# PETROCHEMISTRY

OF THE MAFIC-RICH ROCKS, LAC DES MILLE LACS AREA

# PETROCHEMISTRY OF THE MAFIC-RICH ROCKS,

LAC DES MILLE LACS AREA,

NORTHWESTERN ONTARIO

By

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Lac des Mille Lacs Area, Northwestern Onterio AUTHOR: David Hugh Watkinson, B.Sc. (McMaster University) SUPERVISOR: Dr. T. N. Irvine

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SCOPE AND CONTENTS: An investigation of the petrology and chemistry of two groups of mafic-rich intrusions from the Lac des Mille Lacs area was carried out. The Quetico group consists of hornblenderich ultramafic to mafic rocks; the Shebandowan group consists of serpentinized ultramafic rocks and metagabbro. A spectrographic method was employed to quantitatively determine  $Al_2O_3$ , CaO, Co, Cr, Cu, Mn, Ni, Ti, V and Zr in the rocks. This, and other chemical data, indicate that these two spatially related groups, although mineralogically distinct, have similar chemical features, and have apparently crystallized from compositionally similar magmas under different water vapour pressures. Their similarities to ultramafic rocks from other areas provide some implications regarding ultramafic rock types of orogenic areas.

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#### INTRODUCTION

The Lacs des Mille Lacs Area is located about sixty miles northwest of the cities of Fort William and Port Arthur in Northwestern Ontario (figure 1). The mafic-rich intrusions examined in this study are clustered in two parts of the area (figure 2) that, hereafter, will be referred to as the Quetico and Shebandowan areas.

The Shebandowan area was previously mapped geologically by T. L. Tanton (1938) at a scale of 1 inch to 1 mile. The Quetico area was also mapped by Tanton (1938a), at a scale of 1 inch to 4 miles, and has been remapped by Irvine in 1960 at a scale of 1 inch to 1 mile.

In the present study, field work in the Quetico area was carried out during the summer of 1960 while the author was working with an Ontario Department of Mines field party under the direction of T. N. Irvine. The intrusive bodies in the Shebandowan area were mapped independently during September of 1960. All mapping was done on vertical air photographs on a scale of 4 inches to 1 mile.



Figure I - Index Map Showing Location of the Lac des Mille Lacs Area

### REGIONAL GEOLOGY

#### General Features

The bedrock of the Lac des Mille Lacs area is entirely Precambrian in age. Quartz-biotite paragneiss and metamorphosed basic volcanic rocks are the oldest units, and have been assigned to the Couchiching and Keewatin respectively (Tanton, 1938a; Irvine, 1961). Emplaced into these units are masses of ultramafic, mafic, granitic, and syenitic rocks, probably in that order although conclusive evidence on their relative ages is lacking. The youngest rocks are dikes of diabase which are believed to belong to the Keweenawan magmatic series. Extensive Pleistocene till and local recent fresh water sediment overlie much of the bedrock. The interpretation of the geological succession is summarized in table 1.

### Quartz-biotite Paragneiss

The quartz-biotite paragneiss near Quetico occurs in a narrow belt that is bounded on the north by metavolcanic rocks, and on the south by granite. Its contact with the metavolcanic rocks is a pronounced lineament along which is developed a zone of chlorite schist, and probably, the contact is faulted. The contact with granite is marked by a complex intermingling of the two rock types in the form of a migmatite. The paragneiss itself



Table 1.

TABLE OF FORMATIONS

Quaternary

Recent

Pleistocene

Peat, river deposits, beach deposits Boulder till, silt, sand, gravel

Great Unconformity

Precambrian

Keweenawan

Diabase dikes

Intrusive Contact

Algoman (?)

Red hornblende syenite Quartz diorite, granodiorite Grey granite, pink granite

#### Probable Intrusive Contact

Pre-Algoman (?)

Peridotite, serpentinized peridotite, serpentinite Peridotitic hornblendite, hornblendite, biotitic hornblendite, feldspathic hornblendite Hornblende gabbro, hornblende diorite, anorthosite

#### Intrusive Contact

Keewatin

Metabasalt, meta-andesite, metadacite meta-agglomerate or tuff breccia, chlorite schist, shaly iron formation

Couchiching Quartz-

Quartz-biotite paragneiss, locally containing garnet, staurolite cummingtonite, and sillimanite Quartz-muscovite schist is generally fine grained and weakly schistose. It commonly shows banding because of a variable content of biotite that apparently reflects sedimentary bedding. Relict graded bedding was observed in some outcrops, and chemically, the rock resembles a greywacke (Irvine, 1961). In the parts of the paragneiss that have been examined, quarts, biotite, and plagioclase (generally oligoclase) are ubiquitous. Moderately high grade metamorphism of the original sedimentary unit is indicated by the local presence of one or more of garnet, staurolite, cummingtonite, sillimanite and hornblende.

The large belt of paragneiss shown in the southern part of figure 2 has not been examined during the present study, but is briefly described by Giblin (1962). Apparently it is similar to the northern belt.

### Metavolcanic Rocks

Two belts of metamorphosed volcanic rocks extend from west to east across the Lac des Mille Lacs area. The northerly belt is bounded on the south by paragneiss and on the north by quartz diorite. In contrast, the southerly belt is bounded by paragneiss on the north, granitic rocks on the south, and locally, it is invaded by pink granite and anorthosite. The rocks of both belts are typical Canadian Shield greenstones and represent metamorphosed basic lava flows plus minor amounts of intermediate lava, tuff, agglomerate and intercalated mixed sedimentary rock.

Most of the rocks are faintly schistose to massive. Pillow structures, and porphyritic and amygdaloidal textures are locally developed in the lavas. The northerly belt consists mainly of assemblages of hornblende, plagioclase (albite to andesine), epidote and chlorite, indicating a moderate metamorphic grade. The southerly belt is apparently more chloritic, and possibly its metamorphism is of a lower grade.

# Granitic Rocks

The two belts of paragneiss and greenstone are bordered and invaded by extensive granitic bodies. The most northerly mass shown in figure 2 is predominantly quartz diorite, being composed of quartz, plagioclase (oligoclase-andesine), biotite, chlorite, opaques, and rarely, microcline. The large central granitic belt, in its northwestern part, is a granite composed of roughly equal amounts of quartz, microcline and albite (Irvine, 1961); petrographic data is not available on the remainder of this belt. The granitic pluton underlying Middle Shebandowan Lake consists of quartz, sericitized plagioclase, biotite and chlorite. The mineralogy of the granitic rocks near Greenwater Lake is unknown.

The geologic evidence on the age of the granitic rocks is as follows:

 Quartz diorite contains inclusions of metavolcanic rocks and hornblendite, and is cut by dikes of diabase.

- (2) The central belt of granite is commonly intermixed with the paragneiss forming a migmatite. This granite has not been observed in contact with the quartz diorite, hence their age relation is unknown.
- (3) The Shebandowan granitic rocks intrude paragneiss and greenstone, and probably are younger than the mafic and ultramafic intrusions (Tanton, 1938).

### Mafic-rich Intrusions

The mafic-rich intrusive rocks are, as mentioned previously, clustered in two parts of the Lac des Mille Lacs area.

The bodies in the Quetico cluster are intrusive into paragneiss and metavolcanic rocks, and are included in granitic rocks (figures 2 and 3). Hornblende is the dominant mineral in every body examined, and the principal rock types are hornblende peridotite, hornblendite and feldspathic hornblendite. A few of the dikes are hornblende gabbro or diorite.

The Shebandowan group is entirely emplaced in the metavolcanic belt (figure 4). Most of the bodies are serpentinite, but some partially serpentinized peridotite is present, and a finegrained gabbro or diabase is locally associated. According to Tanton's map, isolated gabbroic and anorthositic plutons are present



in the area, but sufficient time for their examination was not available during the present study.

The two groups of intrusions are described in more detail in subsequent sections.

### Diabase and Quartz Diabase Dikes

Quartz-diabase dikes, having north-south trend, intrude the quartz diorite and metavolcanic rocks in the northern part of the Lac des Mille Lacs area. They have been assigned to the Keweenawan. The dike rock is generally medium-grained, massive, and greenish-gray. It is composed of saussuritized intermediate plagioclase, uralitized augite, interstitial quartz and accessory titaniferous magnetite and pyrite.

The author has observed diabase in only one outcrop in the Shebandowan area. The locality is adjacent to body 'I' (figure 4), and the diabase cuts a metavolcanic rock.





### 7 Diabase

6 Red hornblende syenite



5a Granite b Quartz diorite

4a Partially serpentinized peridotite b Pyroxene hornblendite

c Hornblendite, feldspathic hornblendite

- d Hornblende gabbro, diorite
- e Biotitic hornblendite
- f Serpentinite
- g Anorthosite

3a Metabasalt, meta-andesite

b Meta-agglomerate, tuff

c Shaly iron formation

2 Chlorite schist

la Quartz biotite paragneiss b Garnet quartz biotite paragneiss

Figure 5.

Legend for Accompanying Geological

Maps



Muskeg or swamp



11

Motor road

Geological boundary, defined

Geological boundary, approximate

Strike & dip of schistosity, stratiform foliation

### Pit, trench

Drill hole, indicating plunge









0

0

#### PETROGRAPHY OF THE MAFIC-RICH INTRUSIONS

### Quetico Group

In the Quetico area, mafic and ultramafic rocks have been observed at 35 places, but in figure 2, only the locations of the larger bodies are indicated. The intrusive bodies are widely scattered in both paragneiss and metavolcanic rocks. Granitic dikes cut the intrusion near Baril Lake (figure 2), and inclusions or xenoliths of hornblendite and peridotite occur at several places in the quartz diorite (plate 3, figure 2). Thus, it is clear that some of the mafic-rich rocks are definitely older than the granitic plutons. However, several peridotitic bodies occur in linear groups that are parallel to nearby Keweenawan diabase dikes and transverse to the general trend of foliation in the quartz diorite. Most of these bodies do not show conclusive evidence with regard to age relations, and possibly, they represent later dikes.

The rock types of the mafic-rich intrusions in the Quetico area are variable, but all have an appreciable content of hornblende (table 2). In figure 6, the results of modal analyses are plotted on triangular diagrams that show a tentative classification suggested by Irvine (personal communication) for mafic igneous rocks consisting dominantly of either olivine, pyroxene and hornblende, or pyroxene, hornblende and plagioclase.





altération products

Table 2. MODAL ANALYSES OF THE QUETICO GROUP OF MAFIC-RICH ROCKS

Mineralogy (volume per cent)

Hornblende Peridotitic rocks	160-50	160-76	160-91	160-94	160-87
olivine clinopyroxene hornblende serpentine magnetite biotite chlorite carbonate sulphides	4 20 20 40 13 - 2 1 tr 100+	5 21 26 33 15 tr -	13 25 25 23 13 1 tr 1 tr	11 30 21 25 13 tr tr tr tr	9 33 37 15 5 1 tr 100+
Hornblendite and Feldspathic Hornblendite	160-83	160-115	160-105	160-85	160-111
hornblende biotite plagioclase sphene opaques quartz carbonate apatite chlorite sulphides	98 1 tr 1 1 100+	81 6 11 1 tr - - - 99+	74 8 17 tr tr tr tr 99+	69 20 3 tr 2 tr 3 99+	68 1 28 1 - tr tr tr 2 100+
Hornblendite (body 'c')	160-157	160-161	160-160	160-163	
hornblende biotite olivine orthopyroxene clinopyroxene opaques serpentine iddingsite sulphides	72 1 8 5 4 9 tr tr 79+	69 1 6 4 7 6 3 4 	78 22 	85 15 	

Optical data on the constituent minerals are presented in tables 3 and 4. The refractive indices were determined in white light by immersion in index oils calibrated at 0.002 intervals. 2V was measured by standard orthoscopic universal stage methods.

