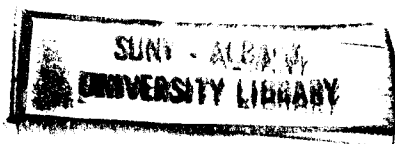


Petrology of the Nemeiben Lake  
Ultramafic and  
Associated Nickel-Sulphide Deposits



A thesis presented to the Faculty  
of the State University of New York  
at Albany  
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Anantaramam Peddada  
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## ABSTRACT

The Nemeiben Lake ultramafic body is located in the center of Saskatchewan, Canada, within the Churchill Province of the Canadian Shield. The ultramafic rocks consist of serpentinites, partly serpentized and unaltered pyroxenite, and unaltered pyroxenite. Associated sulphide mineralization is of disseminated, net texture, and fracture filling types. The ore minerals present are pyrrhotite, pentlandite, chalcopyrite, pyrite, marcasite, violarite, bravoite and native copper. The sulphides are considered to be initially of magmatic origin formed from a sulphide melt separated at a late stage during crystallization of the ultramafic rocks. Subsequent serpentization has locally redistributed the ores.

Serpentinization in the Nemeiben Lake ultramafic rocks was accompanied by introduction of water with no apparent changes of  $\text{SiO}_2$  and  $\text{MgO}$  contents. A minor removal of  $\text{CaO}$  and possible addition of sulfur during serpentization is the only apparent chemical change.

From investigation of co-existing clinopyroxenes, orthopyroxene and olivine and the distribution of Mg and Fe between pyroxenes, it appears that the Nemeiben Lake ultramafic body crystallized at high temperature between  $1100^\circ - 1200^\circ \text{C}$  and in a pressure range between 5-9 Kb.

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## I. INTRODUCTION

### I.1. Location and Accessibility

The ultramafic complex is located in the center of the province of Saskatchewan at north latitudes  $55^{\circ} 15'$ ,  $55^{\circ} 30'$  and west longitudes  $105^{\circ} 00'$ ,  $105^{\circ} 15'$ , 150 miles north of the city of Prince Albert, and 16 miles north of the town of LaRonge within the Churchill Province of the Canadian Shield (Fig. 1). It outcrops on the east shore of Nemeiben Lake, is approximately one mile in diameter and named after the lake, and is subsequently referred to here as the "Nemeiben Lake ultramafic body". The largest and best outcrops occur in the northern portion of the outcrop area.

The most convenient way of reaching the area is by float equipped aircraft from LaRonge. Access to the area is made north of LaRonge by way of Highway No. 2 and by bush road.

### I.2. Physiography and Glacial Geology

The topography along the southern border of Lac LaRonge region is similar to that of other areas of the Canadian Shield. The region is relatively flat, consisting of low irregular hills and ridges separated by areas of muskeg, swamp or thin glacial deposits. Maximum local relief is approximately 200 feet. Lakes form a considerable proportion of the surface of the drift covered area.

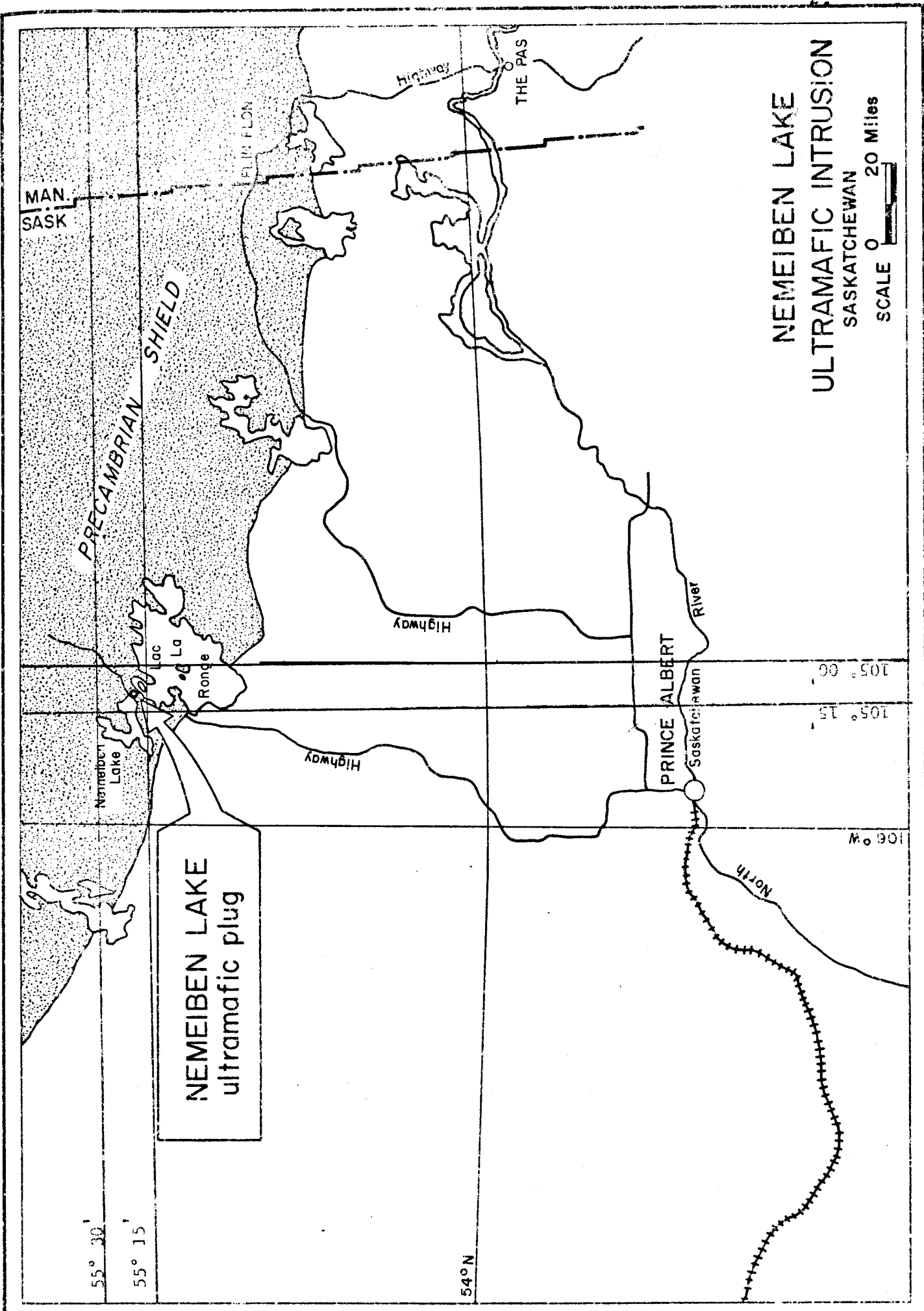


Figure 1. LOCATION MAP

The ultramafic body rises to a maximum elevation 100 feet above the Nemeiben Lake. The outcrops are usually obscured by grass, lichen and weathered debris where little relief occurs, but are fairly clean where relief is present. The body is entirely surrounded by low-lying, often muskeg-covered ground. Nowhere on the surface can ultramafic/wall rock contacts be observed.

### I.3. General Geological Setting

Regional geologic data concerning the Lac LaRonge area (which includes the Nemeiben Lake ultramafic body) have been derived from Padgham (1966, 1969), Pearson (1957), Forsythe (1968, 1971), and Beck (1959). Pearson (1957) and Forsythe (1971) discuss the history and geology of the Nemeiben Lake deposit.

#### I.3.1. Regional Geology

The rocks of the Lac LaRonge area are within the Churchill province of the Precambrian Shield. Granitic rocks underlie most of the area but bands of metasedimentary rocks and local mafelsic, mafic and ultramafic intrusive rocks occur. Migmatites occur locally and inclusions of country rock are common in granites near contacts with sedimentary rocks. The structural trend of the Precambrian rocks is generally northeast in the southern part, whereas in the northern part, the rocks trend sinuously northward.

A complex interference pattern is seen on aerial photographs, with fold axes varying in trend from easterly to westerly (Forsythe, 1971). Forsythe also describes culmination domes and basins which could indicate interference of various fold trends. As well transverse lineaments which trend north-south, north-east, east-northeast, east and east-southeast are described. Forsythe considers that all rock types and fold patterns are transected by these lineaments indicating that the lineaments are late faults and fractures that may mask older faults that have been folded.

Regional dynamothermal metamorphism from upper greenschist to lower amphibolite facies have been recognized in the Lac LaRonge region.

Stratigraphic sequences are imperfectly known at present because sedimentary and volcanic depositional features that might be used to infer the supracrustal rocks have been almost universally destroyed. Potassium-argon ages of igneous rocks and uranium-thorium ages for uraninite from Potassic pegmatites range from 1.5 to 1.75 billion years (Lowdon, 1961). This date corresponds to the Hudsonian orogeny which appears to have involved all the rocks of the region in a period of intense metamorphism. In nearby areas to the west (Money, 1965) and to the east (Davis, 1964) radiometric ages of superior age ( $\pm$  2 billion years) have been recorded in rocks which may have been part of a



basement on which the probably younger rocks of Lac LaRonge region were deposited. No evidence is presently available to suggest rocks which have Superior ages are present in the Lac LaRonge region but radiometric investigations in the region have been confined to rocks strongly affected by the Hudsonian orogeny.

### I.3.2. Local Geology

The Nemeiben Lake ultramafic body is surrounded by granitic rocks. Since this study is concerned with the ultramafic rocks of the area, only a brief description of granitic rocks and of gabbroic dikes which cut the ultramafic body will be given here. The Nemeiben Lake ultramafic rocks are described in detail such as gross distribution of rocks, petrological, mineralogical, and chemical investigations in the succeeding chapters.

#### I.3.2.a. Granitic Rocks

As seen from the geologic map (Fig. 2, in the pocket) the outcrop of granitic rocks in the area is relatively scarce. However, to the east of Miller Lake there are large exposures of the granitic rock unit which consists largely of granodiorite and pegmatite.

The granodiorite gneiss is a medium to coarse grained light pinkish grey rock, possessing a poor to well developed gneissosity, depending on the degree of concentration of the

biotite into lenses and layers. The foliation in the foliated granodiorite is produced by the subparallel orientation of the biotite flakes. The foliated granodiorite weathers light pinkish grey to almost white. Pegmatite is relatively abundant in the granodiorite. Pearson (1957) states that no part of the ultramafic body contains any granitic intrusion of any kind, the ultramafic intrusive is therefore considered to be younger than the surrounding country rocks.

Thin sections from the gneissic and foliated granodiorite indicate the following range in mineralogical composition: 55-58 percent plagioclase, 30-36 percent quartz, 3-8 percent microcline, and 3-10 percent biotite. Accessory and secondary minerals include muscovite and sericite.

#### I.3.2.b. Gabbroic Dikes

Gabbroic dikes occur locally in the ultramafic rocks and drilling indicates numerous narrow bodies at depth. The northeasterly trending dike (Fig. 2) is the largest gabbroic dike in the outcrop area being three to four feet wide. It is a medium to coarse grained, massive, mottled-grey and black rock that is in sharp contact with the serpentinite. It appears to have suffered similar deformation as the ultramafic body and locally is sheared and fractured.

The gabbro consists chiefly of hornblende and plagioclase with minor quartz in parts. In portions of the dyke

there are coarse grained segregations composed almost entirely of hornblende.

#### I.4. Aeromagnetic Map

During the spring of 1953 an airborne magnetometer and scintillation counter survey was carried out in the Lac LaRonge area by Canadian Aero Services Limited for the Department of Mineral Resources. The results of the aeromagnetic survey are reported in Figure 3. Interpretation of this map is based on the magnetic susceptibility of the various rock types. Ultramafic body has a high magnetic susceptibility due to concentration of magnetite and nickeliferous pyrrhotite although no specific magnetic intensity is diagnostic of the ultramafic body comparison with the known outcrop area gives an approximate standard. The 2000 to 2800 gamma counter interval on the map appears to outline the ultramafic body of Nemeiben Lake.

The granitic rock types in the area have uniformly low magnetic response resulting in widely spaced countour lines.

#### I.5. Mineralisation

The Nemeiben Lake ultramafic body is host to nickel-copper mineralisation, occuring as disseminations and some fracture fillings, principally concentrated within the pyroxenite layers of the ultramafic body. The nickel-

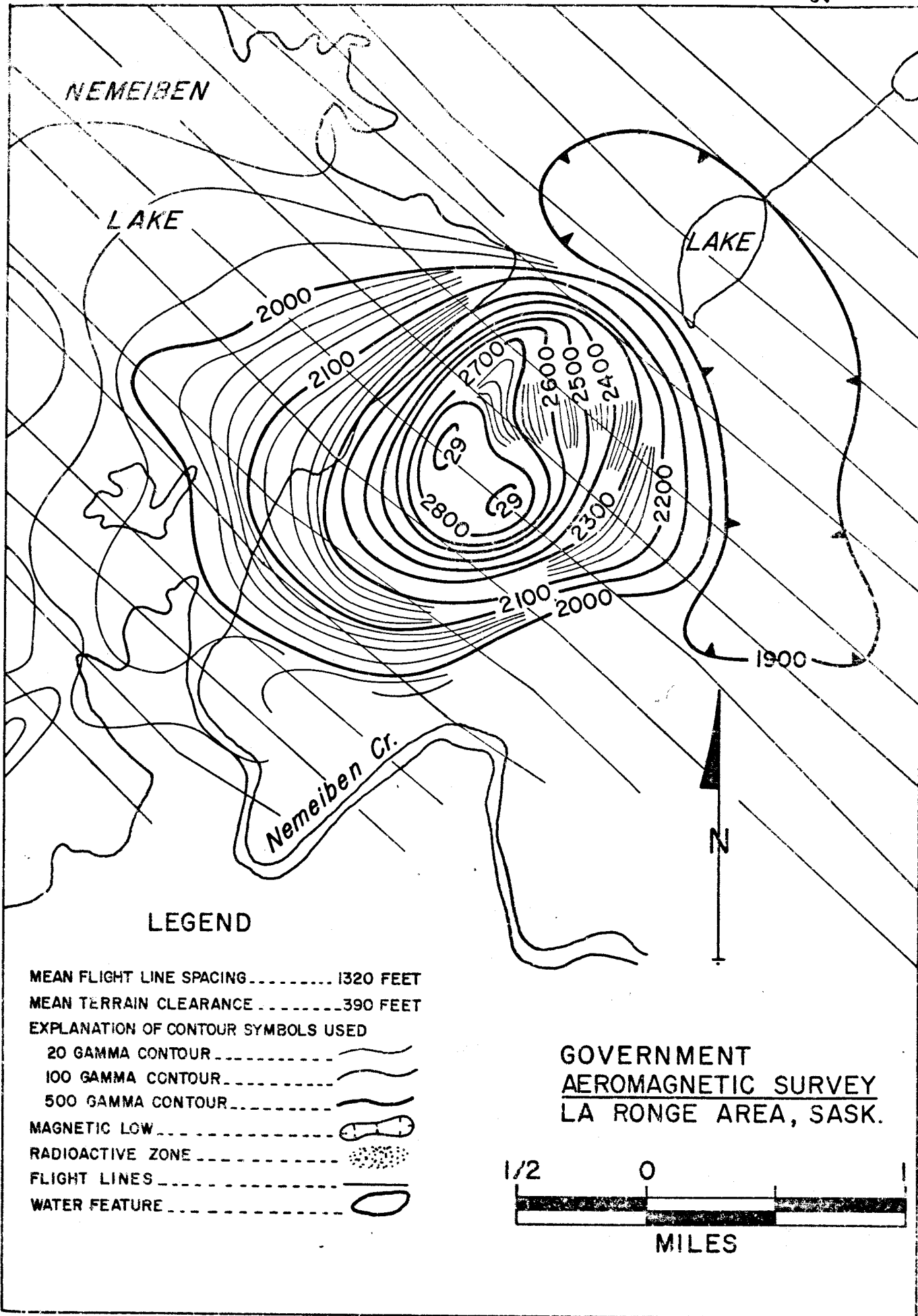


Figure 3. Aeromagnetic map.

copper sulphides which are associated with the ultramafic body are nickeliferous pyrrhotite, pentlandite and chalcopyrite. This ore mineralisation forms diffuse bands or layers in the ultramafic body. Some of the drill core shows the ore minerals occurring as blebs and irregular clusters intimately intermixed with the silicates of the host pyroxenite (Plate 1, Fig. 1) in the fashion of what is accepted to be magmatic sulphide segregation textures (Described later in more detail). In this type of ore there is no evidence in the drill cores of any relationship of the sulphide to fractures or shears. Other occurrences of sulphides as exposed in the cores are irregular concentrations along and beside fractures and incipient fractures. These fracture concentrations only occur within serpentinite and adjacent to it in the cores.

#### I.6. Statement of the Problem:

A pronounced correlation exists between many ores and their host rocks (Buddington, 1933). An excellent example of this is the nickel, copper, cobalt sulfide ores are almost exclusively found in ultramafic and related rocks considered to belong to the peridotite class. Ultramafic rocks are of considerable importance in petrological studies because it is commonly supposed that an ultramafic rock clan of some type is the dominant material of the earth's upper mantle. A popular idea at present time is that the

mantle, is a direct source for the sulfur and metals that are requisite for ore deposits associated with these ultramafic rocks.

The primary objective of this investigation was a detailed study of the Nemeiben Lake ultramafic intrusion and its associated mineralization. Among the more important problems considered were:

- (1) An attempt to provide satisfactory geological and petrological interpretation of the Nemeiben Lake ultramafic body with particular reference to the origin of the nickel-copper sulfide deposits.
- (2) Effects of serpentinization on the chemistry of the rocks.
- (3) Petrogenesis of the ultramafic body; pressure and temperature estimates.

#### I.7. Methods of Investigation

- (1) The field work consisted of mapping the area on the scale of 200 feet to the inch, examination of most of the outcrop area, collection of specimens and the examination of drill core.
- (2) The laboratory work consisted partly of examination of thin sections, study of polished ore sections and polished thin sections to establish the paragenesis of sulphides and to gain insight into the textural relations.

(3) Partial chemical analyses of rock samples for major constituents were determined using conventional x-ray fluorescence method. Base metal analyses were determined primarily by atomic absorption.

(4) Partial chemical analyses and trace element distribution in co-existing silicate phases were determined using electron microprobe supplemented by emission spectroscopy.

## II. NEMEIBEN LAKE ULTRAMAFIC ROCKS

### II.1. Terminology

As used here, ultramafic means a rock which is presumed to be either of magmatic origin or at least to have crystallized at high temperature, and which contains 70% or more mafic minerals, with no accompanying free quartz. This definition seems to be acceptable to most geologists for two reasons, first it can be used as a field term, and second, because it allows inclusion of such rocks as pyroxenites which may not be classed ultramafic in other schemes, such as the one based on a maximum silica content in the rock of 45%.

A serpentinite is defined as a rock which contains 50 percent or more serpentine, usually as a replacement of pre-existing olivine and pyroxenes.

### II.2. Classification of Ultramafic Rocks

Many geologists have dealt with the problem of classification of ultramafic rocks (Hess, 1938, 1955; Smith, 1958, 1962; Thayer, 1960, 1970; Watkinson and Irvine, 1964; Wyllie, 1967), and until recently Precambrian ultramafic rocks have been considered as one group. Hess (1955) states that Precambrian ultramafic rocks occur as small remnants over huge areas and they do not appear to be distributed in belts, although belts of intrusive ultramafic



rocks are now recognized in association with early Precambrian greenstone belts in Canada. The nature and evolution of the greenstone belts, however is imperfectly known, and this factor complicates the classification of certain Precambrian ultramafic rocks.

Thayer (1960) describes alpine-type ultramafic bodies, in part, as being distributed along eugeosynclinal belts which have been subjected to an alpine type deformation. The linear belts of some Precambrian ultramafic rocks (e.g. from Manitoba) appear to be similar in size and shape to typical alpine associations, but the postulate that Precambrian belts of ultramafic rocks and their associated metasedimentary and metavolcanic rocks represent eugeosynclinal belts which have undergone alpine-type deformation is, at this time, not established. For this reason use of the term 'alpine type' as applied in general to Precambrian ultramafic associations is not justified.

Linear belts of Precambrian ultramafic rocks associated with regional fault zones have been recognized by Kilburn, et.al., (1969) who proposed the term 'orogenic association' for these bodies and their associated nickel sulphide deposits. Scotese (1971) is of the opinion that the term 'orogenic' is inappropriate because it refers to, or implies, mountain building processes. "Tectonic" or "fault bounded" would perhaps appear to be more suitable terms for describing these bodies. However, as some

individual bodies or groups of ultramafic bodies are not obviously fault bounded, the term 'discrete' ultramafic body is considered suitable as a general descriptive term for both groups.

The Nemeiben Lake ultramafic body has a nearly - circular outline in plan; is not fault bounded and is a Precambrian ultramafic association, so it can be considered as a 'discrete' ultramafic body.

No gravity survey of the Nemeiben Lake ultramafic is available so that there is no further information concerning the depth and shape of the body below the present ground surface.

### II.3. Gross Distribution

The Nemeiben Lake ultramafic rocks show considerable variation in colour, texture and mineral content as observable in the field and in hand specimens. Some of the samples examined were specimens of fresh drill core (for sampling procedure see Appendix I). The various rock types include pyroxenite, partly serpentized and uralitized pyroxenite and serpentinite. Colour variations in the ultramafic rocks include brown green, pale green, grey green and black and can be used to some extent as criteria for field mapping inasmuch as they represent various rock types. The distribution of these rock types in the study area is shown on the geological map (Figure 2, in pocket).

Pyroxenite is the major rock unit (about 50%) of the ultramafic outcrop area. Generally the pyroxenite is massive and occurs mainly in the eastern and southeastern parts of the ultramafic body. It is a medium to coarse grained rock with a brownish green to pale green colour. Partly serpentinitized and uralitized pyroxenite is the next in abundance (about 45%) and is grey green coloured rock. Serpentinite is a fine grained, greenish black rock comprising approximately 5% of the ultramafic rock outcrops. The process of serpentinitization apparently was irregular and developed most intensively in highly fractured areas in the northern portion of the body.

The relation between each of these ultramafic rocks is not clear and is obscured by weathering and poor exposure.

#### II.4. Structure

Much of the rock in the ultramafic body is massive, but foliation is present in several localities, where it is faintly to moderately well developed. There is a general tendency for the strike of the foliation to parallel to the periphery of the ultramafic body. The north contact dips steeply inward (southward) suggesting that the ultramafic body may be more a laccolith than a plug. This is further suggested by the layering of serpentinitite and pyroxenite within the ultramafic body; this layering is exactly parallel to the contact of the body, as would be expected in a

gravity segregated intrusive body.

The general trend of gneissosity and foliation in the surrounding granitic rocks is in a northeasterly direction.

### III. PETROGRAPHY AND MINERALOGY

#### III.1. Petrographic Classification

Three ultramafic rock groups have been recognized and Table I lists the range of modal composition present within each group. Estimated modal compositions were determined visually from thin sections and are considered to have an accuracy for each major constituent of approximately  $\pm 5\%$ . The ultramafic rock groups are as follows:

##### III.1.1. Serpentinite

The serpentinite is a fine-grained greenish black coloured rock, which is finely fractured, with the fractures carrying fine stringers of pale green serpentine of one mm in thickness in outcrops and drill core samples. Native copper in hematite bearing serpentinites is seen in drill core as fibrous crystals in veins. Two generations of serpentine can be observed. The second generation serpentine cuts across the first generation and occurs mainly as fracture fillings (Plate I, Fig. 2). All vein types of serpentine contain magnetite (Plate II, Fig. 1).

Mesh texture is predominant in the serpentinites. All the original olivine and orthopyroxene has been converted into the serpentine group minerals (lizardite and chrysotile), magnetite ( $>10\%$ ) and talc. Chrome spinel occurring as sub-hedral to euhedral grains are present as accessory minerals,

TABLE I

Range of Estimated Modal Compositions in  
Ultramafic Rock Types of the Nemeiben Lake

	Serpentinite	Pyroxenite	Uralitized and partly serpentized pyroxenite
Olivine			2
Orthopyroxene		40-45	10-20
Clinopyroxene		35-40	10-15
Serpentine	90-98	Trace	10-20
Tremolite		<1	40-50
Talc	<1	Trace	<1
Carbonate	<1		Trace
Opaque Oxides	5-10	1	5
Chrome Spinel	<1		
Sulphides	5-10	10-20	10-15

## PLATE I

Figure 1. Drill core shows ore minerals occurring as blebs and irregular clusters intimately intermixed with the silicates of the host pyroxenite.

Figure 2. Two generations of serpentine. The second generation cuts across the first generation and occurs mainly as fracture fillings in the drill core.

Plate I

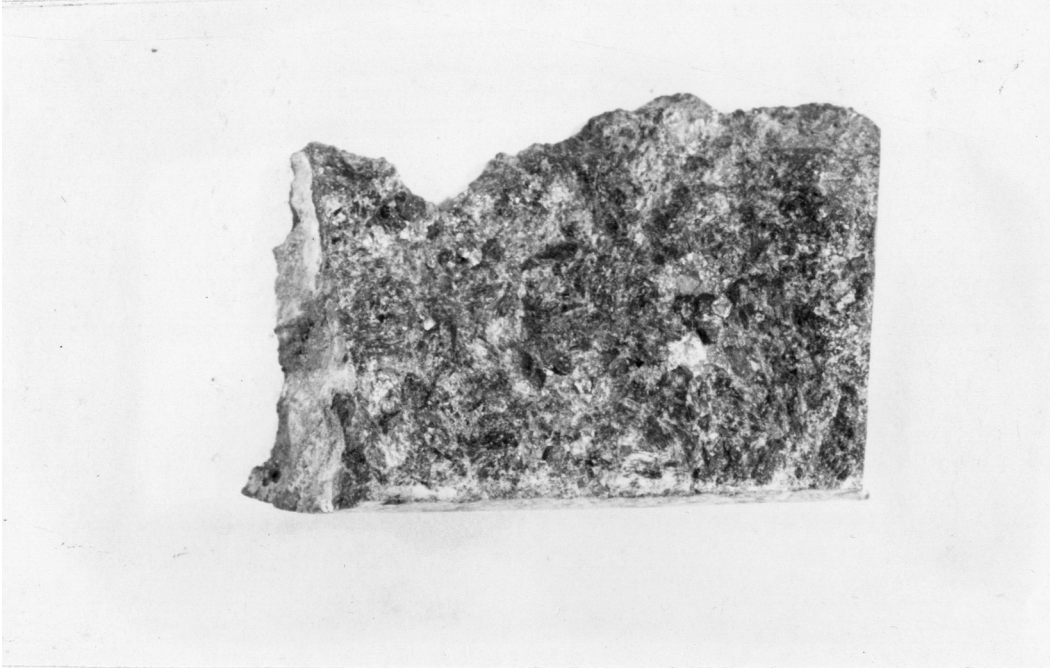


Figure 1

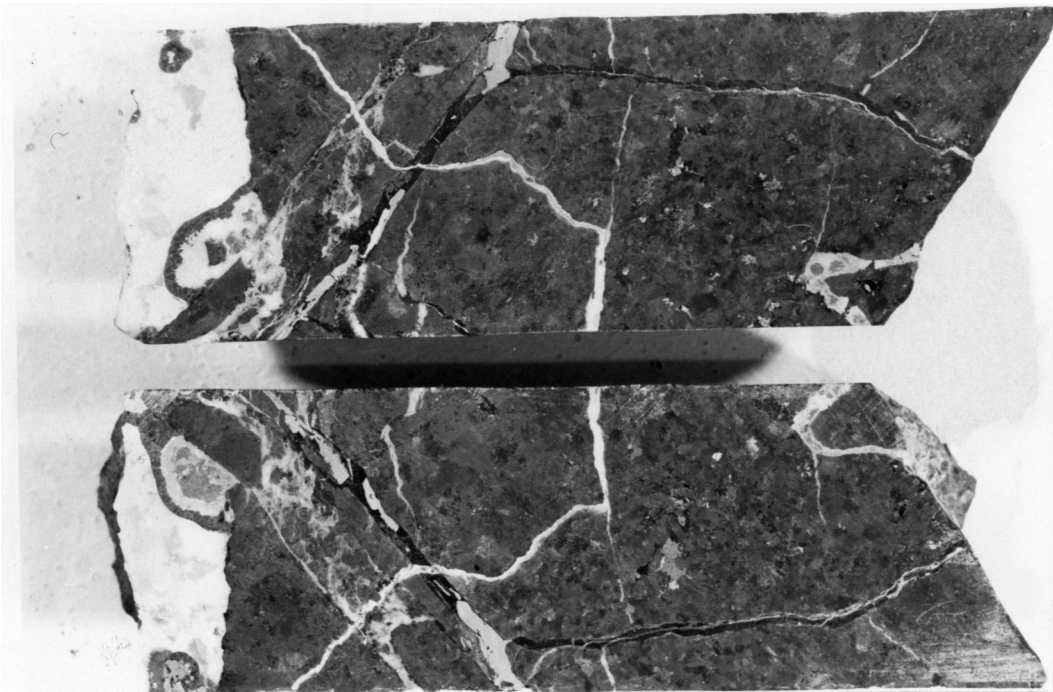


Figure 2



cut by late serpentine veins (Plate II, Fig. 2). Other minor accessory minerals of the serpentinite are talc, carbonates and sulphides. Brucite was not observed in the thin sections.

### III.1.2. Pyroxenite

Microscopically, the pyroxenite has a granular texture. The grain-size varies from 2mm to 5mm and less commonly reaching up to 7 to 8 mm. It consists of about equal proportions of medium to coarse-grained hypersthene and diopside clinopyroxene and locally olivine occurs as minor accessory. The olivine is commonly fresh or altered to serpentine minerals (lizardite and chrysotile). Magnetite, pyrrhotite, chalcopyrite, pentlandite and pyrite may be present as an accessory. As a rule in this pyroxenite the pyroxene is relatively unaltered showing only minor alteration to talc, serpentine.

