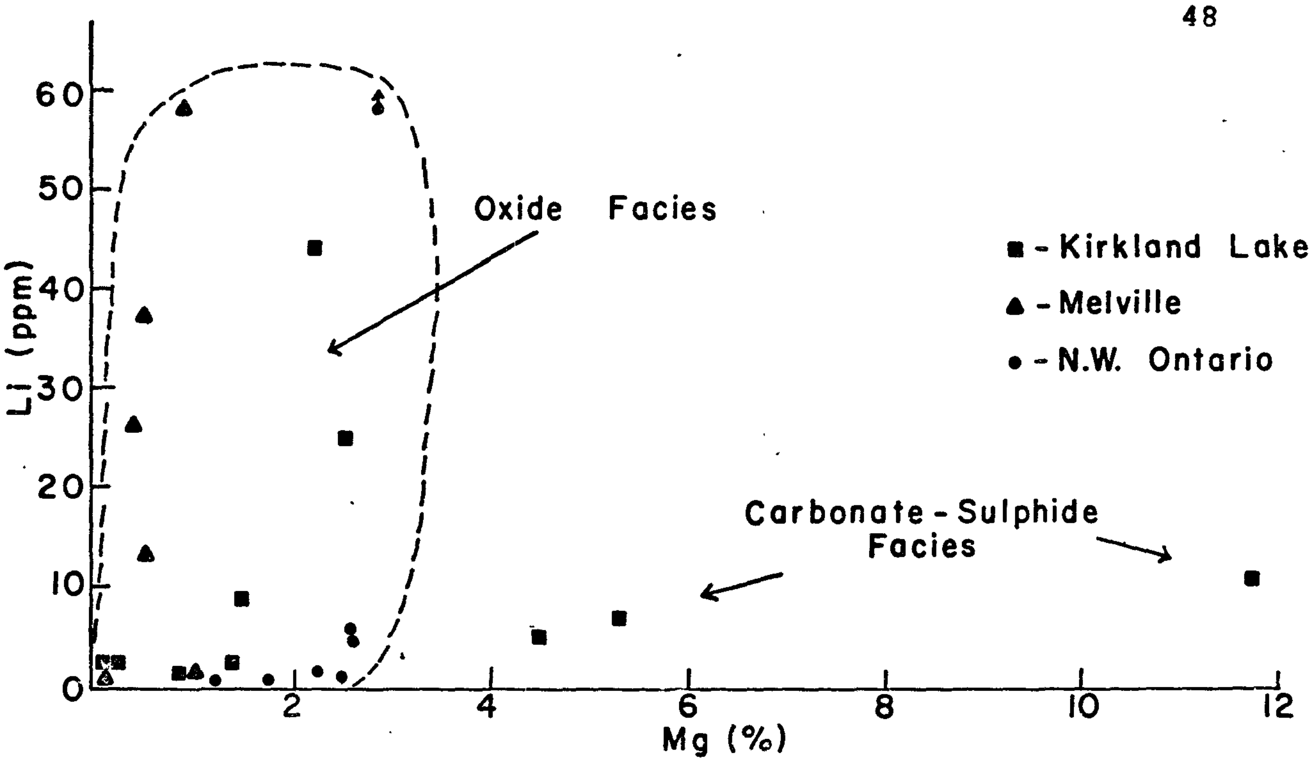


Figure 16. Relationship Between Li and Mg in Iron Formation

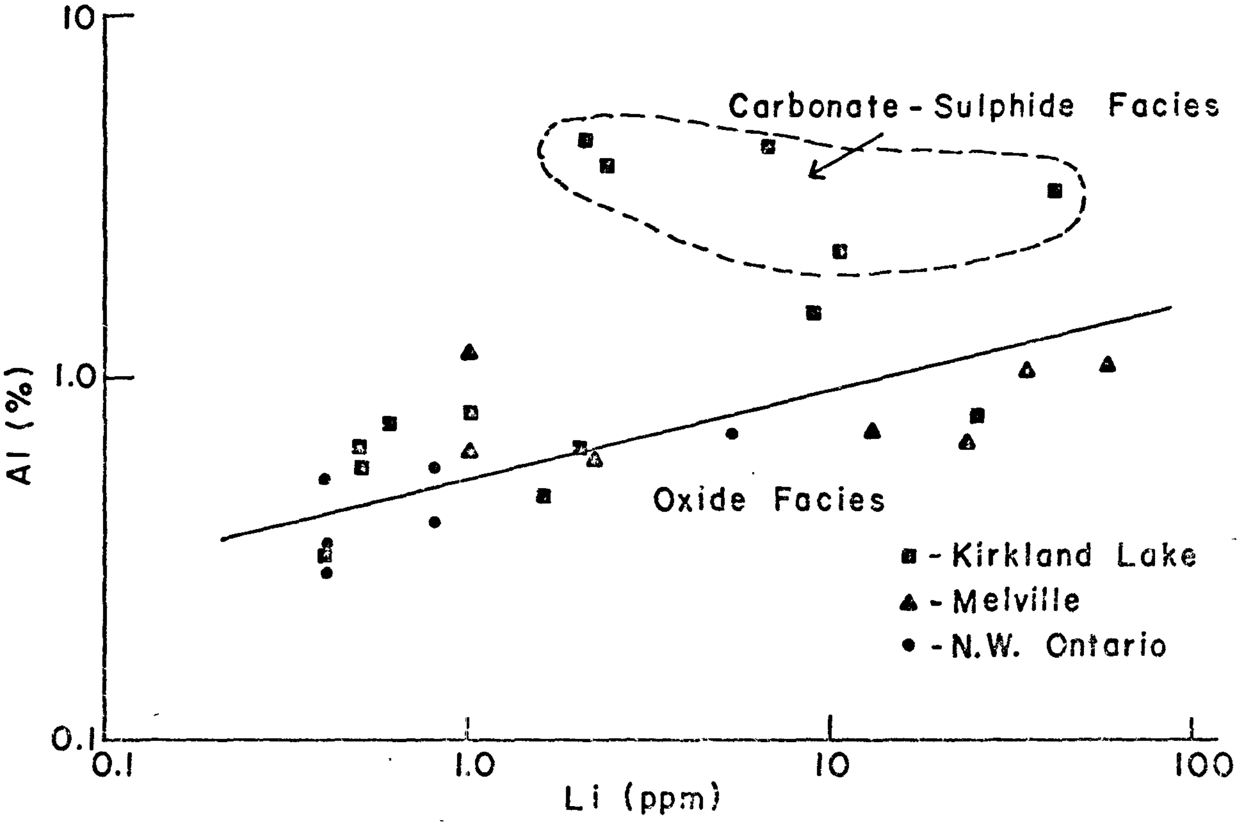


Figure 17. Relationship Between Li and Al in Iron Formation

material makes up a good portion of the rock. This data would indicate that modes of accumulation for the oxide and carbonate-sulphide facies, respectively, are quite different. The Li-Al correlation in the oxide facies would indicate an origin dominated by weathering processes (Ronov et al, op.cit.) whereas the behaviour of Li, in the siliceous detrital fractions of the other facies of iron formation, shows no trend and possibly reflects contributions of volcanic effusives to the depositional basin.

The previous discussion was concerned with the relation of the alkalis, in iron formation, to the major rock-forming elements and, in an indirect way, to the minerals themselves. This gave some implications as to the site location and distribution characteristics of the alkalis (mostly for Li) within the iron formations. The simple mineralogy of the oxide facies is an advantage in this respect since it is essentially a three-component system (magnetite-hematite, quartz and silicates). From an empirical standpoint then, it seems the alkalis are most closely related to the silicate fraction. The next question is, in what way are the alkalis related to the silicates - by substitution or adsorption phenomena? The following experiments shed some light on this question.

E. Leaching Experiment

Ellis and Mahon (1967) found that almost quantitative extraction of Cs occurred from most rocks in hot water/rock interaction experiments. Potassium, Rb and Li are liberated to a lesser extent and are readily taken from solution into secondary mineral structures. Considering the ease with which most alkali metals are ionized and removed from the initial rocks, it was considered feasible to conduct some leaching experiments on the iron formation samples.

Apart from the separation of magnetics and non-magnetics, the fine grain size and variable amounts of clay/silicate minerals and carbonates admixed in the banded ores, makes silicate mineral separation techniques inapplicable for these rocks. A selective chemical attack on the whole rock portion was considered as an alternative approach, following a technique outlined by Hirst and Nicholls (1958) for separating detrital and non-detrital fractions in limestones.

A weak acid attack on the rock will dissolve the alkalis held in the carbonate fraction and those adsorbed elements that can be leached from the other fractions, but should not liberate elements occupying sites within the crystal lattices of the magnetite and silicates. The clay minerals are not destroyed.

1. Leaching Procedure

In a clean 150 ml beaker, 1.00 gm of whole rock powder was weighed, and a 25% acetic acid solution was added. The slurries were subjected to constant agitation (magnetic stirrer) at room temperature for 24 hours. After leaching, the solutions and their residues were filtered on a fast filter paper and washed with de-ionized water. The filter paper and residue were dried in an oven at 100°C for 2 hours, after which the residue was carefully removed from the filter paper, mixed in an agate mortar and then spectrographed according to the procedure outlined earlier.

2. Results

Generally a decrease is seen in total alkali content in the leached residues (Table 10), as a result of liberation of the elements contained in the soluble fraction and adsorbed to minerals. The only sample to have appreciable carbonate present was #14b (9.5% CO_2 - Appendix A), so that a somewhat higher percentage of the whole rock is dissolved compared to the other leached samples (residues were not weighed after leaching to calculate percentage soluble). It is interesting to note that in this one sample of carbonate-sulphide facies of iron formation very little or none of the alkalis were lost through the leaching process. Too few data do not allow any firm conclusion to be made, but it would appear that in sample #14b the alkalis are incorporated exclusively in the structural sites of the minerals (detritals) and none are found in the acid soluble fraction (carbonate). In the residues of the other samples of iron formation (oxide facies), no quantitative extraction has occurred

Table 10. Comparison of Alkali Metals in Leached Residues-Whole Rock Portions of Iron Formation

Facies	Sample #		K*	Rb	Li	Cs	K/Rb	Rb/Cs
Mixed Carbonate-Sulphide	14b	whole	11870	38	2.4	1.3	310	29
		residue	8800	38	2.2	<1	230	38
Oxide	7	whole	420	12	0.6	<1	35	12
		residue	-	3.4	0.5	1	-	3.4
Oxide	DG-15-4	whole	580	29	24	4.7	20	6.2
		residue	-	7.7	16	2.7	-	2.9
Oxide	DG-16-4	whole	2490	55	34	17	45	3.2
		residue	1800	45	32	14	40	3.2
Oxide	MR-1-9	whole	980	11	5.3	3.7	89	3.0
		residue	950	7.3	4.6	2.9	130	2.5

* Spectrochemical determination of K in residues

during leaching so the bulk of the alkali metals must be:

1. occupying structural sites in silicates and clay minerals, or,
2. recrystallization of original colloidal silica and ferric oxide to acid resistant minerals has trapped adsorbed alkalis and not enabled their liberation by weak acid leaching.

F. Alkali Metals in Magnetite Fractions

Some of the magnetite fractions, separated from the whole rock for the purpose of a later section, were analyzed for Li, Rb and Cs. Working with the purified magnetite fractions essentially reduces the system to one component, free of other interfering minerals that may contain alkali metals. The magnetite analyses are presented in Table 11, along with their respective whole rock analyses, for comparison. Separation procedures generally resulted in a 95% magnetite content.

Table 11. Alkalis in Magnetites

Sample #			Li	Rb	Cs
Carbonate-Oxide Facies	14a	whole rock	44	0.6	<1
		magnetite	2.2	0.5	<1
Oxide Facies	11	whole rock	25	3.1	<1
		magnetite	5.5	1.1	<1
Oxide Facies	MR-1-9	whole rock	5.3	11	3.7
		magnetite	8.4	17	4.9

The purified magnetite obtained from #14a contains very little Li compared to the whole rock portion. Contrary to Li behaviour, nearly all of the Rb is contained in the magnetite fraction of #14a.

In #11, only one-fifth of the Li concentration and one-third of the Rb concentration, of the whole rock, is found with the magnetite fraction.

The upshot of all this is that much of the Li appears not to be associated with the magnetite fraction but instead is related to the clay mineral and silicate content (see modal composition - Appendix B). As concerns the Rb, and probably Cs content of the oxide facies, it would seem that much of it is incorporated into the magnetite structure although the mechanism of such a substitution of large alkali ions in the spinel structure is not clear. Relatively higher concentrations of Li, Rb and Cs are observed in the magnetite of MR-1-9 from N.W. Ontario, and are even greater than the whole rock portion. There is the possibility that the magnetite, presuming it was originally deposited as a colloid, may have adsorbed alkali metals present in the depositional environment and has retained such a relation despite subsequent diagenetic and metamorphic effects.

CHAPTER 5

RELATIONSHIP OF IRON FORMATION TO ARCHEAN VOLCANICS

Assessment of the role of volcanism and related processes to iron deposition in the Precambrian is not easily made, since it depends largely upon conclusions drawn from rocks associated with the iron formation. As already discussed, the variations in basinal environments and post-depositional effects (metamorphism) can have marked effects on the geochemistry of the alkali trace elements and their application to problems in petrology. Be that as it may, the close spatial affinity of iron formation to volcanic and igneous activity in the Kirkland Lake area is not easily overlooked and their contemporaneity may imply a genetical relationship between them. Ridler (1970) has gone a step further and demonstrated the development of the Boston iron formation as an integral part of an Archean cycle. The simplified stages of the Timiskaming strata are as follows:

1. An opening phase of coarse sedimentation representing deformation and erosion of pre-Timiskaming volcanic complexes, along the hinge line of the mobile belt.
2. Stages of intermediate alkaline volcanism, hypabyssal intrusions and volcanogenic sedimentation representing

the felsic phase of the volcanic cycle.

3. A closing phase of quiescent volcanogenic sedimentation culminating in iron formation. The alkaline volcanism and iron formation are both anomalously auriferous and would indicate further evidence of their consanguinity (Ridler, 1970).