# Body 'A'

The largest mafic-rich body in the Quetico area is located near Chief Peter Lake (fig. 3), and is 2500 feet by 1500 feet in outcrop dimensions. It consists of almost equal amounts of hornblendite and hornblende peridotite with 5 percent or less feldspathic hornblendite. It is evident in drill core from this body that these rock types may be complexly intermingled, but in outcrop, the peridotite seems more prevalent in the central part of the body.

The hornblende peridotite is an equigranular mosaic of partly altered olivine, clinopyroxene and hornblende (plate h, figure 1). The olivine is colourless and forms equant anhedral grains of 1 - 4 mm diameter. Its refractive index,  $n_y$ , is about 1.692 (table 3), indicating a composition near Fa<sub>18</sub>. Alteration of olivine to serpentine and magnetite is present in all degrees, but generally, individual grains are about two thirds altered. Clinopyroxene occurs as colourless, occasionally twinned, equant grains that are similar in size to those of olivine. Optical properties indicate that it is diopsidic augite (Ca<sub>15</sub>Mg<sub>16</sub>Fe<sub>9</sub>), and apparently, it has negligible variation in composition in the intrusion (table 3). It is not affected by serpentinization but is partly altered to hornblende and accompanying tiny rods or blades of opaque oxides that

Table 3. OPTICAL DETERMINATION OF MINERALS

Specimen	n_ olivine	clinop	clinopyroxene		orthopyroxene	
	У	ny	+2y	25		
160-90	-	1.680	-		-	
160-94	1.693	1.680-1	-		***	
160-87	1.692	1.680-1	54_1/2°			
160-76	1.689	1.682-3	550		-	
160-54	1.690-1	1.680-1	-		-	
160-50	-	1.682	560		-	
160-91	-		54 1/2°		-	
160-157	-	1.683	-		1.692	
W60514	1.691	-	-		-	
W60511	1.693	1.683	49 1/20		-	

Table 4. OPTICAL DATA ON HORNBLENDE

Specimen	n <sup>s</sup>	n: z	-2V
160-94	1.647	1.651	-
160-87	1.647	1.651	
160-50	1.040-7	1.051-2	
160-54	1.040-7	1.051-2	
160-76	1.040	7.025	8c0
100-91	7 61.6	1 601-0	05
100-03	1.040	1.655-6	770
100-115	1.000	1.656	750
T60-85	1.653	1.657-8	810
T60-111	1,652	1.657-8	
160-160	1.645-6	1.652	78 <sup>0</sup>
T60-157	1.649-50	1.654-5	
W60-130	1.647-8	1.652-3	78 <sup>0</sup>
W60511	1.644	1.652	

occur along its cleavages and grain boundaries. Hornblende is pleochroic from colourless to light green. It occurs as: individual anhedral grains; partial rims on clinopyroxene; and irregular patches between olivine and clinopyroxene. When it is in contact with olivine, the hornblende commonly shows a narrow colourless rim (plate h, figure 2). Other minerals, locally present in the hornblende peridotite are biotite, chlorite, carbonate, pyrite, chalcopyrite and nickeliferous pyrrhotite. The weathered surface of the hornblende peridotite is brownish-grey and has a distinctive roughness due to the more rapid weathering of serpentine as compared to pyroxene or hornblende. On fresh surface, the rock is greenishgrey with black mottling caused by the fine grained magnetite in the pseudomorphs after olivine.

With a decrease in olivine and clinopyroxene, coupled with an increase in hornblende, the peridotite grades rather abruptly into hornblendite. Hornblendite is a dark green rock, consisting dominantly of hornblende with accessory biotite, and small scattered grains of sphene, apatite, magnetite and sulphides. The hornblende is pale to dark green in thin section and occurs as ragged anhedral grains, averaging about 3 mm. in diameter. Alteration is minor, but has produced some biotite and chlorite.

Feldspathic hornblendite is a minor rock type in body 'A'. The constituent hornblende is pleochroic in light to dark green, slightly darker than that in the hornblendite. Plagioclase (oligoclase-andesine) makes up less than 20 percent of the rock. It is

interstitial to hornblende and is partially sericitized. Accessory minerals are biotite, sphene, apatite, chlorite and sulphides (plate 5, figure 1). The common grain size is 5-15 mm. in diameter, but a local pegmatitic variant of this rock type contains prismatic hornblende grains, 5-8 cm. in length.

### Body 'B'

The smaller intrusion near Chief Peter Lake consists dominantly of feldspathic hornblendite, grading to hornblende gabbro and less commonly, to hornblendite. The rock types are similar to those described for body 'A'. Hornblende is the dominant mineral and interstitial feldspar is present in all thin sections examined, ranging from a few per cent to nearly 30 per cent. Quartz, in myrmekitic intergrowth with feldspar was observed in one thin section (plate 5, figure 2). The contact of body 'B' and the paragneiss is not exposed in outcrop, but it is evident at four places in drill core available from this body. At two of these, the intrusive rock is distinctly finer grained for about one foot adjacent to the contact; the grain size is about 1 1/2 mm. as compared to 5-15 mm. within the intrusion.

# Body 'C'

The small mafic body situated just north of Baril Lake (body 'C') is mainly biotitic hornblendite that is invaded and altered by granitic rocks and quartz veins. The hornblende is dark green and, in most of the body, averages about 1 mm. in diameter. The biotite is pleochroic from pale reddish-brown to medium brown; it is generally

finer grained than the hornblende, averaging about 1/2 mm. A coarse grained variant of the hornblendite consists of large hornblende grains (approximately 20 mm. in diameter) poikilitically enclosing small grains of olivine, orthopyroxene and clinopyroxene (plate 6, figure 1). The olivine grains are subhedral to anhedral and are 1/2-2 mm. in diameter. Most are partly altered to iddingsite or, more rarely, to serpentine and magnetite. Clinopyroxene occurs as anhedral grains from 1/4 to 1 mm. in diameter. It is generally unaltered but contains considerable magnetite along cleavage traces. Orthopyroxene occurs as small grains in hornblende, and as larger (4 mm.) grains poikilitically enclosing olivine and elinopyroxene. It has faint pink pleochroism and its refractive index, ng, is 1.692 indicating a composition near Eng. The orthopyroxene is marginally altered to iddingsite (plate 6, figure 1).

### Group 'D'

The mafic-rich bodies in the northeast of the Quetico area are enclosed and altered by granite. The rocks consist dominantly of green hornblende or of brown hornblende with green borders. Locally the hornblende appears to be pseudomorphous after pyroxene. Aggregates of talc, carbonate, chlorite, serpentine and magnetite are common and are probably secondary after either olivine or pyroxene or both. Sericitized plagioclase is also evident in some rocks. Sulphides and ilmeno-magnetite are common accessories. Included in this subgroup is a hornblendite body emplaced in the metavolcanic belt. This rock

is composed of hornblende, some of which is apparently pseudomorphous after clinopyroxene, and minor clinopyroxene and magnetite.

### Shebandowan Group

Fourteen bodies of serpentinite or serpentinized peridetite, indicated by Tanton (1938a) in the Shebandowan area, were mapped and sample for this study (figure 4). Most of the bodies are lensoid in shape and elongated subparallel to the schistosity in the enclosing metavolcanic unit. The bodies range from 1/8 to 1 mile in length and are all less than 1/8 mile in width. Unfortunately, bedrock exposure in the area is extremely poor and the contacts between ultramafic and metavolcanic rocks are covered by water or heavy overburden. In no place was a clearly defined contact observed. In the best exposures, the adjacent metavolcanic and ultramafic units are both altered to assemblages of chlorite, talc, serpentine and carbonate, and they are therefore difficult to distinguish. In the volcanic unit, bands of shaly iron formation are contorted in the vicinity of the ultramafic bodies and appear to parallel their contact. The strike of the regional schistosity has a somewhat similar trend. These features suggest forcible intrusion of the ultramafic bodies.

Partially serpentinized peridotite occurs in body 'B' (figure 4), but the most common intrusive rock type is serpentinite. Fine to coarse-grained gabbroic rocks occur both as isolated intrusions and in association with both ultramafic types.

The rocks of body 'B' are medium-grained and in most exposures contain pyroxene and amphibole that can be recognized in hand specimen. Highly sheared serpentinite occurs locally in drill core from the body. In thin section, the peridotitic rocks show olivine, clinopyroxene and orthopyroxene as apparently primary minerals in variable stages of alteration (table 5; plate 2, figure 2; plate 3, figure 1). Olivine now comprises only about 20 percent of the rock. However, alteration has produced serpentine and magnetite pseudomorphs after the olivine, and these minerals respectively constitute about 60 and 15 percent of the rock, indicating that olivine was originally present at about 75 -85 percent. Talc rarely occurs in olivine pseudomorphs, being more common in pseudomorphs after pyroxene. The olivine grains are both rounded and subhedral, and range from 1/8 to 2 mm. in diameter. The smaller grains tend to be rounded possibly indicating partial resorption of originally larger, more idiomorphic grains. The n\_ index of the olivine is about 1.692 (table 3) indicating a composition of Orthopyroxene and clinopyroxene occur in subequal amounts Fazo totalling about 5 percent of the rock. They occur as large grains about 6 mm. in diameter enclosing olivine. Orthopyroxene is the most readily altered mineral of the peridotitic rocks, being converted to assemblages of talc, amphibole, serpentine and magnetite. Prior to alteration, it was apparently slightly more abundant than clinopyroxene, but the latter has remained relatively fresh, showing only slight alteration to amphibole. The clinopyroxene has a n index of 1.683 and a 2V of 49 1/2° which indicate a composition of Call Mgh8Fell.

Table 5. MODAL ANALYSES OF SOME SHEBANDOWAN ULTRAMAFIC ROCKS

	Min	eralogy	(volume	percent)		
	W60509	W60511	W60514	W60515	W60522	W60533
serpentine magnetite <sup>1</sup>	88.8 10.1	64.4 13.0	53.2 17.0	70.5	70.7	74.6
olivine orthopyroxene	-	14.6 tr	21.7	-	-	-
clinopyroxene	0.1	2.5	2.8	-	-	-
talc	1.0	5.4	tr	tr	0.3	4.6
020 02 00	100.0	99.9	+ 99.9	+ 99.9+	100.0	100.0

1. This may include minor sulphides and possibly chromite.

# Table 6. ANALYSES OF GRAB SAMPLES OF SULPHIDE-BEARING ROCKS

Cu	Ni	Pt	Pd
percent		oz/	ton
tr	1.18		0.02
3.44	0.70	0.01	0.08
0.81	0.24	0.03	0.04
2.95	tr	0.03	0.06
1.06	0.26		tr
	Cu pero tr 3.44 0.81 2.95 1.06	Cu Ni percent tr 1.18 3.44 0.70 0.81 0.24 2.95 tr 1.06 0.26	Cu Ni Pt   percent oz/   tr 1.18   3.44 0.70   0.81 0.24   2.95 tr   1.06 0.26

Serpentinite occurs in bodies C,D,E,F,G,H,I and K (figure 4). Of these, bodies C,D and I are highly sheared and occur as a linear group near and parallel to the contact of the metavolcanic and granitic rocks. In hand specimen, serpentinite is fine grained, dark green to black, and massive to schistose. It consists largely of minerals of the serpentine group and magnetite. Talc, chlorite, brown amphibole, biotite, carbonate, chromite and sulphides are present locally. In many of the thin sections taken from the serpentinite, pseudomorphic textures of olivine and pyroxene are clearly evident (plate 1), and it seems apparent that the rock represents complete alteration of dunite or peridotite. In specimens where pseudomorphs are not visible, the rock is commonly sheared, and in some, pseudomorphs may have been destroyed by intense alteration (plate 2, figure 1).