### III.1.3. Uralitized and Serpentinized Pyroxenite

Uralitized and partly serpentinized pyroxenite is a grey green coloured rock, which is basically a more altered variety of the above rock type. The increased degree of alteration may partly reflect the original presence of somewhat larger amounts of olivine. Small olivine crystals, or their relicts which are now in some thin sections completely serpentinized, are found between the coarser

PLATE II

Figure 1. Second generation of serpentine cuts across the first generation and occurs mainly as fracture fillings. All vein types of serpentine contain magnetite.

Figure 2. Chrome spinel occurring as subhedral to euhedral grains in serpentinite.

Plate II



Figure 1

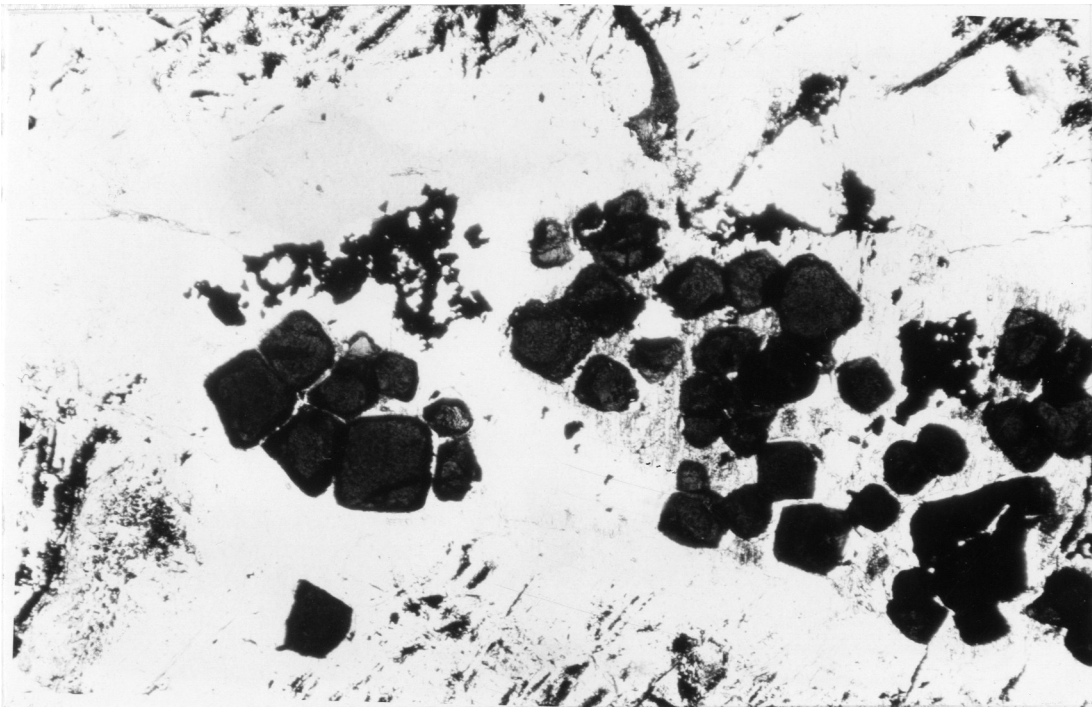


Figure 2

orthopyroxenes. In some sections the orthopyroxene is largely altered to tremolite. Serpentine also occurs as pseudomorphs after the orthopyroxene. The hypersthene is more uralitized than diopside. Accessory minerals are same as in the pyroxenite.

### III.2. Mineralogy

The Nemeiben Lake ultramafic rocks mineralogically consist mainly of olivine, orthopyroxene and clinopyroxene. The alteration products include serpentine minerals lizardite and chrysotile, tremolite, talc and carbonate. The primary mineral assemblage is considered to have been clinopyroxene, orthopyroxene and olivine. Oxide phases which are minor to accessory include magnetite, hematite and chrome spinel. Sulphides occur in all the ultramafic rocks described previously. It was found that disseminated sulphide is about 2% (average) by volume in the ultramafic rocks.

#### III.2.1. Primary Silicate Phases

##### III.2.1.a. Olivine

Olivine is a rare constituent in serpentinites. The olivine grains, on being replaced by serpentine, become rounded serpentine pseudomorphs which are isolated in a matrix of serpentine (Plate III, Fig. 1). Partially serpentized olivine grains poikilitically enclosed in

broad plates of orthopyroxene occur in some partially serpentized pyroxenites. They are subrounded to elongate-oval shaped with maximum dimensions of 5 by 4mm and averaging 3 by 2mm. The serpentine alteration product of olivine has been found to be lizardite in addition to chrysotile. In the initial stages of alteration serpentine occurs as rims around olivine and fillings along cracks in olivine (Plate III, Fig. 2). Serpentinization affects the olivine more than orthopyroxene. In some sections of partly serpentized pyroxenite, serpentine is partly or completely pseudomorphic after olivine leaving the pyroxene relatively unaltered. Irregular fractures in the olivine extend out through the surrounding pyroxene. Table II gives the compositions of the olivine determined by electron probe analyses. The average composition of the olivine is about  $Fo_{87.84}$ .

#### III.2.1.b. Orthopyroxene

Orthopyroxene is a rather prominent mineral in the Nemeiben Lake ultramafic rocks. As seen in thin sections it occurs as broad, ragged plate like crystals ranging up to a maximum size of 8 by 4mm in pyroxenite and partly serpentized and uralitized rocks. It is colourless and pleochroic, has large 2V, negative optic sign and characteristic parallel extinction. The orthopyroxene usually exhibits schiller caused by minute inclusions of clino-

TABLE II  
Composition of Olivines

Oxide	1	2
SiO <sub>2</sub>	39.2	39.4
MgO	46.3	48.2
FeO	12.6	10.8
Total	98.1	98.4

Number of ions on the basis of 4 oxygens

Si <sup>+4</sup>	0.9927	0.9870
Mg <sup>+2</sup>	1.7477	1.7997
Fe <sup>+2</sup>	0.2669	0.2262
Sum	2.0146	2.0259

FO

$\frac{\text{Mg} \times 100}{\text{Mg} + \text{Fe}}$	86.75	88.83
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PLATE III

Figure 1. Olivine grains on being replaced by serpentine become rounded serpentine pseudomorphs, which are isolated in a matrix of serpentine.

Figure 2. In the initial stages of alteration serpentine occurs as rims around olivine and fillings along cracks in olivine.

Plate III

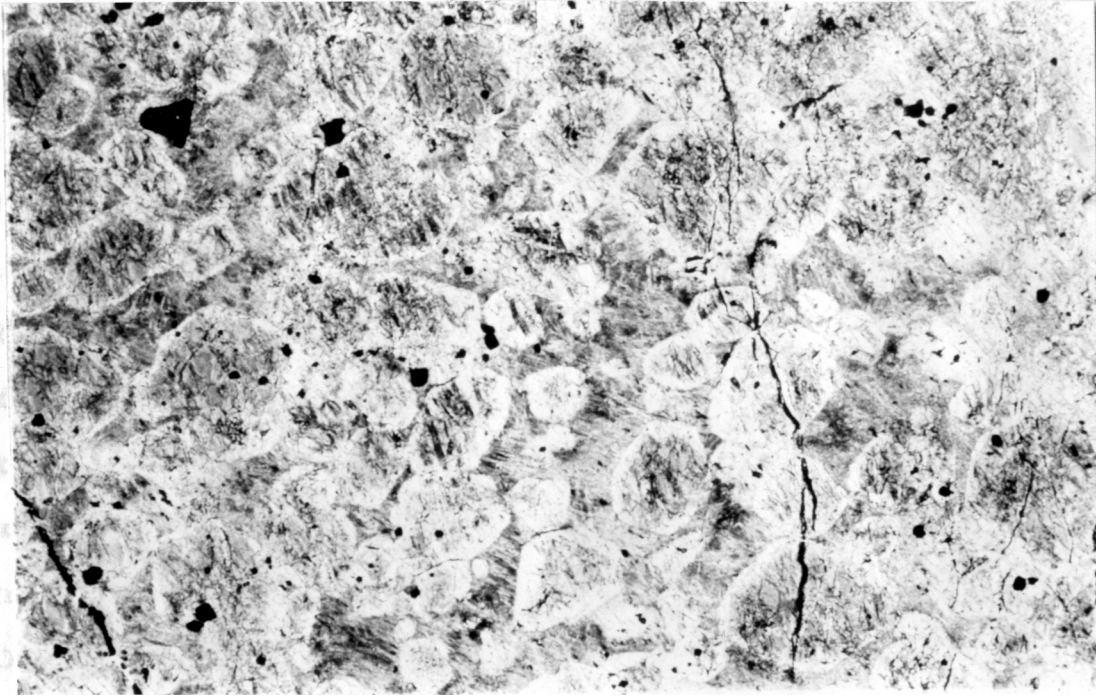


Figure 1



Figure 2



pyroxene along cleavages. Often polysynthetic twinning is observed.

The orthopyroxene is more serpentized and uralitized than diopsidic clinopyroxene, and in pyroxenites it has been replaced by tremolite, and talc. In the uralitized rocks orthopyroxene is readily replaced by colourless tremolite. The process can be seen at all stages of development. Wispy laths to needle shaped crystals of tremolite, aligned parallel to and cross cutting the pyroxene cleavage, increase in abundance until only scattered, highly corroded vestiges of the original pyroxene remain. Orthopyroxene commonly encloses rounded olivine grains or serpentine pseudomorphs after olivine.

As determined by chemical analysis the orthopyroxene ranges in composition between  $En_{90.5-88.05}$  with a mean of  $En_{88.88}$ , which places it in the bronzite field.

### III.2.1.c. Clinopyroxene

Both orthopyroxene and clinopyroxene are present in most ultramafic rocks. The clinopyroxene is optically +ve with a  $2V$  of approximately 60 degrees. Analyses of clinopyroxene from pyroxenite are shown in Table III. The diopside is coarse grained (maximum 1cm) and equigranular. It often shows the pronounced (100) parting of diallage. Diopside is generally less altered than hypersthene.

TABLE III

## Compositions of Ortho and Clinopyroxenes

Oxide	Orthopyroxene		Clinopyroxene	
	1	2	1	2
SiO <sub>2</sub>	54.6	55.3	52.4	52.4
Al <sub>2</sub> O <sub>3</sub>	3.8	2.4	4.6	2.9
FeO	8.3	6.1	3.9	3.0
MgO	31.3	32.6	18.5	19.5
CaO	1.7	1.1	20.1	21.7
Total	99.7	97.5	99.5	99.5
En	87.05	90.5		

## Number of ions on the basis of 6 oxygens

Si <sup>+4</sup>	1.8399	1.9074	1.8128	1.8507
Al <sup>+3</sup>	0.1601	0.0926	0.1872	0.1493
Sum	2.0000	2.0000	2.0000	2.0000
Al <sup>+3</sup>	0.1419	0.1026	0.1978	0.0992
Ca	0.0614	0.0406	0.7450	0.8212
Mg	1.5722	1.6761	0.9539	1.0265
Fe	0.2339	0.1760	0.1129	0.0887
Sum	2.0094	1.9953	2.0096	2.0287
Ca	3.29	2.14	41.12	42.42
Mg	84.19	88.56	52.65	53.00
Fe <sup>+2</sup>	12.52	9.30	6.23	4.58
Al <sub>2</sub> O <sub>3</sub>	3.50	2.43	4.62	2.84
(MgFe)SiO <sub>3</sub>	92.72	95.18	53.52	53.06
CaSiO <sub>3</sub>	3.84	2.84	44.86	44.10

### III.2.2. Alteration Products

#### III.2.2.a. Lizardite

Lizardite, colourless or pale green in Nemeiben Lake ultramafic rocks is the dominant mineral which directly replaces olivine and pyroxenes. The olivine has been altered to mesh textures of lizardite. The mesh rims are made up of length fast fibers with the c-axis laying parallel to the axis of the fibers. The mesh centers are composed of poorly oriented serpentine. The pyroxenes have altered to length fast and length slow fibrous serpentine which in both cases is lizardite.

Chrysotile is usually restricted to veins and mesh rims. The pleochrism (weak greenish) of mesh rims and x-ray powder diffraction patterns suggest the presence of chrysotile. In the more completely serpentized rocks the chrysotile forms cross fiber veins up to 3mm. Both mesh textures and hour glass textures of lizardite are seen in serpentinites.

F. Aumento (1969) showed that lizardite is the predominant serpentine mineral formed during the serpentinization process at low temperature of both ultramafic and mafic rocks of alpine, stratiform and mid-oceanic ridge intrusive settings. The formation of lizardite is therefore apparently independent of such features as tectonic settings, chemical composition of the parent rocks and major chrono-

logical differences. The lizardite from the Nemeiben Lake ultramafic rocks also is in accordance with this observation. Chidester (1962) has described in detail talc-bearing ultramafic rocks from north central Vermont. These ultramafic rocks are typical of those that occur along the Appalachian Mountain belt. Typically these serpentinites occur in schists of the chlorite to garnet zone of metamorphism. As identified by x-ray diffraction, antigorite is the only essential constituent of these serpentinites. Antigorite thus appears to be formed at higher temperatures than lizardite and chrysotile, or is the product of subsequent metamorphism of these minerals.

#### III.2.2.b. Talc

Talc is a common mineral in serpentinites. Two types of occurrences are seen, one in which fine grained talc, mixed with carbonate, formed late veins. The second type of talc is associated with the serpentine mineral lizardite. Here the talc is replacing original orthopyroxene. Talc occurs as wispy flakes irregularly scattered throughout the rock. Many pyroxenes, but never olivine, have been completely replaced by talc.

#### III.2.2.c. Carbonates

The carbonate content of the ultramafic rocks is generally minor with calcite and dolomite both present.

Carbonate alone or in association with fine granular magnetite may occupy serpentine mesh centers or occur as cross cutting late veins in serpentinite (Plate IV, Fig. 1).

#### III.2.2.d. Tremolite

Tremolite varies from colourless to pale green in colour and is weakly pleochroic. It occurs in large fibrous bladed aggregates, many of which can be identified as pseudomorphs after pyroxene. Crystal habit is variable from anhedral grains forming an equidimensional, mosaic to circular, spear shaped grains up to 2mm long. Optical examination of a number of specimens has shown the mineral to be optically negative with  $2V=70-80$  degrees. In many thin sections, tremolite can be observed directly replacing primary pyroxene. Where uralitization is more intense, and the pseudomorphs are destroyed, the amphibole becomes distributed in discontinuous ragged patches.

#### III.2.3. Oxides

Various oxides were identified in the Nemeiben Lake ultramafic rocks. They include hematite, chromian spinel and several textural varieties of magnetite as described below. Some optical properties under reflected light are listed in Table IV.

##### III.2.3.a. Magnetite

Magnetite is present in varying quantities in all the ultramafic rock types. Primary subhedral grains (av. diameter=0.3mm) are often recognizable, but in the serpentinites magnetite of secondary origin is the prevalent type. The oxidation and release of iron from primary iron bearing silicate minerals during serpentinization is a well documented phenomena (Coats, 1966). In the Nemeiben Lake ultramafic rocks magnetite occurs in serpentinized or partially serpentinized olivine and orthopyroxene crystals. In some serpentinites, the mode of occurrence of magnetite occasionally enables an estimate to be made of the primary mineralogy, in which original olivine and pyroxene were altered pseudomorphically to serpentine. The released iron was crystallized approximately insitu as magnetite preserving recognizable ghost outlines and textures of the former grains.

Commonly, however, the secondary magnetite does not show any particular control as regards the amount at any one place or in the locus of deposition. It may be present as clouds of minute particles in serpentine, or irregular shaped longer grains with a more even pattern of distribution, or as dendritic aggregates. Narrow veins and subparallel stringers of fine grained magnetite are also common, occurring alone or accompanying one or more of the other forms. The features of Plate IV, Fig. 2 is interesting, in that it shows linear but highly irregular masses of

PLATE IV

Figure 1. Carbonate in association with magnetite as cross cutting late veins in serpentinite.

Figure 2. Irregular masses of magnetite connected by narrow veinlets of magnetite.

Plate IV

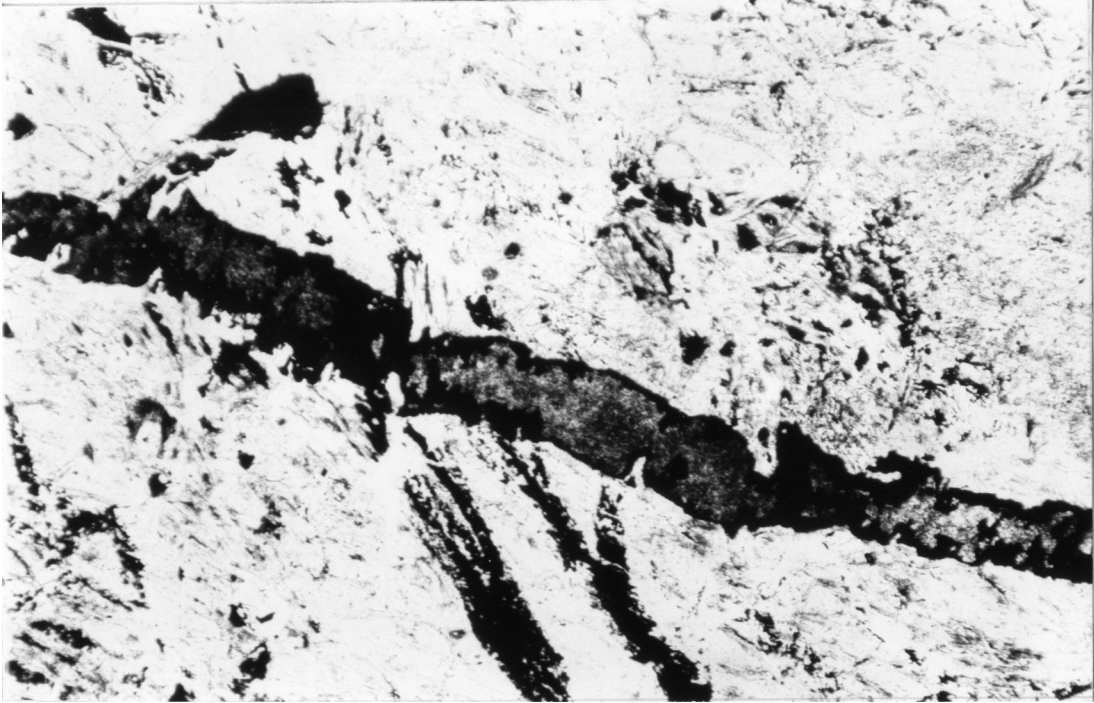


Figure 1

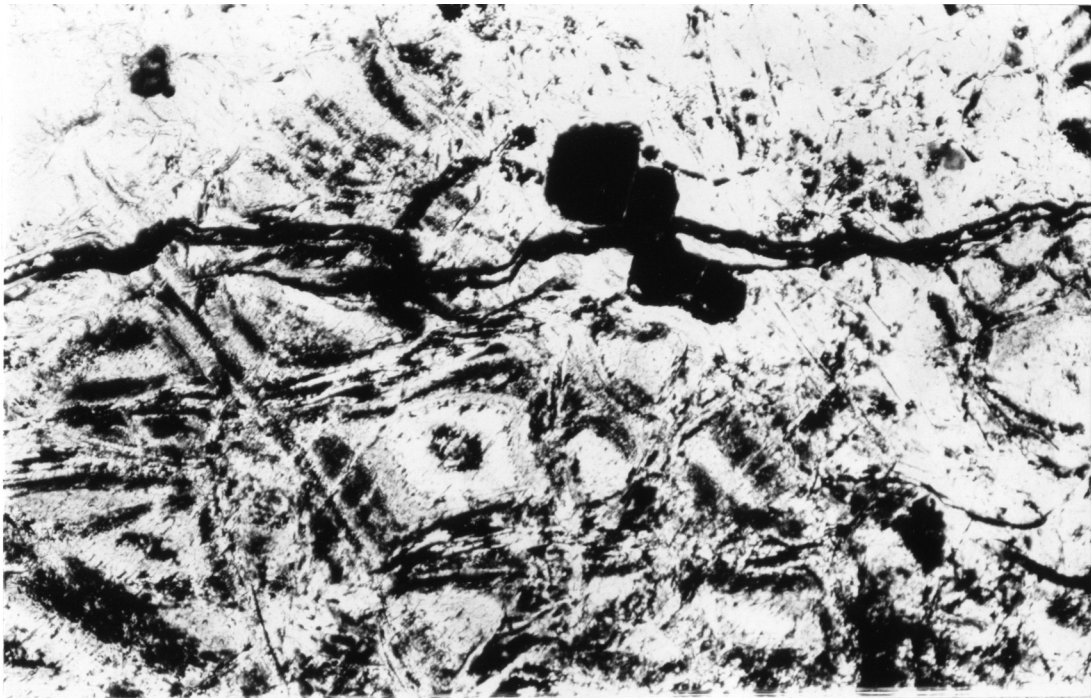
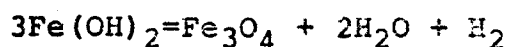


Figure 2



magnetite connected by narrow veinlets of magnetite. This mode of occurrence suggests the accumulation of iron during serpentinization, its movement along fractures and subsequent deposition as an aggregate at some suitable location, including deposition and accumulation in fractures.

In a discussion on the origin of intrusive magnetite Shand (1947) has suggested that residual solutions from a gabbroic magma could contain ferrous iron in the form of a ferrous hydroxide hydrosol. This would be a means to explain the movement of considerable iron during the process of serpentinization. On the breakdown of primary silicates and their replacement by serpentine, the major portions of the iron released would initially be in the form of  $Fe^{++}$  ions (according to this view, but debatable), with the quantities of water necessary for serpentinization necessarily being available, the  $Fe^{++}$  ions, could form a ferrous hydroxide hydrosol or colloidal solution. In this form, transportation of the iron and accumulation at suitable loci could be obtained. Such locations might well be areas of reduced water activity or higher oxygen fugacity (Miyashiro, 1964). Loss of water from the hydroxide brings about oxidation to magnetite according to the equation:



It is suggested that a process of this type could have brought about the aggregates of secondary magnetite in

many of the serpentinites.

#### III.2.3.b. Hematite (Specularite)

Small mica like tabular crystals of steel grey colour and very brilliant metallic luster occur predominantly in veinlets commonly associated with other minerals in serpentized rocks. Both secondary magnetite and hematite appear to have been produced by the serpentization of olivine. This is interesting because hematite is a quite rare product during serpentization. The only other locality with appreciable secondary hematite is the Lizard ultramafic, Cornwall (Green, 1964), but Green does not discuss this aspect (personal communication, F.J. Wicks).

#### III.2.3.c. Chrome Spinel

Chrome spinel occurs both as rather large euhedral grains up to 1 or 2 millimeters in size and as smaller irregular blebs. They occur as disseminated grains seldom making 0.5 percent by volume as estimated from thin sections. Fractures in spinels are filled with serpentine. It is probable that this spinel phase represents a primary magmatic phase which is unaffected by the serpentization process.

#### III.2.4. The Ore-Minerals and their Textures

The normal sulfide assemblage found in most nickel

TABLE IV

Properties of Oxides at Nemeiben Lake

Name	Formula	Colour	X-Nicols
Chromian Spinel	$(\text{MgFe}^{+2})$ $(\text{Cr,Al,Fe}^{+3})_2\text{O}_4$	Reddish brown	completely isotropic
Magnetite	$\text{Fe}^{+2}\text{Fe}_2\text{O}_3$	Grey	isotropic to weakly anisotropic
Hematite	$\text{Fe}_2\text{O}_3$	Greyish white with distinctly bluish tint	anisotropic

deposits related to ultramafic and ultrabasic rocks in Canada is relatively simple, and comprises the primary minerals, pyrrhotite, pentlandite, pyrite, and chalcopyrite, usually in the above order in terms of abundance (Kilburn, et.al., 1969). Partial or complete alteration of pentlandite and pyrrhotite to violarite-bravoite and marcasite-pyrite is common in deposits related to serpentized ultrabasics with either or both supergene or hypogene agencies apparently involved (Kilburn, et.al., 1969). All degrees of alteration pseudomorphism appear, but the primary assemblage generally is preserved, even after extensive recrystallization of silicates and sulfides during serpentization.

Sulphides occur in all the Nemeiben Lake ultramafic rocks described previously. They occur as disseminations and fine fracture fillings. The ore minerals which are present are pyrrhotite, pentlandite, chacopyrite, violarite-bravoite, marcasite-pyrite, native copper and rare platinoid. Some of the optical properties (reflected light) of the sulphides are listed in the Table V.

#### III.2.4.a. The Primary Sulphides

##### III.2.4.a.i. Pyrrhotite (with Ni and Cu)

In general pyrrhotite is the principal sulphide mineral in the Nemeiben Lake ultramafic rocks. Pyrrhotite is seldom found alone and is usually in association with

TABLE V

## Properties of Sulphides at Nemeiben Lake

Name	Formula	Colour	X-Nicols
Nickeliferous pyrrhotite (with Cu)	$\text{Fe}_{1-x}\text{S}$	Pale pine brown	Strongly anisotropic
Pentlandite	$(\text{FeNi})_9\text{S}_8$	Pale creamy to creamy yellow	Isotropic
Chalcopyrite	$\text{CuFeS}_{2-x}$	Brass yellow	Anisotropic
Violarite	$\text{FeNi}_2\text{S}_4$	Grey	
Bravoite	$(\text{NiFe})\text{S}_2$	Brown pinkish	
Marcasite	$\text{FeS}_2$	Yellowish white greenish tint	Very strongly anisotropic
Pyrite	$\text{FeS}_2$	Yellowish white	Weakly anisotropic

pentlandite, pyrite and chalcopyrite. Pyrrhotite characteristically takes a good polish. In most polished sections the pyrrhotite forms rounded to irregular grains ranging in diameter from 0.1mm to 2cm. Grain sizes of 0.5mm to 1cm are particularly common. Irregular contacts between pyrrhotite and the other sulphides are a common feature. Small flames and lamellae of pentlandite are included in the pyrrhotite (Plate V, Fig. 1). Pentlandite-pyrrhotite relations similar to the above are known from almost every nickeliferous pyrrhotite deposit in the world and are accepted as being a result of exsolution from a homogeneous solid solution, not as a result of replacement (Edwards, 1947; Hawley, et al., 1943). The relation between pyrrhotite-pentlandite and chalcopyrite will be discussed later.

#### III.2.4.a.ii. Pentlandite

The main nickel-bearing ore mineral in the Nemeiben Lake ultramafic is pentlandite. It always polishes readily. Pits which originate as a result of octahedral cleavage serve as a distinguishing feature. Fresh pentlandite varies from pale cream to creamy yellow in colour. The pentlandite which has undergone alteration by supergene agencies may have a brownish tint. Pentlandite occurs in two principal textural forms: (1) as fine lamellae oriented parallel to the basal parting of pyrrhotite, and (2) as rims around pyrrhotite grain boundaries. The regular lamellae

parallel to (0001) of pyrrhotite, vary in width, being in many cases less than 1 micron, with a length of approximately 0.03mm, although somewhat longer lamellae have also been observed. Most of the rims of pentlandite around pyrrhotite are 0.1 to 0.2mm thick. Larger, irregular masses of pentlandite may fill the interstices where three or more pyrrhotite grains are close together.

An interesting feature of pentlandite is that it alters readily to the secondary nickel sulphides violarite and bravoite.

In order to distinguish between pyrrhotite and pentlandite, the polished sections were stained with a chromic acid-hydrochloric acid solution following the method of A.M. Graudin as reported by Short (1940). Pentlandite takes on a blue colour when exposed to this solution for about five minutes at 62 F. Pyrrhotite becomes a darker bronze and chalcopyrite and pyrite are unaffected. Pentlandite takes on even brilliant colours with prolonged exposure to this solution. This test proved useful in the identification of pentlandite, especially in the disseminated and weathered ore where pentlandite is very difficult to identify.

#### III.2.4.a.iii. Chalcopyrite

Chalcopyrite is a common mineral in the disseminated sulphides found in ultramafic rocks. It occasionally

forms granular aggregates of small irregularly rounded grains with mutual to slightly interlocking boundaries. Chalcopyrite which is present in Nemeiben Lake ultramafic body is easily identified by its brassy yellow colour and weak anisotropy. The grain size varies from 1mm to 1cm in diameter. Chalcopyrite surrounds pyrrhotite which probably indicates that it is later in paragenesis than pyrrhotite. The pyrrhotite also contains chalcopyrite as irregular shuttle-shaped lamellae about 0.002mm thick and this is most likely an exsolved phase from pyrrhotite. In these occurrences chalcopyrite crosscuts pentlandite. The grain boundary relationships between pentlandite and chalcopyrite are sharp.

#### III.2.4.b. The Secondary Sulphides and Native Metals

The secondary sulphide minerals are violarite, bravoite, marcasite, two textural varieties of pyrite and native copper. Supergene or hypogene alteration of primary sulphides has resulted in the formation of secondary sulphides. Ramdhor (1967) documents an extensive list of opaque minerals (over 26 minerals) associated with serpentinization.

##### III.2.4.b.i. Violarite

Violarite is always observed to be pseudomorphous after pentlandite. It was seen in some polished sections



that the pentlandite has almost been completely altered to violarite and the violarite in turn is altered to bravoite (Plate VI, Figs. 1 and 2). In the Sudbury ores, violarite is found as a near surface intermediate alteration product of pentlandite (Hawley, 1962).