A. Archean Cyclicity

The cyclic nature of Archean volcanic assemblages has been well documented in the literature and so no attempt will be made here to summarize the many data, and proposed models for Archean volcanism. However, C.R. Anhaeusser (1970) has brought together all of the specific studies on cyclic volcanicity and sedimentation, in the Shield areas of the world, to demonstrate the overall nature of Archean cyclicity. His major cycles (one of several types of cycles that he discusses) have been recognized in volcanic belts in Canada, South Africa and Western Australia (Anhaeusser, op.cit., p.1). On comparison of the various lithologies found in them Anhaeusser (op.cit.) groups the rock types into an early volcanic phase and a later sedimentary phase, the predominantly volcanic phase being subdivided into an Ultramafic Group and a Greenstone Group (1970, p.4). The Ultramafic Group is less well known in the fold belts of the Canadian Shield and will not be considered here. His proposed stratigraphic column is presented in Figure 18. The most interesting observation

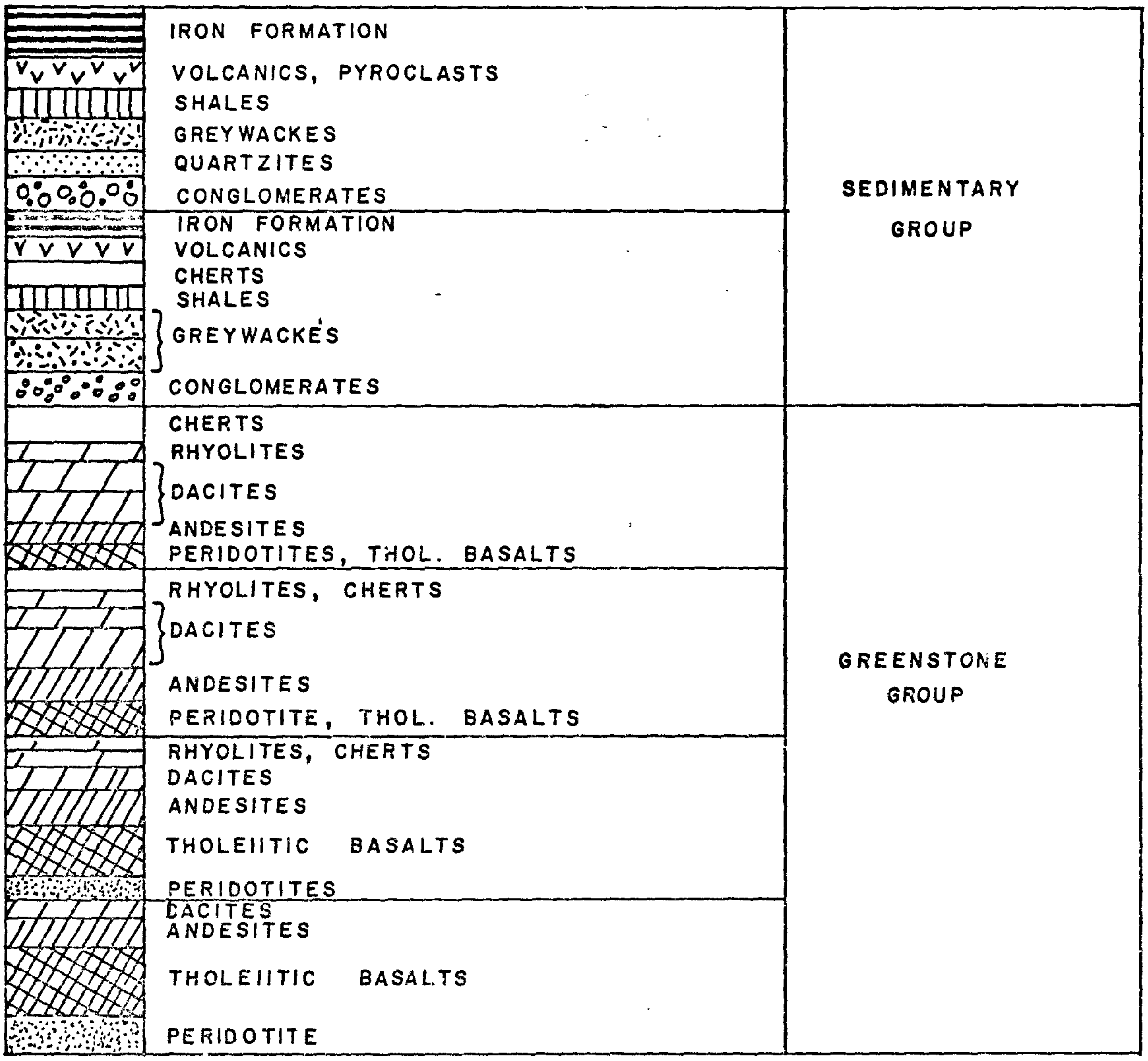


FIGURE 18. HYPOTHETICAL ARCHEAN STRATIGRAPHIC COLUMN (ADAPTED FROM ANHAEUSSER, 1970)

from this generalized Archean stratigraphical column is the common occurrence of banded iron formations and cherts at the top of each major cycle, particularly for the later Sedimentary Group. This portrayal of the Archean bears considerable likeness to the Archean cyclicity observed in the Kirkland Lake area by Ridler (1969). The unique alkaline volcanism of this area together with the well developed iron formation permits a rare opportunity to study the development of these later phases of Archean volcanism and sedimentation, as outlined by Anhaeusser (op.cit.).

B. Timiskaming Volcanics

Cooke and Moorehouse (1969), and Moorehouse (1970) have given an adequate breakdown of the chemistry and petrography of the Timiskaming volcanics in the Kirkland Lake volcanic-sedimentary sequence, however some new analyses of Kirkland Lake volcanics and intrusions are presented here (Appendix A).

There is a predominance of pyroclastic material in the Timiskaming volcanics particularly in the late alkaline effusives. However lava flows do occur and in some instances their primary features are quite well preserved, where there has not been extensive deformation. As expected the primary minerals have been invariably altered in these rocks which precludes the usage of modal nomenclature systems. Consequently the rocks have been classified in accordance with the chemical classification scheme of Irvine and Baragar (1971) with reference to chemical analyses from Cooke and Moorehouse (op.cit.).

C. Geochemistry of Volcanics - Alkali Metals

The alkali metal abundances of the volcanic rocks are presented in Table 12 in which the rocks are listed in order of increasing differentiation. Two analyses of samples from syenite stocks in the area have also been included. The generally increasing abundances of the K, Rb and Cs values quite obviously reflect the differentiation (the Rb increased by two orders of magnitude whereas the K increased by one order of magnitude). However Li does not show an increase with differentiation but is more or less constant throughout the series. This is probably because the amount of Li which can be admitted into the feldspar lattice is generally quite restricted. So instead the Li is concentrated in the mafic silicate minerals, as implied by the increasing Li/Mg ratio with differentiation.

D. Genetic Implications

1. K/Rb ratio

The general geochemical coherence between Rb and K and the constancy of the K/Rb ratio in igneous rocks is well documented in the literature. Using this relationship, the K/Rb ratios for the Kirkland Lake area volcanics and iron formations are plotted in Figure 19A, with the generalized K/Rb "fields" indicated in Figure 19B. The diagrams also show the limits of "normal" K/Rb

Table 12. Comparison of Alkali Metals in Archean Volcanics and Intrusives, Kirkland Lake Area

Rock Type	Sample #	Abundances					Ratios				
		ppm*			per cent**						
		Rb	Li	Cs	K	Na	K/Rb	K/Cs	Rb/Cs	Li/Mg 10^3	K/Na
Peridotite	9	2.0	23	<1	0.04	0.09	210	420	2	0.17	0.44
Tholeiitic basalt	1	23	20	1.1	0.65	2.53	280	5900	21	0.80	0.26
Tholeiitic basalt	2	12	13	<1	0.46	1.28	380	4600	12	0.48	0.36
Tholeiitic basalt	3	9.0	8.6	<1	0.37	1.63	420	3700	9	0.38	0.23
Mafic trachyte porphyry	24	88	13	1.5	3.62	3.08	410	24100	59	0.54	1.2
Mafic trachyte	26	60	20	3	2.32	2.05	390	7700	20	0.44	1.1
Trachyte porphyry	25	300	11	17	3.55	4.56	120	2100	18	2.0	0.78
Leucite trachyte	20	212	29	9.0	7.50	0.45	350	830	24	1.7	16.7
Mafic syenite (Murdock Creek Stock)	12	71	12	2.7	3.35	4.22	470	12400	26	0.69	0.79
Alkali syenite (Otto Stock)	21	109	2.0	<1	5.22	4.63	480	5200	109	0.41	1.1

* geometric means of triplicate spectrochemical analyses; Rb values are from chemical determinations except sample #9 and #3.

** chemical determinations

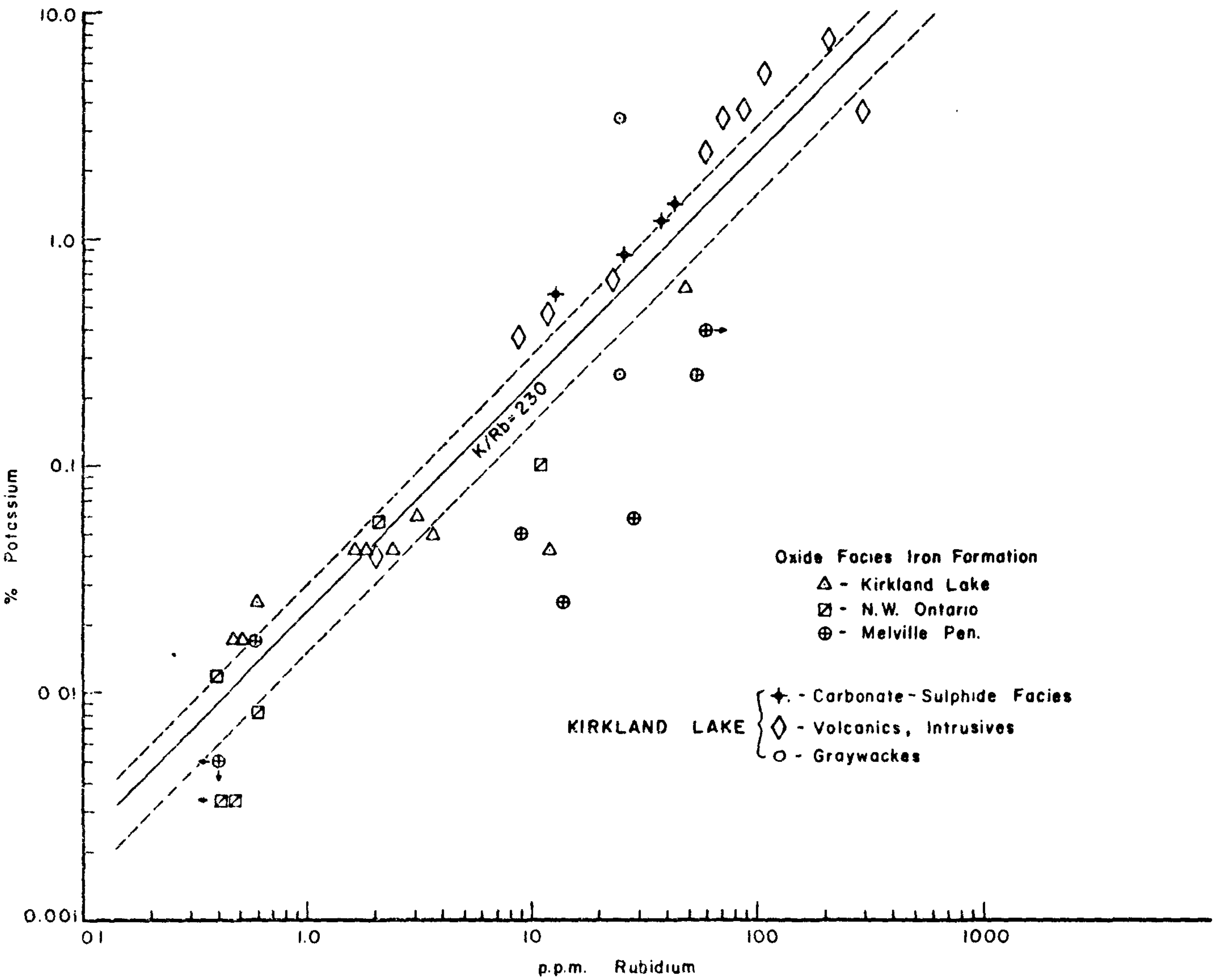


FIG. 19A. RELATIONSHIP BETWEEN K AND RB.

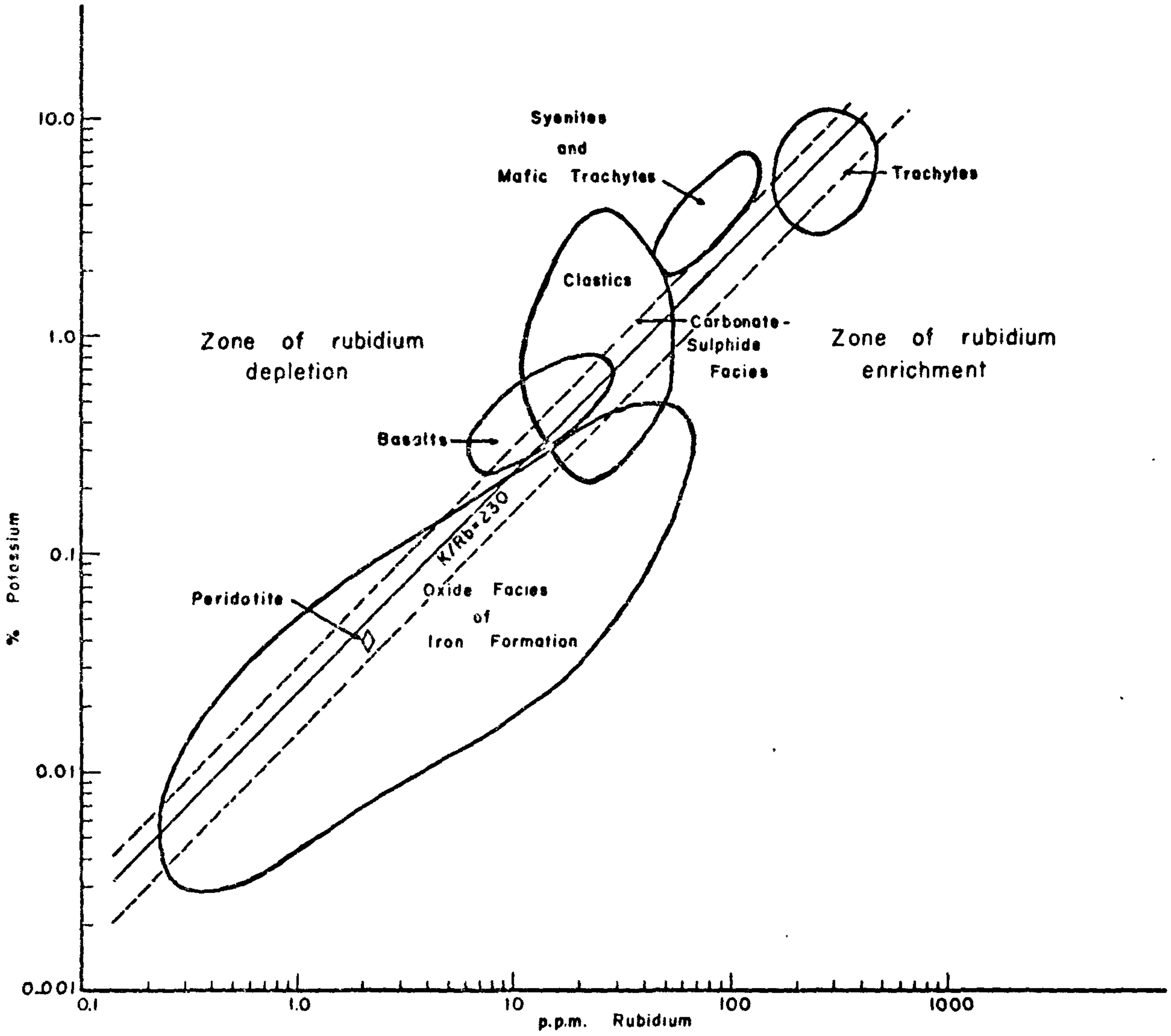


FIG. 19B. K/Rb FIELDS

ratios (Taylor, 1966) to indicate the relative enrichment, or depletion of Rb in the rocks.

A fair correlation is observed between Rb and K in Figure 19A. The oxide facies of iron formation have K/Rb ratios lower than and within the "normal" range. In particular, the Melville samples show a marked enrichment in Rb (low K/Rb ratios) for probable reasons already discussed. The K/Rb "field" for the carbonate-sulphide facies of iron formation and other clastic sediments straddles the "normal" range and is closely associated with the K/Rb ranges for the volcanics and intrusives of the area. This coincidence of K/Rb values may be an indication that the clastic material of these rocks is derived from the contemporaneous volcanism of the area.

S.R. Taylor (op.cit.) has shown that low K/Rb ratios (Rb enrichment) are a common anomaly in several common crustal rocks (late stage granites and pegmatites). The trachytes from Kirkland Lake area show a somewhat variable K/Rb ratio, some are low whereas others are fairly high. However most of the K/Rb values for the volcanics and intrusives are higher than the normal range indicating either Rb depletion, or alternatively an enrichment of K. This may arise from an accumulation of early feldspars, themselves depleted in Rb. In the case of the mafic syenites and trachytes, higher K/Rb ratios may be a result of the feldspars having crystallized with other minerals (biotite, muscovite) having more favorable lattice sites for Rb.

2. K/Na ratio

From an examination of Table 12 it is apparent that another useful chemical guide to the differentiation of these rocks is the K/Na ratio which is generally quite low for the basic rocks and higher, although quite variable, for the late differentiates.

At Kirkland Lake, Ridler (1969) correlated stratigraphic height in the volcanic pile with potash content of the rocks. Using this tool, in conjunction with structural and stratigraphic criteria, he was able to interpret several volcanic cycles in the area. This same approach was used here, but utilizing K/Na ratios rather than absolute abundances, with the intention of including data from the Boston iron formation and its correlatives.

The K/Na ratios are plotted against stratigraphic height in Figure 20 (subdivided into cycles according to Ridler's interpretation of the volcanic stratigraphy). Most of the data and terminology are from Ridler (op.cit.) and reference should be made to this work for further details on the stratigraphy. The plot consists of 86 rock sample analyses (50 analyses from Ridler, op. cit.; 15 analyses from Cooke and Moorehouse, 1969; 1 analysis from P. van de Kamp, 1964, McVittie basalt; 27 analyses from this study, including Boston iron formation, clastic sediments, volcanics and intrusives). The geometric means of the K/Na ratios are indicated by the line drawn through the various stratigraphic units, and at the same time outline the cyclical nature of the K/Na ratios. The ratio approaches a peak in the late differentiates of each volcanic cycle.