The mineral serpentime occurs as fracture filling and in pseudomorphs after olivine and pyroxene. Fractures in the rock are commonly coated with apple-green serpentime having a slicken-sided appearance. The serpentime is fibrous, and aligned both perpeodicular and parallel to the fracture walls. Where pseudomorphous after olivine, it is extremely fine grained (1/8 mm.) and lamellar, fibrous or platy. Mesh and radial replacement textures are common (plates 1 and 2). Serpentime after pyroxene (bastite) may be colourless in thin section but is commonly pale green. Magnetite is commonly associated in amounts of 25 percent (table 5), occurring as fine dust and square-outlined or anhedral aggregates as large as 1/2 mm. in diameter. Some large opaque grains are brownish and may be chromite or highly chromiferous magnetite (specimens W605h0 and W605h3). Tale is relatively abundant in some serpentinite, occurring as aggregates up to 1/2 mm. in diameter. It occurs in pseudomorphs after pyroxene and, less commonly, after olivine. Amphibole occurs as sheaves of brown acicular grains, or deep reddish-brown, pleochroic plates with light green borders. Both habits appear to be formed by alteration of pyroxene, but some large grains may be of late-stage magnatic origin. Disseminated or fracture-localized carbonate is present in some serpentinite.

Fine grained metagabbro occurs to the north and northwest of the ultramafic rocks in bodies B,E,G and H. The contact of these rock types was not observed. The original or primary minerals were apparently calcic plagioclase and pyroxene. Both had a grain size of about 1 mm. They are altered to epidote and minor plagioclase, and to green hornblende.

Bodies 'A' and 'J' are dominantly coarse grained metagabbro. This rock consists of hornblende and epidote, with minor plagioclase and altered ilmenite. Some specimens are quartz-bearing. Fine grained metagabbro crops out to the southeast of the coarse gabbroic rock in body 'A'. A pegmatitic facies of the metagabbro is associated with body 'J'.

### Sulphide mineralization

Sulphide mineralization is associated with both groups of mafic-rich intrusions, and has been described by Cross (1920), Watson (1928), Tanton (1938) and Irvine (1961). Apparently, none of the deposits can be profitably mined at present. The principal sulphide minerals in both groups are pyrite, chalcopyrite, pyrrhotite and pentlandite. Chemical analyses of grab samples are given in table 6. In both groups, the sulphides are characterized by Pt and Pd, as well as Cu and Ni.

The isotopic composition of the sulphur in three grab samples was kindly analyzed by Dr. M. Shima of the Chemistry Department, McMaster University, with the following results.

Sample	Location and associated rock	sS <sup>34</sup> (per mil)
160-143	'I' body, Shebandowan area, peridotite	- 0.338
160-104	'A' body, Quetico area, peridotite	- 0.207
160-54	'B' body, Quetico area, hornblendite	+ 0.148
		+ 0.103

It is notable that the \* value for the sulphur from the Shebandowan peridotite is the lowest, that of the Quetico peridotite similar but slightly higher, and the value from the hornblendite is higher still. A progressive increase in the  $3^{34}/3^{32}$  ratio of sulphides with increasing silica content in the associated rocks has been observed by Thode et al (1961) in several mafic-rich igneous bodies that have

apparently undergone differentiation by fractional crystallization. The low : value for the Shebandowan analysis indicates that the source of the sulphur of sulphide deposit 'I' is probably the ultramafic body itself, and not the nearby granitic pluton.

### CHEMICAL AND SPECTROCHEMICAL DATA

### Sampling and Specimen Preparation

An attempt was made to collect fresh hand specimens representative of the major rock types from each of the mafic-rich bodies visited in the Lac des Mille Lacs region. However, thorough sampling was not possible because of poor exposure. Several of the bodies have been investigated by diamond drilling, and although much of the drill core was available and was sampled, storage and records are poor, and the exact sites at which much of the core was taken are unknown. In addition to the seventeen rocks from the Quetico area and fourteen rocks from the Shebandowan area chosen for analysis, ultramafic and mafic rocks from S. E. Alaska and from the Abitibi area of N. E. Ontario were examined for comparison. The approximate locations of the analysed specimens are indicated on the accompanying geological maps, and brief descriptions of the petrography and geological environment of these specimens are given in the appendix.

Specimens for analysis were broken into pieces of about 1/2-inch diameter which were coarsely crushed in a steel mortar. Effects of weathering and contamination were avoided as much as possible by rejection of fragments showing weathered surfaces and pieces of drill core showing metallic smears from coring bits. The coarse pulp was quartered sufficiently to give a sample of a few grams and this was crushed to pass a 150 mesh stainless steel screen.
Samples of about 5 grams were taken for major element analysis and by repeated quartering, representative portions of about 1/2 gram were obtained for spectrochemical analysis.

Mineral separates for analysis were purified from a 150-200 mesh size fraction by means of a Franz electromagnetic separator and heavy liquids, and by rolling the sized sample on separating paper. The purity of these separates, as estimated from 400 grain counts, is greater than 98 percent.

# Major Element Analyses

Standard wet chemical analyses for major elements were made by the Ontario Provincial Assay Office under the direction of D. A. Moddle. Analyses were obtained for five rock specimens and one hornblende separate from the Quetico area, and for two rock specimens from the Shebandowan area. The results are given in tables 7, 8 and 11.

# Minor Element Analyses

#### Molybdenum-graphite Spectrographic Method

Quantitative spectrographic analyses were made by the author. The analytical method employed the D. C. arc and internal standardization, and is essentially that outlined by Shaw (1960). The Stallwood air-jet was used in sample excitation to minimize selective volatilization and matrix effects, and to stabilize the arc. Molybdenum was used as an internal standard, being introduced as Table 7.

CHEMICAL ANALYSES OF SERPENTINIZED ULTRAMAFIC ROCKS

	W60514	W60533	(A)
$Si0_{A1203}$ $Fe0_{Ca0}$ $Mg0_{Ca0}$ $Na_{20}$ H20+ H20- H20- $T10_{5}$ $Cr_{203}$ $Mn0_{3}$ $V_{203}$	37.16 3.97 6.51 8.54 31.48 4.42 tr tr 6.16 0.26 tr 0.25 0.47 0.17 0.01 nil	37.35 3.75 6.92 7.66 31.96 0.15 nil tr 8.45 0.12 0.10 0.10 0.18 0.57 0.20 0.01 nil	39.74 1.14 3.55 3.22 39.35 0.27 0.08 0.07 10.85 0.32 - 0.32
Total	99.40	97.42	98.91

 (A) Average of four analyses of ultramafic rocks from Massachusetts (Hess, 1938).

Data on the analyzed rocks are listed in the appendix

Specimen Rock Type	160-94 hpd	160-87 pdhb	160-83 hb	160-85 fhb	160-114 marginal hgb	(A)
SiO Al $203$ Fe $03$ Fe $0$ Mg $0$ Ca $0$ Na $0$ K $20$ H $20$ + H $20$ - P $205$ TiO Cr $03$ S $2$ S	41.77 1.99 5.33 8.33 27.07 9.04 0.24 trace 4.10 0.04 trace 0.18 0.39 0.18 0.01 0.39	43.46 2.93 6.21 5.20 25.56 10.61 0.31 0.11 3.95 0.02 trace 0.14 0.43 0.18 0.02 0.68	50.52 2.73 2.38 6.00 18.88 13.88 0.80 0.21 0.77 mil trace 0.15 0.38 0.18 0.02 1.69 0.20	45.64 16.12 1.04 7.20 12.70 10.28 2.87 0.80 1.00 0.02 0.15 1.26 0.25 0.12 0.05 0.57	49.99 11.52 1.42 9.26 10.60 10.35 2.50 0.76 0.84 0.01 0.23 0.83 0.08 0.14 0.04 0.29 1.14	50.83 14.07 2.88 9.06 6.34 10.42 2.23 0.82 0.91 0.23 2.03 0.18
Total	99.06	99.81	98.79	100.07	100.00	100.00

Table 8. CHEMICAL ANALYSES OF MAFIC-RICH ROCKS

(A) Normal Tholeiitic Basalt (Nockolds, 1954).

Table 9.

C.I.P.W. NORMATIVE MINERALOGY

		W60514	W60533
Olivine	Fo	57.43	46.51
	Fa	20.95	15.92
Orthopx	En	-	24.13
	Fs	-	7.48
Clinopx	Di	5.70	
	He	1.66	-
Anorthite		11.95	0.16
Apatite		-	0.25
Chromite		0.74	0.94
Corundum		-	4.21
Ilmenite		0.51	0.40
Larnite		0.78	
Magnetite		0.28	-
Total	× .	100.00	100.00

N.B. In the computation of the norm of W6051h, the FeO / Fe<sub>2</sub>O<sub>3</sub> ratio was corrected to allow an FeO / MgO molecular ratio of 0.2 in the normative femic silicates, similar to that determined from refractive index measurement of the olivine. For W60533, all Fe<sub>2</sub>O<sub>3</sub> was converted to equivalent FeO; the resultant molecular ratio was O.19.

Table 10.

C.I.P.W. NORMATIVE MINERALOGY

		160-94	160-87	160-83	160-85	160-114
Olivine	Fo Fa	39.13 14.17	35.08	1.02	18.73	5.93
Orthopx	En Fs	2.64	3.88	29.15 5.21	-	10.07
Clinopx	Di He	24.55	27.89 7.48	38.14 5.93	11.27	17.64
Feldspar	An Ab	4.50	6.54 2.75	3.21	28.75	17.93
Nepheline Apatite	01	-	-		5.22	0.50
Calcite Chromite		0.92	1.63	3.88	1.31 0.37	0.67
Magnetite Pyrite		3.12	-	3.49 0.37	2.43	2.08
		Approximity of the second sec	ensistementintipataceation	monten in the description	and the second	
Total		100.00	100.00	100.00	100.00	100.00

N.B. In the computation of the norms of specimens showing alteration and oxidation of Fe-bearing silicates, the FeO / Fe<sub>0</sub>, ratio was corrected to allow an FeO / MgO molecular ratio<sup>2</sup> of 0.2 in the normative femic minerals, similar to the ratio determined by refractive index measurements of the olivine.

			an analysis	
		160-115	(1)	(2)
Si0 percent Al 203 Fe $_{203}$ Fe $_{203}$ Fe $_{203}$ Mg $_{20}$ H20+ H20- P205 Tf05 Cr 203 Mn $_{20}$ V 0 C $_{20}$	nt	49.08 5.56 2.78 8.27 16.36 12.80 0.75 0.52 0.55 0.12 tr 0.55 0.22 0.20 0.04 0.14	45.87 8.43 1.94 5.87 21.79 12.22 1.04 0.34 1.79 0.14 0.63	41.20 16.16 4.12 7.04 13.96 12.63 2.27 0.62 0.38 0.29 0.03 1.42 n.d. 0.04
Total		97.94	100.13	100.16
Ba ppm. Co Cr Cu Mn Ni Sr Ti V Zr		105 95 1600 98 1750 360 120 5200 390 62	45 35 2500 - 600 160 220 22	105 88 60 24 940 235 135 4700 760 23
	N	ormative Mine	eralogy of I60-115	
Olivine Orthopyroxene Clinopyroxene	Fo Fa En Fs Di	6.16 2.03 17.24 5.14 34.28	Magnetite Chromite Ilmenite Calcite	4.14 0.32 1.08 0.32
Feldspar	He An Ab Or	8.91 10.36 6.53 3.49	Total	100.00

Table 11. A CHEMICAL ANALYSIS OF HORNBLENDE FROM FELDSPATHIC HORNBLENDITE AND RELATED DATA

(1)(2)From hornblende peridotite (0'Hara, 1961) From hornblendite (Irvine, 1959)

0.877% Mo<sub>2</sub>O<sub>3</sub> in the graphite matrix.