#### III.2.4.b.ii. Bravoite

Ramdhor (1960) considers that bravoite is the most common alteration product of pentlandite. Although the mineral is isotropic it could readily be distinguished from pentlandite on account of its brown-pinkish colour, which is very similar to that of pyrrhotite. In extremely weathered rocks or in the mineralized, serpentized ultramafics all the pentlandite is converted to bravoite. Zonation between bravoite and pyrite is observed (Plate VII, Fig. 1). Close examination of pyrite reveals a distinct zonal structure caused by brownish and yellowish coloration. The innermost zones of such individuals are distinctly brown in colour and were identified as bravoite, which suggests that the zonal development of the pyrite is due to differences in the nickel content.

#### III.2.4.b.iii. Marcasite

Marcasite is a relatively minor constituent of the Nemeiben Lake ultramafic rocks. Marcasite replacing nickeliferous pyrrhotite develops first as fine feathery

forms along cracks and partings of pyrrhotite. Marcasite is also associated with pyrite.

#### III.2.4.b.iv. Pyrite

Two generations of pyrite are clearly seen from polished sections. Massive pyrite 0.5mm appears to be an alteration from pyrrhotite, developed around the margins of pyrrhotite grains. A later generation pyrite also occurs along cross-cutting fractures.

Particularly around pyrite thin layers of chalcopyrite concentration (Plate V, Fig. 7) is noticed. Probably as pyrrhotite is transformed to pyrite, copper which was incorporated in pyrrhotite is released and formed a second generation of chalcopyrite.

#### III.2.4.b.v. Native Copper

Native copper locally is a common minor constituent of a wide variety of rock types, including basic lavas and associated sandstones, shales, and conglomerates (Michigan copper deposits). It has also been reported in the Skaergaard intrusion; East Greenland (Wager, et.al., 1957; p. 865) and Muskox intrusion (Chamberlain, et.al., 1965) discuss the origin of native copper during serpentinization process.

Native copper at Nemeiben Lake occurs in hematite bearing serpentinites and is seen in drill core samples as

fibrous crystals in veins. Native copper may have formed by the reduction of copper-bearing sulphides.

#### III.2.4.b.vi. Platinoid Mineral

White platinoid mineral which is very rare is seen in chalcopyrite (Plate V, Fig. 8). Rucklidge (1969) describes the occurrence of platinum minerals in the ultrabasic rocks from Canada.

## PLATE V

- Figure 1. Large pyrrhotite grain with a few pentlandite lamellae (upper left). Marcasite develops as secondary alteration. Also pyrrhotite has been altered to pyrite (upper right). Within this pyrite, bravoite occurs in the middle. 60x oil.
- Figure 2. Portion of the above figure at higher magnification. 100x oil.
- Figure 3. Consist largely of pyrrhotite and chalcopyrite. Pyrrhotite contains a few exsolution lamellae of pentlandite. Magnetite-silicate veins cutting sulphides. 60x oil.
- Figure 4. Pyrrhotite with marcasite lamellae. 100x oil.
- Figure 5. Shows chalcopyrite veining pyrrhotite. Pentlandite alteration to violarite and bravoite. 60x oil.
- Figure 6. Violarite alteration to bravoite. Chalcopyrite (upper left). 60x oil.
- Figure 7. Chalcopyrite, pyrite, pyrrhotite. Chalcopyrite around pyrite. 100x oil.
- Figure 8. White platinoid mineral in chalcopyrite. 60x oil.

Plate V

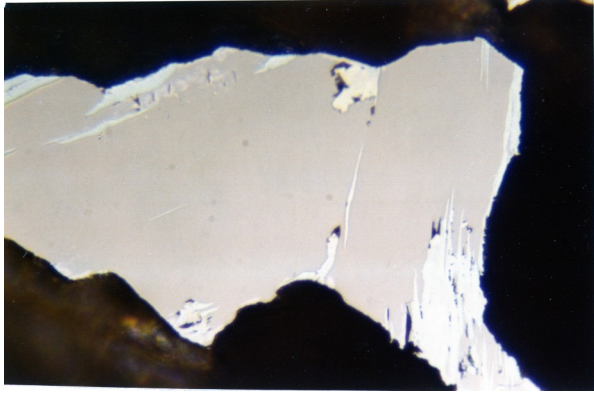


Figure 1

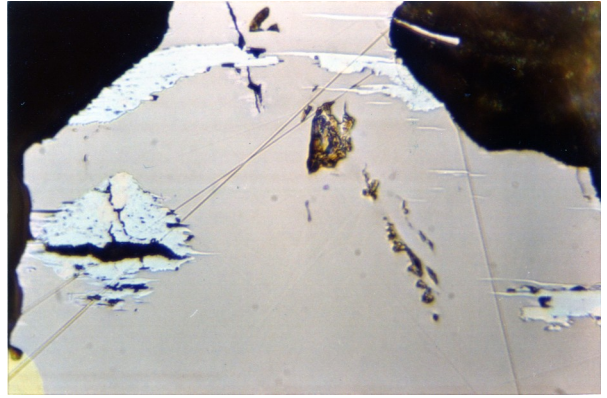


Figure 2

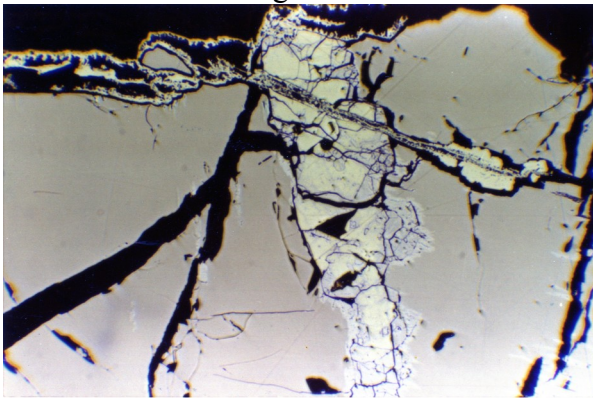


Figure 3

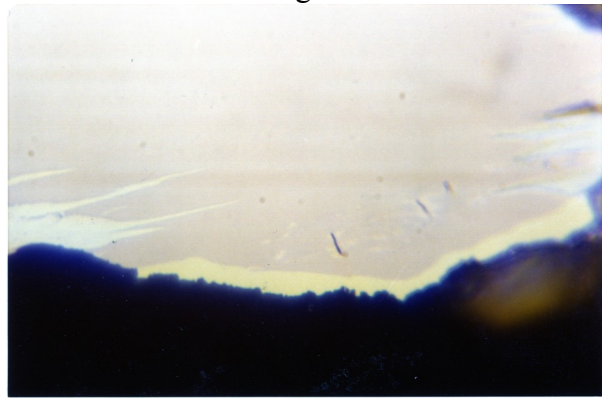


Figure 4

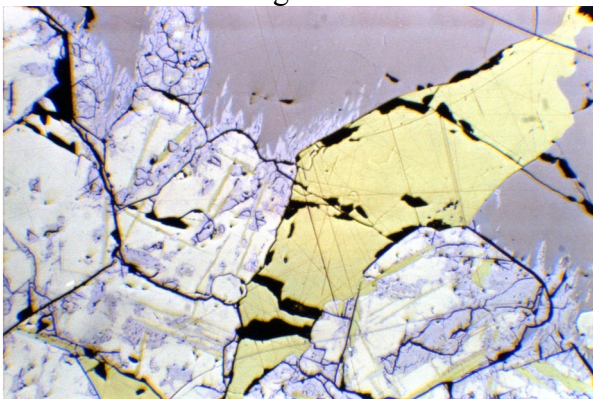


Figure 5

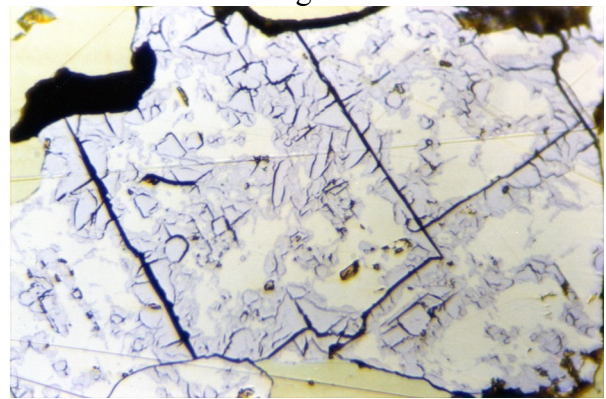


Figure 6

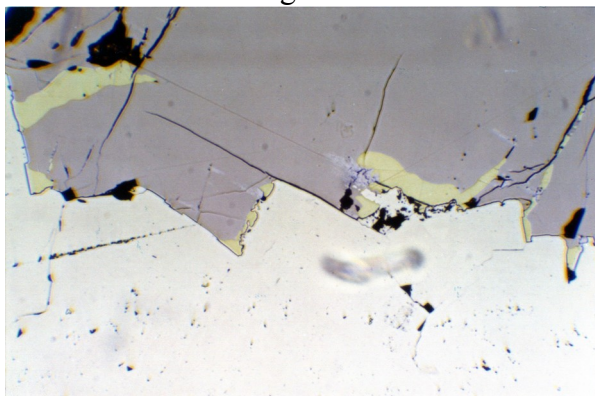


Figure 7

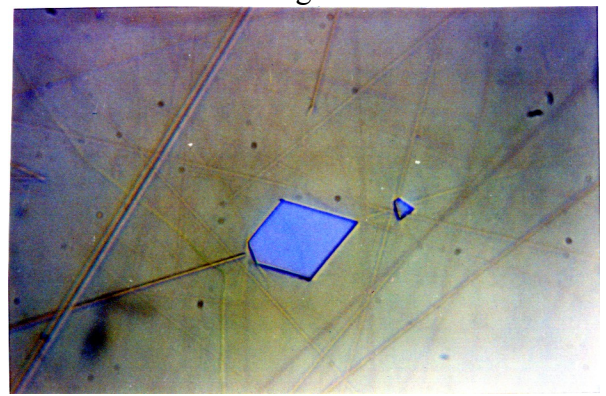


Figure 8

PLATE VI

Figure 1. Violarite alteration to bravoite. Portlandite lamellae on the left side. 12.5x oil.

Figure 2. Violarite alteration to bravoite. Whole mass is violarite. Bravoite in the middle 60x oil.

Plate VI

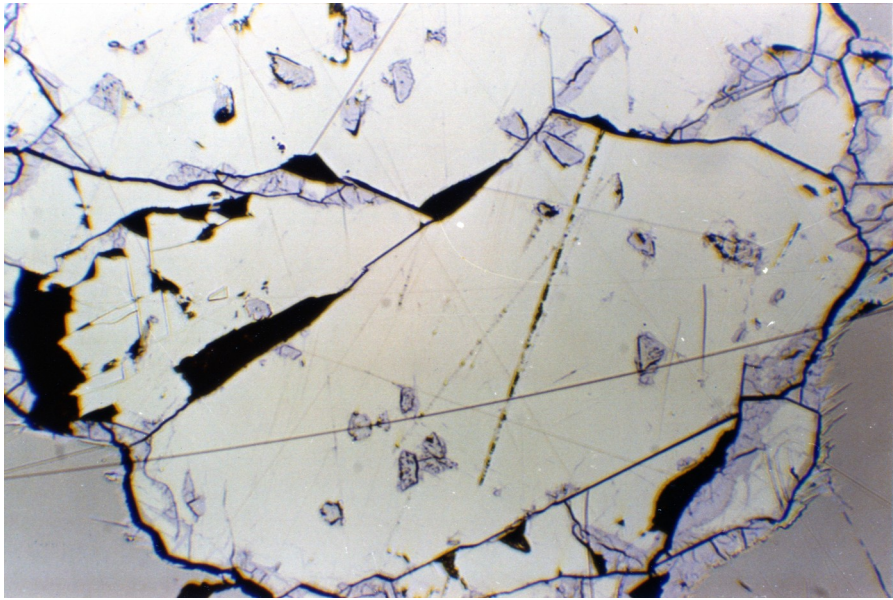


Figure 1

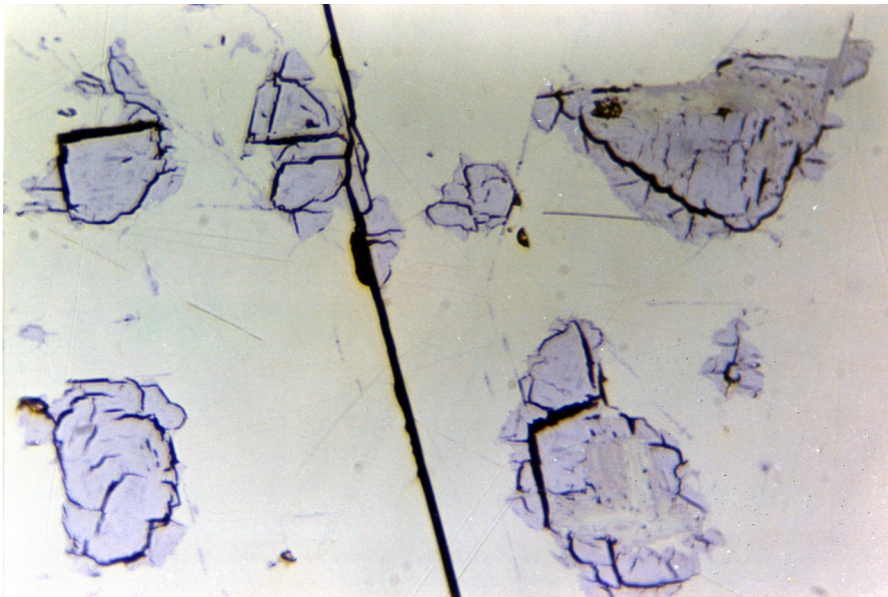


Figure 2

PLATE VII

Figure 1. Zonation between bravoite and pyrite. The inner zones are brown in colour and are identified as bravoite. Outer zone pyrite.



Plate VII

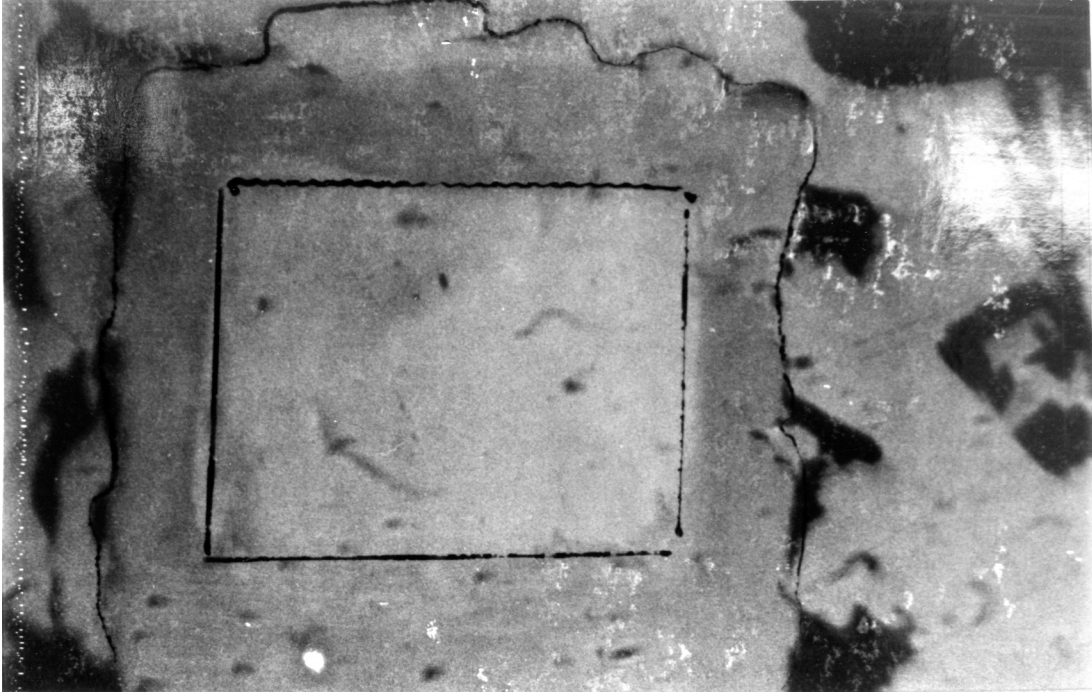


Figure 1

PLATE VIII

Figure 1. Myrmekite texture between pyrite and chalcopyrite. The section also contains pyrrhotite. 1200x oil.

Figure 2. Three fold myrmekite texture between chalcopyrite. Pyrrhotite and pyrite. 1200x oil.

Plate VIII

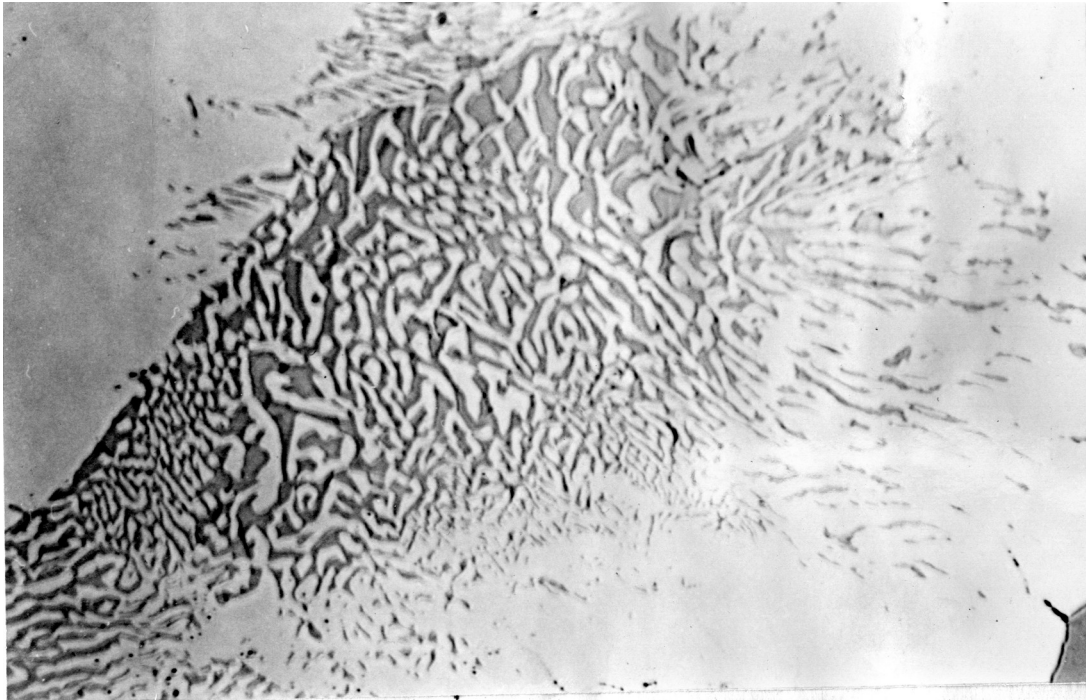


Figure 1

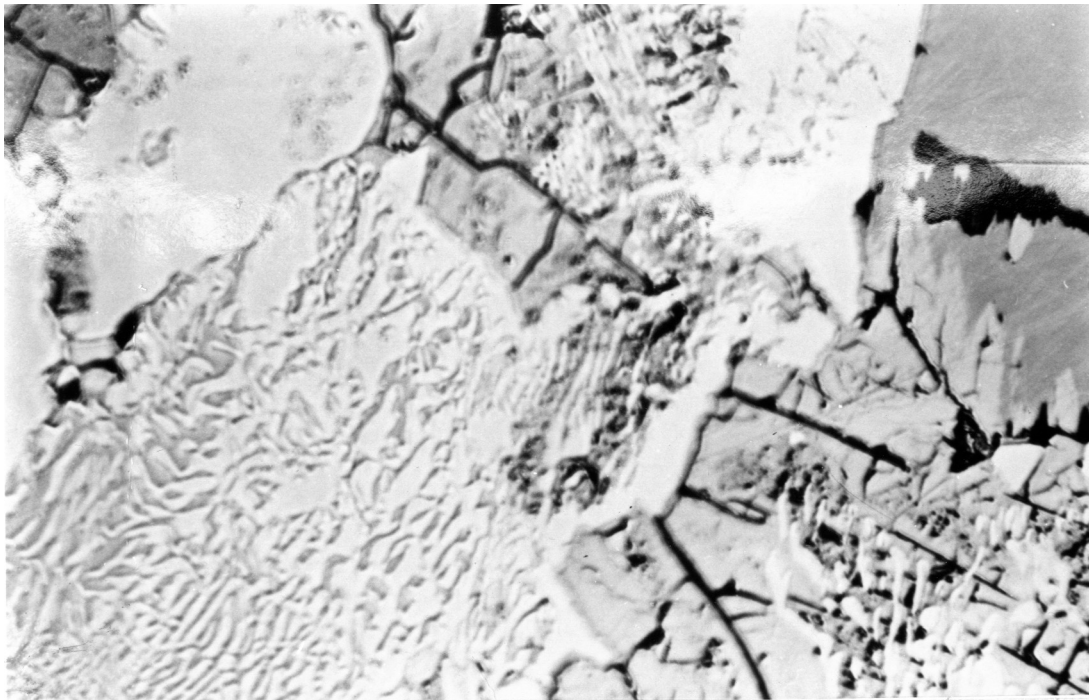


Figure 2

## VI. MINERAL CHEMISTRY

### IV.1. Introduction

Partial chemical analysis were determined on two olivines, orthopyroxene and clinopyroxenes from pyroxenite using an electron microprobe (procedure in Appendix IIc). Table II shows the results for olivine with their atomic ratios calculated on the basis of 4 oxygens per unit formula. Table III shows analyses for ortho and clinopyroxenes with their calculated atomic ratios on the basis of cations per 6 oxygen and a Z group cations to be 2. The olivines could not be separated from the serpentinites, which obstructed the use of other methods to determine the composition of olivines.

### IV.2. Olivine

The olivines give compositions of Fo 86.75 and Fe 38.83 calculated as the molecular ratio  $Mg \times 100 / Mg + Fe$ . Total iron was calculated as FeO. In Figure 4 are compiled data on the composition of olivines in Canadian rocks along with Nemeiben Lake. Smith (1962) states that olivines with high iron content occur locally in the Cordillera or Appalachians, where they are associated with gabbroic rocks. However, magnesium-rich olivines, that is olivines with a forsterite content over 90% are confined to the Cordillera or Appalachian belts and have not been found in the Pre-

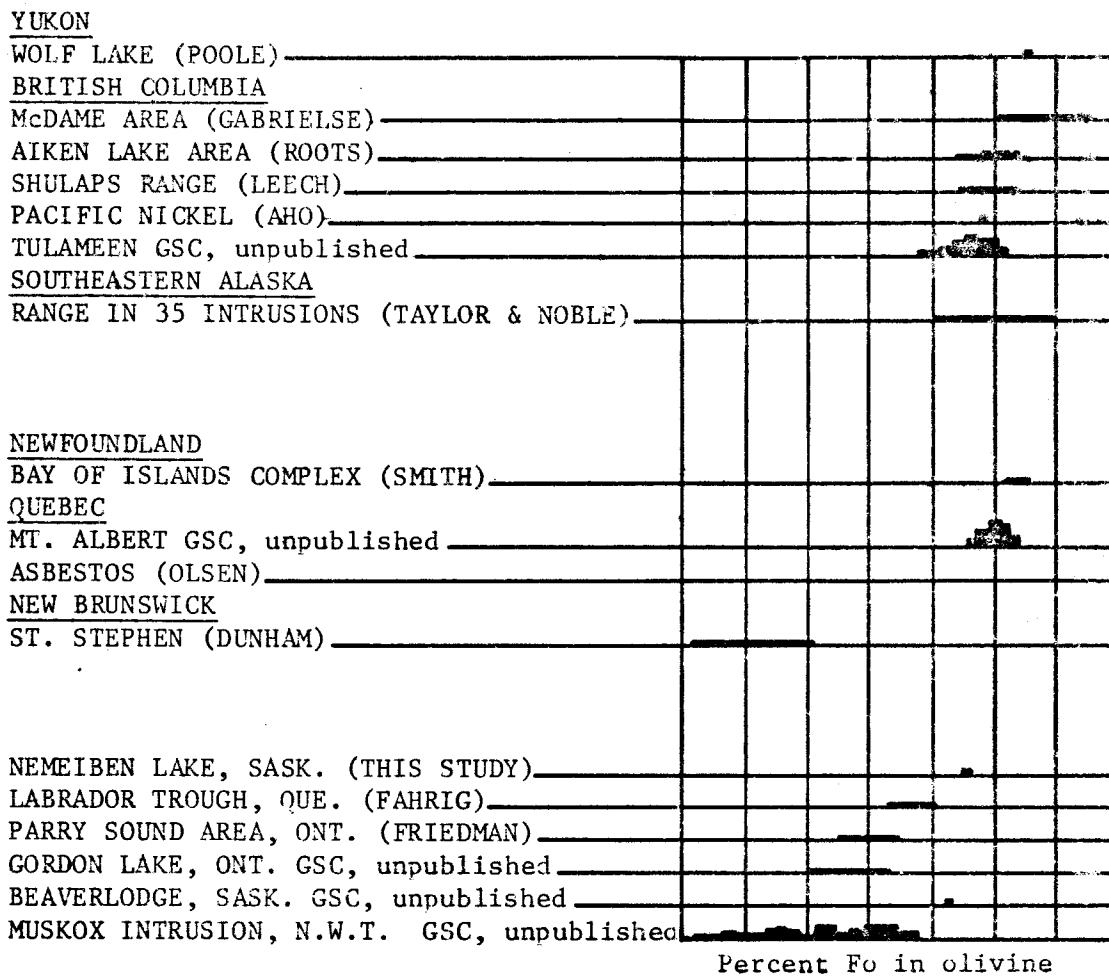


Figure 4. OLIVINE COMPOSITIONS OF CANADIAN ULTRAMAFIC ROCKS

(After Smith, 1962).

cambrian shield. This appears to be a significant relationship with which the Nemeiben Lake olivines are consistent. Fo content however is still high.

In Figure 5 the olivines from Nemeiben Lake ultramafic body are compared in their forsterite contents with magnesium olivines crystallized from basaltic magma, with olivines from peridotite nodules in basalts, and with olivines from ultramafic intrusives in orogenic belts.

D.H. Green (1964) and G.A. Challis (1965, 1966) have made comparisons of the forsterite content of olivine from various ultramafic rocks. Olivines from alpine-type harzburgite and dunite are typically rich in magnesium and have a restricted range in forsterite content. They are similar to olivines in peridotite nodules (Ross, et.al., 1954). Olivine from stratiform rocks (such as Stillwater, Skaergaard, and Bushveld complexes) may be as magnesium rich as those of alpine-type peridotites, but as a result of differentiation the olivines from the stratiform type have a larger range in composition extending to Fo 80 and below.

Challis (1965) and Himmelberg and Coleman (1968) report that the olivine from pyroxenite at Red Hills, New Zealand and from Red Mountain, California is more iron rich than the olivines from the dunites and harzburgites. Loney, et.al., (1971) report that at Burro Mountain, California, the composition of the olivine from the orthopyroxenite is Fo 91.2 which is within the range of olivine compositions

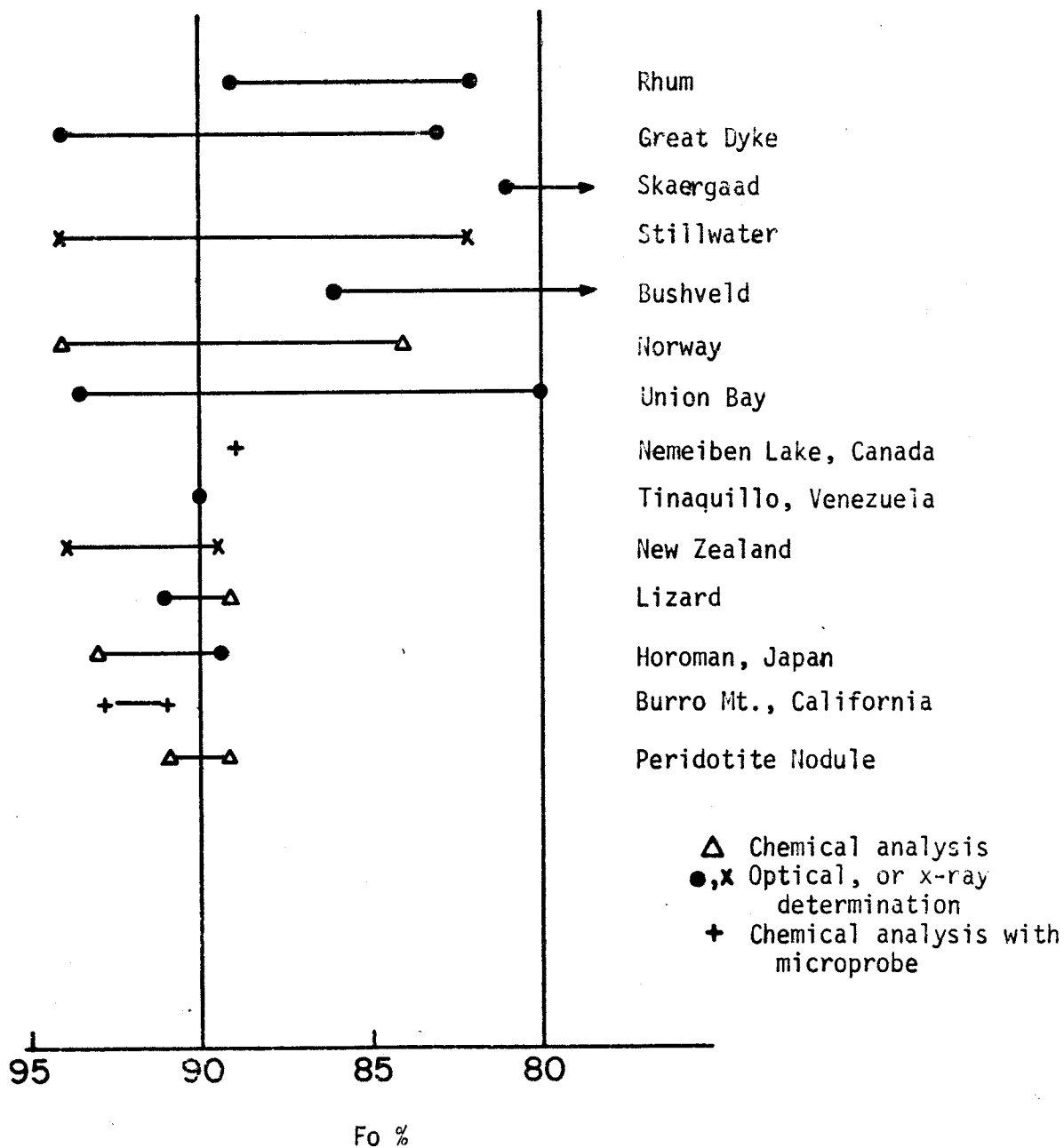


Figure 5. Composition range of olivine (after Green, 1964; Challis, 1966).

from dunite and harzburgite.