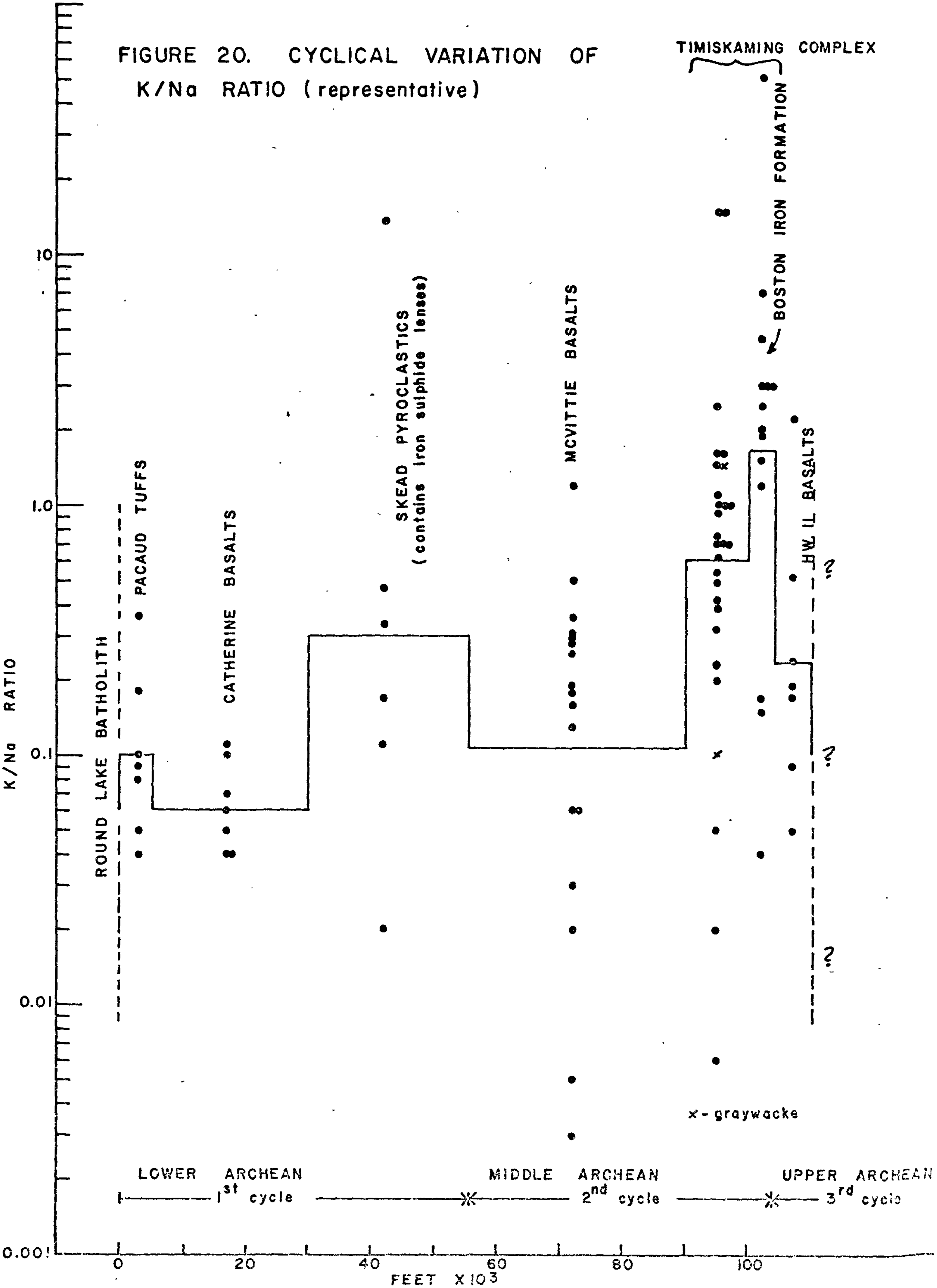


FIGURE 20. CYCLICAL VARIATION OF K/Na RATIO (representative)

Iron formations appear in the volcanic pile at various stratigraphic heights (generally in the end stages of the volcanic cycles, Ridler, op.cit.), but data is available here only for the Boston iron formation. The most notable observation from Figure 20 is that the geometric mean of the K/Na ratios of the Boston iron formation is higher than that for the associated volcanics and intrusives (Timiskaming Complex). The high enrichment of K relative to Na suggests that iron formation is developed at the end of a volcanic cycle, in agreement with Anhaeusser's model of cyclic volcanicity and sedimentation in Archean greenstone belts. However, there is a great variation in the ratios for any one stratigraphic unit (Figure 20), and more data is required before any firm conclusions can be made.

CHAPTER 6

FERRIDES AND MINOR ELEMENTS IN MAGNETITE FRACTIONS FROM IRON FORMATIONS

The purpose of this section of the thesis was to study the abundances of the ferrides and other elements in magnetites from the various iron formations of the Canadian Shield. From the spectrochemical results it was hoped to find significant geochemical characteristics for the ores and rocks of each area.

A. Sampling and Analytical Method

The magnetite samples were purified using the procedure of Kisvarsanyi and Proctor (1967):- approximately 10-15 gm rock sample, powdered to -100 mesh, was transferred to a beaker filled with distilled water. A hand magnet, enclosed by a small beaker, was used to separate the magnetite by stirring the water and the sample. The water was decanted 5-10 times to discard non-magnetics. The magnetite was then checked under a binocular microscope for purity and if the desired purity of 95% was not obtained, the sample was reground in an agate mortar, immersed in a beaker of acetone and separated again. The fine grain size and intergrowth of chert-silicate material with the magnetite prevented a final purity greater than 95%. The Frantz isodynamic separator was tried under various conditions, prior to repetition of the above procedure, but with little benefication of the magnetites.

B. Standards for Trace Elements in Magnetites

A synthetic base approximating that of magnetite was prepared from "Specpure" Fe_2O_3, to which "Spex Mix" was added and a set of standards was obtained by successive dilution with additional "Specpure" Fe_2O_3. A convenient dilution factor was $\sqrt{0.1}$, to give standards containing 1000, 316, 31.6, 10 and 3.2 ppm (Ahrens and Taylor, 1961).

C. Spectrographic Conditions

The dried magnetite was mixed in an agate mortar with strontium carbonate and graphite in a 1:1:1 ratio, using palladium as an internal standard (added initially as $PdCl_2$ solution to buffer and then dried to give a concentration of 0.013% Pd). The Stallwood Jet was also utilized to improve precision.

Spectrographic conditions were similar to those used in the previous section (p.20), except for the following changes:

Electrodes.........Ultra Carbon; sample (anode), preformed electrode 213202 (#5440) U-2 grade; counter electrode, 1/8 in rod, 711202 (U40-2), U-2 grade - pencil point.

Emulsion and Range......Kodak SA#1 and 111-F, 2200-4800Å

Developer....................3 min in Kodak D-19 at 20°C
Excitation Source............Spark ignited unidirectional arc
Screens......................2
Filter.......................none
Exposure time................2 min, single exposure
Electrode packing............manually; 20mg sample, 40 mg buffer
(1:1 $SrCO_3$ and graphite)
Stallwood Jet................A/O_2 atmosphere, 20 CFH
Spectral Lines...............See Table 13

Table 13. Analytical Line Pairs

Internal Standard	Analytical Line, Å	
Pd 3421.2	Al	3082.2
"	Mg	2782.9
"	Co	3453.5
"	Ni	3414.7
"	Cu	3273.9
"	Ti	3349.4
"	Mn	2801.0
"	V	3102.3
"	Ga	2943.6
Pd 3609.5	Cr	4254.3

D. Results and Discussion

The analytical curves for the above elements are presented in Appendix D. The spectrographic results are presented in Table 14, expressed as geometric means of triplicate determinations. The coefficient of variation or relative standard deviation for each element is also expressed in Table 14, based on pooled triplicate analyses. Results are satisfactory for most elements except Al and Mg which are reported as semi-quantitative values, due to lack of appropriate standards. Iron interference was negligible for most elements but caused a slight "toe" on analytical curves for Co and V (Appendix D). Also for Ga, Fe interference was appreciable and a correction was applied. The Ga 2943.63 line was corrected for iron interference from Fe 2943.57 by using a neighbouring iron line, Fe 2945.70, of similar intensity. The ratio of $I_{Fe\ 2943.57}/I_{Fe\ 2945.70} = 0.488$ in the absence of gallium (blank determination), so that the corrected intensity of Ga 2943.63 was found by the following relationship:

$$I_{Ga\ 2943.63} = I_{Total\ at\ 2943} - 0.488 I_{Fe\ 2945.70}$$

The effect of such iron interference on Ga 2943 can be seen in Appendix D-9 and D-10.

Accuracy is difficult to assess but from one arcing of the rock standard W-1, the results for most elements agree with recommended values (Table 15) and suggests that matrix affects had been minimized in the method.

Table 14. Geometric Means of Trace and Minor Element Contents in Magnetites from Iron Formations and Associated Rocks*

Rock Type	Locality	Sample #	Ga	V	Mn	Ti	Cu	Cr	Ni	Co	Mg**	Al**
Oxide Facies of Iron Formation	Kirkland - Larder Lake	6	4	16	409	64	49	nd(<10)	12	7	0.10	0.06
		10	2	nd(<10)	101	nd(<10)	4	nd	12	12	0.14	<0.01
		11	<3	59	438	63	3	nd	20	18	0.28	0.04
		14a†	4	39	376	470	165	28	11	12	0.35	0.5
		18	2	23	58	105	<3	12	11	<5	0.02	0.05
	North Spirit Lake	MR-1-9	nd(<3)	19	>1000	286	5	39	8	<5	1.8	0.4
	Melville Peninsula	DG-7-2	nd	115	424	<10	<3	nd	10	30	0.07	0.10
Trachyte	Kirkland Lake	25	nd	237	419	>>2000	122	68	41	34	0.07	>>0.5
Relative Standard Deviation %			7.1	14.2	8.8	7.1	11.1	12.7	9.2	12.3	9.5	22.6

*-triplicate analyses in ppm, except Mg and Al which are expressed in %

**-semi-quantitative values

nd-not detected with sensitivity limits in brackets

†-mixed carbonate-oxide facies

Table 15. Comparison of Results

Element	Spec.	Recommended Value*
Ga	9.0	16
V	270	240
Mn	1500	1670
Ti	-	6400
Cu	148	110
Cr	215	120
Ni	52	78
Co	29	50

* Fleischer, 1969

E. Geochemical Implications

An examination of Table 14 indicates the variability in content of the trace ferrides in the magnetite fractions of the various iron formations. Magmatic iron oxides are generally higher in trace elements than those from volcanic-sedimentary and metasomatic origins, but if the contents of several elements in magnetite are considered simultaneously, then it is possible in some cases to separate different types of ores and rocks (Frietsch, 1970). In his study of the trace elements in magnetite and hematites from N. Sweden, R. Frietsch demonstrated that Cr, Mg, Ti and Ni show variations in content depending on the mode of formation, whereas other elements are more or less uniformly distributed in the different kinds of ores and rocks. Using such criteria the magnetite analyses of Table 14 were assessed to determine possible modes of formation.

The trachyte-porphyry magnetite (#25) has a comparatively high trace element content, particularly for V, Ti, Cr, Ni and Al, manifesting the magmatic character of this rock type.

Among samples from the Kirkland Lake iron formations one in particular, #14a, contains a comparatively high amount of trace elements (most notable are Ti, Cu, Cr, Mg and Al). As mentioned previously this sample is from a mixed facies of iron formation, and occurs in a hybridized zone adjacent to the Murdock Creek syenite stock in Teck township (Ridler, 1969).

The remaining four Kirkland magnetites are somewhat similar in trace element abundances and may be taken to represent typical magnetite from the iron formations of the area. For ease of comparison a graphical representation of the ranges of trace elements in magnetites from this area and world-wide iron ores of various origins is presented in Figure 21 (adapted from Frietsch, op.cit.; Kisvarsanyi and Proctor, op.cit.). The range of the trace element values of the Kirkland magnetites (including #14a) are very similar to those of known volcanic-sedimentary magnetites with some similarity to contact-metasomatic magnetites also evident. Generally the hydrothermal and magmatic

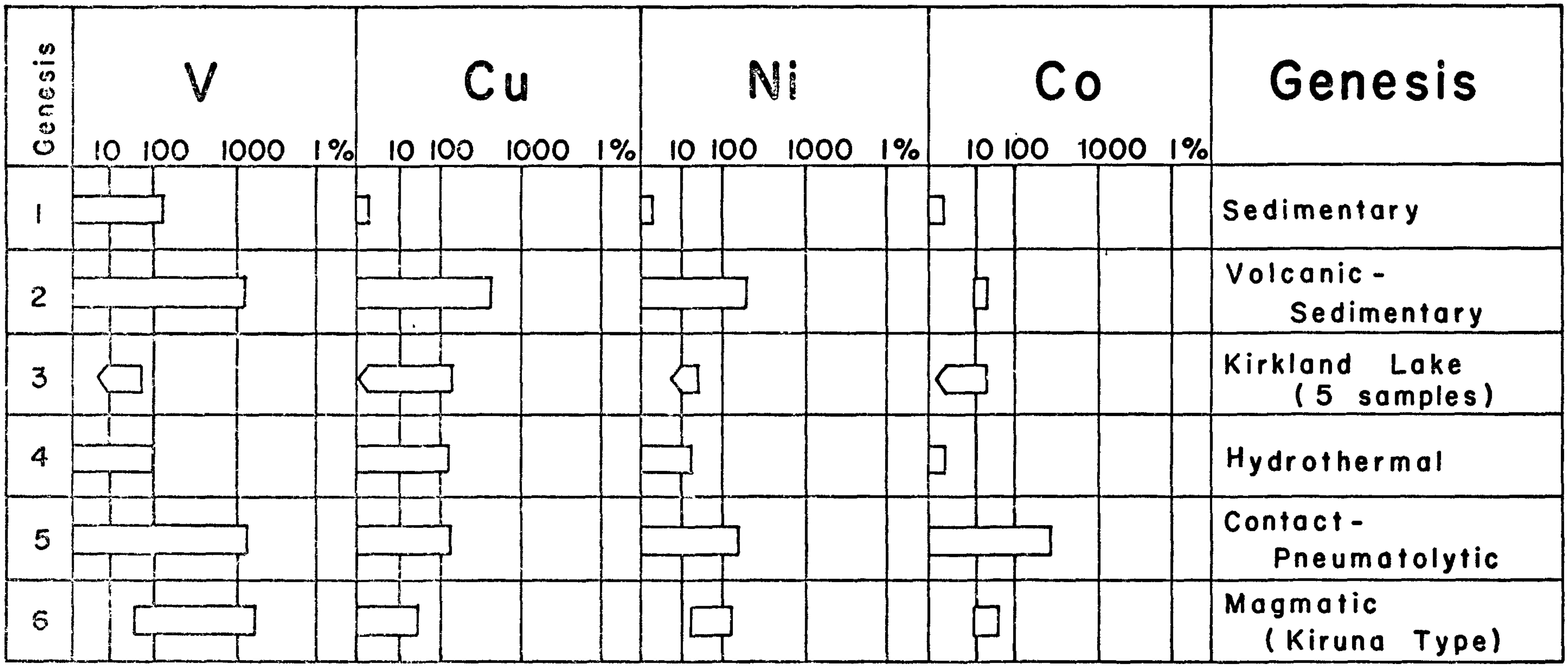


FIGURE 21. Comparison of Trace Element Content in Magnetites from Canadian Shield Iron Formations, with Those of Magnetites from all over the World (iron ores). (Data from Frietsch, 1970; Annersten and Ekstrom, 1971 and this study)