The following elements were determined: Al, Ca, Co, Cr, Cu, Mn, Ni, Ti, V and Zr. A list of the spectral lines and their analytical range, and the relative deviation for triplicate analyses are quoted in table 12. Details of the spectrographic arcing conditions, plate processing and photometry are outlined in table 13. Results are given in tables 14, 15, 16 and 17.

Samples for analysis were thoroughly mixed with an equal. weight of graphite matrix containing the internal standard and were then ground in an agate mortar. Triplicate portions of each mixture were packed into the cavities of 1/8-inch diameter graphite rods. A sample electrode was inserted as the anode in the lower watercooled jaws of the arc-spark stand, and a plain graphite rod was placed in the upper jaws as the cathode. The sample was burned in the arc for approximately 80 seconds at a current maintained at 6 amperes. Spectra were recorded on Eastman Kodak type SAl photographic plates in the wave length region of 2400-3700 Å.

The spectral line transmission values were read from the processed plates by means of an A. R. L. densitometer. Wherever possible, lines were read on the central steps and transmission values (T) in the range 1.5 - 95 were accepted. 'T' values were converted to arbitrary log intensity units (Y values) on a calculating board using calibration curves constructed by the two-step method (Shaw, 1960). Two-step values were read from the spectrum of a matrix of Fe<sub>2</sub>O<sub>3</sub>-MgO-SiO<sub>2</sub>. Y values for the internal standard

Table 12. THE SPECTRAL LINES USED IN THE MOLYEDENUM GRAPHITE METHOD, THEIR RANGE, AND THE RELATIVE DEVIATION OF TRIPLICATE ANALYSES

Element or oxide	Spectral Line	Range	Relative Deviation "C" in percent
AL_O.	2652.489 Å	0.30 + 8 percent	18.0
CaÕ	3158.869	0.07 - 5 percent	15.0
Co	3453.505	15 - 500 ppm	20.7
Cz	3005.057	600 - 20,000 ppm	13.5
Cu	3273.962	4 - 200 ppm	30.7
Mn	2933.063	150 - 9000 ppm	12.7
NI	3003.629	100 - 9000 ppm	25.1
TI	3354.635	300 - 2000 ppm	30.9
T1 <sup>2</sup>	3321.588	1600 - 20,000 ppm	14.7
A	3183.406	35 - 600 ppm	10,9
Zr	3391.975	12 - 500 ppm	19.8
No	2931.209	standard line	

#### Table 13. DETAILS OF THE MOLYEDENUM-GRAPHITE METHOD

30 microns

Spectrograph

JACO 21-foot grating, Wadsworth mount, first order dispersion 5.2 %/mm.

Condensing Optics 25 cm. focal length cylindrical lens (horizontal axis) at the slit; 6.7 cm. focal length cylindrical lens (vertical axis) l6.1 cm. from the slit; 10 cm. focal length spherical lens 58.1 cm. from the slit; are located 72.5 cm. from the slit.

Slit width

Intensity Control

of 0.2; 2 mesh screens for further reduction.

National Carbon Co. graphite (Special grade) sample (anode) 1/8" rod, plain crater 1/16" x 3/8"; counter electrode (cathode), 1/8" rod.

Eastman Kodak Type S.A.1 plate, 2300-3700 Å.

ARL arc-spark stand, water-cooled jaws.

7-step sector at the slit, log intensity ratio

8 mm.; sector height adjusted for steps 2.3.4.5.

Slit length

Electrode Stand

Electrodes

Emilsion and range

Processing

Voltage and Current

Exposure

Sample

Artifical Standards

Photometry

3 minutes development in D19 developer at 20°C., 15 seconds stop bath; 20 minutes acid fix, 20 minutes wash.

220 v. D.C. on open circuit at 6 amperes.

Completion, 80-90 seconds.

1 part mineral or rock to 1 part graphite containing 0.877% Mo.0.20

Prepared from Johnson-Matthey 'Specpure' compounds. Matrix of 310, - 45%, MgO - 45%, Fe<sub>2</sub>O<sub>2</sub> + 10%, mixed with sufficient of the oxides to give Ca, Al, Ti - 5%, Cr, Mi, Mn - 2%, Co, V, Cu, Zr, B - 500 ppm. Five equal dilutions of this to cover a range of 100 fold.

ARL photodensi tometer used; galvanometer readings between 1.5 and 95 were used with plate background adjusted to 100 before each measurement; readings made on step 4 where possible (steps numbered 0~8).

Specimen	Body	A1_0,	Co	Cr	Cu	Mn	Ni	Ti.	V	Zr		
	or Area	per cent	ppm									
160-50	A	2.10	115	2900	68	1100	670	930	110	28		
160-76	A	3.7	160	3600	105	1250	660	2400	195	36		
160-91	A	-2.55	140	3300	75	1400	690	1200	155	38		
160-94	A	1.80	120	2700	60	1300	600	1000	110	29		
160-87	A	2.65	110	2700	33	1250	460	1350	140	100		
160-83	A	5.9	61	2350	175	1350	370	2050	185	14		
160-115	В	st	53	1800	92	1500	390	6100	330	80		
160-105	В	16.0	83	2550	st	1550	440	3800	215	86		
160-85	A	st	43	1800	72	1000	295	6700	290	35		
160-114	В	st	70	2050	57	970	360	9200	470	46		
160-161	C	4.2	100	2300	25	860	510	2050	150	29		
160-160	C	8.1	84	2650	8	1600	480	2300	155	34		
160-163	C	4.3	80	2450	8	1200	520	1100	115	29		
W60-105	D	10.0	78	3300	st	1750	840	7100	245	67		
W60-125	D	11.5	96	1350	st	1900	960	13500	285	110		
W60-139	D	14.5	99	2550	st	1700	940	9100	300	81		
W60-130	D	16.5	84	1100	41	1400	480	1700	160	27		

Table 14. MINOR ELEMENT ANALYSES OF ROCKS FROM THE QUETICO GROUP OF MAFIC-RICH INTRUSIONS

"st" - strong, greater than analysis range. "tr" - trace, less than analysis range. "\*" - sought but not detected.

CaO values all "st".

Specimen	Body	Al 203	CaO per	Co	Cr	Cu	Mn	N1	<b>T1</b>	V	Zr
		cent	cent				pp	ppna			
¥60511	R	3.8	et.	96	2000	8	1000	990	11.00	73	26
W60512	B	5.7	st	86	2800	h	1200	1150	1.850	90	27
W60514	В	5.3	st	140	3500	18	1500	1450	1550	87	27
160509	В	3.8	0.80	130	3100	7	1200	1400	1350	74	25
W60530	E	3.0	1.95	235	4300	8	770	1850	2050	130	12
W60533	F	2.85	0.41	170	4000	16	1050	1400	1100	100	31
W60536	Q	2.75	0.81	190	4200	24	1050	1600	1750	115	34
W60528	E	3.5	3.0	230	4300	30	1050	1900	1500	120	40
w60543	н	1.85	1.20	130	4700	20	1100	2100	730	43	tr
W60540	H	2.00	5.0	190	5000	18	880	3200	1250	100	tr
W60515	C	1.45	st	90	4600	st	1250	3300	340	58	21
W60522	C	0.87	0.26	230	6400	155	650	3700	390	64	tr
W60529	E	st	st	34	2500	19	1200	235	2550	175	29
W60553	J	st	st	37	· 者	st	1400	tr	7700	480	65

Table 15. MINOR ELEMENT ANALYSES OF ROCKS FROM THE SHEBANDOWAN GROUP OF MAFIC-RICH INTRUSIONS

Table	16.	MINOR	ELEMENT	ANALYSES	OF	ULTRAMAFIC	AND	MAFIC	ROCKS	FROM
		OTHER	LOCALITI	EES						

Specimen	Al 0 per <sup>3</sup> cent	Co	Cr	Cu	Mn ppi	N <b>i</b> .	Ti	V	Zr
H-4-4	0.57	165	2100	6	1900	1550	295	38	tr
I-37-2	3.0	87	1800	27	1500	330	1650	160	tr
R-38-2	6.8	75	1350	245	1250	270	33.00	275	tr
I-31-3	6.6	52	930	300	1050	115	4300	450	tr
N-25-1	15	53	200	25	1950	105	1450	200	tr

Duke Island, Southeastern Alaska

HOTOT WLAT ALAS AND	1110
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Specimen	Al_O	CaO	Co	Cr	Cu	Mn	Ni	Ti	V	Zr	
	cent	cent		ppm							
1949-94	5.3	st	120	5400	st	1650	2000	670	87	tr	
1949-2	8.1	4.1	130	2750	14	1350	1400	500	67	tr	
1949-15	5.9	2.60	140	2750	14	1600	1700	480	74	tr	
1949-10	4.4	st	70	3600	71	1850	510	3000	210	28	
1949-39	5.5	st	45	3200	43	1750	440	2900	200	51	
1949-5	st	st	42	2850	20	1100	350	1250	150	tr	
1949-48	st	st	43	2200	22	790	300	1350	135	13	

Table 17. MINOR ELEMENT CONTENT OF HORNBLENDE AND BIOTITE

Element		Hornblende							
or oxide	160-115	160-105	160-160	W60-130	160-85	160-160			
Al_0, percent	13.0	12.0	7.2	11.5	st	st			
Co ppm	95	98	96	135	65	170			
Cr	1600	2700	2750	*	2200	5400			
Cu	98	220	9	37	53	9			
Mn	1750	1850	2500	2250	1050	970			
Ni	360	490	590	520	300	1100			
Ti	5200	3600	1250	1950	9100	7200			
V .	390	280	190	165	520	285			
Z <b>z</b> *	62	63	40	38	35	30			

Table 18. A MINOR ELEMENT ANALYSIS OF THE STANDARD DIABASE W-1 BY THE MOLYBDENUM-GRAPHITE METHOD COMPARED WITH RECOMMENDED VALUES.

Element	Mo-graphite <sup>1</sup>	Recommended <sup>2</sup>
Co	37 ppm	( 38 ppm (spectrographic mean) ( 51 (neutron activation)
Cu	135	110
Mn	1500	1300
Ni	115	82
Ti	8250	(7400 (spectrographic mean)
		(6400 (chemical analysis mean)
V	390	240
Zr	97	1.00

1.

Mean of 5 replicates. Values from Stevens et al (1960). 2.

spectral line were subtracted from those of the analysis line, and the resulting AY values were used for interpolating on working curves.

Working curves were then drawn up using artificial standards consisting of the appropriate weighed spec-pureoxides, diluted sufficiently with the matrix to cover the analysis range. These standard samples were arced, and the resultant  $\Delta Y$  values were plotted as ordinates against log concentration (k). Straight lines were drawn through the means of eight or nine replicate determinations for each element concentration (figures 7 and 8).