The olivine compositions from pyroxenite at Nemeiben Lake ultramafic body are therefore similar to high temperature alpine-type ultramafics. They match closely the analysed olivines from the Lizard, Cornwall; the olivines (optically determined) of the high temperature Tinaquillo Peridotite (Mackenzie, 1960); the olivines from Horoman, Japan (Onuki, 1965); and have a slightly lower Fo content than the olivines (chemical analysis with electron microprobe) of the high temperature Burro Mountain peridotite California (Loney, et. al., 1971).

In summary, the olivines from Nemeiben Lake ultramafic rocks are similar to olivines in peridotite nodules in basalts and ultramafic intrusives in orogenic belts.

#### IV.3. Orthopyroxene

Since  $Al_2O_3$  and CaO contents are the most important criteria in the orthopyroxenes to consider, a discussion of their contents is given below to elaborate the petrological significance of their host rocks.

##### IV.3.1 $Al_2O_3$ Content

The  $Al_2O_3$  content of orthopyroxenes has been discussed by Ramberg and DeVore (1951), Hess (1952), Boyd (1963, 1966), Green (1964), Challis (1965), Onuki (1965) and Loney et. al., (1971).



Hess (1952) suggested that higher pressure favored the formation of more aluminous orthopyroxene, and aluminous hypersthene has been reported from garnetiferous granulites.

Green (1964) considered the distribution of  $\text{Al}_2\text{O}_3$  in orthopyroxenes of various origins and suggested that normal magmatic crystallization yield orthopyroxenes with maximum  $\text{Al}_2\text{O}_3$  contents of 2-3 percent, at least in upper crustal environments. Depending upon the availability of aluminum during crystallization an increase in the  $\text{Al}_2\text{O}_3$  content of orthopyroxene is favored by high pressure, as shown by the experimental work of Boyd (1963, 1966).

The  $\text{Al}_2\text{O}_3$  contents in the orthopyroxenes from Nemeiben Lake are 3.8 and 2.4 weight percent. These values are very close to the orthopyroxene compositions (2.55-3.54) from the Horomon ultramafic, Japan (Onuki, 1965) and comparable to the  $\text{Al}_2\text{O}_3$  contents of orthopyroxene from New Zealand peridotites (1.43-4.09) and Burro Mountain, California (1.3-3.0). On the other hand, orthopyroxenes from Nemeiben Lake ultramafics and recrystallized peridotites in the Lizard intrusion are very similar to each other in  $\text{Al}_2\text{O}_3$  contents, though primary enstatites from the Lizard show far higher  $\text{Al}_2\text{O}_3$  contents than any other orthopyroxenes thus far reported from ultramafic intrusives.

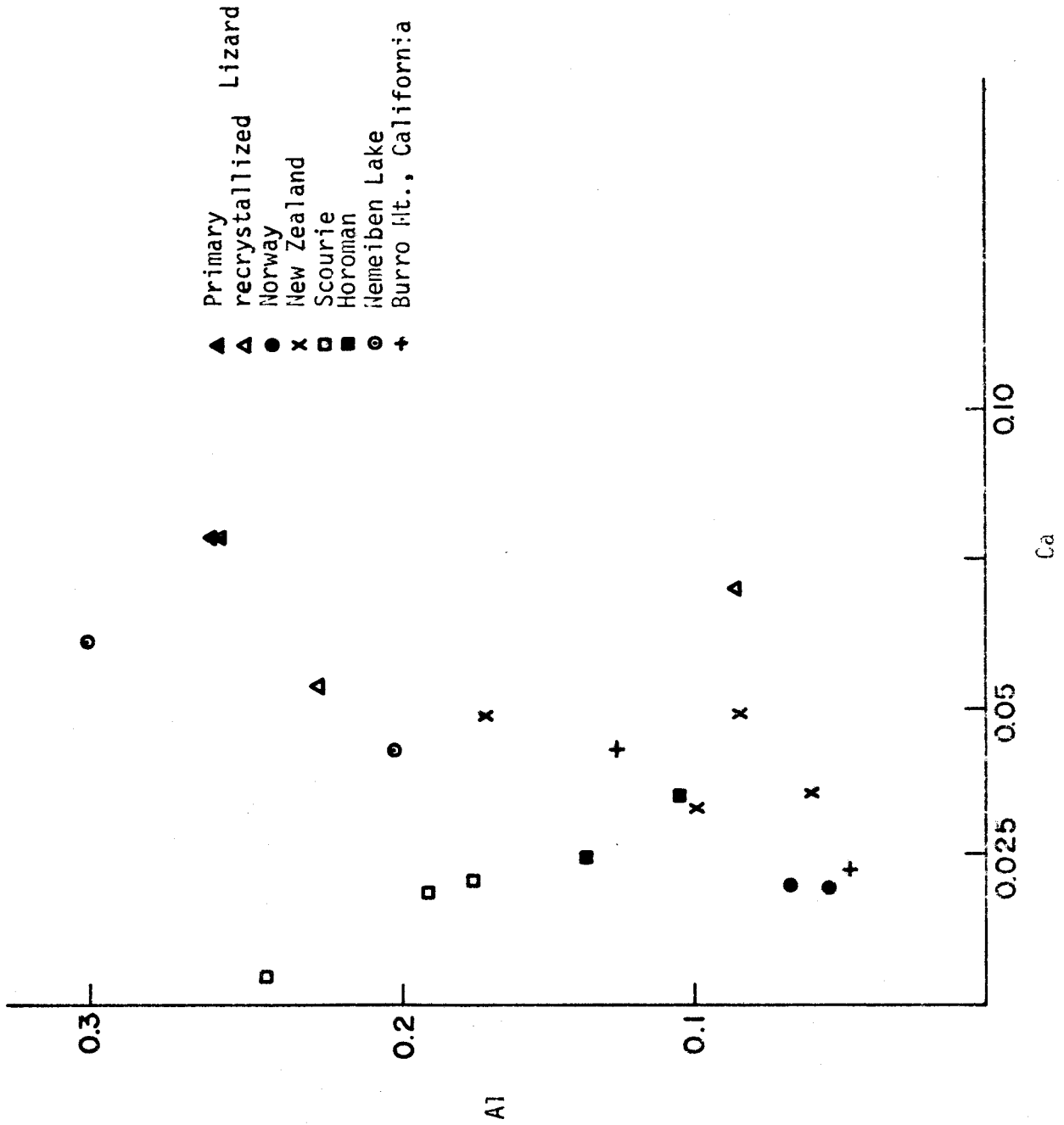


Figure 6. Relation between the atomic proportions of Al and Ca in orthopyroxenes.

Green (1964) considered that high  $\text{Al}_2\text{O}_3$  contents (4.05%-7.09%) of orthopyroxenes in the Lizard high temperature peridotite intrusion were a function of high pressure crystallization, probably in an environment similar to that in which peridotite nodules in basalt crystallized. Similarly the orthopyroxenes from the high-temperature, high-pressure Beni Bouchera peridotite (Kornprobst, 1969) have high  $\text{Al}_2\text{O}_3$  contents (3.27%-5.93%). The  $\text{Al}_2\text{O}_3$  contents of orthopyroxenes from ultramafic nodules and orthopyroxene megacrysts in basalts, which are thought to have crystallized under pressures broadly appropriate to the lower crust or upper mantle, are variable but relatively high, ranging from approximately 2% to 8% (Ross, et.al., 1954; Aoki, 1968; Binns, et.al., 1970).

Fig. 6 compares the  $\text{Al}_2\text{O}_3$  and CaO contents in orthopyroxenes from various ultramafic rocks with respect to the atomic proportions of Al and Ca on the basis of  $\text{O}=6$ .

Orthopyroxenes from garnetiferous peridotites (O'Hara and Mercy, 1963) are not high in  $\text{Al}_2\text{O}_3$  contrary to expectations based on recent experimental work.  $\text{Al}_2\text{O}_3$  in orthopyroxenes may be dissolved as  $\text{MgAl}_2\text{SiO}_6$ ,  $\text{CaAl}_2\text{SiO}_6$ ,  $\text{MgFe}^{+3}\text{Al}_2\text{SiO}_6$ ,  $\text{CaTiAlSiO}_6$  and so on. Therefore Onuki (1965) stated that although Tschernak's molecules are always a function of pressure, other molecules containing Al may not be always related to pressure. Since the ionic radius of Al is intermediate between that of Si and those of Mg

and Fe, the content by Al in Y position of orthopyroxene structure rather than total  $\text{Al}_2\text{O}_3$  may be more useful as a pressure indicator. When the deficiency of Si in Z position is filled with Al atom, the atomic proportion of the remaining Al is then allotted as  $\text{Al}_y$ . A plot of the relation between the atomic proportion of  $\text{Al}_y$  and Ca in orthopyroxenes is shown in Figure 7. However, the relative positions among various ultramafics do not differ between Figures 6 and 7. Plotting  $\text{Al}_2\text{O}_3$  vs.  $\text{Mg} \times 100 / (\text{Mg} + \text{Fe} + \text{Mn})$  the compositions of orthopyroxene from Nemeiben Lake ultramafic body are compared with those from other ultramafic rocks in Figure 8. All the orthopyroxenes in Fig. 8, with the exception of five samples from alpine type peridotites, are limited to values between 89-92. The  $\text{Al}_2\text{O}_3$  contents of the Nemeiben Lake orthopyroxene are higher than those of typical orthopyroxene from alpine-type peridotites and stratiform basic intrusions.

MacGregor (1965, 1967) has stated that in the spinel-peridotite mineral assemblage, the  $\text{Al}_2\text{O}_3$  content of pyroxenes will decrease with increasing pressure, and at constant temperature the aluminum will go into the spinel phase.

Thus it can be emphasized that the bulk chemical and mineralogical compositions have profound effect on the  $\text{Al}_2\text{O}_3$  content of orthopyroxene.

#### IV.3.2. CaO Content

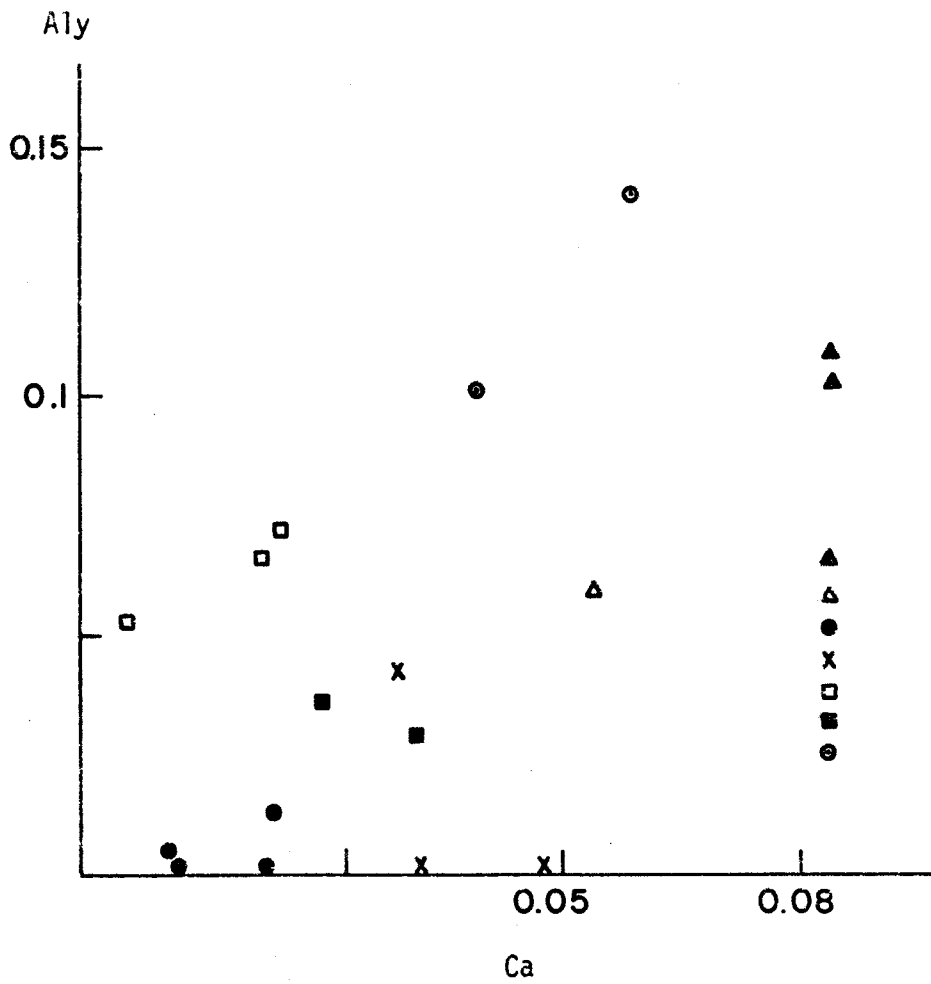


Figure 7. Relation between atomic proportion Aly and Ca in orthopyroxenes. Symbols as in Figure 6.

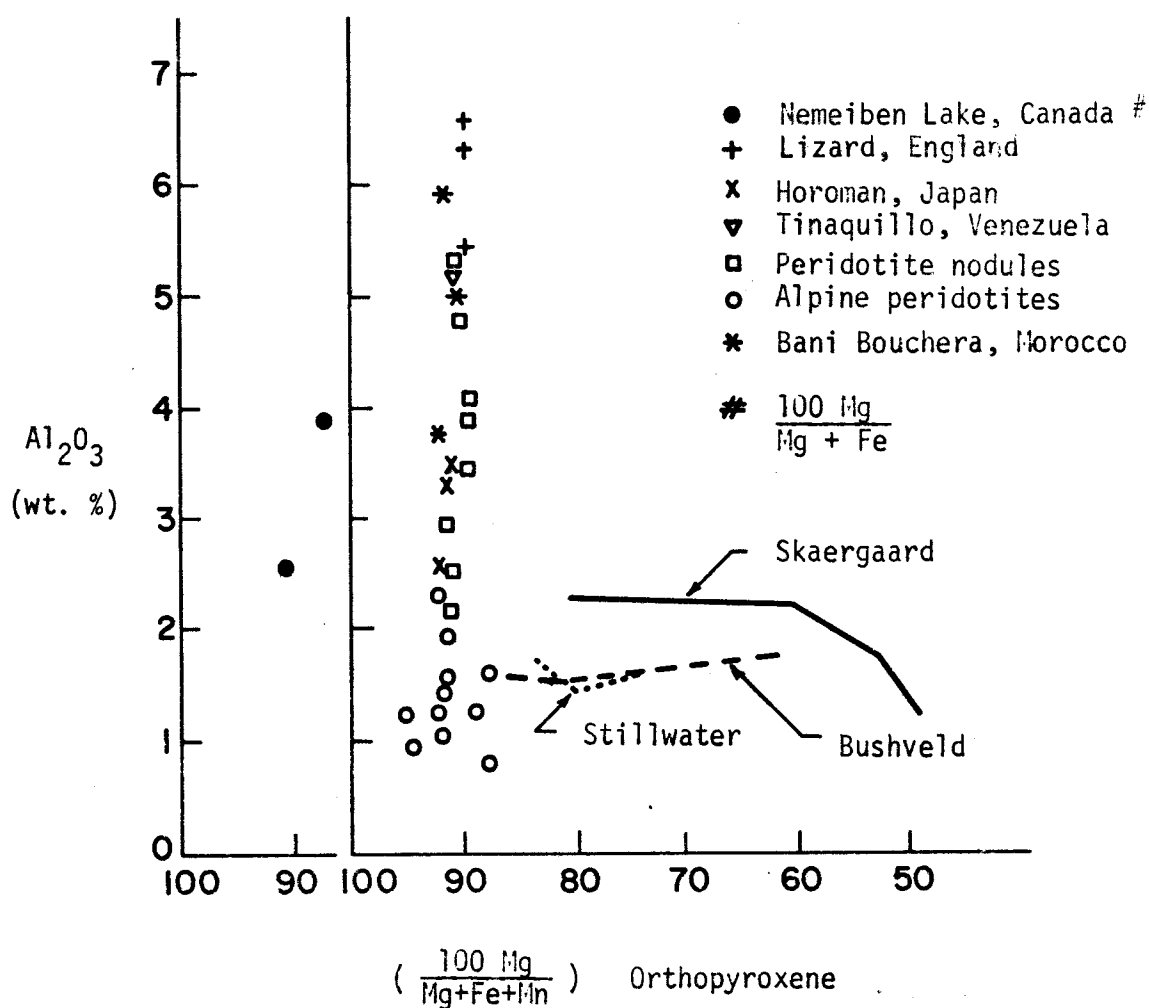


Figure 8.  $Al_2O_3$  contents of orthopyroxene from Nemeiben Lake pyroxenites compared with those from other ultramafic rock occurrences.

In Figure 6 the CaO contents of orthopyroxenes from various ultramafics are plotted with respect to the atomic proportion of Ca on the basis of  $O=6$ . The CaO contents of Nemeiben Lake orthopyroxenes are 1.1 and 1.7. They fall within the highest part of the range given by Ross, et.al., (1954) and Hess (1960) for the orthopyroxenes from intrusive peridotites of ultramafic magma, and correspond to the lower range of the orthopyroxenes from peridotite-inclusions in some basaltic rocks (Ross, et.al., 1954).

Hess (1960) has compared the CaO contents of orthopyroxenes from the layered intrusions of Stillwater, Great Dyke and Bushveld with the orthopyroxenes of the calcium-poor, ultramafic magma series, and with inverted pigeonites and pigeonites. Challis and Lauder (1966) state that the enstatites from the Great Dyke (Worst, 1958) and Stillwater Complex (Jackson, 1961) are not significantly different from those of "alpine" type ultramafics. The low CaO content of enstatites from "alpine" type rocks has been used (Hess, 1960) to support derivation from a Ca-poor ultrabasic magma, as distinct from enstatites with a higher CaO content in the Stillwater and Bushveld Complexes which have been considered as derived from basaltic magma. However the comparison is unsound because enstatites from bronzitites and norites (sometimes feldspar bearing) were compared with those from dunites and harzburgites. In other examples

of layered intrusions derived from basaltic magma, such as the Dawros and Belhelvie intrusions (Rothstein, 1958; 1962) the enstatites are as low in CaO as any from "alpine" type intrusions. The lime content of orthopyroxene has been interpreted as a qualitative and comparative temperature indicator. Kuno (1954) has shown that Ca is more abundant in natural orthopyroxenes formed at high temperatures, and experimental studies by Atlas (1952) and Boyd and Schairer (1964) substantiate this conclusion. The CaO content of orthopyroxene must also depend on the pressure and the composition of the system in which it is crystallized. Since the ionic radius of  $\text{Ca}^{+2}$  is larger than those of  $\text{Mg}^{+2}$  and  $\text{Fe}^{+2}$ , a higher lime content of orthopyroxene will be favored by higher temperature at the time of crystallization, and the maximum solubility of CaO in orthopyroxene at a given temperature and pressure will be obtained only when the system is sufficiently calciferous. Therefore, the lime contents of orthopyroxenes may be the most effective indicator of temperature, if the systems (the host rocks or magmas) are saturated with lime.

Consequently, the relatively high CaO contents in the orthopyroxenes from Nemeiben Lake possibly indicate rather high temperature in comparison to other ultramafic intrusives at the time of crystallization of orthopyroxenes.

#### IV.4. Clinopyroxene

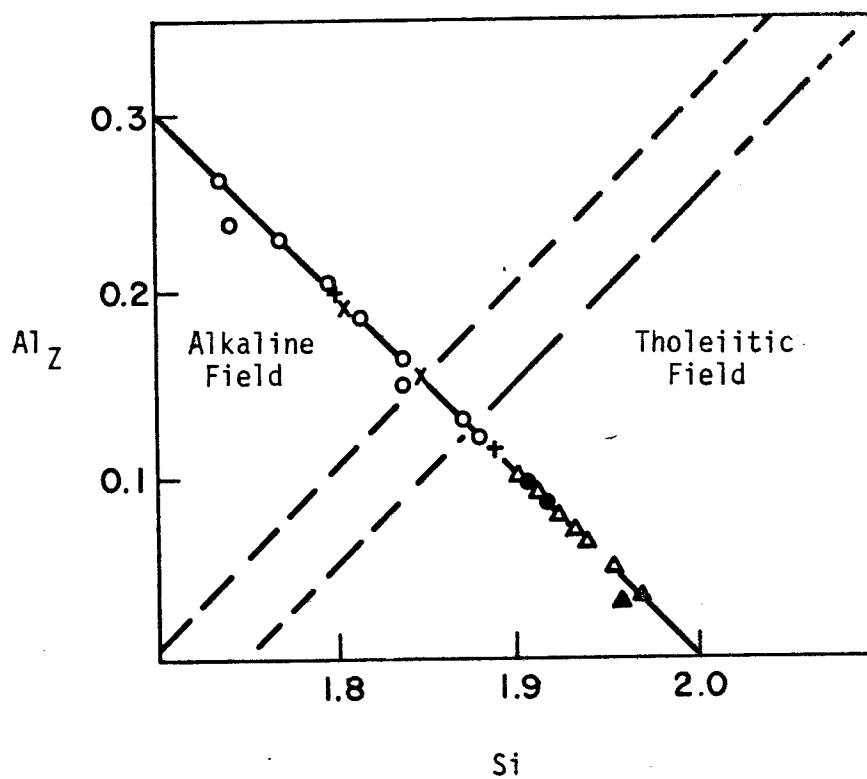


Clinopyroxene, commonly chromian diopside, is usually the last mineral to crystallize in dunites and harzburgites, and if the ultramafic rocks have crystallized from a magma the clinopyroxenes might reflect the composition of the magma.

Kushiro (1960), LeBas (1962), and Rothstein (1962) have stressed the chemical control of Al substitution for Si in igneous clinopyroxenes. LeBas (1962) has shown that if total  $\text{Al}_2\text{O}_3$  is plotted against  $\text{SiO}_2$  clinopyroxenes (excluding Fe-rich pyroxenes) from tholeiitic, alkaline and peralkaline rocks fall into three fairly well defined fields.

Kushiro (1960) has discussed the substitution of  $\text{Al}_2$  for Si in clinopyroxenes from tholeiitic and alkalic magma series and his analysis brings out the chemical control of this substitution in that deficiency of  $\text{SiO}_2$  in the magma increases the  $\text{Al}_2$  content of clinopyroxene. The same feature is brought out by the occurrence of extremely aluminous clinopyroxenes (Lassaites) in metamorphosed limestone xenoliths (Tilley, 1938; Knopf and Lee, 1957).

The relationships between atomic proportion of Si and  $\text{Al}_2$  of clinopyroxenes from various ultramafics including Nemeiben Lake are compared with each other in Figure 9. On this plot Nemeiben Lake clinopyroxenes fall in the higher  $\text{Al}_2\text{O}_3$  and lower  $\text{SiO}_2$  region, namely the alkaline field of igneous rocks.



- Red Hills, Dun Mt., Red Mt.
- Nodules
- ▲ Twin Sisters, Webster
- △ Stillwater, Skaergaard, Bushveld
- x Nemeiben Lake, Canada
- + Lizard

Figure 9. Plot of  $Al_Z$  substitution in clinopyroxenes from ultramafic rocks. In this calculation the Z group has been made equal to 2.

As shown in Figure 10, clinopyroxene from Nemeiben Lake ultramafic body has a relative composition of En 89.42-92.02.  $Al_2O_3$  contents are comparable to those from Horoman peridotite (Onuki, 1965) lower than those of clinopyroxenes from ultramafic inclusions and megacrysts in basalts (Aoki and Kushiro, 1968; Binns, et.al., 1970) and are higher than alpine peridotites and stratiform basic intrusions (cited in Green, 1964). An interesting comparison is that of  $Al^{iv}$  against  $Al^{vi}$  using the suggestion by Thomson (1947) that in silicate structures, Al tends to enter into the tetrahedral site at higher temperatures and into octahedral site at higher pressures. Aoki and Kushiro (1968) compared the properties of  $Al^{iv}$  and  $Al^{vi}$  in clinopyroxenes from various environments. They found that clinopyroxenes from igneous rocks have the Al mostly in tetrahedral sites, whereas those from eclogites have Al mostly in octahedral sites. Clinopyroxenes from granulites and from inclusions in basalts have Al in both sites and fall in a region between the other two. Nemeiben Lake clinopyroxenes along with those of other ultramafic intrusions fall in the field of granulites and inclusions in basalts as shown in Fig. 11.

#### IV.5. Partitioning of Elements

The partition of minor elements between co-existing minerals has been suggested as a generally applicable

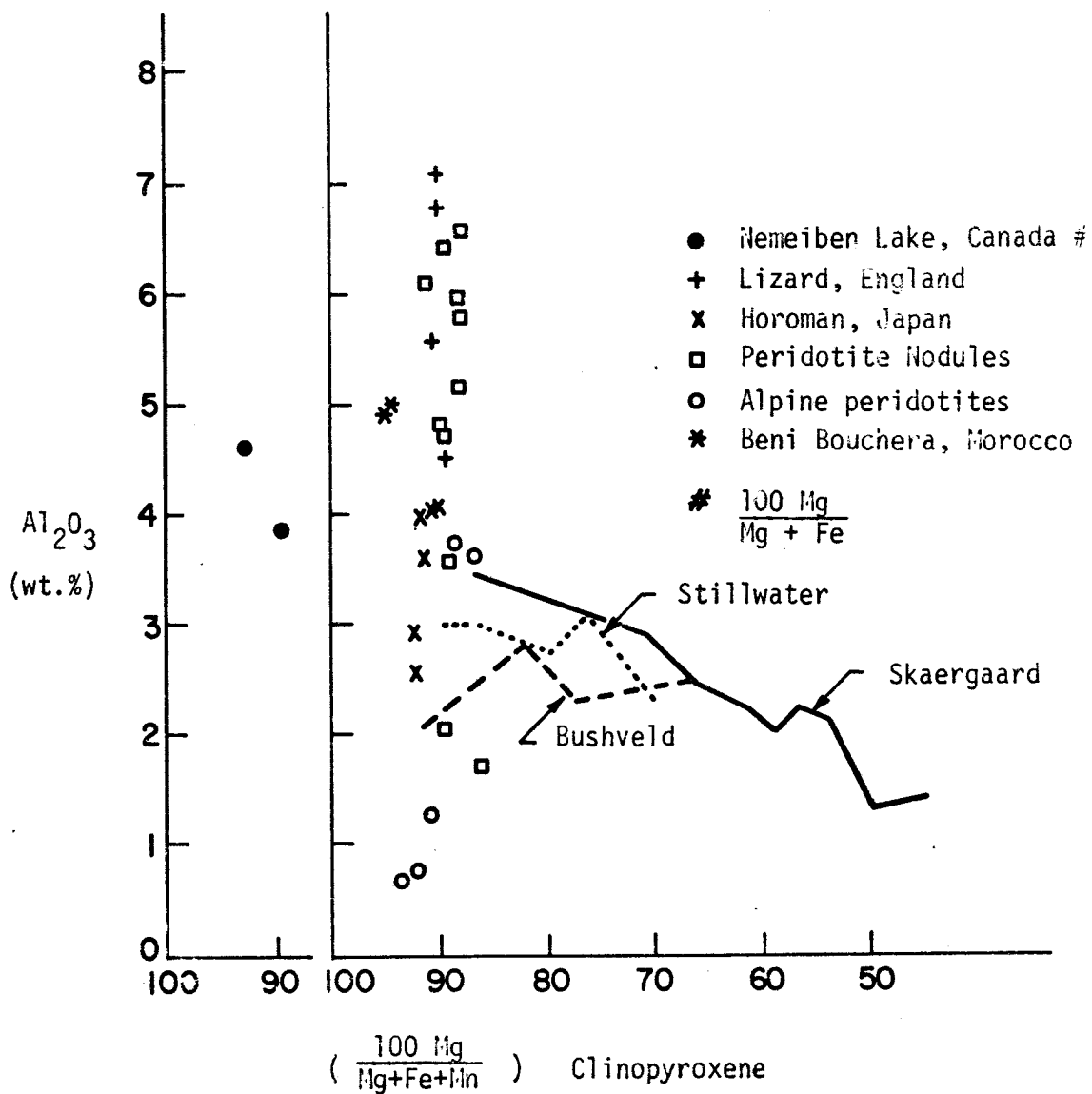


Figure 10. Contents of clinopyroxene from Nemeiben Lake pyroxenites compared with those from other ultramafic rock occurrences.