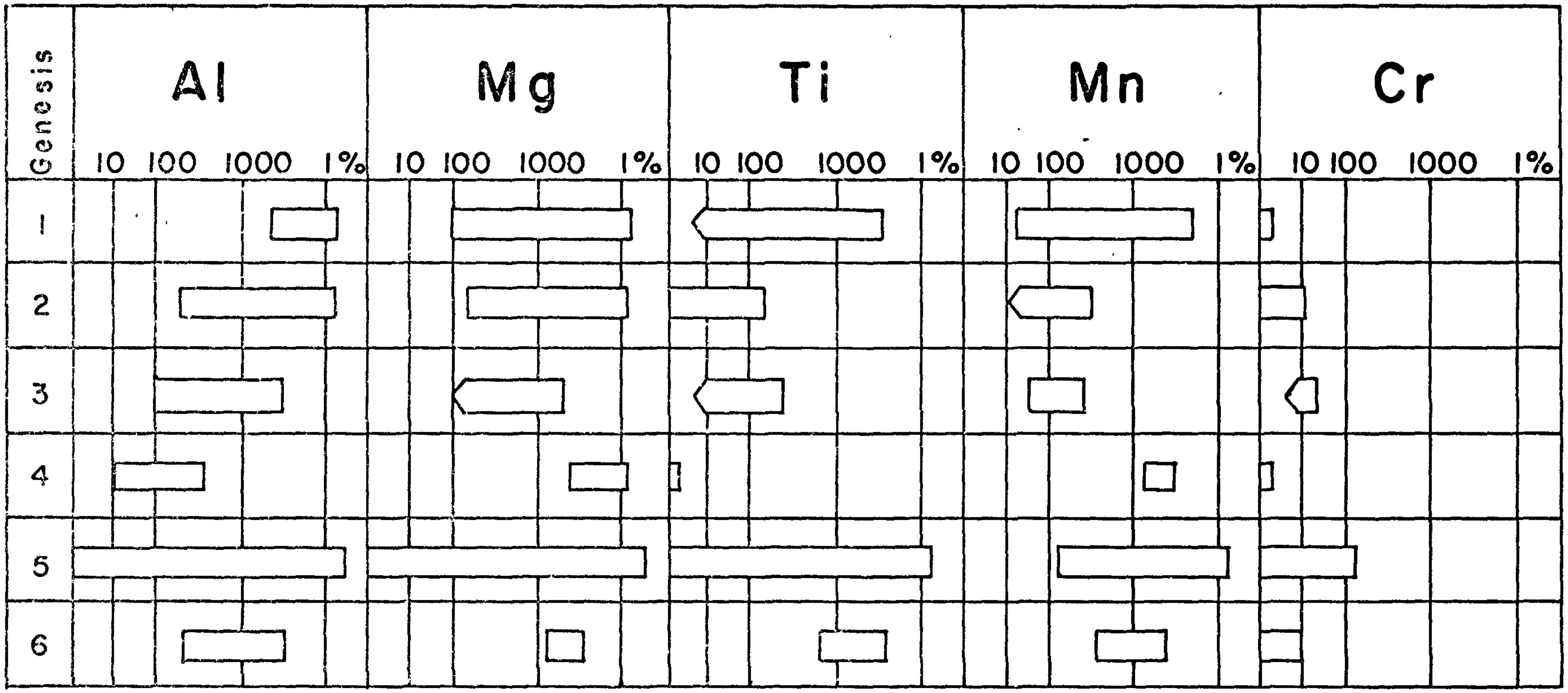


FIGURE 21 continued.

magnetites have quite different values from the Kirkland Lake magnetites. Analyses are too few to make any firm conclusions from this comparison study but the evidence presented here would suggest a "volcanic exhalation" genesis for the iron formation occurrences in the Kirkland-Larder Lake area.

As concerns the N.W. Ontario and Melville Peninsula occurrences little can be said with regard to analyses of a single sample from each area. Trace element content of the magnetite from MR-1-9 is relatively high (Table 14) and for this reason may represent a metasomatic origin for that particular occurrence in N.W. Ontario, an inference admittedly without geological evidence. The magnetite from Melville Peninsula, DG-7-2, which is located 10 miles south-west of the rocks showing alkali metasomatism (discussed previously), has values very similar to the Kirkland-Larder Lake magnetites, and volcanic-sedimentary magnetites.

In his extensive study of trace elements in iron oxides, Frietsch (op.cit.) used "concentration coefficients" in the elucidation of genetical differences between iron ore types.

> "This coefficient (= clarke of concentration) has been obtained by dividing the mean content of an element in the iron oxide with the content of this element in the upper lithosphere. Thus a coefficient higher than 1 means an enrichment of the element in the iron oxide as compared with the

upper lithosphere." (op.cit., p.107).

From Table 16 it is seen that almost all of the concentration coefficients for the ferrides and minor elements in the various samples are less than 1. The magnetite shows a relatively high deficiency in trace elements inferring that the processes giving these magnetites have depleted these elements.

Table 16. Concentration Coefficients-
Magnetites (Clarke, ppm)

	Ga	V	Mn	Ti	Cu	Cr	Ni	Co	Mg^{10^4}	Al^{10^4}
Continental Crust *	19	135	950	5700	55	100	75	25	2.3	8.2
Kirkland Lake**	0.16	0.18	0.22	0.01	0.22	0.13	0.17	0.40	0.05	0.007
N.W. Ontario (MR-1-9)	0.16	0.14	1.05	0.05	0.09	0.39	0.11	0.20	0.78	0.05
Melville (DG-7-2)	0.16	0.85	2.03	0.14	0.25	0.10	0.13	3.00	0.58	1.70

*data are from S.R. Taylor (1964) and D.M. Shaw (1957)

**geometric mean of 5 samples (magnetites)

CHAPTER 7

CONCLUSIONS

Trace element data has been stressed in this study of the geochemistry and modes of formation of the "Algoma-type" iron formations of the Canadian Shield. The various paths of migration and fixation of the alkali metals in iron formations have been outlined.

It is well known that source rock compositions are often reflected in the sediments derived therefrom, however in oxide iron formation admixed clastic material is often lacking, and the mineralogy, textures and primary structures are evidence of chemical precipitates formed in direct response to their environment. An explanation for the presence of alkalis in such rocks is difficult. An intimate association with alkaline volcanic rocks has been demonstrated for the iron formation at Kirkland Lake, and the other iron formations cited are also known to be associated with metavolcanic sequences. It appears then that the alkalis are somehow related to volcanism in the area. In certain cases metasomatism and related processes can be an important factor especially in those occurrences adjacent to intrusive igneous rocks.

The alkali geochemistry of the Boston iron formation and its correlatives, in the Kirkland Lake area, indicates deposition under variable physical-chemical conditions, qualitatively consistent with the lateral facies development advocated by James (1954). A relation is observed between the pattern of alkali element distribution and the facies of iron formation. The oxide facies, as represented by banded magnetite-chert ores, contain very low alkali abundances and exhibit low K/Rb and K/Cs ratios whereas the carbonate-sulphide facies display higher trace element content (a reflection of their clastic nature), with "normal" K/Rb and K/Cs values. As evident in some of the occurrences, the geochemical character of the environments of deposition may be obscured by the effects of local differences - specifically, the geochemical aspect of the surrounding terrain.

As concerns the distribution of the alkalis in the mineral fractions, evidence from leaching tests and analyses of the magnetite fractions has shown that the rare alkalis Rb, Cs, and to a limited extent Li, have been "captured" in the magnetite structure, a phenomena violating the laws of crystal chemistry. For the most part, Li shows a more conformable nature and is related to the clay minerals and detrital silicate fraction of the rocks.

A more direct approach to the genesis of these iron formations was a study of the ferride elements in the individual magnetite fractions. It was deduced that the magnetites are highly depleted in most elements and consequently a magmatic derivation for the iron formation is not likely. One must invoke other modes of origin, the most reasonable being the processes of volcanism, and chemical weathering.

James (op.cit.) has emphasized that the relationship between iron formation and volcanism is structural; not necessarily chemical: the major requirement for deposition of iron formation is a closed or restricted basinal environment. The relatively thin and discontinuous character of iron formations in the Archean are considered due to deposition in small basins ponded by submarine volcanic accumulations (James, op.cit. p.280). The geochemistry of trace elements in these iron formations and associated rocks are more indicative of the actual physical-chemical conditions prevailing in such sedimentary basins. Finally, in synthesizing the above evidence, it would appear that there may be less difference between the volcanic and the weathering hypotheses of origins for iron formation, than has been reported in the literature in the past.

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APPENDIX A

CHEMICAL AND SPECTROGRAPHIC ANALYSES

Bulk chemical analyses are expressed in weight per cent
and were carried out by J.R. Muysson
Trace element analyses are reported as parts per million

APPENDIX A-1

Chemical Analyses

Iron Formation - Kirkland Lake

Oxide facies

	4	5	6	7	8	10	11
SiO_2	77.99	72.02	62.72	36.28	95.32	47.99	50.33
TiO_2	0.04	0.01	0.00	0.02	0.00	0.01	0.04
Al_2O_3	1.51	1.05	1.22	1.40	0.62	0.88	1.47
Fe_2O_3	8.91	17.03	23.77	39.91	0.98	35.20	25.20
FeO	8.31	8.57	10.48	19.34	1.60	13.11	11.28
MnO	0.30	0.13	0.08	0.02	0.07	0.01	0.08
MgO	1.44	1.02	0.81	1.70	0.23	2.21	4.39
CaO	0.27	0.39	0.77	1.13	0.56	0.97	4.82
Na_2O	0.03	0.02	0.01	0.02	0.00	0.13	1.78
K_2O	0.06	0.03	0.03	0.05	0.05	0.02	0.07
P_2O_5	0.05	0.09	0.16	0.26	0.00	0.19	0.28
H_2O+	0.70				0.29		
H_2O-	0.29				0.09		
CO_2	0.04	0.02	0.00	0.01	0.40	0.00	0.04
Cr_2O_3	0.00				0.00		
S		0.03	0.06	0.04		0.00	0.00
Rb_2O				0.0012			
TOTAL	99.94	100.40	100.09	100.16	100.21	100.72	99.78
Fe as Fe_2O_3	18.15	26.55	35.42	61.40	2.76	49.77	37.74
Li	1.0	0.5	0.5	0.6	<0.5	1.6	25
Rb	3.7	2.4	1.8	12	1.7	0.5	3.1
Cs	<1	<1	<1	<1	<1	<1	<1

Description and location of samples given in Appendix B
Trace element analyses by F.G. Alcock

	oxide facies		Mixed Facies c.o.	Mixed Facies c.s.	carbonate facies		sulphide facies
	17 comp.	18	14a	14b	15	16	13
SiO_2	54.71	46.70	49.82	58.07	32.87	30.51	38.91
TiO_2	0.08	0.02	0.24	0.23	0.18	0.58	0.25
Al_2O_3	2.83	1.21	6.36	7.24	4.30	8.17	8.50
Fe_2O_3	22.74	26.50	6.03	4.52	0.35	0.42	23.66
FeO	12.37	12.44	15.43	10.31	6.30	6.64	1.88
MnO	0.07	0.08	0.12	0.09	0.13	0.15	0.00
MgO	2.46	0.24	3.64	2.26	19.43	8.73	0.13
CaO	2.10	7.23	6.07	1.94	6.65	16.09	0.10
Na_2O	0.21	0.00	0.01	1.23	0.02	0.91	3.95
K_2O	0.97	0.02	0.03	1.43	1.02	1.69	0.69
P_2O_5	0.20	0.09	0.16	0.15	0.00	0.18	0.01
H_2O+				0.84	1.03	0.86	0.32
H_2O-				0.09	0.08	0.07	0.69
CO_2	0.51	5.71	8.95	9.46	27.29	23.39	0.06
Cr_2O_3				0.02	0.24	0.07	0.02
S	0.39	0.31	0.92	3.74	0.09	0.02	20.27
Rb_2O				0.0042			
C						0.63	7.76
TOTAL	99.49	100.43	97.31	100.22	99.95	99.10	99.60
Fe as Fe_2O_3	36.49	40.33	23.18	15.98	7.35	7.80	25.75
Li	9.0	2.0	44	2.4	10.8	6.7	2.0
Rb	49	<0.5	0.6	38*	26	44	13
Cs	4.8	<1	<1	1.3	1.0	3.7	<1

* Chemical value
c.o. - carbonate-oxide
c.s. - carbonate-sulphide

	Graywackes		Peridotite	Volcanics		
	19	23	9	1	2	3
SiO_2	44.40	49.55	43.31	53.07	47.10	49.68
TiO_2	0.89	0.90	0.43	1.51	1.38	1.72
Al_2O_3	12.82	13.90	8.96	15.80	14.14	14.93
Fe_2O_3	0.92	3.17	1.54	2.83	3.76	2.77
FeO	7.79	5.28	8.94	8.59	13.56	12.40
MnO	0.21	0.13	0.15	0.32	0.66	0.40
MgO	7.43	6.15	22.54	4.14	4.50	3.73
CaO	8.61	6.34	6.37	7.96	10.56	9.96
Na_2O	2.93	2.94	0.12	3.41	1.73	2.20
K_2O	0.30	4.01	0.05	0.78	0.55	0.45
P_2O_5	0.42	0.58	0.03	0.12	0.15	0.15
H_2O+	2.58	2.81	6.90	1.50	1.65	1.38
H_2O-	0.09	0.14	0.49	0.08	0.09	0.10
CO_2	9.86	4.18	0.02	0.11	0.29	0.50
Cr_2O_3	0.03	0.05	0.40	0.02	0.01	0.01
S						
Rb_2O				0.0025	0.0013	0.0010
TOTAL	99.28	100.13	100.25	100.24	100.13	100.38
Fe as Fe_2O_3	9.58	9.04	11.40	12.38	18.83	16.55
Li	5*	100*	23	20	13	8.6
Rb	25*	25*	2.0	23**	12**	9.0**
Cs	<1*	10*	<1	1.1	<1	<1

* Semi-quantitative values
**Chemical values

	Volcanics			Intrusives		
	20	25	26	12	21	24
SiO_2	53.00	53.15	47.05	55.40	63.60	52.98
TiO_2	0.89	0.71	0.99	0.74	0.25	0.96
Al_2O_3	16.64	21.38	12.45	15.31	18.74	15.73
Fe_2O_3	4.46	3.06	4.65	5.05	1.41	3.03
FeO	4.14	2.04	6.43	2.52	0.93	4.97
MnO	0.11	0.15	0.18	0.12	0.06	0.14
MgO	2.89	0.93	7.55	2.89	0.81	3.99
CaO	2.33	2.63	9.04	4.93	1.41	5.56
Na_2O	0.61	6.14	2.76	5.69	6.24	4.15
K_2O	9.03	4.27	2.79	4.03	6.29	4.36
P_2O_5	0.62	0.13	1.56	0.69	0.12	0.54
H_2O+	2.33	1.39	2.29	0.65	0.13	1.66
H_2O-	0.21	0.10	0.18	0.07	0.09	0.12
CO_2	2.44	3.49	1.69	1.68	0.16	1.59
Rb_2O	0.0232	0.0328	0.0066	0.0078	0.0119	0.0096
TOTAL	99.72	99.60	99.62	99.78	100.25	99.79
Fe as Fe_2O_3	9.06	5.33	11.80	7.85	2.44	8.55
Li	29	11	20	12	2.0	13
Rb	212*	300*	60*	71*	109*	88*
Cs	9.0	17	3.0	2.7	<1	1.5

*Chemical values

Iron Formations - N.W. Ontario

Oxide Facies

	MR-I-1	MR-I-4	MR-I-5	MR-I-9	MR-I-11	MR-I-13
SiO_2	45.19	35.27	44.78	46.17	53.25	42.82
TiO_2	0.03	0.00	0.01	0.03	0.01	0.01
Al_2O_3	1.07	1.00	0.75	1.32	0.64	0.55
Fe_2O_3	18.17	32.54	29.41	18.92	23.24	23.98
Fe O	22.22	25.21	19.19	26.80	18.51	23.73
MnO	0.35	0.36	0.48	0.07	0.02	0.80
MgO	2.81	4.73	3.73	4.33	2.12	4.15
CaO	5.06	0.93	1.34	0.48	1.99	3.29
Na_2O	0.006	0.005	0.005	0.017	0.012	0.008
K_2O	0.069	0.015	0.010	0.118	0.004	0.004
P_2O_5	0.11	0.45	0.30	0.29	0.10	0.21
CO_2	4.37	0.00	0.00	0.07	0.00	0.00
Rb_2O	tr	tr	tr	0.0012	tr	tr
C				0.90		
TOTAL	99.46	100.51	100.01	99.52	99.90	99.55
Fe as Fe_2O_3	42.87	60.56	50.74	48.71	43.81	50.35
Li*	0.8	<0.4	0.8	5.3	0.4	0.4
Rb**	2.1	0.4	0.6	11	<0.4	<0.4
Cs***	3.5	<1	<1	3.7	<1	<1