Correction for background intensity was negligible except on the lower-most steps of the spectral lines. Correction was made by setting the transmission scale to zero in a clear area of the plate near the spectral line; the wave-length of this area of similar background was determined by intensity comparison with the spectrum of the  $Fe_2O_3$ -MgO-SiO<sub>2</sub> matrix. This method of correction gave straightline working curves for Al, Co, Mn, Ni, Ti<sub>1</sub> and Ti<sub>2</sub>. The background correction was insufficient at the lowest standard concentration for some lines, where high background intensity on the lowest spectral step resulted in 'tails' in the working curves. This curvature is apparent in the curves for Ca and V, and to a lesser degree, for Cr, Cu and Zr.



Figure 7. Working Curve for Co 3453



# Precision and Accuracy of the Molybdenum-Graphite Method

A single classification analysis of variance was made for each of the spectrographically analyzed elements. The resultant variance  $(s^2)$  within replicates for each element is interpreted as yielding an estimate of the precision of the spectral line determinations. Replicate values for each sample analysis were included in the analysis of variance programmed for the Bendix G-15 computer by Dr. G. V. Middleton. Standard deviation (s) and relative deviation (C = x / s) were calculated for each spectral line as indicated in table 12.

A Bartlett test of homogeneity of variance within elements (Dixon and Massey, 1957, p. 179) was made on Ca, Co, Cr, Ai, V and Zr. At the 5 percent level of significance, the variance of V is homogeneous throughout the analysis range. All the other elements have significant inhomogeneity, but only Ca gave a highly significant non-homogeneous variance. Most of this inhomogeneity is probably due to the spectrographic technique. At the high and low ends of the spectral line range, error in densitometer readings is appreciable. This is, for example, evident for the working curve for cobalt at low concentrations (fig. 7). On the other hand, manganese has a consistent spread of values (fig. 8) and would, presumably, show much smaller inhomogeneity, especially since the range of Mn values of analyzed specimens is small.

The accuracy of the molybdenum-graphite method is indicated in table 18 by a comparison of analyses of the standard diabase, W-1, with the recommended values given by Stevens et al (1960). Another indication is the comparison in table 19 of the data on the same specimen

Floment	Method	n dia Ministry ny kaodim-kaodim	alan an an an thu an	n nama ang kang kang kang kang kang kang kang		Specimen	No.	ana in grand grand and in this	1997 - Antonio Maria and Maria An
or oxide		160-94	160-87	160-83	160-85	160-114	W60514	W60533	160-115 hb
Al <sub>2</sub> 03	chem	1.99	2.93	2.73	16.12	11.52	3.97	3.75	5.56
~ )	spec	1.80	2.65	5.9	st	st	5.3	2.85	st
Cr	chem	2700	2900	2600	1700	500	3200	3900	1500
	spec	2650	2700	2350	1800	2050	3500	4000	1600
Mn	chem	1390	1390	1390	929	1080	1320	1550	1550
	spec	1300	1250	1350	1000	970	1500	1050	1750
Ti	chem	1100	800	900	7550	4970	1500	1100	3300
	spec	1000	1350	1950	6700	9200	1550	1100	5200
V	chem	70	140	140	340	270	70	70	270
	spec	110	140	185	290	470	87	100	390

Table 19. COMPARISON OF DATA DUPLICATED BY WET CHEMICAL AND SPECTRO-GRAPHIC METHODS

1. Chem-values converted from oxide analyses by wet chemical methods. Spec-spectrographic determinations

N.B. Al<sub>2</sub>0<sub>3</sub> values in percent; all others in ppm.

Table 20.

SPECTROGRAPHIC DATA ON GABBROIC ROCKS

	Ba		Sr	MgO		FeOL
1949-5	50	ppm	180	15.0	percent	5.5
1948-48	120		120	15.5		6.4
W60529	40		105	10.5		6.6
W60553	80		125	6.4		12.5
160-114	140		165			

1. Total Fe as FeO.

material duplicated by chemical and spectrographic methods.

Application of this method appears to be limited to maficrich rocks of bulk composition very close to that of the matrix used in the construction of the working curves. For the least mafic rocks, where an independent determination of any value was available (as for the standard rocks Gl and Wl, and for the rocks analyzed for major elements), the Mo-graphite spectrographic value was in almost every case higher than the independent value. The intensity of spectral lines appears to be enhanced by elements more strongly concentrated in the least mafic rock types. This is not unlike the matrix effect observed by Turekian, Gast and Kulp (1957) in the spectrographic determination of strontium.

## Aluminum

Determination of aluminum using the molybdenum-graphite method is not entirely satisfactory. The working curve for  $Al_{2652}$ shows a fairly large spread of values, and the precision is rather poor. Comparison of chemical and spectrographic values suggests that accuracy is fairly good for compositions close to the matrix used for preparation of the working curve (i.e., values near 2 - 4 percent  $Al_{2}O_{3}$ ), but it is poor for the relatively aluminous hornblenderich rocks. Accuracy of the lower portion of the analytical range is unknown, but is probably better than that higher in the range as optimum spectral intensity and minimum background are encountered in this lower portion. Unfortunately, the majority of specimen values are in the upper range.

#### Calcium

Calcium oxide was determined only in the range 0.07 - 5 percent and was, therefore, measurable only in the serpentinite from the Shebandowan area. The precision of the Ca<sub>3158</sub> spectral line is fairly good; its accuracy can be estimated only from the two methods of analysis for W60533.

#### Cobalt

Although the spread of working curve intensities for cobalt is relatively large, the accuracy, as indicated by an analysis of the standard W-1, seems excellent. The range of cobalt values is small and from the central part of the working curve, hence the determined

values are assumed to be good estimates of the true amount. This is notable in as much as the Co<sub>3453</sub> line is at the highest wave-length region examined and near the region of cyanogen band spectral masking.

## Chromium

The agreement of spectrographic and chemically determined chromium values is remarkably good (table 19). This is the only estimate of the accuracy of the chromium determination in as much as the value of W-1 was considerably lower than the trace level of the working curve range. Background effects for the Cr line, as for all lines at the lowermost wavelengths of the examined spectrum, are negligible. These factors along with evidence of good precision indicate that this method for chromium determination is highly satisfactory.

#### Copper

The determinations of copper are extremely erratic, with large deviation in values noted within replicates. However, the copper analysis of W-l is reasonably accurate. Copper is the most volatile of the elements sought, but the arcing conditions should have nullified the erratic behaviour due to selective volatilization. Neglecting the possibility of copper contamination, it appears that the major source of between-replicate variation must be due to inhomogeneity of the sample. If a major part of the copper is contained in sulphide minerals, irregular distribution of sulphide grains should cause poor precision yet not greatly affect accuracy.

## Manganese

The Mn<sub>2933</sub> spectral line gives one of the lowest relative deviation values, indicating good precision. Accuracy of the line is also good (table 18 and figure 7), and matrix and background effects are slight. Due to fairly constant manganese concentrations in the specimens, the intensity of the Mn line is quite similar to that of the Mo<sub>2934</sub> standard line. This similarity and the proximity of the two lines are additional features which recommend this method for the determination of manganese.

#### Nickel

The working curve for the determination of nickel is acceptable, but as is indicated by the relative deviation for the Ni<sub>3003</sub> line, reproducibility is only fair. Accuracy is difficult to assess because the value obtained for the nickel content of W-1 was read from an extrapolation of the working curve below the lowest standard concentration. Background masking is apparently not significant, but may be sufficient to account, in part, for the high W-1 value.

## Titanium

Due to the large range of titanium abundance, two spectral lines were used for its determination. At higher concentrations, Ti<sub>3321</sub> gives good reproducibility and fair accuracy. Ti<sub>3354</sub> gives the poorest precision of any of the spectral lines used in this work, but it is apparently fairly accurate for low concentrations of titanium in specimens similar in composition to the standard matrix. Due to the matrix effect, accuracy is lessened for determinations of rocks of composition different from the standard matrix.

## Vanadium

The  $V_{3183}$  spectral line shows the lowest relative deviation for replicate analyses of any of the lines used in the present work. However, the vanadium determination of W-1 indicates that the analyses are not particularly accurate. The working curve for vanadium is acceptable but shows a slight tail at low concentrations. It was found that considerable error resulted in the use of  $V_{3185}$  for analysis, possibly because of calcium-vanadium coincidence at this wavelength (Shaw, 1958).

#### Zirconium

Zirconium values are from the lowest part of the spectral line range, but their accuracy, as determined by replicate analyses on W-l, seems excellent, and the precision of the Zr<sub>3391</sub> line is intermediate in the range encountered for all elements. This is notable in as much as the line is in a region showing some masking by the cyanogen band spectrum.

#### Other elements

Mr. N. B. Church kindly made spectrographic determinations of the concentrations of barium and strontium in a specimen of the 'chill zone', in a separate of hornblende from the Quetico group, and in two specimens of gabbroic rocks from each of the Shebandowan and Abitibi areas. He also made spectrographic determinations of Fe and Mg in the latter four rocks. The values obtained are given in table 20. Only the gabbroic rocks were analyzed because, in the mafic-rich rocks, the concentrations of these elements would lie outside the range of the spectrographic method employed and matrix effects would probably be high. In fact, the Ba and Sr values obtained were all near the lower limit of detection.

A quantitative determination of boron was attempted by the molybdenum-graphite method. However, even the strongest boron line is too weak for quantitative determination in most specimens. Masking of the two major boron lines is a further complication. A significant increase in boron content with degree of serpentinization like that indicated by Turekian and Wedepohl (1961) was not apparent in a qualitative examination of the boron data.

Platinum and palladium are reported to occur in the sulphides in the mafic-rich intrusions in both the Shebandowan and Quetico areas (Cross, 1920; Watson, 1928; Irvine, 1961). A qualitative spectrographic search was made for these elements in the rocks, but neither was detected. It is noted that masking is strong for all but one of the strongest Pd spectral lines in the wave-length region examined.

## PETROCHEMISTRY OF THE QUETICO AND SHEBANDOWAN GROUPS

# Effects of alteration on chemistry

#### Shebandowan group

Before any petrological interpretation of the chemical data can be attempted, the nature and extent of the alteration of the rocks and its effect on the chemistry must be evaluated. Secondary mineralogy is developed in both groups of mafic-rich rocks, and in the Shebandowan rocks, its development is extreme.

The pseudomorphic textures present in many of the rocks from the Shebandowan group might suggest that the alteration was a volumefor-volume replacement of primary olivine and pyroxene by minerals of the serpentine group and, to a lesser extent, by magnetite, talc, chlorite, amphibole and carbonate (plate 1). The reaction for volumefor-volume serpentinization of olivine is considered by Turner and Verhoogen (1960) to be approximated in the equation

> $5 \text{ Mg}_2\text{SiO}_4 + 4 \text{ H}_2\text{O} \longrightarrow \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 4\text{MgO} + \text{SiO}_2$ olivine serpentine

They indicate that the excess MgO and SiO<sub>2</sub> are removed in solution. However it is noted that expulsion of large amounts of material as indicated by the above serpentinization reaction need not be required

if the Fe content of the olivine and its oxidation be considered. In olivine with one quarter mole percent fayalite  $(Mg_{1.5}Fe_{0.5}SiO_{l_1})$ , the Mg/Si ratio is the same as in serpentine  $(Mg_3Si_2O_5(OH)_{l_1})$ . On alteration, the Fe is removed from the olivine structure and partially oxidized to form magnetite. Thus the removal of Mg inferred by a constant volume alteration is not necessary. In the rocks under study, the removal of Mg is minor, as the olivine contains about one fifth molecular Fe<sub>2</sub>SiO<sub>1</sub>.