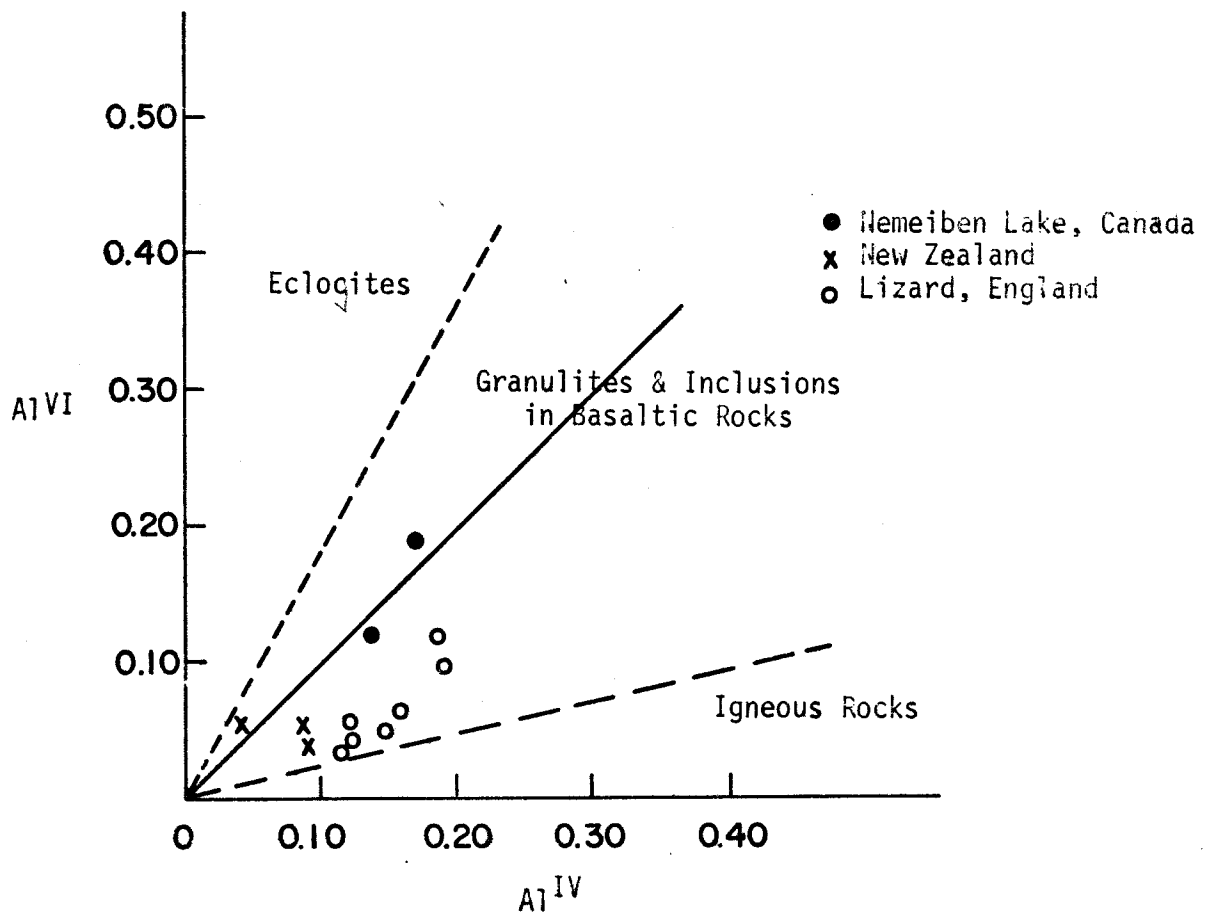


Figure 11. Plot of Al<sup>VI</sup> against Al<sup>IV</sup> for Clinopyroxenes from Nemeiben Lake compared with other ultramafic rocks.

geothermometer (Friedman, 1949; Holland, 1956; McIntire, 1963; and many others). Barton (1970) and Barton and Skinner (1967) have pointed out the advantage of using the distribution of elements between co-existing minerals as opposed to using the element content of a single mineral in the estimation of environmental conditions. Study of the distribution of elements among co-existing minerals potentially gives us information both of petrogenetic significance and of the attainment of chemical equilibrium and the indication of physical conditions of formation of the rock. To be useful, these results must first be analysed in terms of the solid solution relationships and other di-ochic substitutions in the minerals.

The partition of elements between co-existing pyroxenes has been discussed by many authors namely Ramberg and DeVore (1951), Kretz (1961), Bartholomé (1962), Muller (1961, 1962a,b).

#### IV.5.1. Iron and Magnesium in Co-existing Pyroxenes

The distribution of Mg and Fe<sup>+2</sup> between orthopyroxene (Ca-poor) and clinopyroxene (Ca-rich) which are presumed to be in equilibrium has been expressed most simply by Bartholomé (1961, 1962):

$$K_T = (\text{Fe}^{+2}/\text{Mg})_{\text{Opx}} / (\text{Mg}/\text{Fe}^{+2})_{\text{Cpx}}$$

Concentrations of Fe and Mg are expressed in mole fractions in above equation. In the more complex equation derived by

Ramberg and DeVore (1951) and used by Kretz (1961, b) the term  $K_D$  is the reciprocal of  $K_T$ . Because of the inability to distinguish quantitatively between  $Fe^{++}$  and  $Fe^{+++}$  by means of the microprobe, the Fe contents of the silicates under consideration have been given in terms of total Fe as FeO. The distribution coefficients  $K_D$  for Nemeiben Lake pyroxenes have been calculated using  $(Fe^{++} + Fe^{+++})$  for iron contents and the relation Mg:total Fe gives a better approximation to the bulk chemical reactions involved in exchange equilibrium between these minerals. The average  $K_D$  value for the Nemeiben Lake pyroxene pairs is 0.8086.

Muller (1961), Kretz (1961) and Bartholomé (1962) have examined K'Mg-Fe between natural pyroxenes from various geological environments and concluded that pyroxenes behave as ideal solutions. Kretz (1961) has given  $K_D$  values with a range of 0.51 to 0.602 for high grade metamorphic assemblages, from 0.689 to 0.769 for rocks crystallizing from a magma, particularly the differentiated basic magmas such as the Skaergaard, Stillwater, and Bushveld complexes, and from 0.769 to 1.1 for co-existing pyroxenes from peridotite nodules in basalts. Sexana (1968) found the  $K_D$  value ranged between 0.501 and 0.647 (average 0.556) for 41 metamorphic pyroxene pairs, while for 13 igneous pyroxenes pairs it ranged between 0.536 and 0.857 (average 0.717). Atkins (1969) has given an average  $K_D$  value of

0.76 from Bushveld pyroxene pairs and he considers the lower  $K_D$  value to be a function of different P-T conditions relative to those existing for the Skaergaard and Stillwater intrusions (Brown, 1957; Hess, 1960; Kretz, 1961b). The average  $K_D$  value for Nemeiben Lake pyroxene pairs is higher than the average value for igneous pyroxene pairs particularly differentiated basic magma. If variations in  $K_D$  are related essentially to the temperature of crystallization of pyroxene pairs, provided that they are ideal mixtures of Mg and  $Fe^{+2}$ , then  $\ln K_D$  may be used as a rough temperature (and pressure) scale (Ramberg & DeVore, 1951). This has been done by Sexana (1968), who noted the close similarity in shape between the pyroxene solvus and the curves resulting from a plot of  $\ln K_D$  against  $(Mg, Fe)SiO_3$ . Nemeiben Lake pyroxene pairs plotted on a diagram such as that given by Sexana (1968, Fig. 2), plot above the range of other plutonic igneous pyroxenes. The very different  $K_D$  values of Nemeiben Lake pyroxene pairs show that, if the temperature dependency of  $K_D$  is valid, then these pyroxenes have crystallized well above the liquidus temperatures of the other igneous intrusions cited such as the Skaergaard, Stillwater or Bushveld.

The distribution of Mg and Fe in co-existing clinopyroxene and orthopyroxenes from Nemeiben Lake pyroxenite is shown in Fig. 12; also shown is the tentative diagram from Kretz (1963), in which  $K_D$  and temperature are correlated.



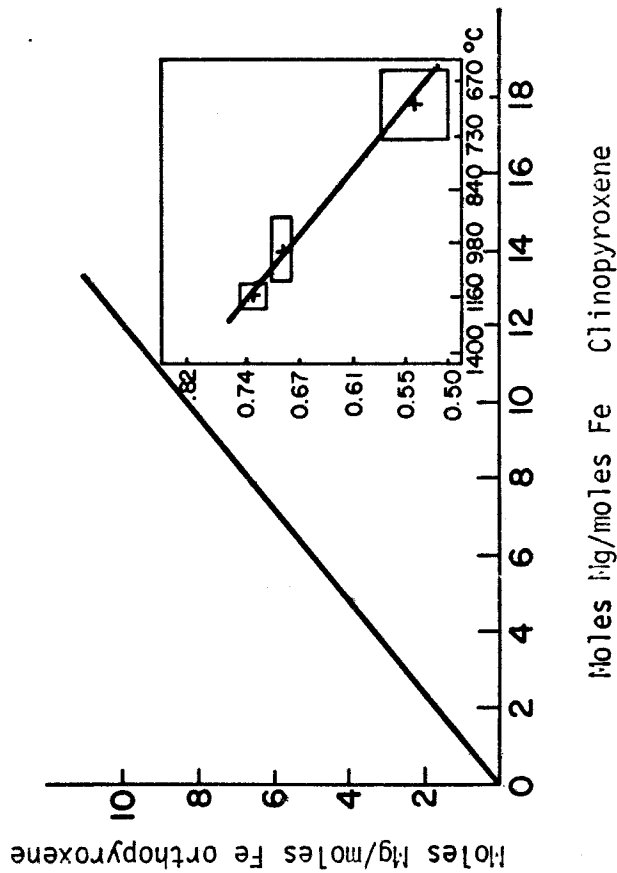


Figure 12. The distribution of Hg and Fe between orthopyroxene and clinopyroxene of the Nemeiben Lake rocks.

Inset: the diagram of Kretz (1963) relating the Hg/Fe distribution coefficient of co-existing pyroxenes with temperature.

Using Kretz's diagram the  $K_D$  value of Nemeiben Lake ultramafics yields a temperature of around  $1350^\circ\text{C}$ .

However, Kretz (1963), and O'Hara & Mercy (1963) have expressed doubts as to the dependence of  $K_D$  for pyroxenes solely on variations in P-T conditions. Brown (1967) considers that the distribution of Mg and  $\text{Fe}^{+2}$  between igneous pyroxenes in equilibrium crystallization is complicated by too many unknown factors to allow for precise evaluation at present.

It has long been established that the distribution coefficient in general is dependent mainly upon temperature (Albee, 1965), less so on pressure and, in some cases upon concentrations of other elements. Binns (1962) found that the  $K_D$  values of pyroxene pairs in the high grade metamorphic terrain around Broken Hill, Australia did not follow the pattern predicted by Kretz (1961b, 1963), but that  $K_D$  was also composition dependent. The dependency of  $K_D$  upon temperature is usually treated on the assumption that the co-existing minerals form ideal solid solutions. Since it has been established that the orthopyroxene series is not completely an ideal mixed crystal series (e.g. Ramberg & DeVore, 1951; Burns, 1968) the  $K_D$  values cannot be used directly as rigorous indicators of temperatures of crystallization. (cf Sexana, 1968). Moreover the relatively high  $\text{R}_2\text{O}_3$  content of Nemeiben Lake pyroxenes is likely to affect the Mg- $\text{Fe}^{+2}$  distribution

(Brown, 1961). Thus as shown by Binns (1962) the  $K_D$  values will vary with variations in the  $Fe^{+2}/Mg$  ratios of the pyroxenes.

The  $K_D$  values for pyroxene pairs from Nemeiben Lake are comparable with  $K_D$  values from Horoman, Japan  $K_D=0.76$  to 0.79 and the  $K_D$  in the Lizard intrusion pyroxenes is very close to 0.73. The pyroxenes from peridotite inclusions in basaltic rocks have  $K_D$  values in the range 0.75 to 0.85. These values are not greatly different from those of Nemeiben Lake. Peridotite inclusions are currently considered as xenoliths of the mantle materials, and Green (1964) has considered that the primary peridotites crystallized under conditions similar to that indicated for the peridotite inclusions.

#### IV.5.2. Partitioning of Fe and Mg between Olivine and Orthopyroxene

Since the appearance of Ramberg and DeVore's paper (1951), naturally occurring olivine-orthopyroxene assemblages have been investigated by Ross, Foster, and Meyers (1954), Ringwood (1961), Bartholomé (1962), O'Hara (1963), and many others. Mueller (1964) attempted to predict the effect of temperature on  $Fe^{++}-Mg^{++}$  partitioning on the basis of thermodynamic considerations, utilizing data from experimental studies by Bowen and Schairer (1935), Muan and Osborn (1956), and Ernst (1960). However, because none of

these experimental studies were specifically designed to investigate element partitioning, there was insufficient data available for the precise determination of the temperature dependence of partitioning.

The distribution of Mg and total Fe between the mineral pair olivine-orthopyroxene from Nemeiben Lake ultramafic is illustrated in Figure #13 along with other ultramafic bodies. Experimental investigations (Larimer, 1969; Medaris, 1969) have established that the distribution of Mg and Fe between olivine-orthopyroxene is relatively insensitive to changes in temperature.

Williams and Engster (1969), also have recently shown that the distribution of iron and magnesium between olivines and pyroxenes is independent of temperature and cannot be used as a geothermometer. Olivine-orthopyroxene pairs from Nemeiben Lake pyroxenites plot close to the distribution curve determined experimentally at 900°C and 500 bars pressure (Fig. 13). With the exception of one plot, olivine-orthopyroxene pairs from alpine peridotites (Green, 1964; Challis, 1965) cluster about the experimental curve and presumably represent equilibrium assemblages.

Olivine-orthopyroxene pairs from Nemeiben Lake ultramafic rocks and alpine peridotites plot close to the experimental curve, emphasizing the mineralogical and chemical similarities between these two groups.

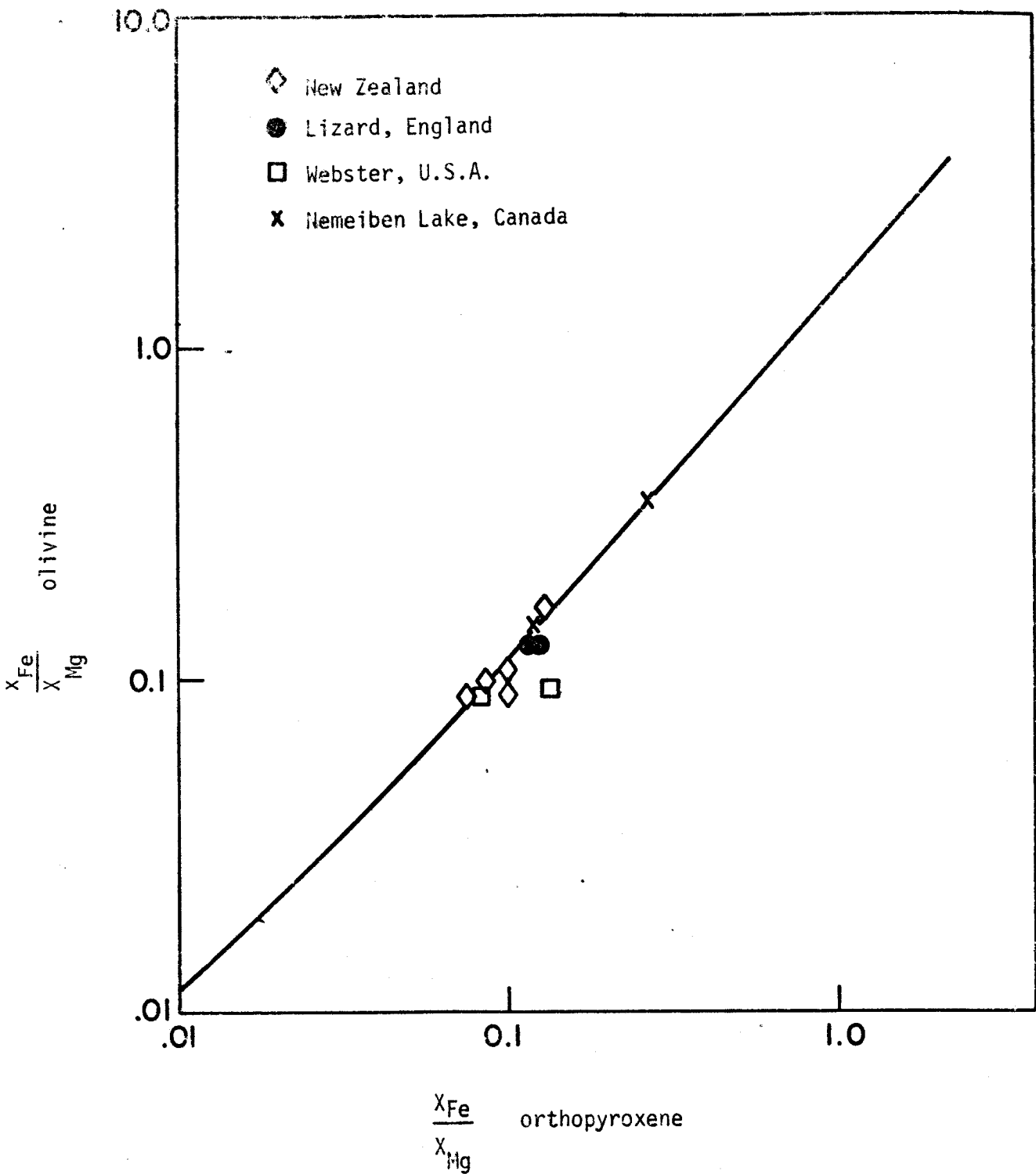


Figure 13. Comparison of experimental partitioning at 900°C with compositions of co-existing olivine and orthopyroxene in natural rocks. Experimental curve is shown by solid line.

#### IV.5.3. Nickel Fractionation between Olivine and Clinopyroxene

The nickel fractionation data from Makaopuhi lava Lake (Häkli and Wright, 1967) apparently indicates that by determining the concentration of nickel in co-crystallizing olivine and clinopyroxene, it is potentially possible to estimate the crystallization temperature to a considerable degree of accuracy. Nickel is a good choice as a trace element for this purpose for two reasons:

- (1) Nickel has an affinity for the earliest minerals to crystallize, with the result that its distribution is sensitive to temperature over a wide range of liquidus temperatures.
- (2) The determination of even a low nickel concentration can be carried out conveniently and with sufficient accuracy using an electron probe microanalyser.

However, a great deal of experimental data must yet be gathered, particularly in regard to the influence of pressure and chemical composition upon the numerical value of the partition coefficient, before the fractionation of nickel between olivine and clinopyroxene can be used as a reliable geothermometer. Using Häkli and Wright's (1967) data, the Nemeiben Lake ultramafic body crystallization temperature is estimated at  $1165^{\circ}\text{C}$  (average).

#### IV.6. Temperature-Pressure Estimates based on Clinopyroxene Composition

The stability relations of high pressure mineral assemblages in ultramafic rocks have now been experimentally established (summarized by O'Hara, 1967a and MacGregor, 1967). The most striking feature of these experiments is the successive accommodation of  $\text{Al}_2\text{O}_3$  in plagioclase, spinel, and garnet in the increasing pressure, resulting in the facies diagram for lherzolite depicted in Figure 12.3 of O'Hara (1967b).

O'Hara (1967b) has further refined this facies diagram by deriving a petrogenetic grid based on the composition of clinopyroxene co-existing with olivine, orthopyroxene, and an aluminous phase, either plagioclase, spinel, or garnet. A specific point is located on the petrogenetic grid by calculating from a clinopyroxene chemical analysis the factors  $\alpha_c$  and  $\alpha_c$ , related to the  $\text{CaSiO}_3$  and  $\text{R}_2\text{O}_3$  contents, respectively, of the clinopyroxene (O'Hara, 1967b p. 395), and plotting these values in relation to two intersecting sets of contours for  $\alpha_c$  and  $\alpha_c$  on the grid. Because total Fe is ordinarily given as FeO in probe determinations, values of  $\alpha_c$  and  $\alpha_c$  obtained from probe analyses will plot on the grid at slightly higher temperatures and lower pressures than would be the case if independent determinations were made for  $\text{Fe}_2\text{O}_3$  and FeO. Clinopyroxene compositions from Nemeiben Lake ultramafic rocks

plot at uniformly high temperatures between  $1100^{\circ}\text{C}$  and  $1200^{\circ}$  and a pressure range 5 to 9 kbars. (Fig. 12.4, O'Hara's 1967b).

In addition to Nemeiben Lake ultramafic, high temperature recrystallization has so far been recorded in five other ultramafic masses. The lizard peridotite (Green, 1964) has been recrystallized under conditions prevailing in the spinel lherzolite field, but plagioclase appears in the later anhydrous assemblages. Kornprobst (1969) has proposed that the Beni Bouchera peridotite in Morocco was derived by partial fusion of a fragment of upper mantle at about  $1500\text{ C}$  and 25 kbars, followed by re-equilibration with decreasing temperatures and pressures in spinel lherzolite field. The Miyamori peridotite, Japan (Onuki, 1965), and the Dawors peridotite in Ireland (Rothstein, 1957; 1958), have been recrystallized at lower pressures within the plagioclase lherzolite field. The Horoman ultramafic complex, Japan, has been interpreted as a layered intrusion (Nagasaki, 1966; Onuki, 1965) but application of O'Hara's grid and textural relations described by Nagasaki suggest that subsequent to intrusion, the Horoman complex may have been recrystallized at temperatures and pressures within the plagioclase lherzolite field.

It should be emphasized that O'Hara's petrogenetic grid is provisional at present, the experimental control of the grid is provisional at present, the experimental control



of the grid being more precise for the garnet lherzolite field than for the spinel and plagioclase lherzolite fields. Thus, petrogenetic interpretations based on the present form of O'Hara's grid will need to be re-evaluated as additional experimental data become available.

#### IV.7. Ca/Ca+Mg+Fe ratios in Clinopyroxenes

From experimental work by Boyd and Schairer (1964) and Davis and Boyd (1966) the solubility of  $\text{MgSiO}_3$  in co-existing clinopyroxene has been shown to be largely a temperature effect, and much less a pressure effect. In Figure 14 the diopside solvus in the system  $\text{CaMgSi}_2\text{O}_6 - \text{Mg}_2\text{Si}_2\text{O}_6$  at 1 atm from Boyd and Schairer and 30kb from Davis and Boyd is drawn together with the Ca/CA+Mg+Fe ratios of clinopyroxenes (average) from Nemeiben Lake ultramafic. The equilibrium temperature for the clinopyroxenes derived in this way lies between  $1100^\circ - 1170^\circ \text{C}$ .

The experimental data referred to above do not take into account the influence of Fe, and the influence of trivalent cations on the pyroxene field is not yet quantitatively known. However by taking Fe and Al into account the equilibrium temperature will be decreased.

#### IV.8. Summary on Temperature and Pressure estimates of the Nemeiben Lake Ultramafic Body

It is difficult to fix the absolute P-T conditions for

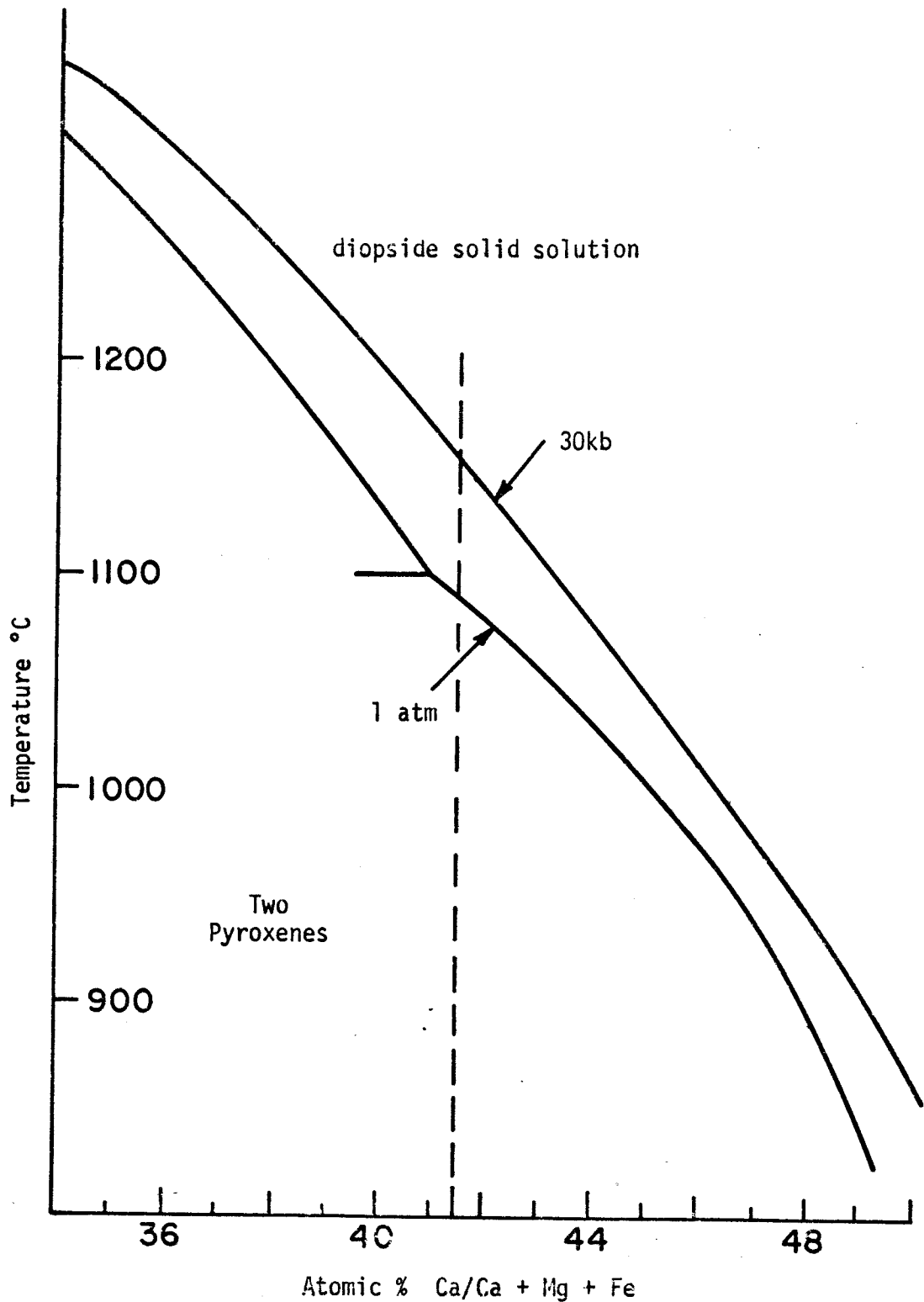


Figure 14. The diopside solvus in the system  $\text{CaMgSi}_2\text{O}_6 - \text{Mg}_2\text{Si}_2\text{O}_6$  at 1 atm from Boyd and Schairer (1964) and at 30kb from Davis and Boyd (1966). The composition of the clino-pyroxenes (average) from Nemeiben Lake are indicated (dashed line).

the crystallization of the Nemeiben Lake ultramafic body because of the uncertainties involved when comparing results derived from synthetic, or natural systems in the laboratory with actual rocks. However, on the basis of chemical studies on the rock forming minerals, even though the data is limited, the following points can be summarized.

1. Various writers have suggested that the  $\text{Al}_2\text{O}_3$  content of pyroxenes is a pressure controlled feature, e.g. Hess (1960), Green (1964). The orthopyroxenes of Nemeiben Lake intrusion contain about 3.06 (average)  $\text{Al}_2\text{O}_3$ . These values although below those observed in pyroxenes from peridotite nodules, are higher than those from layered mafic intrusions, such as Stillwater. They correspond to the values obtained by Green (1964) on recrystallized peridotite assemblages from the Lizard area and suggest pressures intermediate between upper mantle and upper crustal environments.
2. The equilibrium temperature for clinopyroxenes using  $\text{Ca}/(\text{Ca}+\text{Mg}+\text{Fe})$  ratio lies between  $1100^\circ\text{C}$ - $1170^\circ\text{C}$ . This is lower than the temperature found from Mg-Fe distribution using Kretz's diagram (about  $1350^\circ\text{C}$ ). Peters (1968) found similar discrepancies when estimating the equilibrium temperature of pyroxenes from the Tolalap serpentinite. He explained the discrepancy by showing that the high  $\text{Al}_2\text{O}_3$  contents of the pyroxenes tend to shift the  $\text{Ca}/(\text{Ca}+\text{Mg})$  ratios to higher values because  $\text{Al}_2\text{O}_3$

tends to increase the miscibility gap between enstatite and diopside.

3. The temperature of crystallization using  $\text{Ca}/(\text{Ca}+\text{Mg}+\text{Fe})$  ratio in clinopyroxenes ( $1100^{\circ}\text{C}$ - $1170^{\circ}\text{C}$ ) is very close to the one determined from nickel fractionation between olivine and clinopyroxene ( $1165^{\circ}\text{C}$  average).
4. Using O'Hara's petrogenetic grid, clinopyroxenes compositions from Nemeiben Lake ultramafic rocks plot at high temperatures between  $1100^{\circ}\text{C}$  and  $1200^{\circ}\text{C}$  and a pressure range of 5 to 9 K-bars.
5. By summing up, the best possible temperature and pressure conditions which can be attributed to the Nemeiben Lake ultramafic body are between  $1100^{\circ}\text{C}$ - $1200^{\circ}\text{C}$  and 5 to 9 K-bars respectively.

## V. GEOCHEMISTRY OF ELEMENTS

### V.1. Introduction

In this section the distribution and variation of each element (Silica, Alumina, Iron, Magnesium, Titanium, Calcium, Nickel, Copper, Chromium) is discussed and a comparison is made of the data from this study with the values reported in the literature for similar rocks.

Partial chemical analysis (See Appendix II for various procedures of chemical analysis) of bulk rock samples of the serpentinites and other ultramafic rocks are given in Table VI. For comparison purposes an attempt was made to recalculate the serpentinite analyses to an original water free composition (assuming a water content of 10% by wt.). Following the discussion of the problem of serpentinization it was decided that such recalculations of the bulk rock serpentinite analyses provide the best available approximations to the primary pre-serpentinization compositions of these rocks. Partly serpentinized pyroxenite, and uraltized pyroxenite analyses were not recalculated to a water free basis.