* Analyses by D. Goodale
** Analyses by M. Raudsepp
***Analyses by F.G. Alcock

Iron Formation - Melville Peninsula

Oxide Facies

	DG-2-4	DG-7-4	DG-15-4	DG-16-4	DG-17-4	DG-3-2	DG-9-2
SiO_2	46.70	71.09	48.12	59.78	6.61	41.27	38.47
TiO_2	0.03	0.03	0.02	0.04	0.03	0.01	0.01
Al_2O_3	2.20	1.33	1.25	1.91	1.99	1.11	1.18
Fe_2O_3	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	0.00
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_2O	0.10	0.01	0.00	0.01	0.01	0.01	0.00
K_2O	0.02	0.06	0.07	0.30	0.47	0.03	0.00
TOTAL	100.92	100.60	100.32	100.90	99.04	99.80	98.43
Fe as Fe_2O_3	50.03	28.06	50.98	39.20	90.97	58.02	58.63
Li*	1.0	13	24	34	58	2.2	1.0
Rb**	0.6	9.0	29	55	60	14	0.4
Cs***	1	1.0	4.7	17	17	2.1	1

* Analyses by D. Goodale

** Analyses by M. Raudsepp

***Analyses by F.G. Alcock

NOTE: Major element analyses for above samples are incomplete

APPENDIX A-2

Semi-quantitative Spectrographic Analyses of Various Rocks in the Kirkland Lake Area

Iron Formation - Oxide Facies

	27	28	29	30	31	32	33
Li	1	2	<1	<1	1	<1	<1
Rb	1	5	1	1	1	<1	1
Cs	<1	<1	<1	<1	<1	<1	<1
K%	<0.05	<0.05	<0.01	<0.01	<0.01	<0.01	<0.05

APPENDIX A-3

Normative Composition of Kirkland Lake Volcanics and Intrusions*

	Tholeiitic basalts			Mafic trachyte		Trachyte	Leucite trachyte	Mafic syenite	Alkali syenite
	1	2	3	24 (porphyry)	26	25 (porphyry)	20	12	21
Q	4.74	-	4.26	-	-	-	1.45	-	-
Co	-	-	-	-	-	2.46	3.57	-	-
Or	4.74	3.39	2.82	26.38	16.91	25.81	56.20	23.49	36.24
Ab	31.53	16.13	20.83	34.19	21.00	42.40	5.79	38.45	54.65
An	26.30	30.37	31.06	11.72	13.74	12.44	7.90	4.30	4.45
Ne	-	-	-	2.37	2.66	8.36	-	7.14	-
Ol	-	8.14	-	9.84	20.73	4.88	-	9.57	1.12
Opx	16.36	19.13	19.19	-	-	-	19.77	-	0.25
Cpx	10.87	18.48	15.94	10.33	17.50	-	-	12.32	1.28
Mt	3.05	2.04	3.05	2.63	2.68	2.36	2.63	2.31	1.44
Il	2.16	1.99	2.53	1.37	1.42	1.01	1.31	1.01	0.34
Ap	0.26	0.33	0.33	1.17	3.36	0.29	1.37	1.42	0.25
color index	32.44	39.78	40.71	24.27	42.33	8.25	23.71	25.21	4.43

*Calculated from chemical compositions in Appendix A - cation norms calculated using Fe^{+3} and Fe^{+2} separately

APPENDIX B

SERIAL NO.	FIELD NO.	LITHOLOGY	SAMPLE LOCALITY & DESCRIPTION

B-1 Kirkland-Larder Lakes Area

B-2 Northwest Ontario

B-3 Melville Peninsula

Symbols

Twp - township

I.F. - iron formation

f.g. - fine grained

H/S - hand specimen

T/S - thin section

APPENDIX B-1

Sample Localities and Descriptions - Kirkland-Larder Lake Area

I. IRON FORMATIONS

(a) Oxide Facies

Samples #4-#8 inclusive are from Peria pit site of Adams Mine, Boston Twp.

#4	F-16-8	Lean I.F.	Non-banded; very f.g. (<1mm), magnetite occurs as disseminations in chert. Mode - 24.9% quartz/chert 15.4% magnetite 55.0% f.g. magnetite-chert matrix 4.7% chlorite/actinolite
#5	F-16-9	Oxide I.F.	Well banded sedimentary rock - alternating layers of chert and magnetite (grain size <1mm) with variation in thickness of layers. Magnetite layers are up to 1/2 in. thick; chert layers vary from fine laminae to beds several inches thick.

#6	F-16-11	Oxide I.F.	As above
	F-16-12	"	As above; magnetite is associated with silicates. Mode - 35.0% quartz/chert 28.3% magnetite 36.7% actinolite/grunerite (?) and chlorite
#7	F-16-13	"	1/4 to 1/2 in. thick alternating bands of magnetite and chert; disseminated sulphides; complexly folded.
#8	F-16-14	Cherty Quartzite	Massive chert bed containing disseminated graphite, which imparts black color to outcrop. Aggregates of actinolite needles rim occasional bleb of magnetite (T/S). Mode - 84.0% quartz/chert 12.3% actinolite/chlorite 3.7% magnetite
#10	F-17-7	Oxide I.F.	Boston twp., North Pit site - Adams Mine. Well banded, alternating layers of magnetite/hematite and jasper (fine laminae to 1/2 in. bands).

			Mode - 54.6% quartz/chert 23.6% magnetite 13.1% hematite 8.7% actinolite trace of garnet
#11	F-18-7	Oxide I.F.	Boston twp., 1.9 mi W of old Dane Station on Dane Highway. Interbanded magnetite-silicic tuff; much epidote associated with wispy seams of magnetite. Mode - 53.3% epidote/chlorite 22.9% magnetite 21.4% quartz 2.3% plagioclase trace of garnet
#17	F-21-7	"	Boston twp., Adams Mine composite of ore from South and Central Pits. 200 mesh powder.
#18	F-22-1	"	S. McVittie Twp., 1.0 mi W of Tournene L. on Hwy. 66. Bed of shaley oxide I.F. (up to 1 ft thick) occurs in carbonate rich graywacke. I.F. contains some very fine laminations of jasper. The bed is traceable along strike for several hundred yards.

b. <u>Carbonate-Sulphide Facies</u>

#14a F-21-11F) E. Teck Twp., 2 mi S of Kirkland L.
) Mixed Facies
#14b F-21-1Cs) of I.F. town at contact of Murdock Creek syenite stock.

Brown-green carbonate containing lean oxide I.F. and sulphide lenses; minor banding developed.

(1) F-21-11F is sample of lean oxide I.F. and carbonate

(2) F-21-1Cs is sample of carbonate and sulphide rich segment.

Mode (1) -

42.8% ferroan dolomite
37.2% quartz/chert
9.8% magnetite
8.6% epidote/chlorite
1.6% euhedral pyrite

Mode (2) -

54.2% quartz/chert
42.4% ferroan dolomite
3.4% pyrite/minor magnetite

#13 F-20-2 Sulphide I.F. Hwy. 11 at Eby-Otto Twp line, adjacent to NW edge of Otto stock.

Carbonaceous-pyritic shale

F-20-3 " As above.

H/S -massive, dull grey-black in color with abundant fine to medium grained quartz clasts.

			T/S -f.g. clay-silt matrix containing very angular quartz grains (>1mm in size); discontinuous lenses of graphite and silt-sized material are present.
#15	F-21-5	Carbonate I.F.	S. Gauthier Twp., Hwy. 66 - Misema River bridge. Foliated, light-green colored carbonate laced with stockwork of milky quartz veins. T/S -f.g. mosaic of quartz and carbonate with minor chlorite/mica. K-ferricyanide stain for carbonate differentiation indicates 24.5% ferroan dolomite.
#16	F-21-6	"	Lebel Twp., W of Crystal L. at railway cut, adjacent to Hwy.66 crossing. Outcrop is massive, pastel-brown colored carbonate, weathering to an ochrous brown gossan and cut by stockwork of quartz veins. T/S -exhibits clastic texture and consists of subrounded to rounded silt-sized grains of "buff" chert, quartzite and

feldspar in an argillaceous-carbonate matrix. Anhedral grains and masses of ankerite have crystallized out of the matrix.

Mode - 56.1% argillaceous-carbonate matrix
28.2% ferroan dolomite
14.4% rock fragments
0.3% clear quartz (vein)

II. GREYWACKES

#19	F-22-2	Greywacke/grit	Host rock for #18 I.F. - same location. Rock is well foliated, and rich in carbonate. No T/S or H/S.
#23	F-22-9	Greywacke	W Lebel Twp., behind N. Institute of Technology, Kirkland Lake. Dark-green in color, medium to coarse grained graywacke. No T/S or H/S.

III. PERIDOTITE

#9	F-16-15	Altered Peridotite	Boston Twp., Peria Pit site at Adams Mine.

Massive, dark grey-green color, altered to magnesian schist.

IV. VOLCANICS

#1	F-16-2	Tholeiitic Basalt	Boston Twp., Peria Pit site at Adams Mine. Massive, f.g., dark green basic lava. No T/S - see normative composition.
	F-16-3	Basic Lava - Greenstone	As above. Massive, f.g. and dark green in appearance. Mineralogy includes quartz, actinolite, feldspar and traces of sulphides (T/S).
#2	F-16-5	Tholeiitic Basalt	Same location and description as above. See normative composition
#3	F-16-7	"	" " " "
#20	F-22-5	Leucite Trachyte	Lebel Twp., 0.3 mi SW of Crystal L. at Hwy. 66 roadcut. H/S -grey-green in color and porphyritic T/S -(stained) f.g. altered feldspar groundmass containing K feldspar phenocrysts and disseminated opaques

(magnetite).

*Reference - chemistry agrees with chemical analysis of leucite trachyte (sample 3) of Cooke and Moorehouse, p.122, 1969.

See normative composition - the quartz and corundum in norm must be consequence of loss of alkalis and addition of silica during alteration (op.cit., p.126).

#25 F-23-2 Trachyte Porphyry E. Lebel Twp., 0.4 mi S of Crystal L. near Hwy. 66.

H/S -grey-brown in color and porphyritic, laced with fine stockwork of carbonate veins (dolomite - as indicated by X-ray diffraction methods).

T/S -f.g. groundmass containing altered phenocrysts of feldspar. Minerals are sericitized, chloritized and carbonatized.

#26 F-23-3 Mafic Trachyte E. Lebel Twp., S of Crystal L. on power line.

H/S -green-black in color, f.g.

T/S -phenocrysts of nepheline and feldspar in a feldspathic groundmass that still shows some flow texture. Groundmass consists of largely K feldspar, and some chlorite, epidote and carbonate. Phenocrysts are rimmed with chlorite and magnetite.

*Reference - (p.125, op.cit.) chemical composition is close to leucitic trachyte but normative and modal nepheline is present. High CaO and MgO content appears in normative diopside and olivine.

V. INTRUSIVES

#12 F-20-1 Mafic Syenite S. Teck Twp., Hwy. 112 roadcut in Murdock Creek syenite stock.

H/S -dark red-black, medium grained in appearance with abundant ferromagnesium minerals and feldspar. No T/S; see normative composition which is nepheline bearing. Higher CaO and MgO content than common syenite as reflected in normative Di and Ol.

#21 F-22-6 Alkali Syenite W. Otto Twp., 2.0 mi N of Round L. in large circular depression in

			Otto Stock. H/S -very coarse grained red feldspar with interstitial biotite and green clusters of aegerine (?) needles. No T/S.
#24	F-23-1	Mafic Trachyte Porphyry	S. Teck Twp., 0.3 mi W of Hwy. 66 and Hwy. 112 junction, behind Forest Ranger headquarters. H/S -fresh surface is grey-green in color showing blue-green phenocrysts. Weathers to a brown-grey color. T/S -(stained) altered phenocrysts of plagioclase and ferromagnesians in a f.g. feldspathic matrix; plagioclase phenocrysts contain small blebs and/or marginal zones of K feldspar. Ferromagnesians are replaced by magnetite and chlorite.

Miscellaneous samples - no chemical analyses, only trace element analyses (semi-quantitative):

#27	F-16-10	Oxide I.F.	Boston Twp., Peria Pit site, Adams Mine. Well banded with alternating layers of magnetite and chert.
#28	F-16-16	Lean I.F.	Same location as #27. Black cherty quartzite with lenses of sulphides and disseminated magnetite.
#29	F-21-12	"	Boston Twp., North Pit site, Adams Mine. Same description as above.
#30	F-17-4	Cherty Quartzite	Same location as #27. Black, flinty appearance containing disseminated pyrite and magnetite; near contact of overlying pillow lavas.
#31	F-17-5	Lean I.F.	Same location as #27. Cherty quartzite with some disseminated magnetite.

#32	F-17-6	Oxide I.F.	Same location as #27. Banded rock very rich in magnetite with few interlayers of chert.
#33	F-18-6	"	W. Boston Twp., road-cut on Dane Hwy., 0.2 mi SW of Helent Lake. Interlayered magnetite and black cherty quartzite with associated tuffaceous laminations that are differentially weathered.

APPENDIX B-2

Sample Descriptions - N.W. Ontario

Samples collected by M. Raudsepp. All samples are of oxide facies iron formation, each sample being from a different iron formation; associated with felsic and mafic metavolcanics. Samples collected in areas not adjacent to granitic intrusions, except for MR-I-1 which is from a contact aureole of a gabbro.

H/S - well banded, with alternating layers of magnetite and chert; bands varying from 1-10 mm in width. The iron formations have been complexly folded in places.

T/S - mineralogy consists of magnetite, chert, and iron silicates in varying proportions. Minor amounts of calcite and sphene are present. Silicates are predominantly amphiboles of the cummingtonite-grunerite series.

Modes- in volume per cent

Sample #	Magnetite	Quartz	Silicates
MR-I-1	50	31	19
MR-I-4	58	10	32
MR-I-5	44	27	29
MR-I-9	37	25	38
MR-I-11	37	34	29
MR-I-13	32	26	42

APPENDIX B-3

Sample Descriptions - Melville Peninsula

Samples collected by D. Goodale. Oxide facies of iron formation; mineralogy and structure are similar to other banded iron formations described previously. One exception is DG-9-2 which contains hematite as the only iron oxide present. Generally, silicate content (amphibole, chlorite, etc.) is lower in these rocks compared to above occurrences. Extensive recrystallization has occurred in country rock adjacent to the iron formation. In Borealis 4 occurrence the iron oxides have undergone considerable recrystallization (Goodale, 1971).