Moreover, there are textural features that suggest that the rocks were, to a considerable extent, closed to components other than water, oxygen and carbon dioxide during moderate alteration. For example, talc tends to concentrate in areas pseudomorphous after pyroxene rather than olivine, probably reflecting the higher silica content of pyroxene. The small amount of talc that does occur in the olivine pseudomorphs, indicating some excess of silica on serpentinization of the latter mineral, may be due to slight mobility of silica released on alteration of pyroxene. The silica mobilization would, however, be only on a microscopic scale.

'Bastite', the serpentine mineral after pyroxene, is a darker green colour than the serpentine after olivine, probably because it has a higher Fe/Mg ratio. It is likely that the primary olivine and pyroxene had nearly similar Fe/Mg ratios. If the serpentinization of olivine did take place in a system closed to SiO<sub>2</sub>, some Fe<sup>++</sup> had to oxidize to Fe<sup>+++</sup> which formed magnetite with additional Fe<sup>++</sup>. This

would reduce the Fe/Mg ratio in the serpentine pseudomorph after olivine. The fact that the serpentine did not develop homogeneous colour suggests that the system was not open to extensive movement of Fe and Mg even on a microscopic scale during alteration. Chemical mobility of minor elements during alteration will be discussed further in a later section.

There may have been some expansion of the rocks on alteration, but this is difficult to recognize especially if shearing has destroyed the pseudomorphic texture. The shearing may be due in part to expansion on alteration.

## Quetico group

Alteration of the rocks of the Quetico group is developed to a lesser degree than that of the Shebandowan group.

Olivine is only partially altered to serpentine and magnetite, and little or no talc is present. In body 'C', olivine is partially converted to serpentine and magnetite, and to iddingsite. Iddingsite is also developed as a marginal alteration of orthopyroxene (plate 2, figure 2).

Clinopyroxene in bodies 'A', 'B' and 'C' is not serpentinized although it is altered to hornblende (and some magnetite) along grain boundaries and cleavage traces. However, this development of hornblende is, for the most part, interpreted as a late stage magnatic reaction, rather than a later alteration process. The hornblende is

similar to that developed as an apparent primary phase in the hornblendite and feldspathic hornblendite.

Some biotite has formed as an alteration of hornblende. This occurs to a minor extent in bodies 'A' and 'B' and may be due to late magnatic phenomena. However, biotite constitutes up to a quarter of some rocks in body 'C' and it may be that potassium (and possibly sodium) have been added during the emplacement of the later granitic bodies that occur near to and cut this ultramafic mass.

In the feldspathic rocks, plagioclase is generally clouded and may be highly altered to a fine-grained micaceous material or sericite.

The mafic-rich rocks which outcrop within large areas of granitic rocks (group D) are highly altered. Plagioclase is almost entirely sericitized, and the olivine and pyroxene are converted to fine grained aggregates of talc, chlorite, serpentine and carbonate. The effect of the alteration on the chemistry of these rocks cannot be readily estimated.

Except for the apparent addition of potassium in the biotiterich rocks, there is no evidence for large scale migration of chemical species other than  $H_2O$ ,  $CO_2$  and  $O_2$  in most of the Quetico rocks. Zoning in the hornblende grains (plates 4 and 5) indicates that an overall equilibrium distribution of Fe and Mg was not achieved and may indicate that migration of these elements was limited to a microscopic scale.

#### Chemical comparison between groups

# Major elements

Chemical analyses were made of the following rock specimens from the Quetico area: hornblende peridotite, I60-94; peridotitic hornblendite, I60-87; hornblendite, I60-83; feldspathic hornblendite, I60-85; and a fine-grained hornblende gabbro, I60-114. From the Shebandowan group, a serpentinite, W60533, and a partially serpentinized peridotite, W60514, were analyzed.

The Shebandowan rocks are chemically similar to average Alpine type serpentinites (Hess, 1938) out have a higher Fe/Mg ratio. They are also slightly higher in  $Al_2O_3$  and lower in  $SiO_2$  and structural water (table 7).

The Quetico peridotitic rocks are chemically similar to most peridotite except that they are somewhat rich in CaO, and their Fe/Mg ratio is relatively high. The feldspathic hornblendite is much like tholeiitic olivine basalt (Nockolds, 1954) except that  $SiO_2$  is slightly low and Al<sub>2</sub>O<sub>3</sub> is high; the Fe/Mg ratio is lower in this case.

Chemical variation in the two groups with the sum of normative olivine and orthopyroxene is indicated in figure 9. Although the number of analyses is small, there is a smooth variation trend for nearly every plot. The chemical similarity of the Shebandowan and Quetico rocks is notable in as much as they exhibit widely differing mineralogy. The similar Fe content is particularly striking.







Specimen 160-114 is a hornblende-rich gabbroic rock from the fine grained contact zone of body 'B' near Chief Peter Lake. It is of interest because it could represent a 'chill zone' of a magma giving rise to the mafic-rich rocks, and thus it may have a composition not unlike that of the original magma. The existence of dikes of similar mineralogy near the large intrusions is a further indication of the existence of such a magma. If this interpretation is correct, it should be possible to derive the other rock types from this composition. However, it can be seen from the analyzes (table 8) and the variation diagram (figure 9) that this composition is not intermediate for all elements and that it is commonly irregular compared to the other analyzes. This may be due to the following reasons:

1. The specimen contains a relatively high percentage of sulphide minerals, suggesting that it may be a contaminated rock.

2. The magma may have assimilated some of the enclosing paragneiss yielding anomalous chemistry.

3. The major rock units analyzed from the Quetico group are from body 'A', whereas specimen I60-114 is from the nearby but more feldspathic body 'B'. It is possible that I60-114 could represent the magma giving rise to body 'B' only. Such a magma could be a residual liquid of the magma that gave rise to body 'A' or possibly, the olivine in 'A' was carried in suspension in such a liquid.

#### Minor elements

Spectrographic analyses were made of fourteen rock specimens from the Shebandowan area and seventeen from the Quetico area. Chemical similarities or difference between the two groups are difficult to evaluate due to the large number of rock types analyzed, but to give some numerical indication of difference, a discriminant function maximizing the differences between the two groups (Fisher, 1950) has been evaluated using a Bendix computer. The result shows that the inter-group difference is highly significant at the five percent significance level; the major contributors to the discriminant function are

74.9 percent Ti Ni 14.2 8.0 Cr

Total 99.2

Al, Co, Cu, Mn and Zr together contribute the remaining 0.8 percent.

The number of major element analyses is too small to permit a consideration of correlation between elements, but statistical methods have been applied to the minor element analyses. Intragroup correlation is indicated in the correlation coefficient matrices ('r' matrices) for the two rock groups (table 21). It is interesting that the pairs of elements Ti and V, Ni and Cr, which contribute most highly to the discriminant function have two of the highest positive correlation coefficients for both rock groups, and that in many cases



Abitibi Group - 1949 - 94, sp'd dunite; - 2, - 15, sp'd peridotite; - 10, - 39, pyroxenite

• indicates trace; in indicates strong



Figure 12. Plot of Minor Element Data for the Quetico Mafic-rich Group

160-50,-76,-91,-94,-87 - hornblende peridotite 160-83,-115,-167,-163,-160, W 60-105,-125,-130,-139 - hornblendite 160-85,-105,-114 - feldspathic hornblendite

				Shebando	wan Group	p			
	Al	Co	Cr	Cu	Mn	NI	T1.	V	Zr
Al	1								
Co	367	1							
Cr	793	.630	1						
Cu	629	024	.578	1					
Mn	.624	778	762	200	1				
Ni	805	.328	.868	.776	574	1			
T1	.727	.141	560	785	.132	706	1		
V	.291	.604	067	444	286	276	.760	1	
Zr	.564	122	552	259	.503	630	·h29	.425	1

ROCKS OF THE MAFIC-RICH INTRUSIONS

Table 21.

CORRELATION COEFFICIENT MATRICES FOR MINOR ELEMENTS IN THE

Correlation is significant at the 95 percent level if the absolute value of the coefficient is greater than 0.576.

	Quetico Group									
	Al	Co	Cr	Cu	Mn	Ni	T <u>1</u>	V	Zr	
Al	1									
Co	641	1								
Cr	412	.817	1							
Cu	.415	-,161	.214	1						
Mn	.113	042	• 369	•528	l					
Ni	438	.645	.868	.184	• 364	1				
Ti	.774	644	487	. 244	079	374	1			
V	.592	552	478	.210	096	435	.869	1		
Zr	.239	113	043	.256	. 396	058	.205	.249	1	

Correlation is significant at the 95 percent level if the absolute value of the coefficient is greater than 0.532.
correlation between element pairs is very similar for the two different rock groups. Analytical data for the four pairs of elements having the highest correlation coefficients are plotted graphically in figures 13, 14, 15 and 16. It is notable that these two mineralogically different groups have very similar correlation trends.

Sub-grouping of rock types was not possible in the statistical treatment because of the small number of analyses. However, in figure 16 it can be seen that inclusion of data for the highly sheared serpentinite in the Co-Ni correlation has decreased the correlation coefficient to a value below the significance level. The correlation diagrams grouping also indicate that the Quetico 'D' group has characteristics somewhat different from the other Quetico rocks.

Interpretation of the statistical treatment is limited because it has not been possible to weight the data according to the abundances of the different rock types analyzed. This is evident for example, in the estimation of the contribution of Ti to the discriminant function. Allowance for the proportion of gabbroic rocks from the Shebandowan area was not possible, and since the data indicates that Ti is strongly concentrated in the least mafic rocks of each group, the Ti contribution to the calculation of the discriminant function may have been underestimated. V is similarly concentrated in the least mafic rocks, whereas Ni and Cr are concentrated in the most mafic assemblages. In stressing the number of ultramafic rock analyses at the expense of the gabbroic rocks, the apparent difference between the two mafic-rich groups has probably been overestimated.



Figure 14. V-Ti correlation of analyzed specimens



Figure 16. Co-Ni correlation of analyzed specimens

Examination of figure 15 indicates that the possible consideration of a non-linear correlation function is justified for some elements.

It seems apparent that, although the abundance levels of the various elements are not strictly comparable due to the varied rock types in the two areas, general levels and correlation of elements are similar for the two groups. The latter is especially evident if, in some cases, the most highly altered rocks are disregarded (especially Quetico group 'D', and Shebandowan sheared serpentinites).

Average concentration levels of the major rock types are tabulated in table 22. Data from the three bodies enclosed and altered by granite are omitted from the averages. When spectrographic data is not available (CaO and  $Al_2O_3$ ), data from wet chemical analyses is presented. Note that a relatively smooth variation from one rock type to another is indicated except for the fine grained gabbro where only one analysis is available.

Element or oxide	1.	2.	3.	4.	5.	6.
Al_0, percent	3.1	2.6	6.5	14	-	**
CaO	2	10	14	10	-	-
Co ppm	160	130	81	62	34	37
Cr	4100	3000	2600	2050	2500	*
Mn	1100	1300	1350	1250	1200	1400
Ni	1750	620	540	370	235	tr
Ti	1250	1400	2900	6500	2550	7700
V	88	140	190	350	175	480
Zr	27	46	35	62	29	65

Table	22.	AVERAGE	CONCENTRATION	LEVELS	OF	MINOR	ELEMENTS	IN	MAJOR
		ROCK TY	PES.						