### V.2. Silicon

This element is estimated to constitute about 27.2 wt. percent (as Si) of the crustal rocks. Variations in silica content ( $\text{SiO}_2$ ) are one of the most significant factors in

TABLE VI

## Average Compositions of Nemeiben Lake Ultramafic Rocks

OXIDE %	* SERPEN- TINITES	** PARTLY SERPEN- TINIZED PYROXENITE	** URALITIZED PYROXENITE	PYROXENITE	*** GABBRO
SiO <sub>2</sub>	46.32	48.48	52.43	54.31	52.15
MgO	37.90	29.12	20.55	23.20	9.1
CaO	0.25	12.92	17.30	13.31	10.9
Al <sub>2</sub> O <sub>3</sub>	1.16	01.89	3.12	2.20	17.7
FeO	14.25	7.41	6.38	6.78	6.5
TiO <sub>2</sub>	0.09	0.16	0.19	0.16	0.37
<u>Trace Elements (ppm)</u>					
Ni	3000	1203	360	558	57
Cr	3637	3590	3205	3557	40
Cu	1520	458	173	203	122
Zn	84	79	83	72	34

\* recalculated anhydrous

\*\* not recalculated anhydrous but made to 100%

\*\*\* raw gabbro results

the differentiation of igneous rocks. The variation in silica content for different ultramafic rocks from Nemeiben Lake is shown in Fig. 15. As in the case of most major elements, the silica content of the rocks under consideration is reflected in the nature and amounts of the dominant mineral phases present, and its variation explained accordingly. The silica content of Nemeiben Lake ultramafic rocks, as is to be expected, is low in serpentinites and partly serpentitized pyroxenites (reflecting the relative abundance of olivine compared to pyroxenite and gabbro).

In the ultramafic rocks silica content shows a tendency to vary sympathetically with Ca. This can be interpreted to indicate that both of these elements increase in amount during fractional crystallization of the ultramafic magmas (provided that one accepts the interpretation that pyroxenites represent a differentiation product of peridotites or ultramafic magma).

### V.3. Magnesium

The variation of magnesium content in the Nemeiben Lake ultramafic rocks is shown in Fig. 15. The main hosts for magnesium in ultramafic rocks are olivine and pyroxene. In Nemeiben Lake ultramafic rocks the adjusted (recalculated on water free basis) serpentinite has MgO content of 37% indicating the predominance of olivine, partly serpentitized pyroxenite has a MgO content of 29% reflecting lesser

amounts of olivine than in more serpentized rocks, whereas pyroxenite has an average of 23% MgO reflecting the relative absence of olivine. The gabbroic rocks contain 12% MgO which is a reflection of a significant decrease in the content of ferromagnesian minerals.

The Mg content normally decreases during a fractional crystallization sequence and there is usually a sympathetic relationship with nickel contents.

#### V.4. Calcium

In ultramafic rocks free of plagioclase, calcium is concentrated in paragenetically later formed clinopyroxene and amphibole, whereas olivine and orthopyroxene are calcium poor. In the gabbroic rocks calcium content is high due to an abundance of basic plagioclase. This relationship among calcium contents in the Nemeiben Lake ultramafic body is shown in Fig. 15. Data for average calcium content are given in Table VI.

#### V.5. Aluminum

Figure 16 shows the variation of aluminum in different Nemeiben Lake ultramafic rocks and for comparison the aluminum contents of different rock types from the literature are given in Table VIII.

Aluminum may substitute in Y or Z positions in the general pyroxene and amphibole group formulas. In order



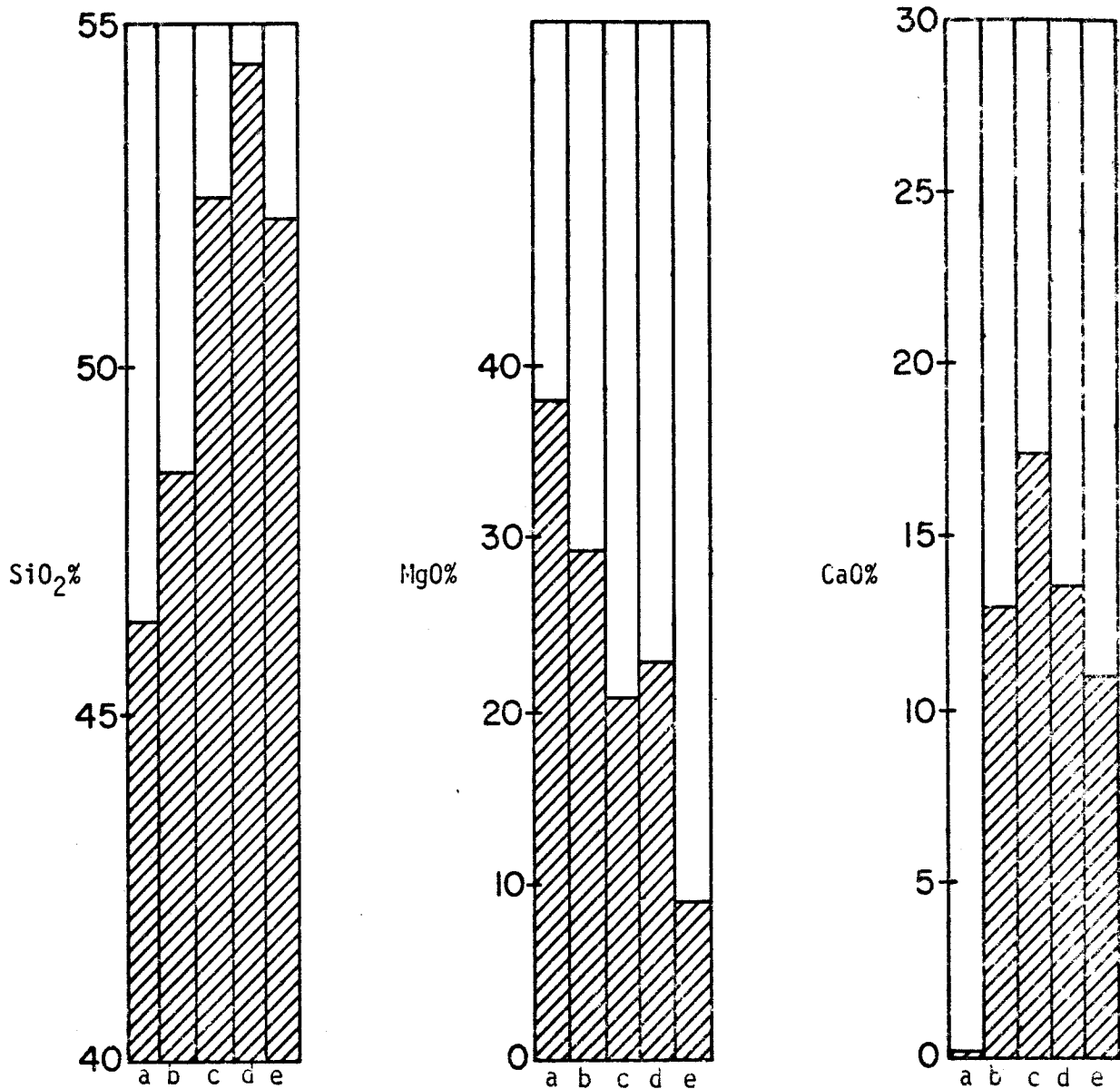


Figure 15. Average chemical composition of Nemeiben Lake ultramafic rocks.

- a. Serpentinite
- b. Partly serpentinized pyroxenite
- c. Uralitized pyroxenite
- d. Pyroxenite
- e. Gabbro

to maintain neutrality the substitution of ions of different charges in the (X,Y) group requires complementary substitutions in either W or Z positions in the pyroxenes and in the X or Y positions in the amphiboles.

Three analyses of bronzites have 2.69, 1.50 and 1.52 wt.%  $\text{Al}_2\text{O}_3$  respectively (Deer, et.al., 1963). Two diopsides from ultramafic rocks have 1.87 and 2.08 wt.%  $\text{Al}_2\text{O}_3$  (Deer, et.al., 1963). Sixteen analyses of diopside-salite from clinopyroxenites of the Urals have a range of 1.19 to 7.24%  $\text{Al}_2\text{O}_3$  and an average of 3.82%  $\text{Al}_2\text{O}_3$  (Malakhov, 1964). The serpentinites from Nemeiben Lake are relatively low in alumina, averaging about 1%. There is a slight increase as the rocks become pyroxene rich (pyroxenite, uralitized and partly serpentitized pyroxenite). Followed by a marked increase as plagioclase becomes an important constituent in gabbroic rocks.

#### V.6. Iron

Variation of iron content of the ultramafic rocks and the gabbroic rock is shown in Figure 16. The range of total iron is 14.25%-6.5%. In the Nemeiben Lake serpentinites much of the variation in iron content can be related to the variation in the amount of the sulphide phases present.

#### V.7. Titanium

Figure 16 shows the variation in titanium content from Nemeiben Lake ultramafic rocks, the  $\text{TiO}_2$  content has a range 0.09% to 0.10%. The gabbroic rock has  $\text{TiO}_2$  0.37%. Turekian and Wedepohl's (Table VII) titanium value for ultramafic is low probably because of inclusion of dunite and other olivine-rich rocks.

Figure 17 shows a plot of Ti content of orthopyroxene against that of co-existing clinopyroxene from Nemeiben Lake along with other ultramafic and related rocks and the relation is discussed under the heading chromium.

#### V.8. Chromium

Chromium contents of the Nemeiben Lake ultramafic rocks are compared with average chromium contents of ultramafic rocks from the literature and are given in Table IX. Chromium content in the ultramafic and mafic rocks given by Goldschmidt (1954, p. 549) is 1000-4400 ppm and 100-400 ppm respectively, and in this respect, the Nemeiben Lake ultramafic do not show any abnormality. Yefimov and Ivanova (1963) have observed that pyroxenites and wehrlites do not contain chromite, but the principal mineral diopside carries up to 0.34%  $\text{Cr}_2\text{O}_3$ , with the magnesian varieties being richer in chromium. They also observed that enstatite from harzburgite contained 0.3%  $\text{Cr}_2\text{O}_3$ .

Most of the chromium in serpentinites from Nemeiben

TABLE VII

Analysis of Ultramafic Rocks from the Literature

Oxide	Ultramafic I	Ultramafic II	Ultramafic III
SiO <sub>2</sub>	43.9		
TiO <sub>2</sub>	0.03		
Al <sub>2</sub> O <sub>3</sub>	3.8		
FeO	12.1		
MnO	0.209		
MgO	33.8		
CaO	3.5		
K <sub>2</sub> O	0.004		
Trace elements			
Ni	2000ppm	2000ppm	2000ppm
Cu	10	10	20
Zn	50	50	30
Cr	1000		2000
Co	150		200

I. Turekian and Wedepohl (1961)

II. Taylor (1966)

III. Vinogradov (1962)

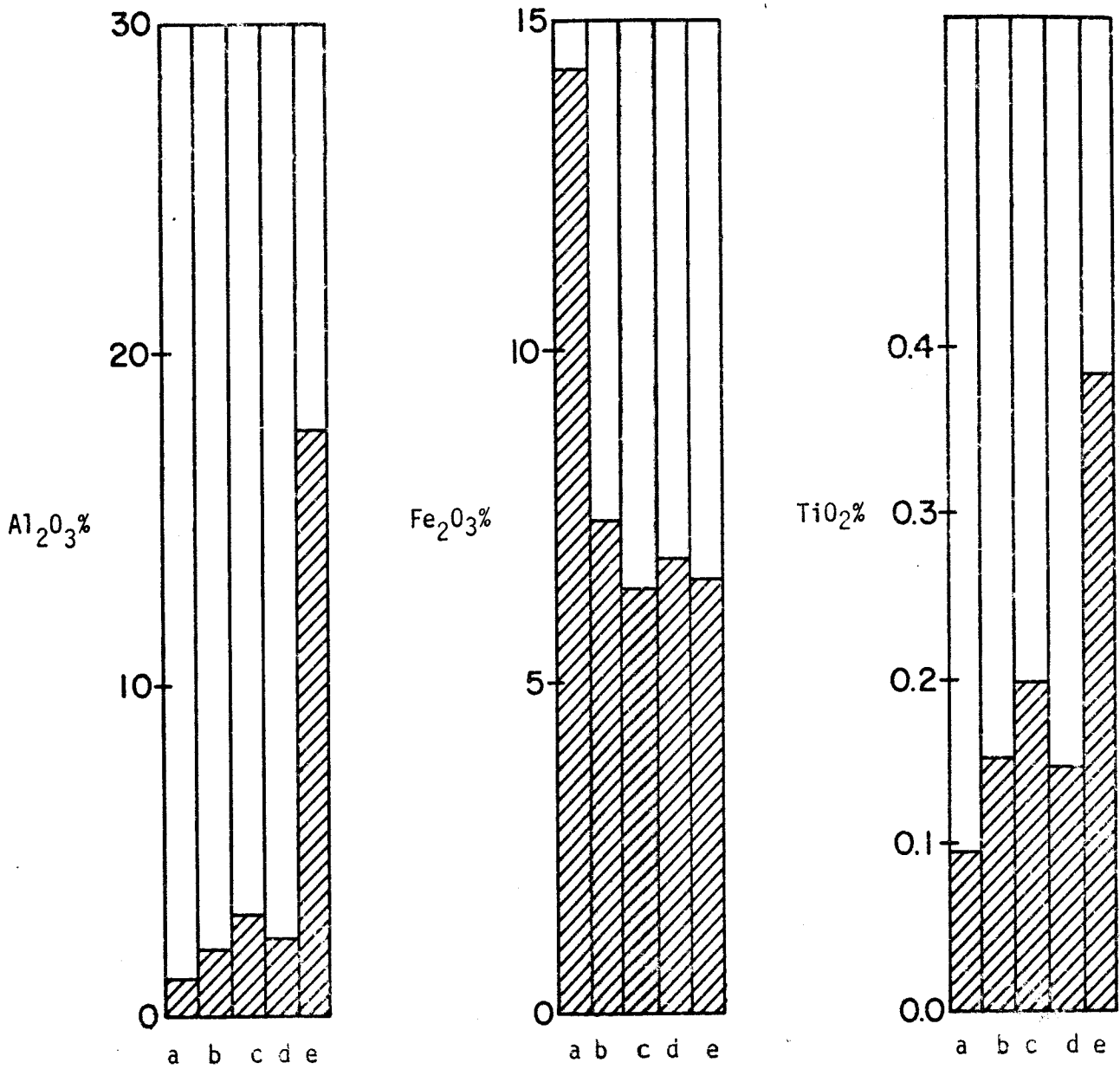


Figure 16. Average chemical composition of Nemeiben Lake ultramafic rocks.

- a. Serpentinite
- b. Partly serpentinized pyroxenite
- c. Uralitized pyroxenite
- d. Pyroxenite
- e. Gabbro

TABLE VIII

## Alumina in Ultramafic Rocks of Urals

Rock type	%Al <sub>2</sub> O <sub>3</sub>	No. of analyses	Range from to	
			Min.	Max.
Dunites	0.75	342		
Harzburgites	2.06	400		7.74
Lherzolites	2.63	10	1.57	9.98
Wehrlites	3.90	20	0.34	9.91
Enstatites and Bronzites	3.68	18	1.05	11.69
Websterites	3.34	11	1.12	9.25
Diallagites (or Clino- pyroxenites)	3.48	176	0.37	12.95

Source: Malakhov, 1964.

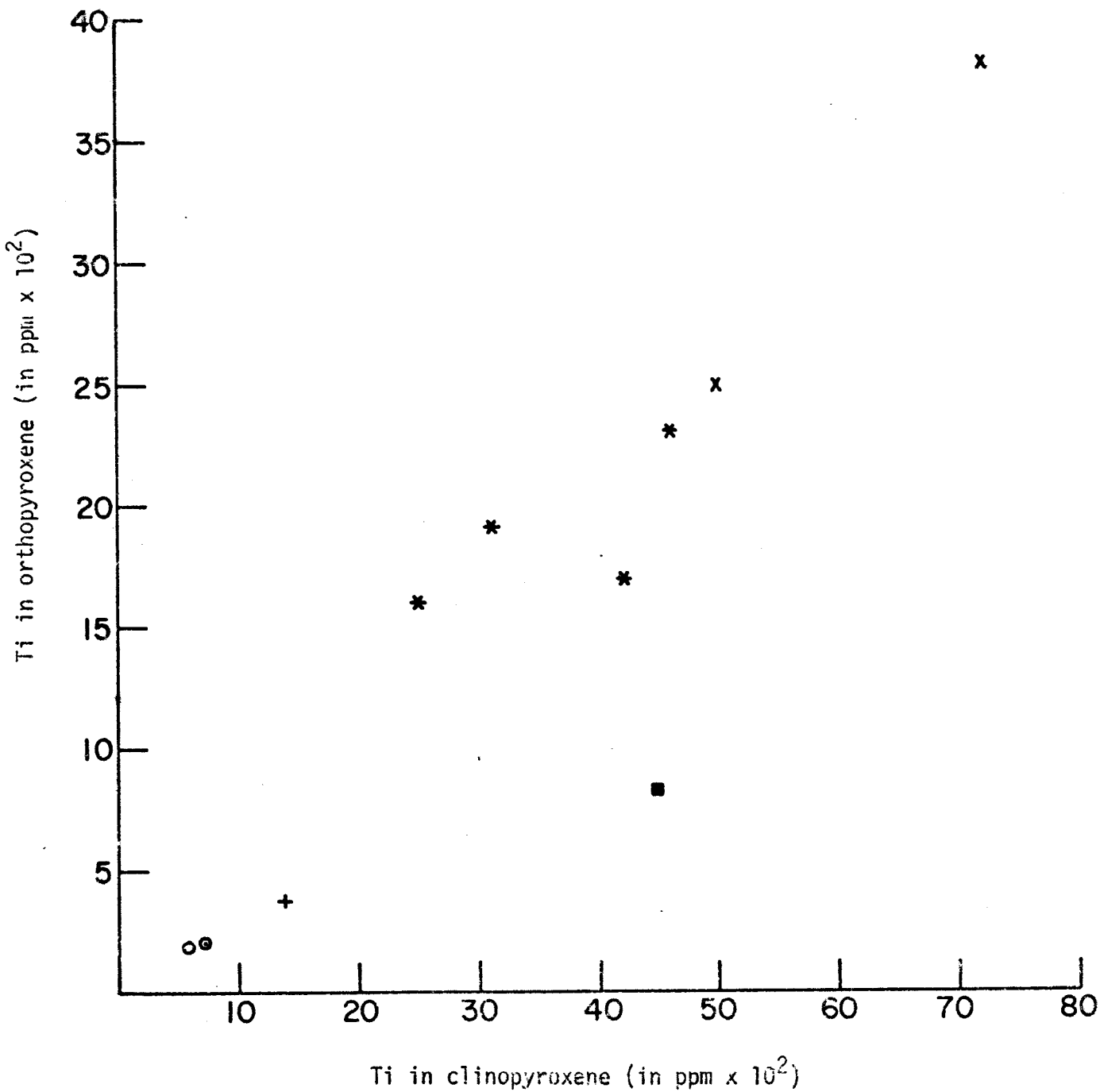


Figure 17. Plot of the Ti content of orthopyroxene against that of co-existing clinopyroxene. Symbols as in Figure 18.

TABLE IX

## Average Chromium Content of Ultramafic Rocks

Rock Group	Chromium (in ppm)	Source
Ultramafic	2000	Taylor (1966)
Ultramafic	1000-4400	Goldschmidt (1954)
Mafic	100-400	"
Ultramafic	1600	Turekian & Wedepohl (1961)
Ultramafic	2980	Stueber & Goles (1967)
Alpine type Intrusions	2370	"
Dunites	2480	"
Pyroxenites	2590	"
Serpentinites (Nemeiben Lake)	3500	
Pyroxenites (Nemeiben Lake)		



Lake is concentrated in the chrome spinel. In the pyroxenites Cr is more enriched in clinopyroxene (av. 4000 ppm) than co-existing orthopyroxene (av. 2500 ppm).

Chromium initially enters the chrome spinels, especially chromite. Olivine discriminates against Cr (Turekian, 1963) but shows a wide range of values because inclusions of chrome spinels cannot be mechanically separated from olivine grains. Cr greatly prefers pyroxene as shown by Wager and Mitchell (1951), Turekian (1963), McDougall and Lovering (1963), and others. Early pyroxene incorporates great amounts of Cr causing chrome spinel to cease to crystallization. Carstens (1958) finds more Cr in clinopyroxene than co-existing orthopyroxene. Fig. 18 shows a plot of the chromium content of orthopyroxene against that of co-existing clinopyroxene from Nemeiben Lake ultramafic rocks and other rocks from literature.

The distribution of Ni, Cr, and Ti between co-existing pyroxenes from Nemeiben Lake ultramafic rocks is similar to that observed for other igneous pyroxenes pairs. (Carstens, 1958; Atkins, 1969). Chromium and titanium values for co-existing pyroxenes from Nemeiben make pyroxenites are given in Table XI. In general the clinopyroxene contains larger quantities of Cr, Ti, while the orthopyroxene is richer in Ni. These data are consistent with observations on the distribution of these elements in metamorphic pyroxene pairs (Howie, 1955; Engel, Engel & Havens, 1964, Leelanendam,

TABLE X

Ni, Cu, Co(ppm), Values in Minerals from  
Nemeiben Lake Ultramafic (Microprobe determinations)

Rock pyroxenite	Elements	Olivine	Orthopyroxene	Clinopyroxene	Serpentine
Specimen No's					
125	Co	160	70	40	70
	Ni	2030	610	340	230
	Cu	40	30	30	0
92	Co	170	90	60	50
	Ni	1840	410	250	250
	Cu	30	40	40	30
127	Co	150		40	70
	Ni	1910		330	240
	Cu	20		40	50
156	Co	180	100	50	30
	Ni	1860	530	300	450
	Cu	20	20	30	20
75	Co			40	
	Ni			230	
	Cu			30	
85	Co	190	90	60	90
	Ni	1510	400	230	370
	Cu	20	60	30	10
135	Co		120	60	
	Ni		410	190	
	Cu		50	40	
98	Co	170	70	60	60
	Ni	1850	540	310	580
	Cu	20	30	30	20

TABLE XI

Ti and Cr values in Minerals from Nemeiben Lake  
Ultramafic Rocks (Emission Method)

Number	Orthopyroxene		Clinopyroxene	
	Ti	Cr	Ti	Cr
72 (pyroxenite)	0.02%	0.2%	0.07%	0.4%
102 (pyroxenite)	0.02%	0.3%	0.07%	0.4%

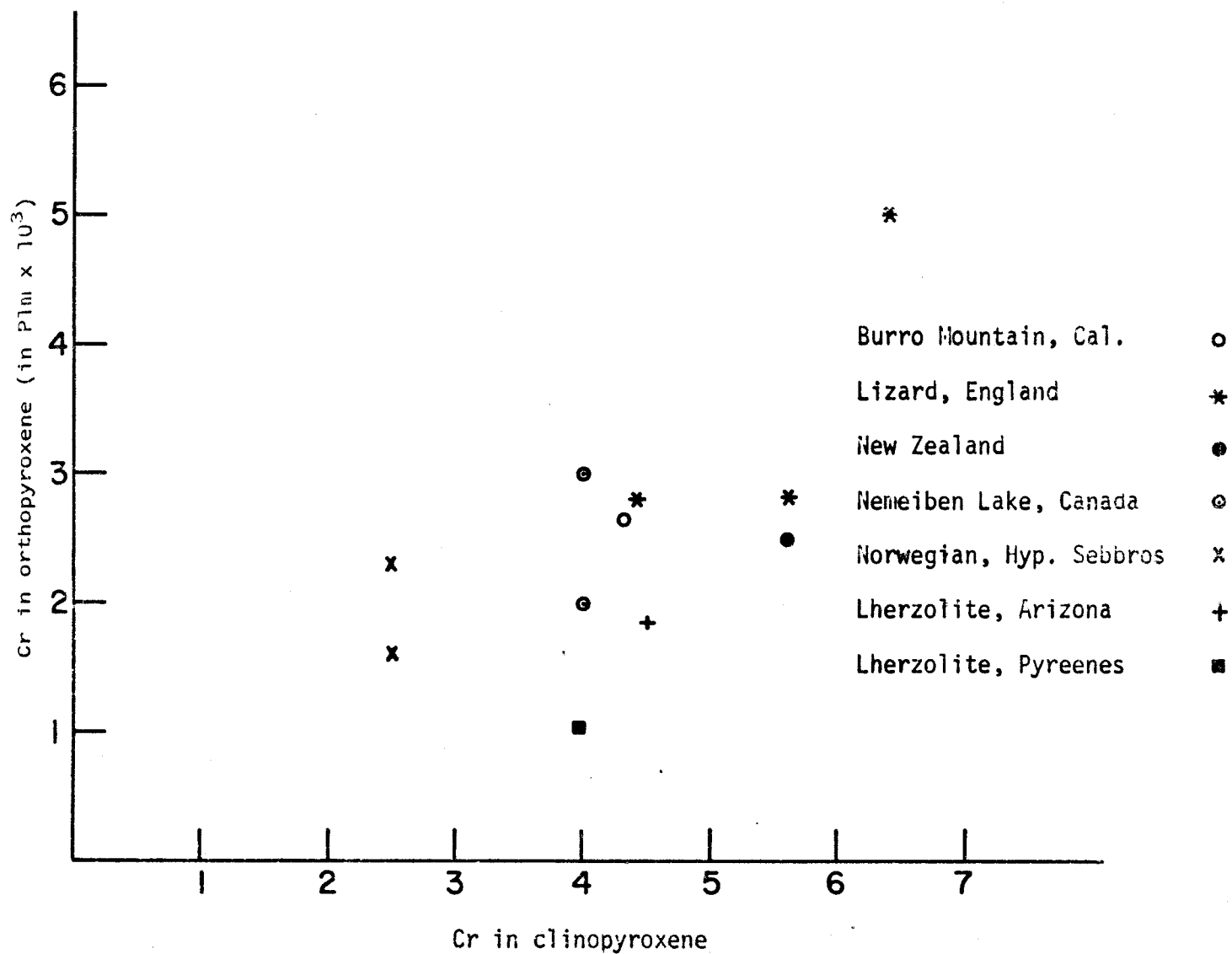


Figure 18. Plot of the Cr content of orthopyroxene against that of the co-existing clinopyroxene.

1967). The three elements under consideration are all transition metals and with the exception of Ti (possibly) they have a crystal field stabilization energy appropriate to an octahedral environment.

The distribution of these elements in both igneous and metamorphic pyroxenes suggests that  $O(\text{Cpx}) = O(\text{Opx})$ , where  $O$  is the energy between the  $t$  and  $e$  levels in octahedral co-ordination (Burns & Fyfe, 1967). This would also explain why the distribution of Cr is not proportional to the number of octahedral sites: orthopyroxene has twice as many such sites as clinopyroxene.

If it is assumed that members of the transition metals group are approximately favored as in  $\text{Fe}^{+2}$  in octahedral sites in pyroxenes, and the crystal field stabilization there energies cause only minor differences within the group, then the ratio of transition metal ion to  $\text{Fe}^{+2}$  gives a corrected measure of the distribution of such transition metal ions for pyroxene pairs with very different  $\text{Mg}/\text{Fe}^{+2}$  ratios. However, Curtis (1964) found that trends established using raw trace element concentrations give the same results for distribution of such elements with magmatic variation as do the trends established using corrected data (c.f. Fig. 5 and Fig. 6, Curtis, 1964).

#### V.9. Copper

Copper has generally been considered to be the most

thiophile of the elements group  $\text{Cu}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Co}^{+2}$  and  $\text{Fe}^{+2}$ , and consequently it does not exhibit as marked a tendency to be incorporated into silicate structures as do the other three and it is probable that in a rock analyses having high copper values much of the copper is present as a sulphide. Sandell and Goldich (1943) noted in their study of magmatic rocks a marked parallelism between copper and sulphur contents. Furthermore, the values that they obtained suggest that copper is present dominantly as the mineral chalcopyrite. This is in accordance with the conclusions of Newhouse (1936) who found that chalcopyrite is a very common constituent of many igneous rocks and virtually the only copper sulphide.

In Nemeiben Lake ultramafic rocks, copper is present in all mineral phases in small amounts. The relative distribution in rocks and minerals is shown in Table X and XIII. The copper values in silicate mineral phases appears unrelated to Cu values in the whole rocks; the small amounts in the olivines, clinopyroxenes, orthopyroxenes, amphiboles, probably include Cu in the mineral lattices.

As previously mentioned, examination of polished thin sections, indicated small chalcopyrite in association with pentlandite and pyrrhotite (with Cu, Ni) as disseminated grains in the Nemeiben Lake ultramafic rocks are most common. Chemical analysis of the rocks showed most of the copper is in the sulphide phase.

The  $\text{Cu}^{+2}$  (0.72) ion is closest in size to  $\text{Fe}^{+2}$  (0.76) where as  $\text{Cu}^{+}$  (0.96) is similar in size to  $\text{Na}^{+}$  (0.95). Ringwood (1955a) indicates Cu-O forms a weaker and more covalent bond than either Na-O or Fe-O. He concludes that Cu does not readily enter silicate minerals, being present in silicates only to a limited extent; e.g. it is found in plagioclase in  $\text{Na}^{+}$  positions and in ferromagnesian minerals in  $\text{Fe}^{+2}$  sites.

The dominant characteristic of the behavior of Cu is its tendency to complex in the magma rather than form independent ions. When sufficiently concentrated it separates as a sulfide phase. This behavior was identified in the Skaergaard intrusion by Wager and Mitchell (1951). Here, they also found that there is a sharp drop in the Cu content of the silicate minerals where heavy sulfide precipitation first occurs, though, the Cu content of the whole rock was high. Copper values of silicate phases in the Nemeiben Lake ultramafic rocks are low, and copper occurs predominantly in the sulphide phase.