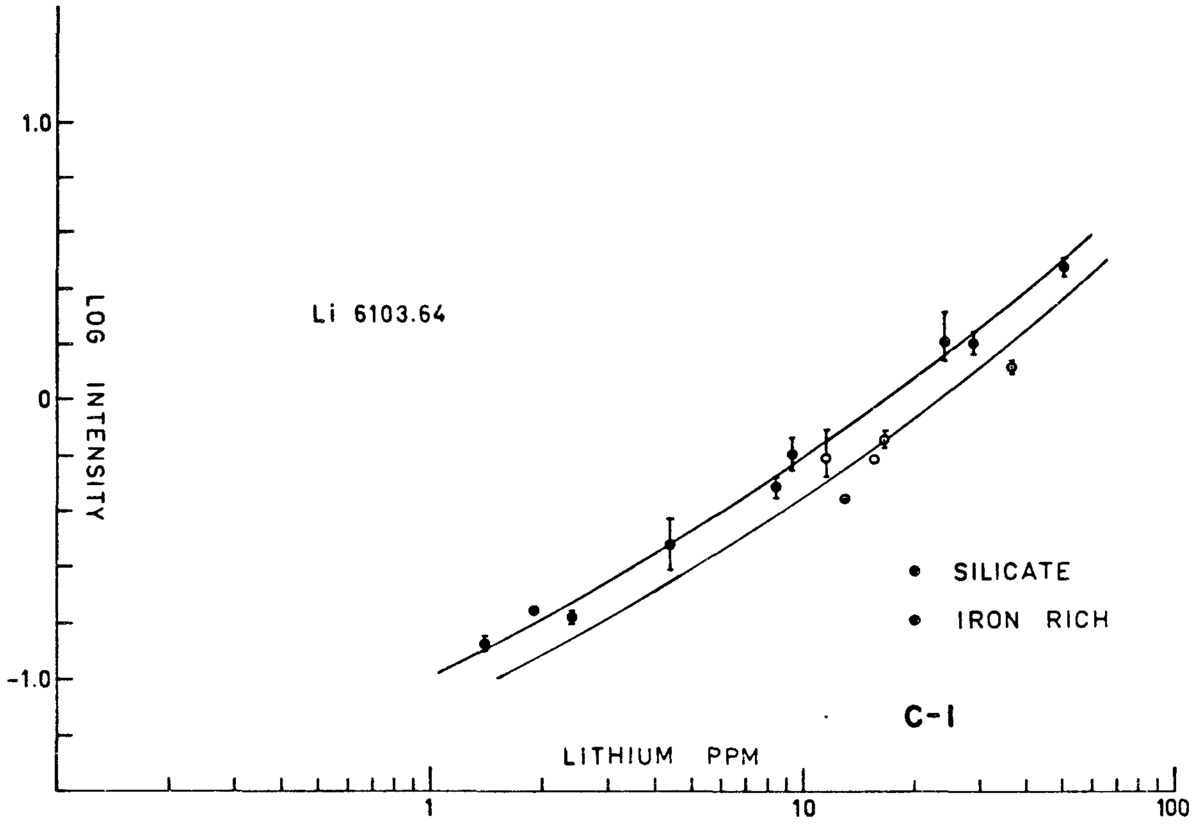
Modes - in volume per cent

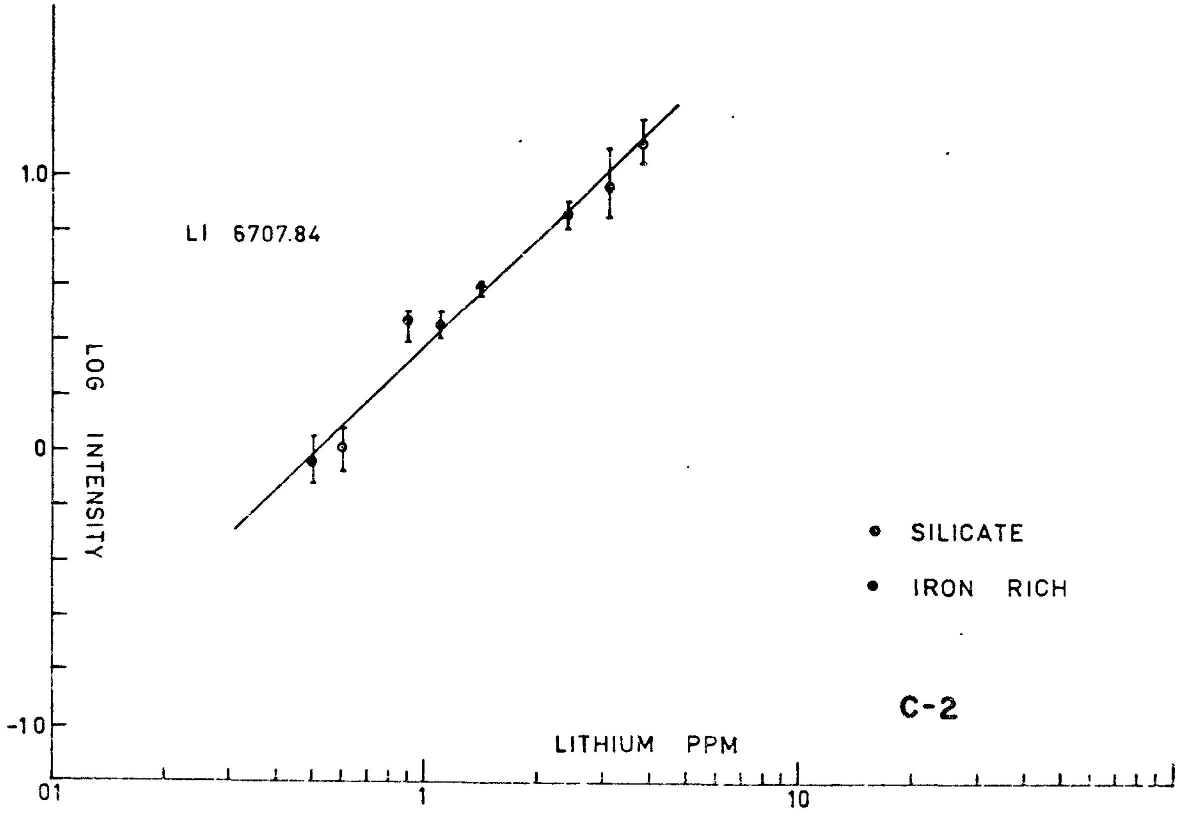
Sample #	Magnetite	Hematite	Quartz	Silicates
DG-2-4	-	-	-	-
DG-7-2	-	-	-	-
DG-7-4	30	-	66	4
DG-15-4	44	-	54	2
DG-16-4	31	-	64	5
DG-17-4	68	-	7	25
DG-3-2	52	-	45	3
DG-9-2	-	52	48	-

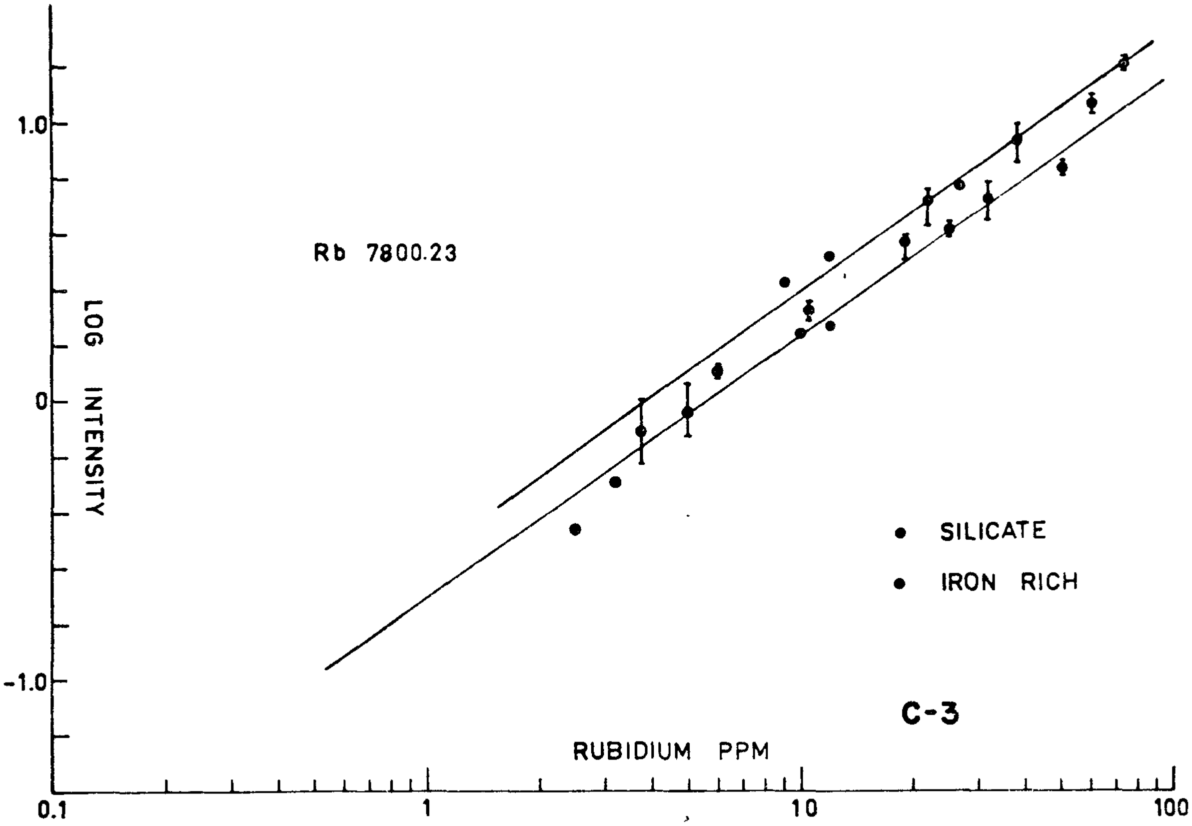
APPENDIX C

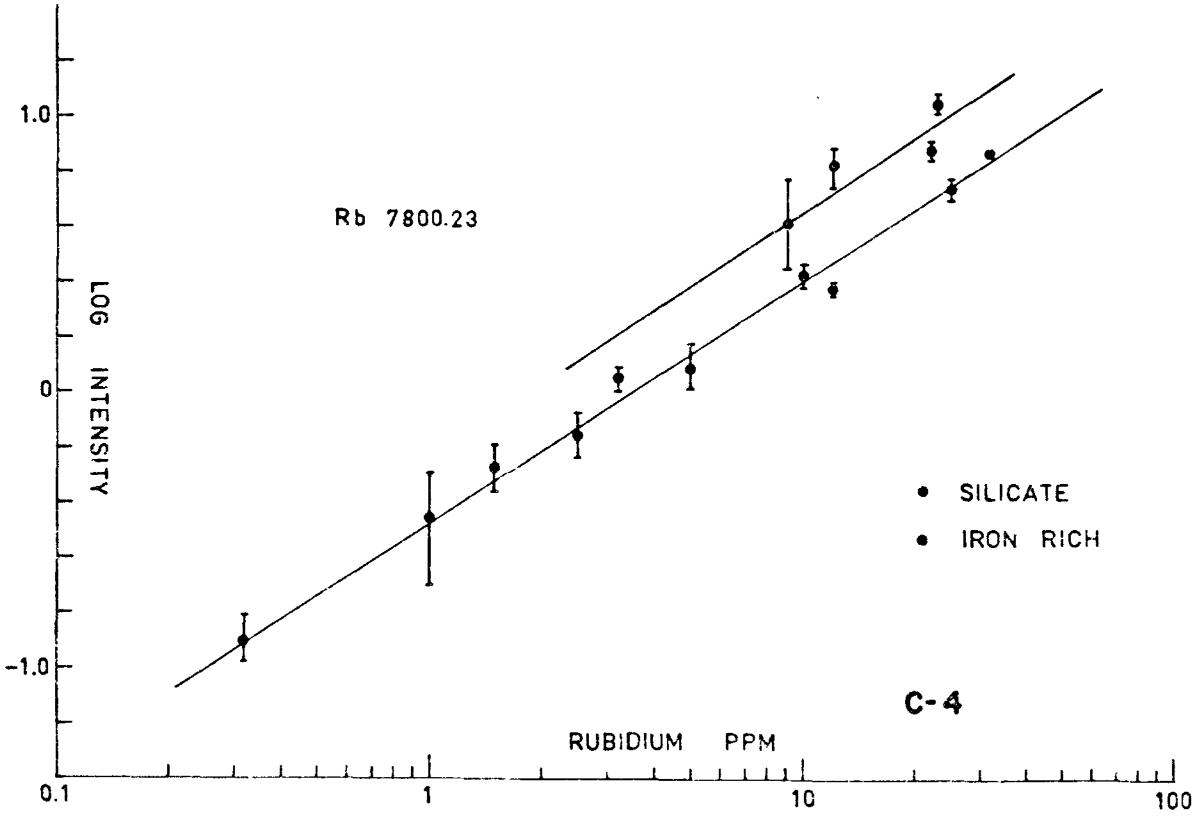
ANALYTICAL CURVES FOR ALKALI METALS

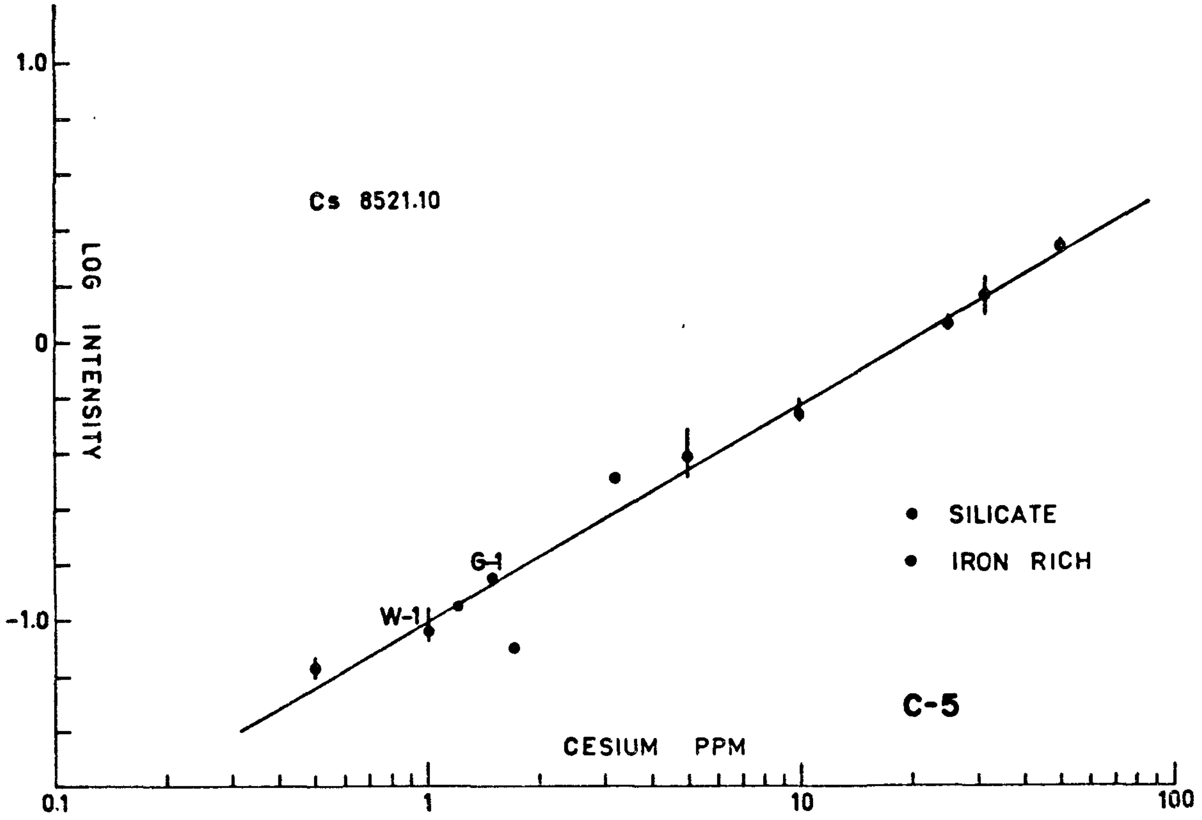
C-1 - Lithium
C-2 - "
C-3 - Rubidium
C-4 - "
C-5 - Cesium
C-6 - Potassium