1. Ultramafic rocks, Shebandowan area. (12 specimens)

2. Peridotitic rocks, Quetico area. (5)

3. Hornblendite, Quetico area. (5)

4. Feldspathic hornblendite, Quetico area. (4)

5. Fine-grained gabbro, Shebandowan area. (1) 6. Coarse-grained gabbro, Shebandowan area. (1)

# Table 23. MINERALOGIC COMPOSITION OF ANALYZED ULTRAMAFIC ROCKS, ABITIBI AREA.

		(volume	percent)		
	1949-2	1949-15	1949-94	1949-10	1949-39
Serpentine	45	64	60		-
Bastite	16	17	16	16	22
Orthopyroxene	7	-	-	-	-
Talc	22	3	· 1	-	3
Clinopyroxene	tr	4	14	79	74
Magnetite	9	12	4	l	l
Amphibole	tr	tr	1	3	tr
Muscovite	-	-	-	l	-
Chlorite	-	-	1	Bite	-
Total	99+	100+	100	100	100+

# Petrological comparison

The mafic-rich rocks of the Lac des Mille Lacs area are considered to be of magnatic origin, modified to a greater or lesser extent, by alteration. It might be argued that the hornblendebearing rocks of the Quetico group are the result of metamorphism of olivine-pyroxene assemblages rather than products of primary magnatic crystallization but in thin section, the rocks have textural features typical of igneous rocks. In some peridotitic rocks, hornblende is zoned and rims the clinopyroxene, or separates it from olivine (plate 4, figure 2).

Presumably, the magna crystallized olivine and clinopyroxene as the early major minerals, and then hornblende appeared in the later magmatic stage as discrete grains and as a reaction product after clinopyroxene. The lighter coloured, presumably more magnesian border of some hornblende against olivine probably represents a local approach to equilibrium with this earlier mineral. In hornblendite and feldspathic hornblendite, hornblende is apparently an early primary Some hornblendite consists of large hornblende phenocrysts in phase. a fine grained matrix of hornblende and plagioclase, and some contains large hornblende grains poikilitically enclosing subhedral olivine and pyroxene (plate 6, figure 1). In the feldspathic rocks, partially sericitized plagioclase or quartz-feldspar micrographic intergrowths are interstitial to large zoned hornblende grains (plate 5, figures 1 and 2). Interstitial micrographic intergrowths are common to many

mafic igneous rocks but are rare in metamorphic rocks. The different rock types indicate a sequence of mineral assemblages formed by fractionation of a magma at different stages of crystallization. The order of appearance of the minerals in the crystallization sequence was apparently; olivine, clinopyroxene, hornblende, plagioclase and quartz. Sphene is a common accessory in the feldspathic hornblendite and may be a late magmatic mineral that followed plagioclase in the crystallization sequence.

The presence of a fine grained border facies in body 'B' and the existence of nearby dikes of similar mineralogy indicate that this body may have been intruded as a liquid. Body 'A' was apparently forcibly intruded into the enclosing paragneiss. It may have been partly consolidated but apparently was hot enough to convert the paragneiss locally to a sillimanite-bearing gneiss. The development of minor granitoid gneiss immediately adjacent to the intrusion may indicate that partial melting of the paragneiss occurred. There is no positive evidence that the rocks of body 'A' crystallized from a magma free from suspended olivine, but the anhedral shape of the olivine crystals, their lack of apparent zoning and the absence of a porphyritic texture in the peridotite are suggestive of this.

The crystallization of the Shebandowan ultramafic rocks in situ from a magma of equivalent chemistry is, however, not feasible. From their experimental investigations, Bowen and Tuttle (1949) indicate that the temperature required for the existence of such a magma is extremely high. The enclosing volcanic rocks in the

Shebandowan area do not show evidence of even moderate contact metamorphism, but their deformation suggests forcible intrusion of the bodies accompanied by major shearing. The texture of the ultramafic rocks indicates that unlike the Quetico peridotitic rocks, they may represent accumulated olivine and possibly, pyroxene crystals. These masses of accumulated mafic crystals could have been emplaced along faults and shear zones as relatively cool masses of crystal mush, possibly lubricated by small amounts of basaltic liquid. Such a lubricant could have been pressed out on emplacement, giving rise to the associated gabbroic rocks.

In most occurrences, the fine grained gabbroic rocks of the Shebandowan area occur to the north or northwest of ultramafic bodies. The author has noted that this gabbro is strikingly similar to gabbroic rocks from the upper portion of ultramafic sills in the Abitibi area of Northeastern Ontario. The origin of the latter has been ascribed to crystallization differentiation in the sill (Satterly, 1951) although Taylor (1955) argues for coincidental intrusion of later gabbro along zones of weakness in the sills. The similarity of the gabbro in the two areas and the fact that, in both, it apparently consistently occupies a specific position with regard to the ultramafic rocks would seem to preclude a coincidental relation to the latter. The common association of gabbro with ultramafic rocks of the Alpine type is emphasized by Thayer (1960). The low Fe/Mg ratio of the fine grained gabbro in the Shebandowan area (table 20) compared to other gabbroic rocks may be indicative of a genetic relation with the ultramafic rocks.

The relation of the coarse grained gabbro and the anorthosite in the Shebandowan area to the fine grained gabbro and the ultramafic rocks is less clear. Coarse and fine grained gabbro occur together in body 'A', but their contact was not observed. The few discrete small bodies of coarse grained gabbro that have been mapped are close to the ultramafic bodies and the two may well be genetically related. The anorthosite, however, is relatively removed, and its chemistry and mineralogy have not been studied.

### Comparison with experimental data

The mineral assemblages occurring in the Quetico group of mafic-rich intrusions and their apparent history of crystallization are strikingly similar to the products observed by Yoder and Tilley (1956) in a tholeiitic basalt crystallized at different temperatures under 5000 bars water pressure. They report the following sequence of assemblages with decreasing temperature (c.f. figure 17):

livine + magnetite	
byroxene + olivine + magnetite ) byroxene + hornblende + magnetite ) hornblende + magnetite ) hornblende + sphene + magnetite ) hornblende + plagioclase + sphene + magnetite)	plus glass

All assemblages were associated with a glass phase above the temperature of beginning of melting,  $750^{\circ} - 800^{\circ}$ C. Melting was not complete below  $1125^{\circ}$ C. It is notable that in the basalt, plagioclase is not compatible with pyroxene and olivine at pH<sub>2</sub>O greater than 2000 bars (figure 17). It seems probable that the same incompatibility existed in the Quetico intrusions during their crystallization in as much as plagioclase occurs with hornblende but not with the olivine or pyroxene.

At atmospheric pressure, the melting range of tholeiitic basalt only extends from 1090° to 1235°C. The assemblages observed by Yoder and Tilley are:



Figure 17 · Projection of the natural tholeiite basalt — water system after Yoder and Tilley (1956).

olivine + iron ore ) plus pyroxene + olivine + iron ore ) glass plagioclase + pyroxene + olivine + iron ore)

These mineral assemblages correspond fairly well to the ultramafic and gabbroic rocks in the Shebandowan group prior to their alteration.

As with the Quetico group, this correspondence suggests that these rocks had a common source in a magma of basaltic character, but it also suggests that, unlike the Quetico group, the Shebandowan intrusions crystallized in an environment of relatively low water pressure. It should be noted that the conditions of formation of the natural and experimental assemblages are different in that:

1. The rocks are not basaltic, but more mafic-rich than the tholeiite of the experiment. In the Quetico group, the most felsic differentiate, feldspathic hornblendite, is near basalt in composition (table 8). In the Shebandowan group, the proportion of gabbroic to ultramafic rocks is not known, precluding an estimate of bulk composition of the initial intrusions. However, in view of the similarity in the products, this difference in chemistry has apparently affected only the proportion of the assemblages.

2. The rocks evidently formed at a lower  $pO_2$  than did the experimental assemblages. Oxygen pressure was not controlled in the experiment and all charges contained magnetite. Conditions of low  $pO_2$  for the rock genesis are indicated by the relatively high Fe/Mg ratio of the silicates. Magnetite in the rocks appears texturally

to be largely due to alteration and recalculation of the norms of rocks analyzed for major elements to give the femic silicates an Fe/Mg ratio equivalent to that determined optically for the olivine and pyroxene resulted in little or no normative magnetite. Low p0<sub>2</sub> should encourage precipitation of olivine from a magma equivalent to olivine basalt.

3. Probably it was the amount of water in the intrusions that was nearly constant during magnatic crystallization rather than  $pH_20$  as in the experiment. Thus in the Quetico group,  $pH_20$  (and  $pO_2$ ) may have been increasing as the magma solidified and the Fe/Mg ratio of the mafic minerals would not increase noticeably.

4. The rocks probably represent differentiates formed by a series of successive fractionations of one magma. The experimental assemblages for each stage, represent one fractionation of the same starting magma for different crystallization periods.

Although there are the above limitations to the comparison of the natural and experimental assemblages, they do not appear to have been of major importance in the present case. The main difference appears to be compositional, but even this may not be too significant in as much as the tholeiitic basalt used by Yoder and Tilley contains nine percent normative olivine. Thus it seems that the Quetico rocks could be derived from the crystallization under high  $pH_2^0$  of a magma near olivine tholeiite in composition, and the Shebandowan rocks may be interpreted as crystallizing under low  $pH_c^0$  from a magma of similar chemistry. This of course, carries

the sweeping assumption that the gabbroic and possibly, the anorthositic rocks in the Shebandowan area are genetically related to the ultramafic rocks, that their chemistry is complementary to that of the latter, and that the volume of these feldspathic differentiates is sufficient to give the implied bulk composition.

Finally, supplementing the experimental evidence for the genetic relation of these two groups are the following:

 The mafic-rich rocks were emplaced as two separate groups closely associated in space and, as closely as can be estimated, in time. They are emplaced in rocks of similar tectonic setting.

They have contrasting mineralogy but many chemical simi larities. This is most obvious in trace element trends and correlation.

3. The Fe/Mg ratio of the constituent mafic minerals is similar and relatively high in both groups.

4. Both groups have associated sulphide deposits of similar mineralogy and chemistry.

Thus, it is not unreasonable that the two groups of mafic-rich rocks have originated from a common magma type but have crystallized under different values of water-vapour pressure.

# Minor element variation

The chemical variation apparent in the rock analyses is indicated in figures 9, 11 and 12. The major part of the variation in the Quetico group is due to the appearance or disappearance of phases in the assemblages through the sequence hornblende peridotite, peridotitic hornblendite, hornblendite and feldspathic hornblendite. In as much as hornblende is common to all rocks of this sequence, its chemical variation is probably indicative of the chemical variation in The refractive index of hornblende increases in the rock the magma. sequence as listed above, and as the increase is due primarily to an increase in the Fe/Mg ratio, it is presumably an indirect index of degree of fractionation of the parent magma. Chemical variation in the hornblende as a function of the refractive index, n,', is plotted in figure 10. As shown, Al203, Ti and V vary directly, whereas Co, Ni and Mn vary inversely with the refractive index. Cu, Cr and Zr have irregular trends.

The variation of elements through the rock sequence (figure 9) is probably affected very little by the chemical variation within minerals, with the possible exception of aluminum. The decrease of Co, Cr, and Ni through the sequence largely reflects the preference of these elements for the early crystallizing olivine and clinopyroxene (and possibly, chromiferous magnetite). On the disappearance of these minerals, the hornblende contribution is diluted by increasing proportions of felsic minerals. The Al<sub>2</sub>O<sub>3</sub> variation is the inverse of this, Al<sub>2</sub>O<sub>3</sub>

occurring dominantly in the late plagioclase and not the early mafic minerals. The Ti variation is probably controlled, for the most part, by the crystallization of accessory sphene in the later differentiates. Variation in Ti content of the hornblende adds to this trend. The variation in V is parallel with that of Ti, and appears to be controlled by the increase of V in hornblende with fractionation.