#### V.10. Nickel

Nickel exhibits a strong tendency to become enriched in the ferromagnesian minerals of early crystallization. This feature, first noted by Vogt (1923) has subsequently been investigated and confirmed by many geologists, e.g. Wager and Mitchell (1951), and Goldschmidt (1954).

The rockforming minerals in the Nemeiben Lake ultramafic rocks differ considerably in their nickel and cobalt content as shown in Table X. In the order of decreasing nickel content the minerals can be arranged in the series olivine, orthopyroxene, serpentine, clinopyroxene and the same series holds for decreasing cobalt content.

The Ni/Co ratio is higher in olivine and hypersthene than in diopside and serpentine. Thus the principal concentrator and carrier of nickel is olivine and to a less degree, hypersthene. The clinopyroxene (diopside) is distinguished by the lowest nickel content. Cobalt is enriched mainly in olivine. There is considerably greater variation in the content of nickel than cobalt in the different minerals.

Figure 19 shows the tendency for sympathetic variation of Ni with Mg in olivine, orthopyroxene and clinopyroxene from pyroxenite of the Nemeiben Lake ultramafic rocks. Vogt (1923) presented extensive evidence that Ni is camouflaged by Mg and this view has been supported by more recent authors (Wager and Mitchell, 1951; Snyder, 1959). Ringwood (1955a) however, considers the Ni-Mg diadochy illusory and inconsistent with ionic radii and electronegativities of the two doubly charged ions. These properties and others (Ahrens, 1964) are given in Table XII.

The ionic radius of  $Ni^{+2}$  is intermediate between



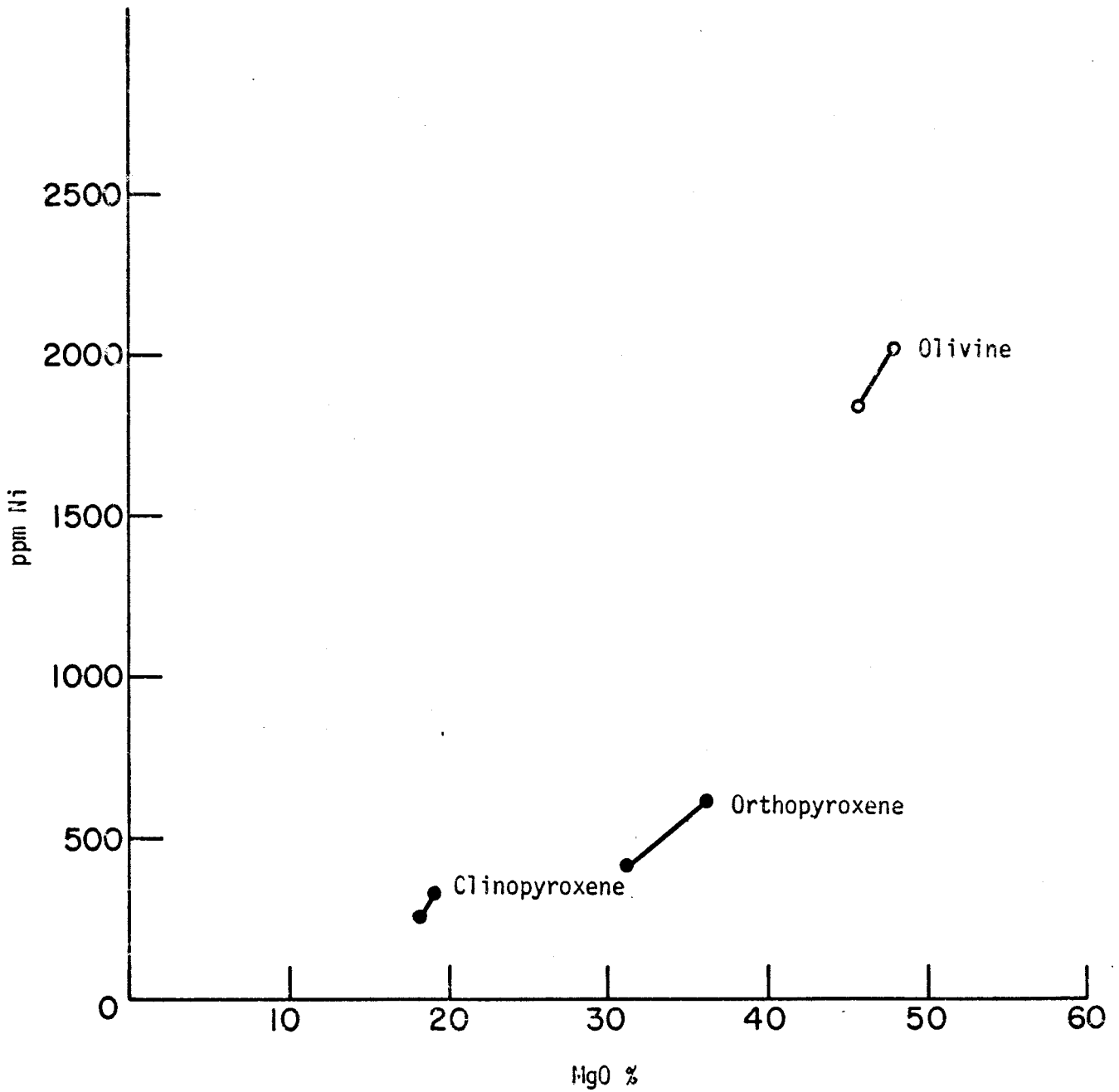


Figure 19. Sympathetic variation of Ni with Mg in co-existing olivine, orthopyroxene and clinopyroxene from Nemeiben Lake ultramafic rocks.

TABLE XII

Ionic Radii and Electronegativities  
and other Properties of Mg, Fe, and Ni

Element	Assignment of valence electrons	Radius $R^{+2}$ cation $A^{\circ}$	Second ioniza- tion potential (I volts)	Electro- negati- vity (e)	Field function $I/R^{+2+10}$
Mg	$s^2$	0.65	15.03	1.23	2.3
Fe	$a^6s^2$	0.74	16.18	1.64	2.2
Ni	$a^8s^2$	0.69	18.15	1.75	2.6

TABLE XIII

Nickel, Copper Values (ppm) of the Sulphide Phase,  
Whole Rock and Silicate Phase

Whole Rock	Nickel		Whole Rock	Copper		Ni/Cu in sulphide
	Sulphide*	Silicate		Sulphide*	Silicate	
Serpentinites (core)						
1868	1640	228	599	520	79	3.15
3949	3300	649	1698	1500	198	2.2
5531	4500	1031	2314	2250	64	2.0
5128	700 (weathered)		33	5	28	
Serpentinites (surface, weathered)						
885	122	763	26	2	24	
3116	2500	616	915	800	115	
1035	210	825	163	85	78	
Pyroxenites						
674	425	249	216	200	16	2.12
666	515	151	333	325	8	1.58
396	200	196	133	125	8	1.6
426	45	381	66	53	13	0.8

\* Sulphide phase is determined by absorbic acid leach method.  
The limitations of this method are described in Appendix III.

those of  $Mg^{+2}$  and  $Fe^{+2}$ ; Greenland and Lovering (1966) point out that on size considerations alone, if  $Ni^{+2}$  replaces  $Mg^{+2}$ , the  $Ni^{+2}/MgO$  ratio should increase during differentiation, where as if it replaces  $Fe^{+2}$ , the  $Ni^{+2}/FeO$  ratio should decrease. Both ratios decrease, and on this basis Ringwood (1955a) has advocated the importance of an  $Ni-Fe^{+2}$  substitution relationship. Goldschmidt (1954) and Ahrens (1953) have stressed that electropositive forces associated with  $Ni^{+2}$  are stronger than those of  $Mg^{+2}$  and  $Fe^{+2}$ , as evidenced by the strong ionization potentials and the field function. This latter parameter in fact shows the same sequence as the enrichment order, that is,  $Ni:Mg:Fe$ . Moreover Ahrens (1964) has discussed the possibility that due to this greater positive field function  $Ni^{+2}$  could be preferentially accepted into the structure site before  $Mg^{+2}$  and  $Fe^{+2}$ .

Taylor (1966), in summarizing the status of the problem, indicated that the convenient size  $Ni^{+2}$  (0.72) and  $Co^{+2}$  (0.74) between  $Mg^{+2}$  (0.65) and  $Fe^{+2}$  (0.76), together with the melting point data for the oxides, would suggest that the sequence of entry into crystal lattices would be  $Mg^{+2}$ ,  $Ni^{+2}$ ,  $Co^{+2}$ ,  $Fe^{+2}$ , particularly as there are no charge balance problems. However he was unable to explain the more favorable entry of Ni than Co into early ferromagnesian mineral lattices. He believed that both Ni and Co occupied the  $Fe^{+2}$  sites.

Burns and Fyfe (1966) pointed out that melting point data alone are not necessarily a guide to bond energies, nor to the order of preference that an element will show in incorporation in natural minerals of basaltic systems. But greater confidence in prediction can be placed in lattice energies, which for example, indicate that Ni-O bond energy is larger than those of Mg-O and Fe-O in solid phase. These observations appear consistent with the behaviour of Ni shown in the Nemeiben Lake ultramafic, and probably crystal-field theory provides the most satisfactory explanation of this behaviour.

Thus a number of reasons have been suggested to explain the behaviour of nickel during fractional crystallization processes, and it appears possible that this behaviour is affected by a number of different factors in varying degrees. It is possible that a better understanding of this important element might be obtained by the close study in the laboratory of the crystallization of spiked rock melts, both natural and artificial.

## VI. SERPENTINIZATION

The Nemeiben Lake ultramafic pluton has undergone various degrees of serpentization and uralitization. The process of serpentization apparently was irregular and most intense in highly fractured areas in the pluton. The mineralization of Nemeiben Lake ultramafic has been affected to some degree by serpentization. Serpentinization process has been discussed here appropriate to Nemeiben Lake ultramafic body.

In general of all the minerals present in ultramafic rocks, olivine is the one that appears to be most readily converted to serpentine, and orthopyroxene is also susceptible to serpentization. The serpentization of peridotites has for long been a controversial subject both as regards the origin of the water producing the reaction and the nature of reaction involved (see Turner & Verhoogen, 1960, p. 316-321). In particular, it is uncertain whether the reaction involved is principally a constant volume reaction, involving addition of water and leaching of MgO, FeO, SiO<sub>2</sub> etc., or constant composition reaction, involving addition of H<sub>2</sub>O without leaching and hence a large volume increase.

Hostetler, et.al. (1966) argued that no evidence exists to support massive introduction of Si and Mg into the country rock surrounding serpentinites. They cite the presence of

brucite in many serpentinites thereby reducing the amount of Mg that must be removed. They also point out that the tectonic environment of alpine serpentinites is compatible with volume increase and suggest incremental expansion of the body under going serpentinization as it tectonically ascends. Thayer (1966) has recently argued the case of serpentinization being essentially a constant volume metasomatic process which requires the removal of about 30% by weight of the original bivalent oxides and  $\text{SiO}_2$  in the peridotite. In discussing the problem of serpentinization, De Waal (1971) expressed the opinion that it involves both removal of ions, especially magnesium, and some degree of expansion, but these two factors might vary in intensity relative to each other from one locality to another.

Edel'shtein (1963) has studied the nickel contents of ultramafic rocks, both fresh and serpentinized, from the southern Urals. He concludes that the nickel content of a serpentinite is directly related to that of the parent rock from which it was derived, a conclusion which agrees with Faust et.al., (1956) and Faust (1963). Stueber and Goles (1967) also commented at length on the lack of any pronounced geochemical distinction between fresh and serpentinized ultramafic rocks, noting that abundances of Na, Mn, Cr, Sc and Co all failed to exhibit any effect which could be assigned to serpentinization alone.

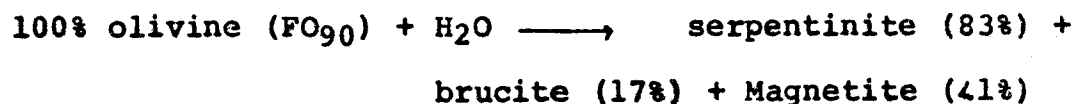
The original amounts of olivine and orthopyroxene

cannot be determined in the completely serpentized rocks from Nemeiben Lake since the ghost or relicts of primary textures are destroyed. Bulk chemistry of the rocks and mineralogy along with individual textures in minerals are considered here.

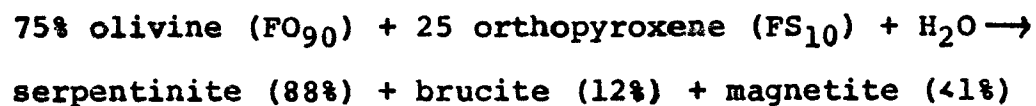
Nemeiben Lake serpentinites do not contain brucite and magnetite content has a range of 5-10%. The silica content of serpentinites (recalculated anhydrous) is 46% which indicates large amounts of pyroxene.

Many authors discussed the problem of serpentization using generalized reactions. The following two reactions are used by Coleman and Keith (1971):

(a) Dunite



(b) Harzburgite



Upon complete serpentization, harzburgites containing approximately 25 wt. percent orthopyroxene contain less than 12 wt. percent brucite. However, when orthopyroxene exceeds 40 wt. percent in harzburgites there is enough silica available to produce entirely serpentine without any brucite.

Another factor that obviously limits the amount of



brucite in the ultramafic rocks during serpentinization is the iron content of olivine and orthopyroxene. It is well known that serpentine, for some reason accommodates very little iron in its unit cell; in fact, persual of the more reliable analyses available in the literature (Deer et.al., 1963; v.1,2,3,4) shows that iron very seldom constitutes more than 1% of the total number of  $R^{+2}$  cations in the serpentine unit cell. This phenomena is borne out by the exudation of dust like particles of magnetite during the serpentinization process.

Any oxidation in the system causes the extraction of the ferrous oxide in the form of magnetite, which lessens the number of superfluous  $R^{+2}$  cations that can go into brucite. Accordingly one can argue that the greater the amount of magnetite present in serpentinite, the less brucite will form (according to De Wall, 1971).

The only textural evidence for expansion in the Nemeiben Lake serpentinites are single chromite grains showing expansion fractures filled with serpentine minerals (Plate IX, Fig. 1). Plate IX, Fig. 2 shows serpentine vein cutting across orthopyroxene and sulphide grain.

From the limited chemical data and from the above discussion it can be suggested that serpentinization in Nemeiben Lake rocks was accompanied by the introduction of water with no changes in relative amounts of  $SiO_2$  and  $MgO$ . A minor removal of  $CaO$  during serpentinization is the only apparent chemical change.

PLATE IX

Figure 1. Single chrome spinel grains showing expansion fractures filled with serpentine mineral.

Figure 2. Serpentine vein cutting across orthopyroxene and sulphide grain.

Plate IX



Figure 1



Figure 2

## VII. ULTRAMAFIC ROCKS AND SULPHIDE MINERALIZATION

### VII.1. Introduction

In this chapter, some general characteristics of nickel deposits are reviewed. Some controversy exists in geological thought as to the origin of nickel-copper sulphide deposits; with magmatic and hydrothermal theories of origin having been proposed. This controversy initially arose over the origin of the extensive Sudbury nickel-copper deposits and has since been extended to other ore bodies. These theories of ore genesis are discussed in some detail and the possible origin for the Nemeiben Lake sulphide deposit is discussed in the light of the observed data.

### VII.2. General Characteristics of Nickel Deposits

A pronounced correlation exists between many ores and the particular rocks in which they occur (Buddington, 1933). As a typical example, nickel-copper and cobalt sulfide ores are almost exclusively located in ultramafic and related rocks, commonly considered as belonging to the peridotite class. Fig. 20 shows the ultramafic rocks and associated nickel deposits in Canada. The strong spatial relationship between nickel deposits and nickel bearing igneous rocks is so well established as to require little extra emphasis here. The association of nickel bearing

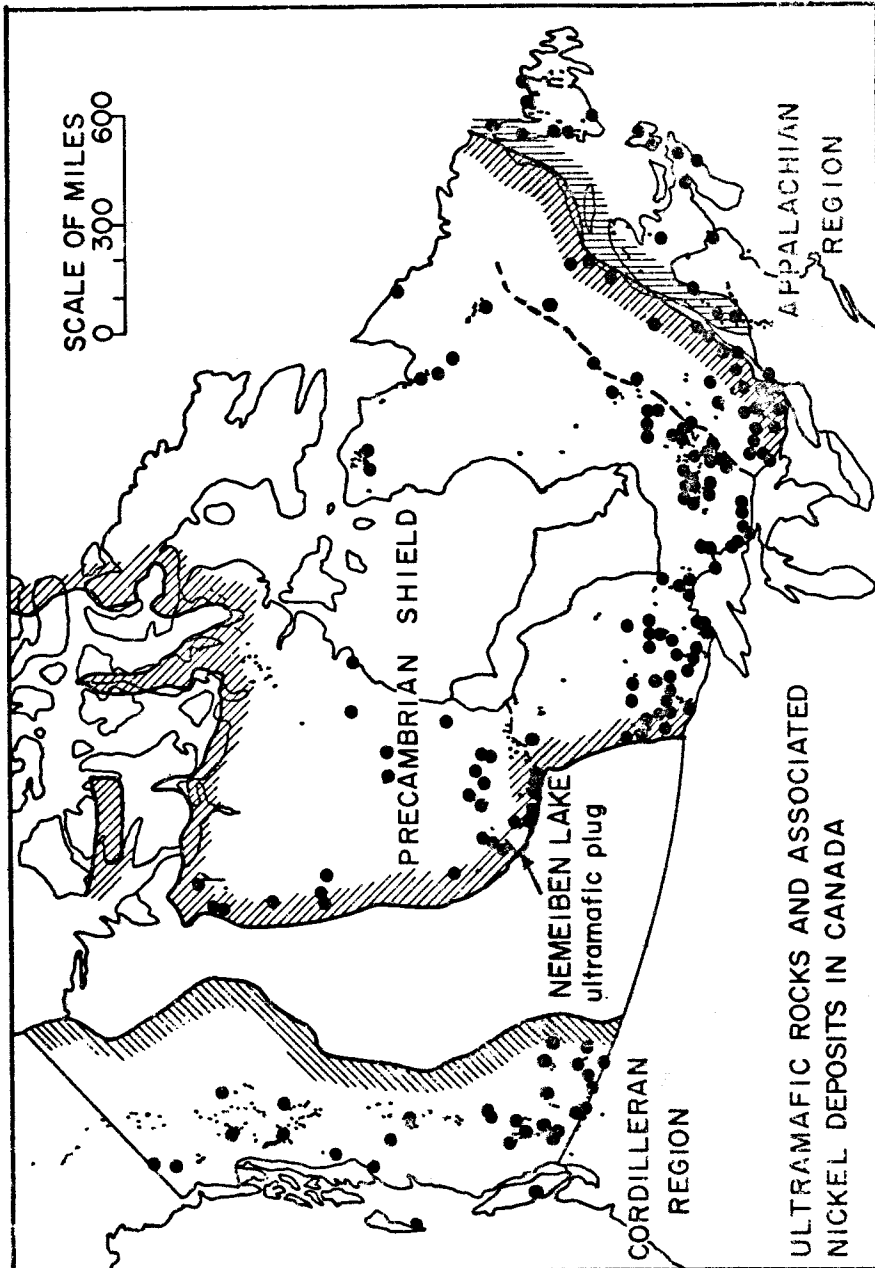


Figure 20.    :: Ultramafic Rocks  
              ● Nickel Deposits: Producers, past, present and non-producers

sulphides with nickel rich silicate rocks was first pointed out by Vogt (1923), who also noted a relationship between the nickel content of sulfides and the nickel content of associated silicate rocks. Wilson (1953), and Wilson and Anderson (1959) have drawn attention to the same relationship citing numerous Canadian examples.

There are two principal types of nickel deposits, primary and secondary:

- (1) The primary sulphide deposits consist of pyrrhotite and pentlandite with or without accompanying chalcopyrite and closely associated with norite or peridotite.
- (2) Secondary nickeliferous laterite deposits, occurring as weathering mantles that overlie peridotite (the nickel silicate variety) and serpentinite (the nickeliferous iron variety).

Considering primary nickel deposits themselves, a division into two broad groups can be made; those of magmatic affiliation and those of hydrothermal affiliation. Deposits of magmatic affiliation are divided into two types: (1) ultramafic, such as the Thomson nickel belt of Manitoba, or (2) mafic, as at Sudbury. Deposits of hydrothermal affiliation are those occurring as veins, generally with abundant gangue minerals. They are divided into two types: (1) simple, such as the niccolite bearing veins in granite that occur in the Yellowknife area; and (2) complex, such as the silver-cobalt-nickel arsenide veins in the Cobalt area (Ontario). Fig. 21 shows the relative abundances of the various types of nickel deposits,

and current production from these types in Canada. It is apparent that only the mafic and ultramafic deposits are of current economic importance. Almost 80% of Canada's nickel production is from mafic rocks and the balance from ultramafics. Without the enormous production from Sudbury, however this situation would be reversed, with the ultramafic deposits contributing twice the amount of nickel as that from the mafic type.

The significance of the ultramafic association is emphasized by the fact that of the seven current nickel producing areas in Canada, four are clearly of the ultramafic type. Kilburn et.al., (1969) have grouped ultramafic host rocks into three general types, two of which are of importance in Canada. In the first type the ultramafic rocks are intruded along belts of major crustal dislocation (faulting). The Thomson belt, running for 100 miles along the boundary between the Churchill and Superior subprovinces of the Canadian Shield, is a good example of this orogenic type. The second or volcanic type consists of concordent sills or dikes distributed through volcanic belts. There is an extensive development of this type of ultramafic rock through the Archean greenstone belts of northern Ontario and adjacent parts of Quebec. Nickel-copper sulphides in the ultrabasic sills of the shield have commonly segregated through gravity settling as bands or layers and lenses along the base of the sill and in some cases may have

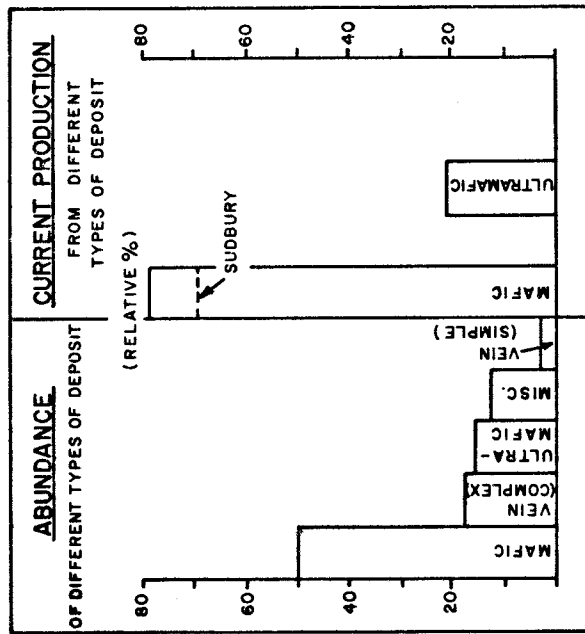


Figure 21. relative abundances of the various types of nickel deposits, and current production from these types in Canada. (After Chamberlain, 1968)



penetrated the wall rock of this lower contact. Segregation in this form is less common for the bodies that have been introduced along orogenic belts. These bodies more often tend to contain disseminated ore, although the Thomson ore body is a prime example of a sulfide ore body that has been injected into the wall rock. Further reflecting the relative minimization of segregation processes within the bodies of the orogenic belts, the ultramafic host rock is more homogeneous than that of the bodies intruded along volcanic belts. These latter bodies may often be differentiated into mafic as well as ultramafic rock types. Serpentinization has affected these rock types to a greater or lesser extent.

### VII.3. Theories on the Genesis of Nickel Sulphide Deposits

In general three possible modes of origin for the disseminated sulphides in ultramafic rocks can be considered. First as igneous origin; nickel-copper sulphides are one example of a comparatively small group of ore deposits that are truly magmatic, being the result of the crystallization of a relatively dry sulphide melt which segregated as an immiscible liquid during the cooling of a mother silicate magma. The sulphur is assumed to have come from the same source as the silicate magma, and to have been introduced or carried with it. A second theory is that sulphides may have been deposited from hydrothermal

fluids derived from an igneous source at depth. The source of such fluids normally would be a more siliceous and volatile-rich magma than that from which ultramafic rocks are usually considered to be derived. The third theory is that the nickel may well have been derived from the silicate magma, but the sulphur was introduced from an external source either while the magma was still liquid or after solidification.

#### VII.4. Origin of Nemeiben Lake Nickel-Copper Deposit

Nemeiben Lake nickel-copper deposit is considered of magmatic origin. The criteria of phase relationships of sulphides, and the distribution of nickel and origin of ore textures are used to emphasize the magmatic origin for the Nemeiben Lake nickel-copper deposit.

##### VII.4.1. The Phase Relationships of the Sulphides and the Origin of the Textures

The relationships between the different minerals and the origin of the texture can be explained in terms of phase-diagrams. The development of sulphide minerals of the Nemeiben Lake ultramafic can be best approximated by the Cu-Fe-Ni-S system, and the various ternary sub-systems. During the last 10 years many of the phase relations involved in the orthomagmatic ores found in mafic and ultramafic rocks have been investigated in detail especially

by the Carnegie Institution. A vast amount of experimentation by numerous workers has been directed toward an understanding of phase relations in the component portions of the Cu-Fe-Ni-S system. A complete review of all previous studies is not presented here. Comprehensive reviews of phase relations in the binary systems may be found in Hansen and Anderko (1958), Pearson (1958), Kullerud (1964), and Elliot (1965). Kullerud, et.al., (1969) has discussed the phase relations in the Cu-Fe-S, Fe-Ni-S, and Cu-Ni-S systems. Relations in the Cu-Fe-Ni system have been studied by Bradley, Cox and Goldschmidt (1941). Craig and Kullerud (1969) has discussed the phase relations in the Cu-Fe-Ni-S system.

Table XIII gives the Ni, Cu values of the sulphide phase as deduced from the differences in analysis. (For procedure see Appendix III).

Naldrett and Kullerud (1966) have investigated the portion of the Fe-Ni-S system inside which the compositions of most pyrrhotite-pentlandite ore deposits fall, paying particular attention to the limits of the  $Fe_{1-x}S-Ni_{1-x}S$  (or monosulphide) solid solution at temperatures below  $600^{\circ}C$ .

If a sulphide phase (in Fe-Ni-S system) contains less than 10 percent Ni all the pentlandite present has resulted in exsolution from nickeliferous pyrrhotite. Pentlandite as a separate sulfide phase may appear in the system at a

maximum temperature at  $610^{\circ}\text{C}$  (Kullerud, 1963).

The maximum stability temperature of pentlandite is not increased by the presence of Cu and pentlandite cannot crystallize directly from the quaternary system, Cu-Fe-Ni-S (Craig and Kullerud, 1967). Craig and Kullerud (1967) indicated that 4-5 percent nickel in solid solution in the pyrrhotite does not significantly affect the solubility of copper in pyrrhotite. Therefore, considerable amounts of chalcopyrite would exsolve from copper saturated pyrrhotite on cooling from  $700^{\circ}\text{C}$  to  $450^{\circ}\text{C}$ . This chalcopyrite is present as round or euhedral bodies or as lamellae parallel to the pyramidal plane of pyrrhotite. Craig and Kullerud (1967) consider that the presence of magnetite will have little or no effect on the sulphide assemblages and that much, if not all of the chalcopyrite observed in the Ni-Cu ores will dissolve at  $550^{\circ}$  to  $650^{\circ}\text{C}$  into a Fe-Ni-Cu monosulphide solution. Yund and Kullerud (1966) indicated that the solubility of copper in the Fe end member of the pyrrhotite  $\text{Ni}_{1-x}\text{S}$  at  $500^{\circ}\text{C}$  (Moh and Kullerud, 1963). Studies by Naldrett, Craig and Kullerud (1966) have shown that at  $600^{\circ}\text{C}$  the bulk compositions of many Ni-bearing pyrrhotite-rich ores lie within the confines of the Fe-rich portion of monosulphide solid solution. Thus if equilibrium prevailed during and after ore deposition (to at least as low a temperature as  $600^{\circ}\text{C}$ ), all sulphide contained nickel now present would have originally have

been either incorporated in the pyrrhotite, or distributed between pyrrhotite and chalcopyrite (which takes up to 15% Ni in solid solution at 600° C Craig and Kullerud, 1967 ). When the Cu or Ni content is less than 2 percent (e.g.; Alexo, Marbridge and many other ores) the copper as well as the nickel will be accommodated within pyrrhotite structure. The temperatures of appearance of other phases of chalcopyrite-pentlandite, and pyrite would then depend primarily upon the Cu and S contents of the primary sulfide phases (Naldrett, et. al., 1966). The maximum temperature at which chalcopyrite and pentlandite could exsolve together from pyrrhotite is about 575° C.

Naldrett, et. al., (1966) showed, that even as low as 300° C pyrrhotite will readily accept in excess of 15 wt.% Ni into solid solution. They also reported that the first appearance of pentlandite through exsolution from pyrrhotite (and hence reduction in Ni content of the pyrrhotite) could not have occurred above 400° C in deposits such as Alexo and Marbridge. The low Ni contents of typical pyrrhotites co-existing with pentlandite must be interpreted to indicate re-equilibration of phases at low temperatures.

From the above work it can be concluded that pentlandite and probably chalcopyrite would not crystallize directly out of a sulphide melt with the sulphide bulk composition inferred for the Nemeiben Lake ultramafic ore deposit (Cu, Ni values in sulphides). The primary textures observed

in Nemeiben Lake ultramafic body would have resulted from exsolution of pentlandite and chalcopyrite from a mono-sulphide solid solution. This exsolution would continue until an essentially Cu and Ni-poor pyrrhotite results.