1.0
0
-1.0
LOG INTENSITY
Li 6103.64
● SILICATE
● IRON RICH
C-I
LITHIUM PPM
1
10
100

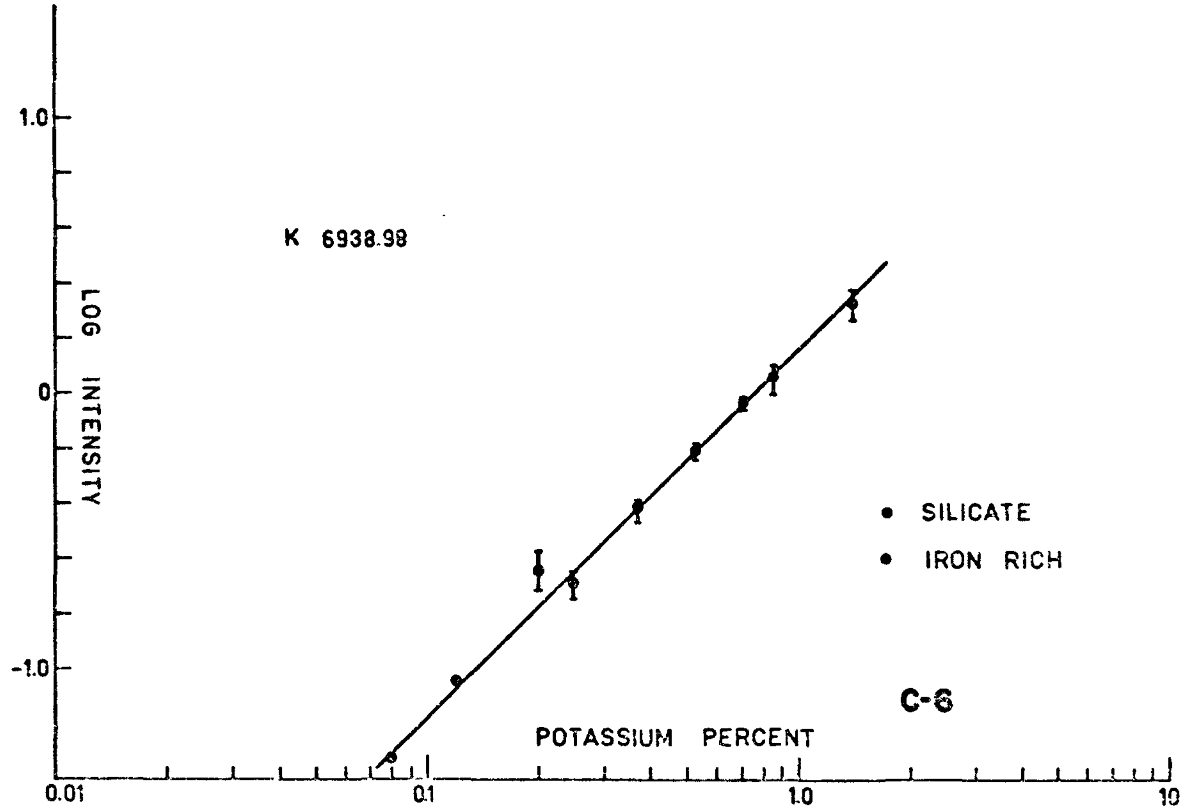

1.0
0
-10
LOG INTENSITY
LI 6707.84
○ SILICATE
● IRON RICH
C-2
LITHIUM PPM
01
1
10


Rb 7800.23
LOG INTENSITY
1.0
0
-1.0
● SILICATE
● IRON RICH
C-3
RUBIDIUM PPM
0.1
1
10
100


Rb 7800.23
LOG INTENSITY
1.0
0
-1.0
● SILICATE
● IRON RICH
C-4
RUBIDIUM PPM
0.1
1
10
100


Cs 8521.10
LOG INTENSITY
1.0
0
-1.0
G-1
W-1
● SILICATE
● IRON RICH
CESIUM PPM
0.1
1
10
100

C-5


K 6938.98
LOG INTENSITY
1.0
0
-1.0
● SILICATE
● IRON RICH
POTASSIUM PERCENT
0.01
0.1
1.0
10

C-6

APPENDIX D

ANALYTICAL CURVES FOR FERRIDES AND MINOR ELEMENTS IN MAGNETITES

D-1 - Vanadium

D-2 - Copper

D-3 - Titanium

D-4 - Chromium

D-5 - Manganese

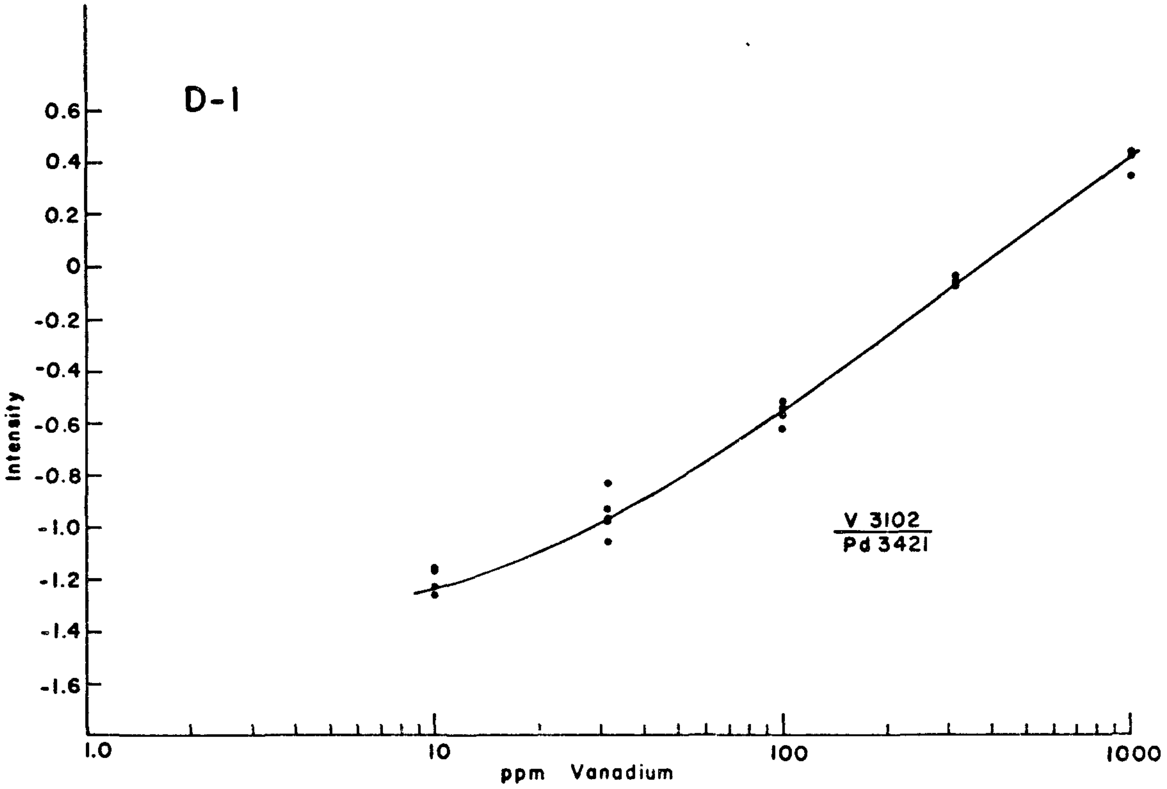
D-6 - Cobalt

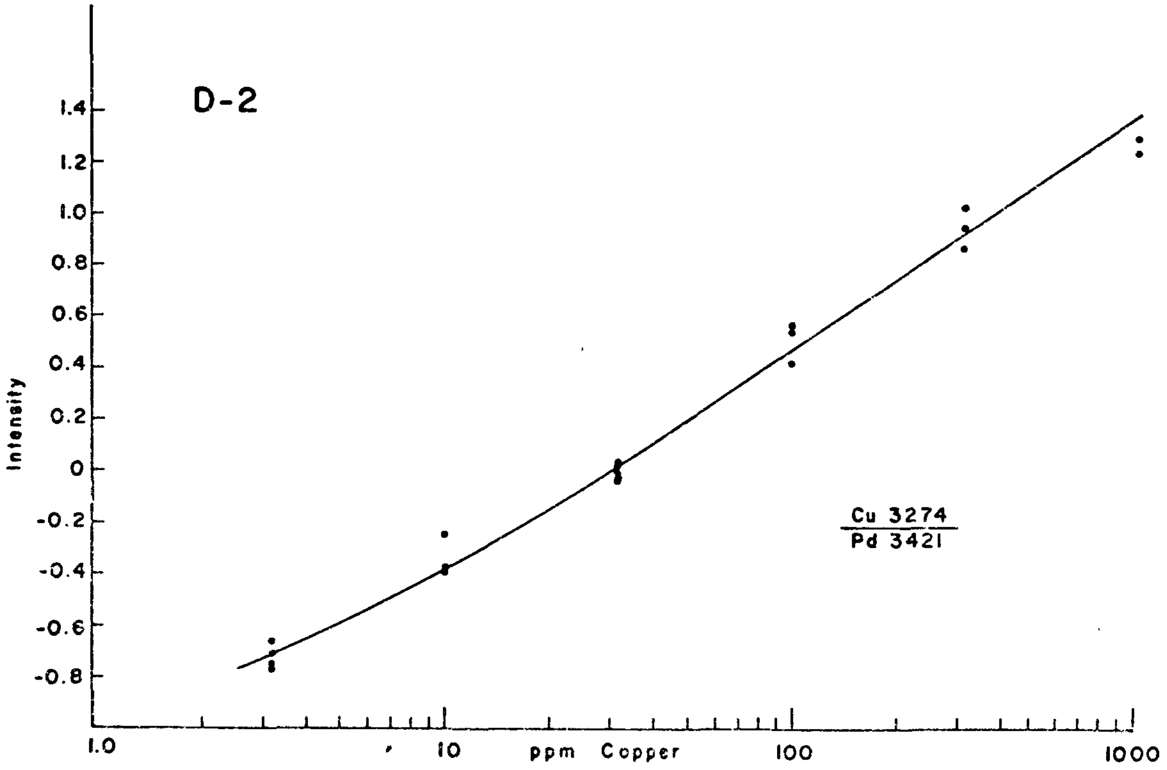
D-7 - Nickel

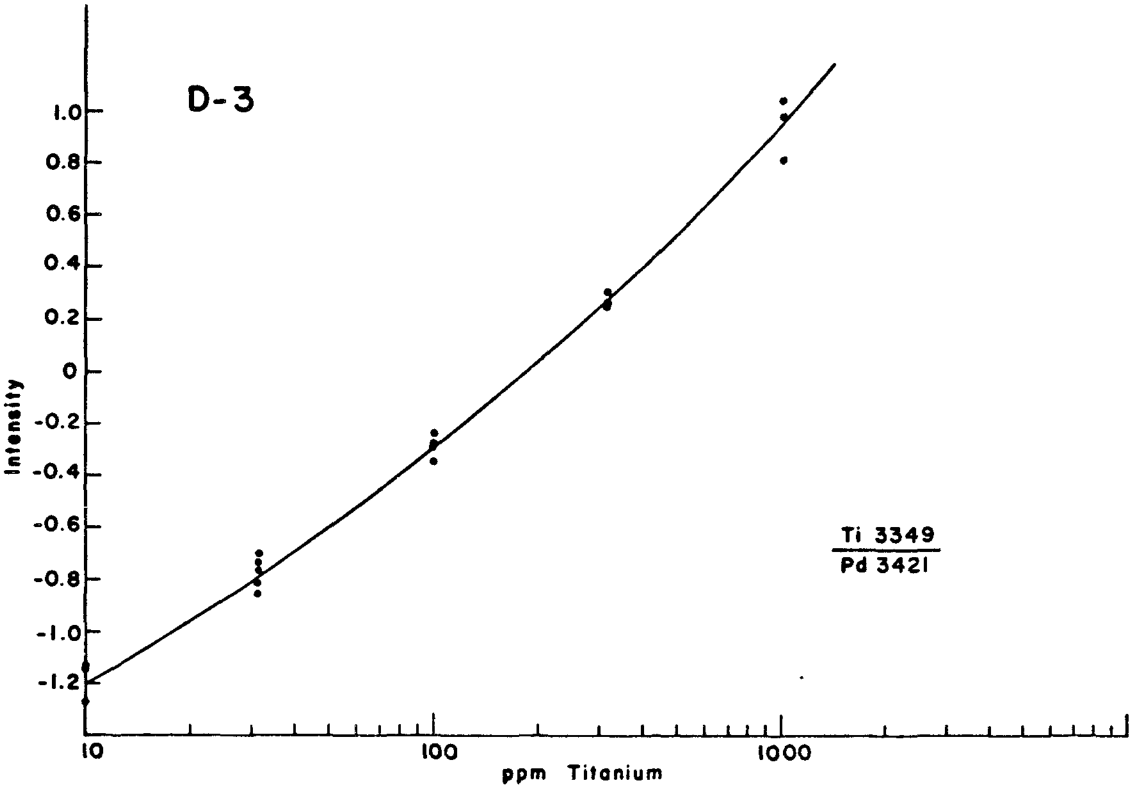
D-8 - Magnesium

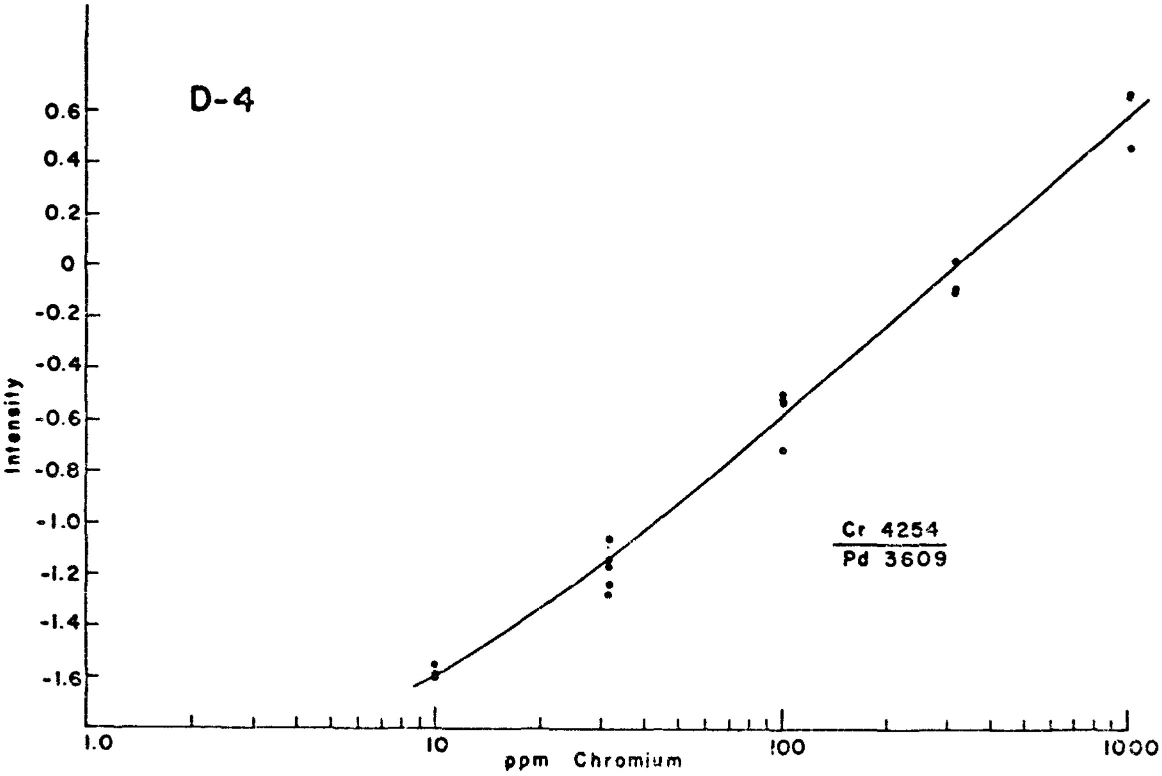
D-9 - Gallium, corrected for Fe interferences