In the analyses of the Shebandowan ultramafic rocks, variation with degree of alteration is noted for some elements (figure 11). The analyses of the least altered peridotitic rocks are plotted to the left, followed by serpentinite and sheared serpentinite analyses. Al<sub>2</sub>O<sub>3</sub> and, possibly, Ti seem to vary inversely with degree of alteration: Ni and Cr vary directly with alteration. The other elements show either little variation (Mn, V), or irregular trends (Cu, Zr, Co). It is difficult to determine whether or not the variation is an effect of the alteration or whether it reflects primary characteristics of the rocks that control alteration. The fact that the partially serpentinized peridotite of body 'B', and the highly sheared and altered rock (W60509) from the same body are very similar chemically, argues against large scale migration of minor elements on serpentinization. Possibly, the most highly altered rocks were originally dunite, or peridotite low in aluminous pyroxene. These are rocks which would be most easily serpentinized and sheared, and the relatively high proportion of olivine (and possibly accessory chromiferous magnetite) would be sites for the large concentrations of Ni and Cr.

The possibility that some of the Ni variation is due to traces of nickeliferous sulphide minerals cannot be disregarded. This is especially true where high Cu content of the rock is indicated (figure 11). However, sulphides are present in only minor amounts, and the nickel (and copper) content of these sulphides is not great (table 23).

# COMPARISON WITH OTHER ULTRAMAFIC INTRUSIVE ROCKS

The two groups of mafic-rich intrusions in the Lac des Mille Lacs are are relatively distinct mineralogically despite being in fairly close proximity and having the same relative age. Both groups are emplaced in steeply dipping metavolcanic rocks and metasedimentary rocks derived from greywacke, and both are **post**dated by granitic intrusions. These relations are typical of the orogenic association of Alpine type ultramafic rocks (Turner and Verhoogen, 1960, p. 310).

The characteristic features of Alpine type ultramafic intrusions have been summarized by Hess (1955) and Thayer (1960). They indicate that these features are common to ultramafic rocks in orogenic zones in most parts of the earth. However, Noble and Taylor (1960) and Irvine (1961) have pointed out that the ultramafic bodies in the mountain belt of Southeastern Alaska are distinctly different from the common Alpine type despite having similar size, shape and tectonic environment. According to Irvine (1960), both types may be comprised of dunite, peridotite and pyroxenite, these rocks being typically free of plagioclase, and both may have associated gabbro although the latter shous no consistent structural relation to the ultramafic rocks. The major difference between the S. E. Alaskan and common Alpine types is that the former is extremely rich in CaO. This is evident in the abundant presence of diopside or diopsidic augite as the sole pyroxene and in the fact that hornblendite is the most common rock type. In the common

Alpine type, both orthopyroxene and CaO-rich clinopyroxene may occur, but orthopyroxene is generally predominant; hornblendite is not commonly present. Further, the S. E. Alaskan ultramafic rocks are also characterized by crude concentric zoning of rock types, whereas the distribution of rock types in common Alpine type intrusions is not regular. Shearing and intense alteration to serpentine, magnetite and talc are features of the common Alpine type; serpentinization of the Alaskan type rocks is relatively slight.

The similarity of the two groups of mafic-rich rocks in the Lac des Mille Lacs area to the two major orogenic types is in some respects, remarkable. Many features of the rocks of the S. E. Alaskan type occur in the Quetico group: the rock types of the largest intrusion exhibit crude concentric zoning; hornblendite is the most common rock type: the pyroxene is generally diopside or diopsidic augite: serpentinization and shearing are not extreme. The main difference is that the Quetico intrusions definitely include a larger proportion of feldspathic differentiates. For comparison, several specimens from the Duke Island ultramafic complex in Southeastern Alaska have been analyzed spectrographically in the present study. The rock types are dunite, olivine pyroxenite, hornblende pyroxenite and hornblende gabbro; they have been described in detail by Irvine (1959). The Shebandowan intrusions are like the common Alpine type in that they are largely serpentinized peridotite and dunite. The ultramafic and mafic rocks in the Abitibi area of Northeastern Ontario were chosen as representative of the common Alpine type: they have been mapped and described

by Satterly (1951) and Taylor (1955). Several typical specimens from Satterly's collections were also analyzed spectrographically for comparison here. They include serpentinized dunite and peridotite, pyroxenite and metagabbro. Modal mineralogy of these rocks is presented in table 23.

A strict comparison of the Quetico and Alaskan rocks is difficult because of certain mineralogical differences. However, the Alaskan rocks are silica-poor and alumina-rich compared to their nearest analogues in the Quetico rocks. This is indicated by the fact that orthopyroxene occurs locally in some Quetico rocks, and by a comparison of analyses of constituent hornblendes (table 11). The mafic silicates in both groups have comparable, relatively high Fe/Mg ratios, but the Quetico group does not have the large proportion of primary magnetite that is present in several of the Alaskan bodies. There is little difference in the minor element content of the two groups, except that Cr and Zr are relatively low in the Alaskan rocks. Ni is also low, but it is strongly concentrated in the dunite (tables 14 and 16).

Similarity of the Shebandowan and Abitibi rocks is quite striking. The major rock units are very similar in mineralogy and in minor element abundance levels (tables 15 and 16). This is true not only for the ultramafic rocks, but also the fine grained gabbroic rocks. The main difference is that pyroxenite is present in the Abitibi intrusions but not at Shebandowan. Other differences are that, in the Abitibi rocks, Ti, Zr and Fe are lower. The low Fe content is indicated by a low magnetite abundance (table 23), by the presence of olivine of composition

Fo<sub>96</sub> (Taylor, 1955), and by comparison of the Fe/Mg ratio determined spectrographically (table 20). The similarity of the Abitibi rocks to the common Alpine type has been indicated by Taylor (1955), and the inclusion of the Shebandowan rocks in this type seems justified.

Noble and Taylor (1960) believe that the ultramafic rocks of S. E. Alaska have originated by crystallization from ultramafic magmas and propose that these magmas are generated along linear belts by fusion of an ultramafic substratum. By analogy with their experimental work on the melting of basalt under high pH20 and low pO2, Burnham and Hamilton (1962, personal communication) estimate that the Alaskan rocks could be completely melted at temperatures less than 1300°C and, perhaps as low as 1000°C at a pH20 of about 10 kilobars and a  $p0_2$  of  $10^{-10}$  to  $10^{-15}$  bars. Thus the magma generating the Quetico rocks, having a more basaltic affinity, may well have been completely liquid at temperatures considered to be in the common magmatic range. A similar magma, at the same temperature, but at a lower pH\_0 would probably consist of olivine crystals plus liquid. This may be the condition in which the Shebandowan rocks and many Alpine type ultramafic bodies were intruded. The crystallization of rocks of the Lac des Mille Lacs area under low p0, would have the effect of making such a magma with basaltic affinity behave more like an ultramafic magma during crystallization in that it would hold Fe in the ferrous state and thus decrease the ratio of SiO, to cations available to the silicates.

From this study, it can be appreciated that the effects of  $H_2^0$ and  $O_2$  have an important bearing on determining the character of ultramafic rocks.

# APPENDIX

#### Sample Locations and Descriptions

### Quetico Area

- 160-50, -54, -76, -87, -91, -94 Partially serpentinized hornblende peridotitic rocks from the western mafic intrusion near Chief Peter Lake (body 'A'). -54, sulphide bearing. Latter four from drill core.
- 160-83, -85 Hornblendite and feldspathic hornblendite, from drill core, western body, Chief Peter Lake.
- 160-105, -115 Felspathic hornblendite and hornblendite, from drill core, eastern body, Chief Peter Lake (body 'B').
- 160-114 Feldspathic hornblendite, ('chill zone'), from drill core, eastern body, Chief Peter Lake.
- 160-157, -160, -161, -163 Hornblendite, 160 and 163 biotitic, 157 and 161, olivine and pyroxene bearing; from drill core near Baril Lake (body 'C').
- W60-105 Highly altered talcose pyroxene-hornblendite, emplaced in metavolcanic rocks, NW of Baril Bay, Lac des Mille Lacs (group 'D').
- W60-125, -139 Highly altered talcose feldspathic hornblende peridotite, (group 'D') -125 included in quartz diorite, north shore, Lac des Mille Lacs, -139 from island in lake.
- W60-130 Hornblendite, in quartz diorite, from island in Lac des Mille Lacs (group 'D').

### Shebandowan Area

W60511, 12, 14 Partially serpentinized peridotite, 'B' body.

- W60509 Highly sheared chlorite-serpentine rock from drill core, 'B' body.
- W60515, 22 Sheared serpentinite, 'C' body.

W60528, 30	Talcose serpentinite with remnant primary texture, 'E' body.
W60533	Serpentinite, remnant primary texture, 'F' body.
W60536	Talcose serpentinite, remnant primary texture, 'G' body.
W60540	Talcose serpentinite, little primary texture, 'H' body.
W60543	Talcose serpentinite from drill core, 'H' body.
W60529	Fine-grained metagabbroic rock, 'E' body.
W60553	Coarse-grained metagabbro. 'J' body.

# Abitibi Area, Ontario

From a collection made by H. S. Armstrong and J. Satterly while mapping for the Ontario Department of Mines.

1949-94 Dunite-peridotite, Harker Township, Claim No. 40537.

-02 Peridotite, Harker Twp, Claim No. 40537.

-15 Serpentinized dunite-peridotite, Harker Twp., North of Claim No. 10533.

-10 Clinopyroxenite, Harker Twp., Claim No. 10691.

-39 Clinopyroxenite, Harker Twp., Claim No. 9862.

-05 Enstatite metagabbro, Harker Twp., North of Claim No. 11079.

1948-48 Metagabbro, Harker Twp., west half, 800' S. of 4400 W of 3 mile post, North body.

### Duke Island, S. E. Alaska

Collected by T. N. Irvine

H-4-4 Dunite, Judd Harbor Ultramafic outcrop.

R-38-2 Olivine pyroxenite, Hall Cove Ultramafic outcrop.

I-37-2 Olivine pyroxenite, Hall Cove Ultramafic outcrop.

I-31-3 Hornblende pyroxenite, Judd Harbor.

N-25-1 Hornblende gabbro from the north side of the Hall Cove outcrop.

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Figure 1. Serpentinite, Shebandowan area. White serpentine is pseudomorphous after rounded olivine grains, white-grey bastite after pyroxene; opaque is magnetite and, possibly, chromite. Plane light.



Figure 2. Serpentinite, Shebandowan area. As in Figure 1, crossed nicols.

PLATE 2



Figure 1. Mesh texture in serpentinite from Shebandowan area. Primary texture apparently has been obliterated by intense serpentinization. Crossed nicols.



Figure 2. Peridotite, Shebandowan area. Orthopyroxene enclosing subrounded olivine is marginally altered to fine-grained talc and bastite. Plane light.

PLATE 3



Figure 1. Peridotite, Shebandowan area. Subhedral olivine partially serpentinized, orthopyroxene entirely altered to talc and bastite. Plane light.



Figure 2. Hornblendite inclusions in quartz diorite along the north arm of Bedivere Lake.

PLATE 4



Figure 1. Peridotite, 'A' body, Quetico area. Equigranular serpentinized olivine, clinopyroxene and hornblende. Plane light.



Figure 2. Peridotite, 'A' body, Quetico area. Green hornblende with colourless margins where in contact with olivine. Plane light.



Figure 1. Feldspathic hornblendite from body 'B', Quetico area. The rock is comprised of dark to light green 'zoned' hornblende, interstitial partially sericitized plagioclase and spatite. Plane light.



Figure 2. Feldspathic hornblendite from body 'B', Quetico area. A syrmekitic intergrowth of quartz and plagioclase is interstitial to large hornblende grains. Crossed nicols.