#### VII.4.2. Nickel Distribution and Origin of Textures

In a study of the distribution of nickel in some mineralized basic intrusions in Finland, Häkli (1963) observed that the nickel content in olivine increases with the increasing nickel content of the sulphide phase. This positive correlation becomes even more pronounced when the atomic ratio Ni/Mg is plotted against nickel percentage of the sulphide phase, that is, when the magnesium percentage of olivine is taken into consideration. A similar relationship exists between the pyroxenes and amphiboles and the co-existing sulphide phase, although for the amphiboles the concentration is not as pronounced. (See Figs. 15,16,17, Häkli, 1963). It thus appears that there is a tendency towards equilibrium in the distribution of nickel between the primary silicate and sulphide phases of basic and ultrabasic rocks.

Shteinberg and Malakhov (1963) have found in the ultramafic rocks of Urals that the sulphide nickel in peridotite forms 'in situ' at the expense of silicate nickel as a result of the relative immobility of nickel and mobility of sulfur. This is proved by the constancy of the

total nickel content and the considerable variation in the ratio of sulfide nickel to silicate nickel. Usually the content of sulfide nickel is proportional to the sulfur content.

The distribution of nickel and copper between silicate and sulphide phases in some Nemeiben Lake ultramafic rocks was determined. Table XIII shows the range of values. As the fine grain size of much of the disseminated sulphides in the rocks made mechanical separation of the silicate and sulphide fractions impractical a process of sulphide solution was used to leach sulphides from the silicate and associated oxide fractions. (The solution process and its limitations are described in Appendix III). The subtraction of nickel and copper values of the sulphide phase from the whole rock nickel and copper values then yields the limiting nickel, copper values in the silicate and oxide phases. The nickel content of olivine from pyroxenite is about 1800 ppm. If a rock containing 100% olivine is serpentinized the nickel content of the rock should be about 1600 ppm (allowing for the dilution via serpentinization). The whole rock analysis of the serpentinites however has given nickel values of about 3000 ppm, which is apparently higher than if derived wholly from serpentinized olivine. The nickel content of the serpentinites excluding the sulphide phase is 375 ppm (average). A likely explanation of the higher nickel content of the sulphide fraction is

the primary magmatic sulphides which are originally present in the ultramafic rocks prior to serpentinization. During serpentinization process the nickel is released from the silicate phase and formed sulphides as shown previously in the ultramafic rocks of Urals (Shteinberg and Malakhov, 1963). The Ni/Cu ratios in sulphide phase are higher in serpentinites compared with the pyroxenites, which suggests that some of the sulphides are formed at the expense of silicate contained nickel.

Recent experimental work by Kullerud and Yoder (1963) has demonstrated that sulphur readily reacts with many of the common rock-forming silicates over wide temperature pressure ranges to produce sulphides and oxides. Phase relations in the system Fe-S-O-SiO<sub>2</sub> at 800° C and 2000 bars were deduced by experiments with fayolite and varying amounts of sulphur. In one experiment with 33 1/3 mole percent S, the derived products were pyrrhotite, magnetite, quartz, and pentlandite. Sulphur can thus react with and cause the breakdown of silicates such as olivine to produce pyrrhotite and pentlandite. Kullerud and Yoder believe that magnesium in silicates probably does not react with sulphur to form sulphides but that the process readily takes place with elements such as iron, manganese, nickel, cobalt, and copper. Naldrett and Kullerud (1965) have since described two examples where evidence suggests a sulphurization process of this type may have taken place



adjacent to ore deposits.

Examination of polished thin sections of partly serpentized and uralitized ultramafic rocks showed amphiboles replacing pyroxenes embedded in a continuous matrix of sulphide minerals composed of pyrrhotite, pentlandite and chalcopyrite. It was also observed that the sulphides occupy an interstitial position between silicates.

The grain size of nickel-copper sulphides in serpentinites, however falls into two distinct size ranges, i.e. fine and coarse. The fine sulphides have a maximum grain size of about one micron (probe determination) and are rather uniformly dispersed through serpentine pseudomorphs of olivine crystals.

The coarse grained sulphides occur interstitially between olivine pseudomorphs and orthopyroxene; however, in some instances they are also encountered in cross-cutting fractures, suggesting an origin as primary magmatic sulphides as described above. As already pointed out, the sulphide mineralization can be classified into three types, disseminated, net texture, and semimassive. Plate X, figures a-e illustrate examples of the textures as in specimens of polished drill core. Disseminated ore consists of evenly distributed worm-like particles of sulphide. Amalgamation of net texture sulphide into larger and more irregular areas forms the semimassive types illustrated in Plate X, figures a-e.

PLATE X

figures; Polished drill core showing types of sulphide textures. Sulphide light, Silicate dark.

- a) Disseminated 1 percent sulphides.
- b) Disseminated 3 percent sulphides.
- c) Net texture 3.5 percent sulphides.
- d) Net texture and semimassive, 4.5 percent sulphides.
- e) Semimassive, 15 percent sulphides.

Plate X

Figure 1

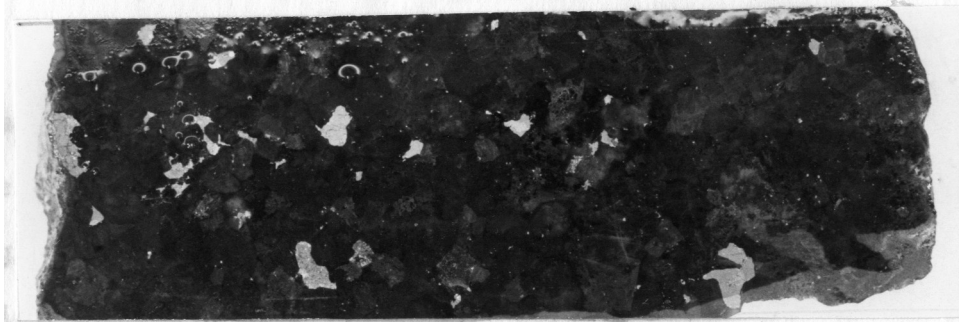


Figure a

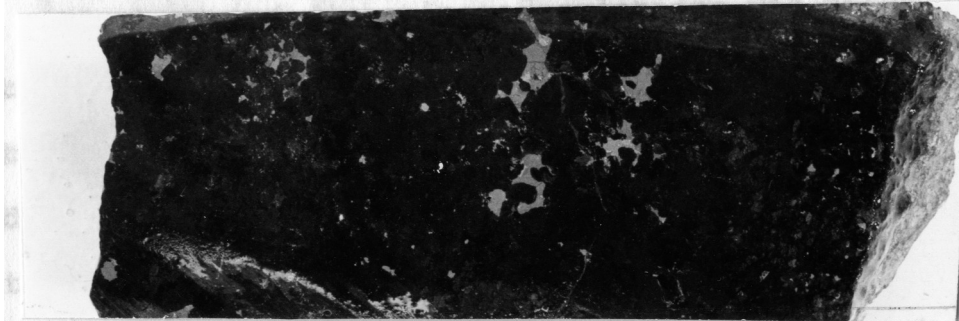


Figure b

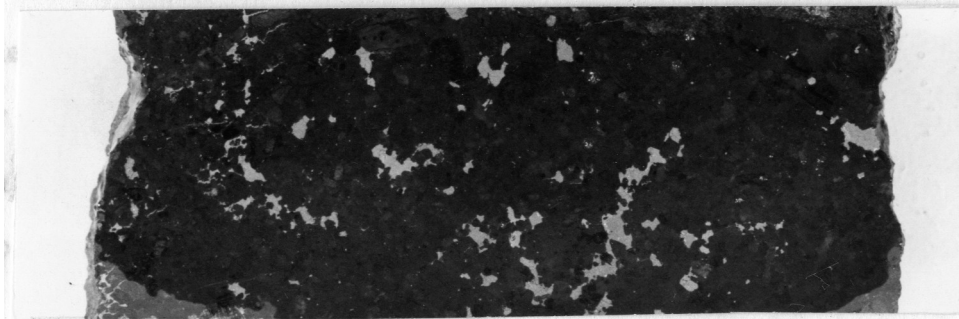


Figure c

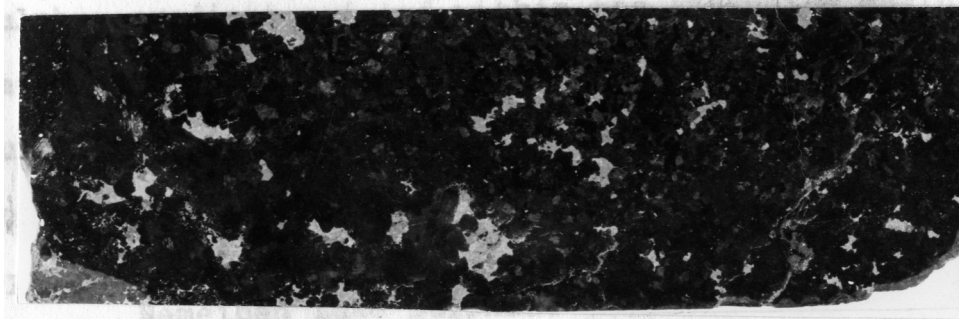


Figure d

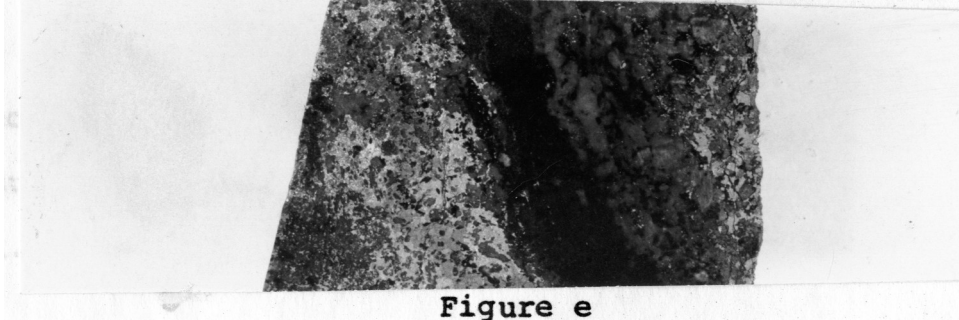


Figure e

The sulphides occur mainly in the ultramafic body at Nemeiben Lake. Exploratory drillhole information indicates the subparallel sulphide zones in at about 800 feet and the high grade ore zone at the base of the ultramafic body, which suggests magmatic accumulation origin.

Occurrence of disseminated sulphides was noted locally but is more pronounced near the northeast portion where the potential ore is located at the base of the ultramafic body. The disseminated nature of the sulphides suggests late magmatic crystallization. The occurrence of sulphides in the serpentinite in a similar way, may be preserved during the first alteration stage (Kilburn, et.al., 1969) subsequently with continued alteration remobilization will occur. Polished thin section study revealed sulphide relationship to microfractures and local migration.

The limited evidence available suggests that a primary sulphur gradient existed within the intrusion during magmatic stage which controlled the formation of early sulphides. This gradient was modified to some extent during serpentinitization.

#### VII.5. Summary of Evidence bearing on Interpretation of Nemeiben Lake Sulphide Ores

The evidence pointing to the development of the nickel copper deposits by crystallization from an immiscible sulphide liquid are as follows:

1. The ore bodies are entirely within the ultramafic

intrusive mass.

2. Potential ore body occurs in the lower part of the ultramafic complex.
3. The ore mineral assemblage is identical with those occurring in other nickel-copper sulphide deposits that have been interpreted as magmatic segregates.
4. The compositional and textural relations of the sulphide ores suggest that the first mineral to crystallize was a pyrrhotite solid solution from which pentlandite and perhaps a chalcopyrite were exsolved.

### VIII. SUMMARY AND CONCLUSIONS

The major points concluded from this study of ultramafic related, nickel-copper ore deposit are as follows;

1. The ultramafic body is considered to be of Churchill age, intruded at some stage of the Hudsonian Orogeny which terminated approximately 1700 million years ago.
2. The ultramafic rock types at Nemeiben Lake are classified as serpentinites, pyroxenites, and uralitized and partly serpentitized pyroxenites.
3. Olivine from these rocks have an average composition of  $Fo_{87.8}$ . Orthopyroxene ranges in composition between  $En_{90.5-87}$  with an average of  $En_{88.8}$ , and clinopyroxene has an average composition of  $Ca_{41.7} Mg_{52.8} Fe_{5.4}$ .
4. X-ray diffraction and optical studies indicate the presence of lizardite and chrysotile in the serpentinite.
5. Disseminated sulphide minerals contained in the ultramafic body are pyrrhotite, pentlandite, chalcopyrite, pyrite, marcasite, bravoite, and violarite. Copper and a platinoid mineral present as native minerals.
6. The ore mineral assemblage, pyrrhotite-pentlandite-chalcopyrite, the compositional and textural relations of the sulphides of potential ore grade, the occurrence of sulphides in the lower part of the ultramafic body and the disseminated nature of sulphides, all suggest a late magmatic crystallization from an immiscible

sulphide liquid.

7. Serpentinization in Nemeiben Lake rocks was accompanied by the introduction of water with no apparent changes in the relative amounts of  $\text{SiO}_2$  and  $\text{MgO}$ . A minor removal of  $\text{CaO}$  during serpentinization is the only apparent chemical change. The  $\text{Ni/Cu}$  ratios in the sulphide phase are higher in serpentinites compared with the pyroxenites, which suggest that some of the sulphides are formed at the expense of silicate contained nickel. Textural examination of serpentinites further revealed relationship of sulphide to microfractures and other features indicating local migration.
8. The mineral chemistries of olivine, orthopyroxene and clinopyroxene from Nemeiben Lake ultramafic body indicate that these minerals have been crystallized at higher temperatures, and it is inferred that these minerals have been crystallized under physico-chemical conditions similar to that estimated for other high temperature ultramafic bodies.
9. For the Nemeiben Lake ultramafic body the preferred temperature and pressure conditions are  $1100^\circ - 1200^\circ \text{C}$ , and 5-9 K-bars respectively.
10. In describing the classification of ultramafic rocks from the Precambrian Shield areas some workers have stated that the terms ultramafic of alpine-type or orogenic association is not justified. In the Nemeiben

Lake ultramafic rocks no evidence was found that orogenesis and alpine-type deformation have not occurred. However, some chemical properties of minerals are similar to high temperature alpine peridotites. To understand and compare the alpine-type ultramafic rocks and the ultramafic bodies in the Precambrian Shield a detailed study of Precambrian ultramafic bodies (e.g. in Saskatchewan and Manitoba) is warranted.



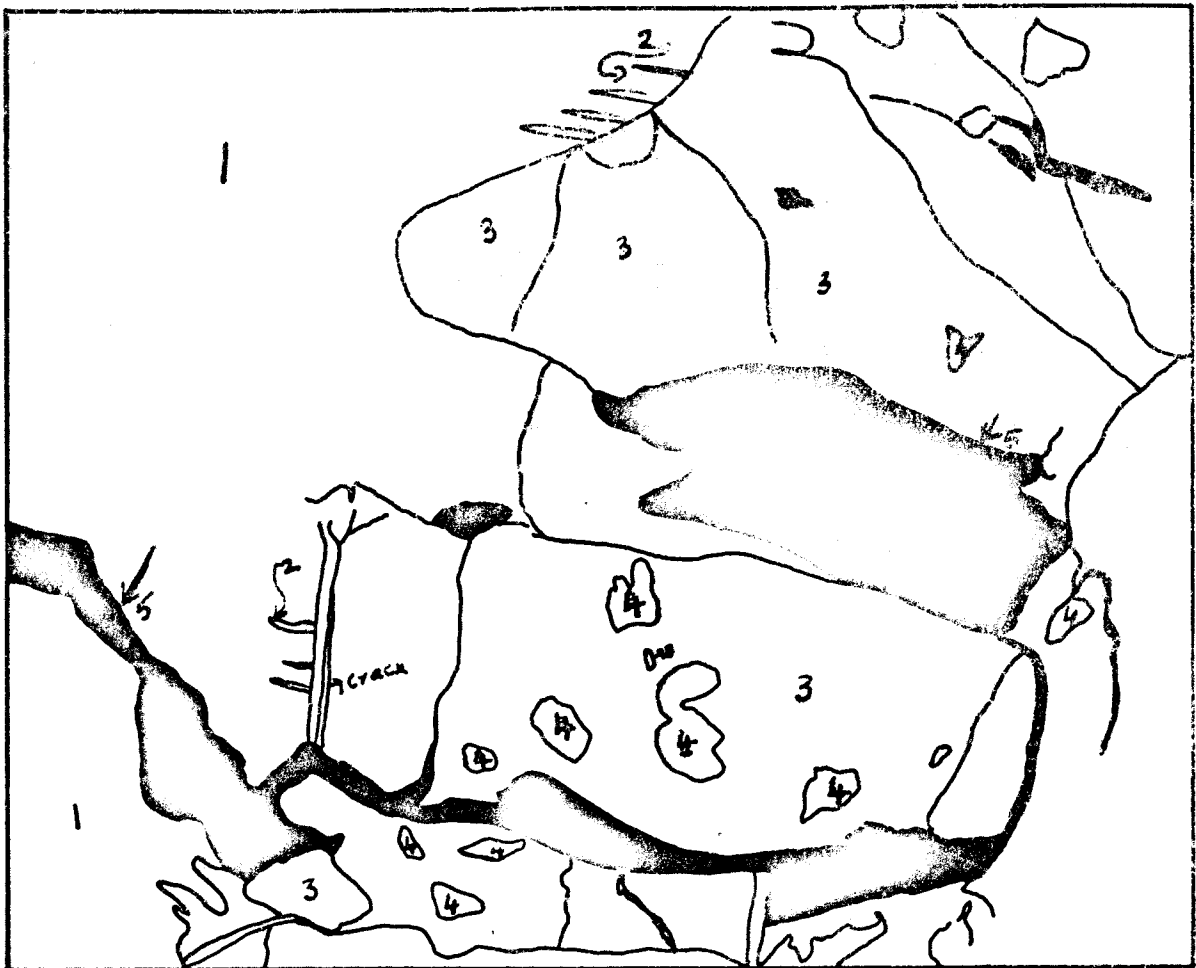


Figure 22. Tracing from a photomicrograph. Violarite (3) alteration after pentlandite (2) containing bravoite (4). Secondary gangue minerals mostly carbonate and magnetite (5). Pyrrhotite (1) with lamellae of pentlandite (2).

## IX. SUGGESTIONS FOR FURTHER RESEARCH

As in most studies many problems arose which could not be adequately studied in the time available. The author would like to mention a few of these problems which can be further investigated.

1. The age relations between the country rocks and the ultramafic intrusive body are not clear. To better understand the age relationships, an adequate age determination on ultramafic rocks (primary and altered) as well as K-Ar determination on the country rocks, where suitable sample material is available is worth investigating.
2. As far as is known at this time, no isotope data from ultramafic rocks exists from the Saskatchewan and Manitoba regional nickel belt. Studies of  $O^{18}$  and D/H isotope data in samples representing primary and altered (most serpentized) rock facies of the Nemeiben Lake ultramafic body could provide some information on (a) possible lines of petrogenesis, and (b) the temperature of formation of some minerals. This may also provide some information on the nature of alteration or serpentization in the Nemeiben Lake ultramafic body and should also provide a basis for comparison with other available isotope data from ultramafic rocks.
3. Variation in the chemistry of the individual minerals

in the serpentinite needs to be investigated in greater detail. Careful separation of the minerals and analyses for major and minor elements may reveal variations that are not apparent from analyses of bulk rock samples. X-ray diffraction and electron microscopy studies on chrysotile fibers is useful in an effort to explain the variations in the physical properties of the fibers.

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APPENDIX I  
SAMPLING & PREPARATION OF ROCKS

A. Sampling

Detailed sampling was carried out over a 6400 by 4000 feet area which includes all the outcrop area of the Nemeiben Lake ultramafic body. Hand specimens were collected for petrographic and mineralogic studies. Selective drill core samples, made available by the National Nickel company, were collected at regular intervals. Most of the samples (hand specimen and drill core samples) were analysed for the major and some minor components using x-ray fluorescence and atomic absorption techniques at the Department of Geology, State University of New York at Albany.

B. Preparation of Rocks for Chemical Analysis

The rocks were cleaned to remove weathered material and lichens, then washed with water and dried. The rocks were first split using a manually operated hydraulic rock crushing machine. The material obtained was passed through a jaw crusher and the particle size was reduced to 1/8" diameter, and possible iron contamination was removed using a magnet. One half of the total rock sample was passed through a roller crusher and the material was passed through -200 mesh sieves and stored for chemical analysis.

APPENDIX II  
ANALYTICAL TECHNIQUES

A. X-Ray Fluorescent Analysis

The following elements, expressed as oxides, were determined by x-ray fluorescence:  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , total Fe as  $\text{Fe}_2\text{O}_3$ , MgO, CaO and  $\text{TiO}_2$ . The analyses were made in the Department of Geological Sciences, State University of New York at Albany.

A comparative method was chosen based on the use of analytical curves prepared by the use of appropriate standards (See Table 14). A lithium tetraborate fusion followed by briquetting was used (Alder, 1966). All standards and samples were prepared in like manner. Fusion was chosen to minimize the differences between standards and specimens with regard to absorption effects, enhancement effects and physical characteristics such as particle size, homogeneity and crystal form.

(1) Sample Preparation

1.2 grams of sample were mixed with 2.8 grams  $\text{Li}_2\text{B}_4\text{O}_7$  in an agate mortar and transferred to a graphite crucible large enough to accommodate the charge, so that during early sintering the sample did not rise out of the crucible, due to the evolution of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  and other volatile material. Fusion was done in a Huppert furnace at  $1100^\circ\text{C}$  for 20 minutes

and cooled in the crucible. The bead was broken then ground in the Spex mixer mill with tungsten carbide grinding balls. About 1 gm. of sample was stored for atomic absorption. The remainder was pressed into a pellet with 3 mm sample thickness for infinite thickness required by elements sought. 10% by weight boric acid was added as a binder, and boric acid was used as a backing for strength. These pellets were pressed for thirty seconds at 35,000 Psi and stored in a dessicator.

## (2) Standards

Working curves were prepared from the following primary standards: PCC-1, DTS-1, 99A, CAAS-1a, T-1.

Since the iron and calcium values are high in some samples, synthetic standards were prepared in suitable ranges.

Siemens SRS-1 sequential spectrometer, with 4000 watt constant potential Kristallaflex generator was used.

Operating conditions of the instrument are given Table 15.

## B. Atomic Absorption Technique

The following trace elements in the whole rock were determined using Perkin Elmer Model 303 atomic absorption spectrophotometer: Ni, Cr, Zn, Cu.

### (1) Procedure

TABLE XIV

## Concentration Range of Standards

Element	Expressed as Oxide	Range
Si	SiO <sub>2</sub>	40.45 - 65.2
Al	Al <sub>2</sub> O <sub>3</sub>	0.55 - 20.5
Fe	Total Fe	6 - 20
Mg	MgO	43.56 - 4.0
Ca	CaO	0.15 - 20.0
Ti	TiO <sub>2</sub>	0.02 - 0.6

## Standards Used

PCC-1	U.S.G.S. Standard
DTS-1	U.S.G.S. Standard
CASS# 1a	Certified Standard Spectroscopy Society of Canada
T-1	Standard Geochemical Sample, Msusle Tonalite
99-A	National Bureau of Standards, Standard Reference Material, feldspar.

Synthetic standards were prepared in suitable ranges for calcium and iron.

TABLE XV

Operating Conditions of the Siemens SRS-1 Spectrometer

Oxide	Wavelength A°	Tube voltage	Tube current	Target	Crystal used
SiO <sub>2</sub>	7.126	33kv	32Ma	Cr	PET
Al <sub>2</sub> O <sub>3</sub>	8.339	42	50	Cr	PET
Fe <sub>2</sub> O <sub>3</sub>	1.937	20	20	Cr	LIF
MgO	9.889	30	64	Cr	KAP
CaO	3.360	20	20	Cr	PET
TiO <sub>2</sub>	5.5065	20	30	Cr	LIF

TABLE XVI

Atomic Absorption: Instrumental Data

Element	Cu	Ni	Zn	Cr
λA°	3247	2320	2138	3579
Silt	4	3	5	3
Oxidizer	Air-Acetylene-----			
Burner	Boling-----			

1 gm of the fusion sample was weighed exactly and the wt. was recorded. The sample was transferred to a 50 ml beaker and 5 ml of 1:1  $\text{HNO}_3$  was added and heated slowly, on a hot plate, until dissolved. 1 gm tartaric acid was dissolved in approximately 10 ml di-ionized water in a 100 ml volumetric flask. The fusion solution was added, and washings from the beaker used to bring the new solution to volume. This solution was stored in polyethylene bottles ready for trace element determination.

## (2) Standards

Standards of suitable ranges were made from stock solutions. Blanks were prepared by using fused  $\text{LiB}_4\text{O}_7$  and following the solution procedure. These were used to correct for apparent %A due to characteristics of the sample solution.

## (3) Instrument Settings

Instrument data for the atomic absorption analyses as shown in Table 16.

## C. Microprobe Analysis

Partial electron probe analyses of minerals olivine, orthopyroxene and clinopyroxene along with trace elements Ni, Cu, Co are shown in Table 10. The analyses were carried out with a Geoscan Electron probe micro analyser

in the research laboratory of the Autokumpu Co. Finland, by the courtesy of A. Häkli. Trace elements were determined at 40 kv/0.6 micro A and the major components at 25 kv/0.1 micro A. The detailed procedure and the standards used were described by Häkli and Wright (1967) and Häkli (1968).

#### D. Emission Method

Titanium and chromium were determined in co-existing orthopyroxene and clinopyroxene mineral separates from pyroxenite. 10 mg of sample were mixed with 90 mg of a mixture of 7 parts spectrographically pure graphite and 2 parts spectrographically pure  $\text{GeO}_2$  for 1 minute in a plastic vial with a plastic ball in a Wig-L-Bug. General graphites type 216 S electrode was hand-packed and type 216 U counter electrode was used. The sample was arced for 2 minutes using a Bausch and Lomb dual grating spectrograph, ARL high precision source unit, DC mode, resistance 25 ohms, current 9 amps approximately. Kodak plate Sa-1 was developed with D-19, for 4 minutes. 30,000/inch grating displayed  $\lambda 2490\text{Å} - 3410\text{Å}$  first order, 15,000/inch grating displayed  $\lambda 3300 - 4700\text{Å}$  first order, 2250 - 3000  $\text{Å}$  second order.

Quantitative estimates were made visually by comparison with a standard plate.

### APPENDIX III

#### COPPER-NICKEL ANALYSIS OF THE SULPHIDE PHASE: PROCEDURE AND LIMITATIONS

The fine grainzize of much of the disseminated sulphides in the Nemeiben Lake ultramafic rocks (in particular serpentinites) made mechanical separation of the silicate and sulphide fractions impractical. A procedure of sulphide solution was used to leach sulphides from the silicate and associated fractions. This is of particular importance for nickel because it may be several times more abundant in the silicate plus oxide component of a sample than in a sulphide component. The method used for copper-nickel employs a cold leach with a mixture of ascorbic acid and hydrogen peroxide to selectively dissolve the sulphides. This method has been extensively used in the Soviet Union (Yegorova, 1938; and Smirnova, et.al., 1968). The details of this method described by Lynch and reported by Cameron, et.al. (1971) are given below as used here.

#### A. Analytical Procedure

##### (1) Decomposition of the Sample

Weighed 1 gm of the ground rock sample into a clean dry 50 ml beaker. 35 ml of ascorbic acid-hydrogen peroxide mixture was added and allowed to stand approximately 18 hours with occasional mixing.



This solution was diluted to 50 ml with di-ionized water and vigorously shaken to mix thoroughly, then centrifuged for 5 minutes. The clear supernatant solution was stored.

Parkin Elmer Model 303 atomic absorption spectrophotometer was used to determine Ni and Cu. Standards of suitable ranges were made from stock solutions.

## (2) Preparation of Reagents

One percent acid solution: 5.0 gms ascorbic acid was dissolved in metal free water and diluted to 500 ml with metal free water. This solution should be prepared freshly just prior to using.

Ascorbic acid-hydrogen peroxide mixture: 200 ml of 30 percent hydrogen peroxide was added to 500 ml 1% ascorbic acid solution and mixed thoroughly. This solution was made each day.

## B. Limitations

Using 1 gm sample of the serpentinite and the above concentrations of solutions did not yield good recovery of the Cu, Ni values in the sulphide phases. The procedure was repeated using 0.1 gm sample of the serpentinite and 7 ml of ascorbic acid-hydrogen peroxide mixture and diluted to 10 ml with metal free water. Then the recovery of the Cu, Ni, values in the sulphide phases was quite

satisfactory. Unaltered pyroxenite from Nemeiben Lake gave good recovery for the Cu, Ni values in the sulphide phases, where as serpentinites are not so consistent.

Smirnova, et.al., (1968) have stated that common sulphide minerals of ultramafic rocks are decomposed in an ascorbic acid-hydrogen peroxide mixture within a few hours.

Cameron, et.al., (1971) stated for ultramafic rocks which have been serpentinized or altered in other ways that the ascorbic acid-hydrogen peroxide leach method is not so reliable. They pose the question whether the metals bonded within silicate alteration products and oxides are also stable to ascorbic acid-hydrogen peroxide leach. Changes that accompany serpentinization include the reduction of metal sulphides or of metals bound within primary silicates (Ramdhor, 1967) to metal alloys such as awaruite,  $Ni_3Fe$ . A sample of Josephinite, composed of a mixture of awaruite and native copper, tested by Lynch decomposed when attacked for several hours with ascorbic acid-hydrogen peroxide mixture.

The weathered serpentinites from Nemeiben Lake have not responded well to the ascorbic acid-hydrogen peroxide leach technique. It may be said that the nickel from weathered products of sulfides, and other silicate alteration products is not attacked by ascorbic acid.

This may answer the question posed by Cameron, et.al., (1971).