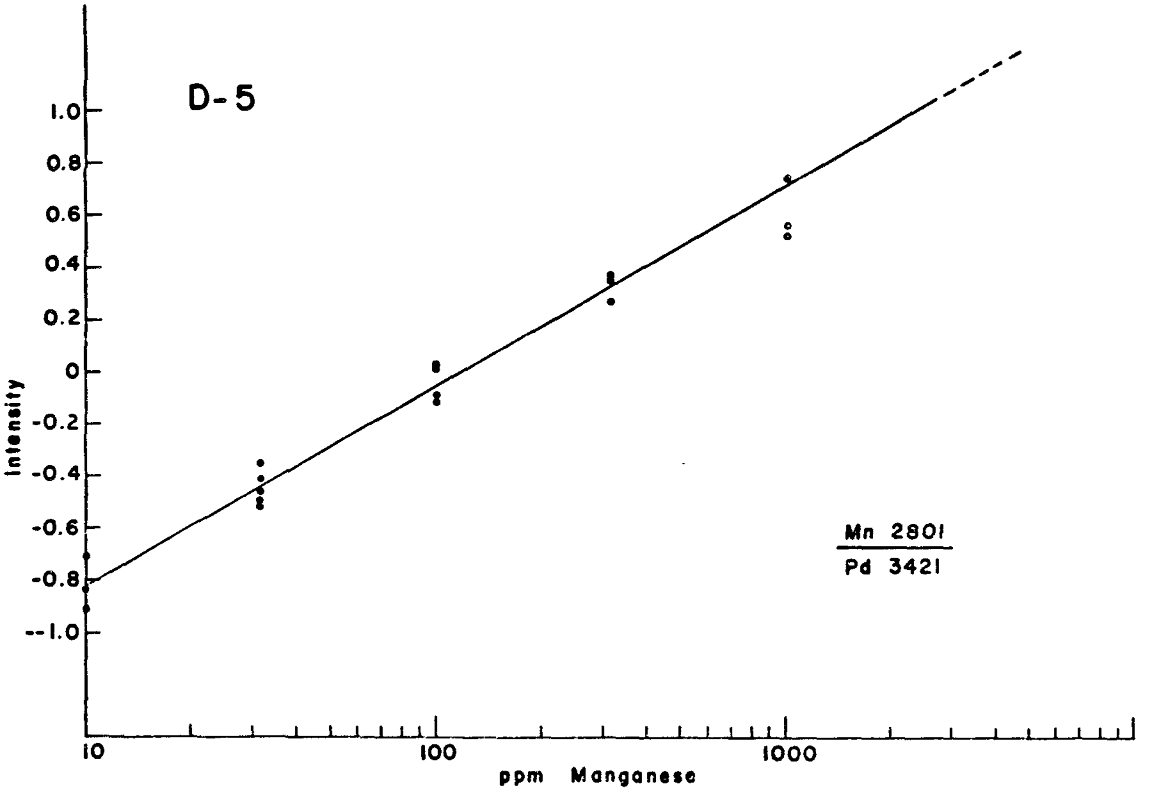
D-10 - Gallium, uncorrected curve

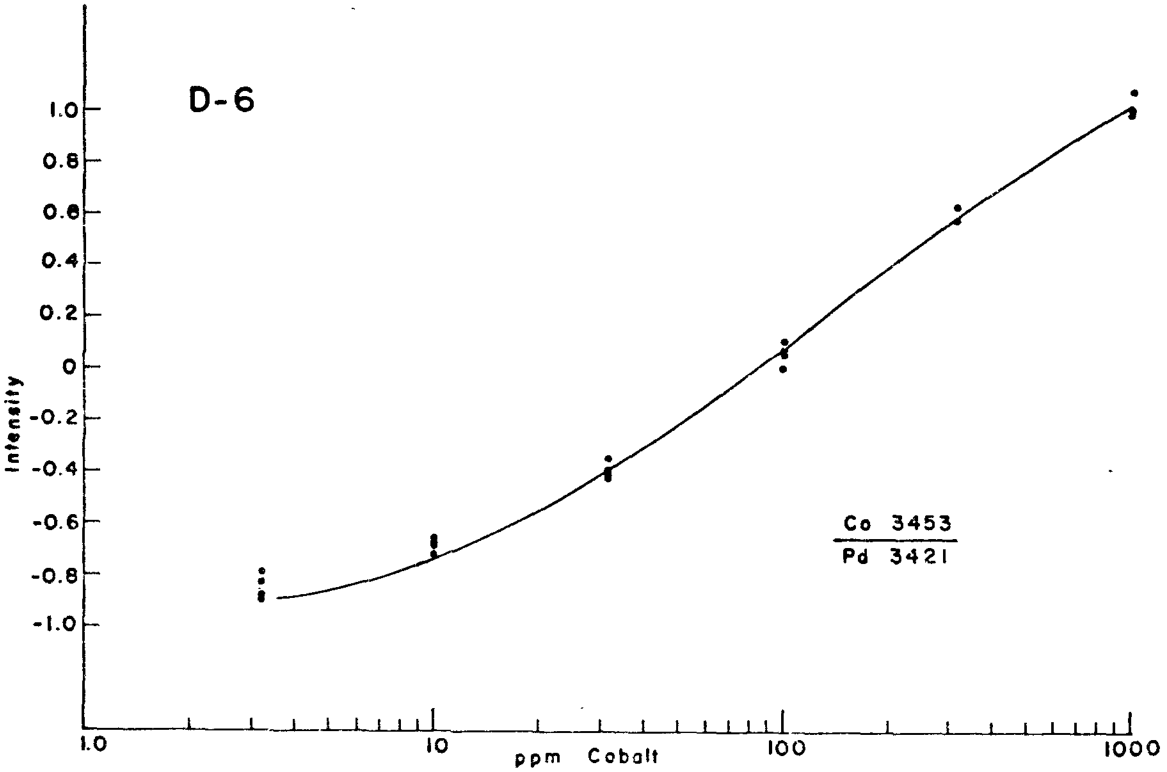

D-1
Intensity
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
-1.6
1.0
10
100
1000
ppm Vanadium
V 3102
Pd 3421

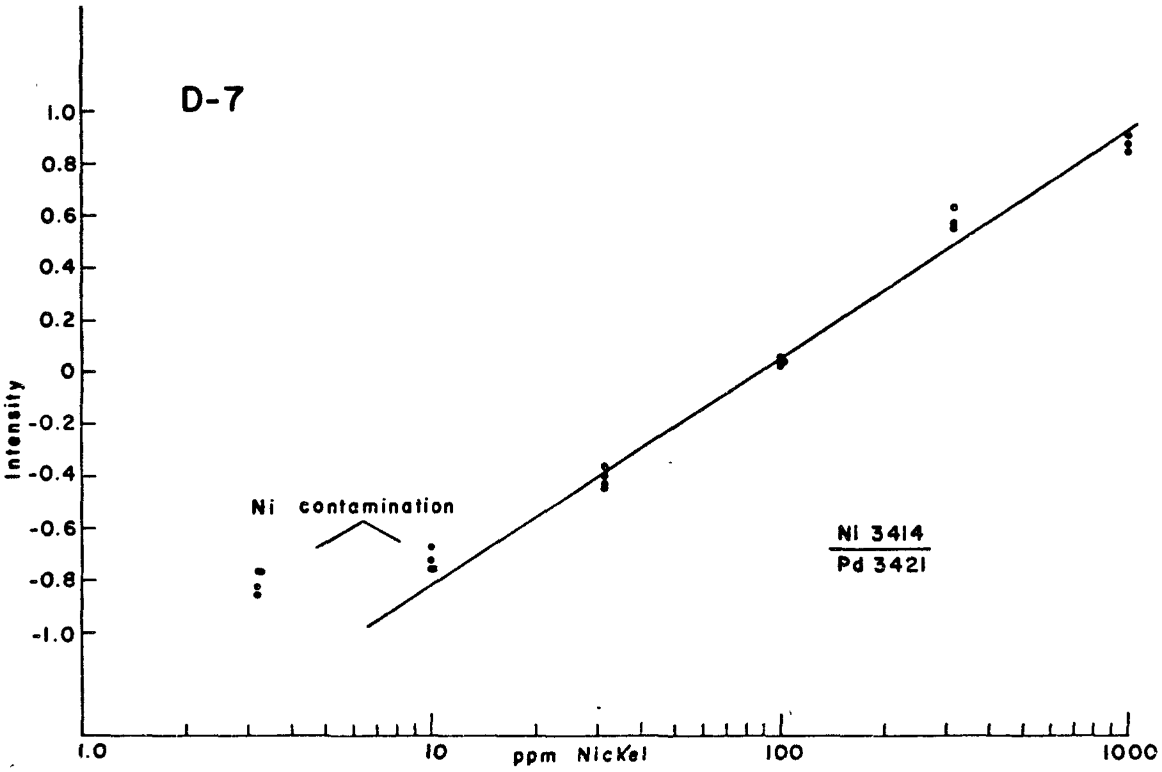

D-2
Intensity
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
1.0
10
100
1000
ppm Copper
Cu 3274
Pd 3421

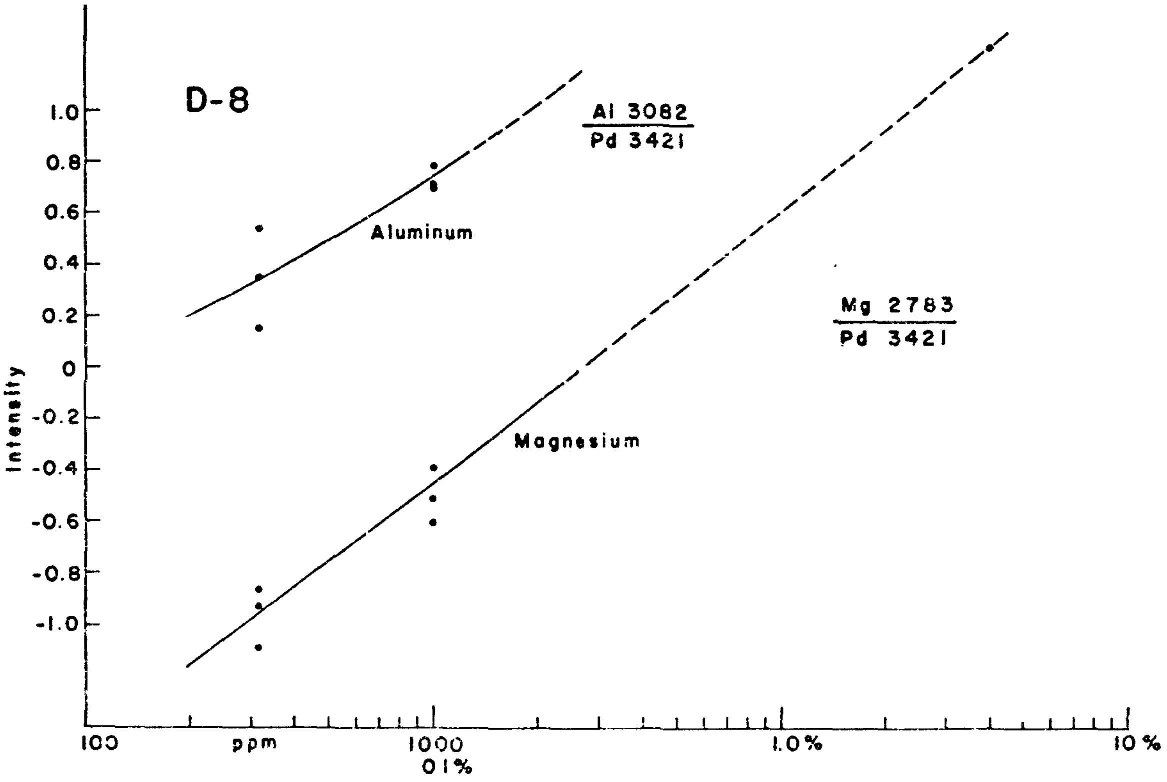

D-3
Intensity
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
10
100
1000
ppm Titanium
Ti 3349
Pd 3421

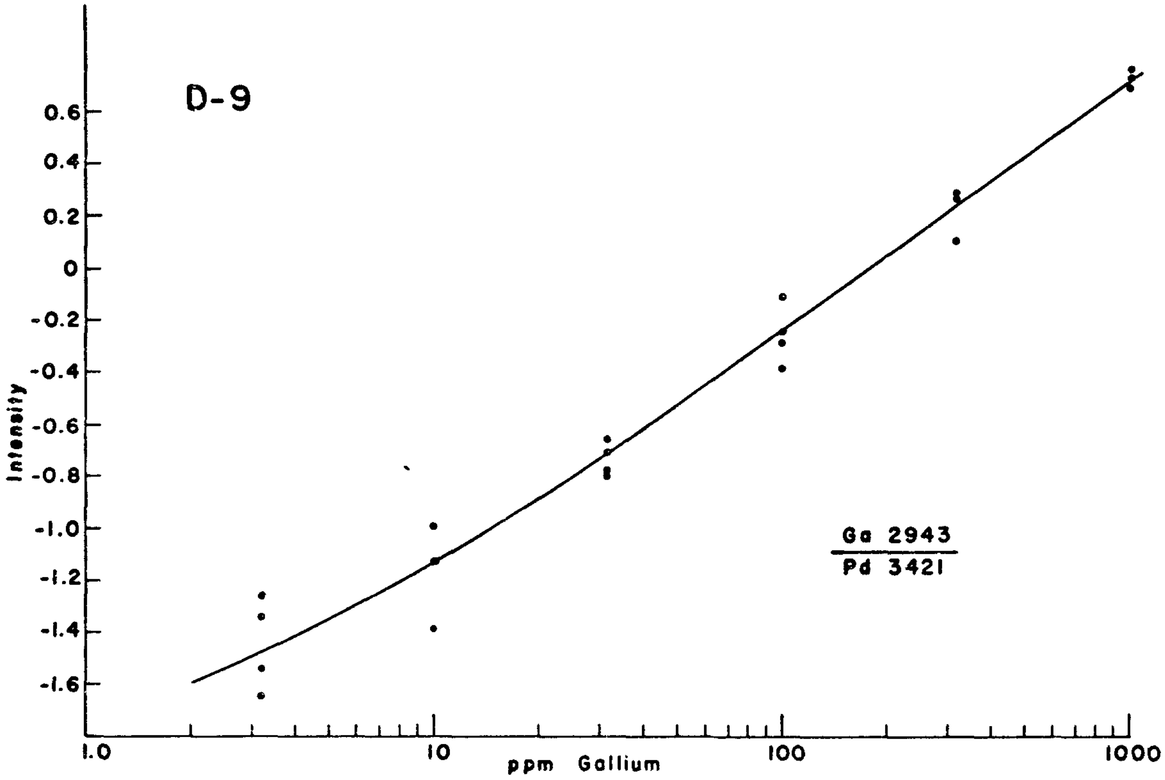

D-4
Intensity
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
-1.6
1.0
10
100
1000
ppm Chromium
Cr 4254
Pd 3609

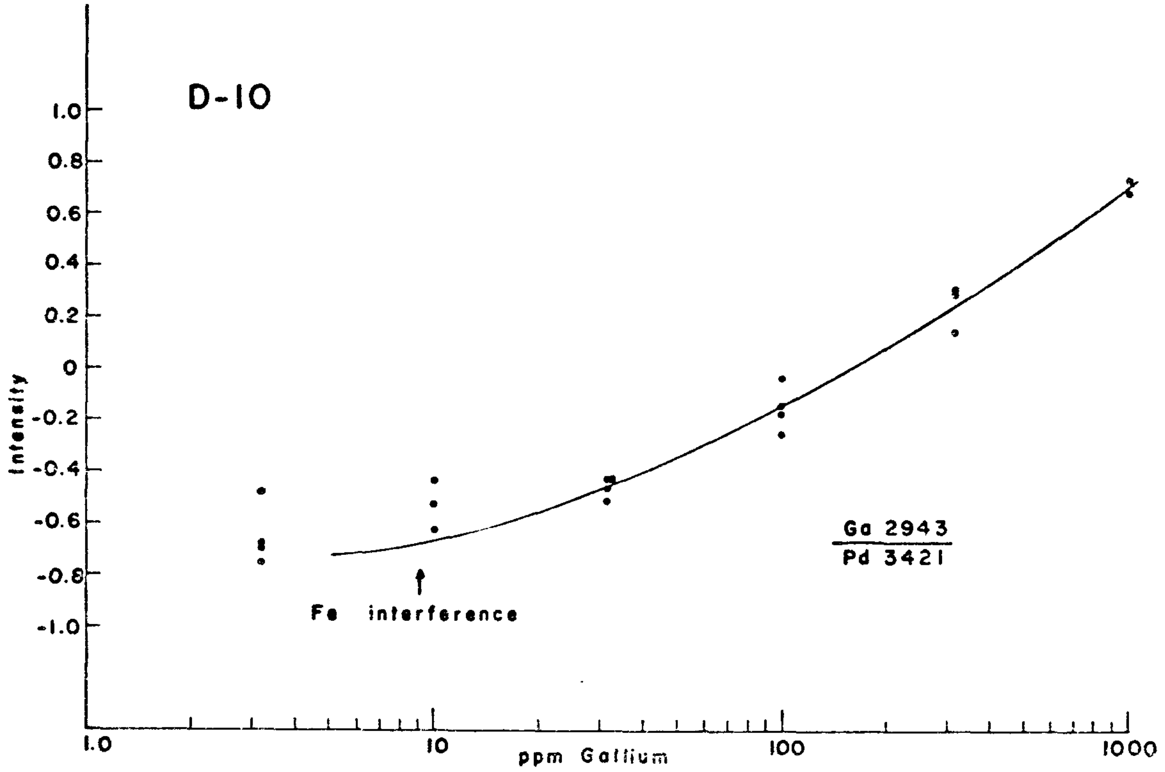

D-5
Intensity
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
--1.0
10
100
1000
ppm Manganese
Mn 2801
Pd 3421


D-6
Intensity
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
1.0
10
100
1000
ppm Cobalt
Co 3453
Pd 3421


D-7
Intensity
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
Ni contamination
Ni 3414
Pd 3421
1.0
10
ppm Nickel
100
1000


D-8
Intensity
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
Al 3082
Pd 3421
Aluminum
Mg 2783
Pd 3421
Magnesium
100
ppm
1000
0.1%
1.0%
10%


D-9
Intensity
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
-1.6
Ga 2943
Pd 3421
1.0
10
100
1000
ppm Gallium


D-10
Intensity
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
Fe interference
Ga 2943
Pd 3421
1.0
10
100
1000
ppm Gallium