NOBLE METAL CONCENTRATIONS IN SELECTED KOMATIITIC AND THOLEIITIC ARCHEAN VOLCANIC ROCKS FROM MUNRO TOWNSHIP, ONTARIO

42°

# NOBLE METAL CONCENTRATIONS IN SELECTED KOMATIITIC AND THOLEIITIC ARCHEAN VOLCANIC ROCKS FROM MUNRO TOWNSHIP, ONTARIO

By

WILLIAM EDGAR MACRAE, H. B. Sc.

(Geology, Lakehead University)

A Thesis

Submitted to the School of Graduate Studies in Partial Fulfillment of the Requirements

for the Degree

Master of Science

McMaster University

May, 1982

- Title: Noble Metal Concentrations in Selected Komatiitic and Tholeiitic Archean Volcanic Rocks from Munro Township, Ontario.
- Author: William Edgar MacRae, H.B. Sc. (Geology, Lakehead University)

Supervisor: Dr. James H. Crocket

Number of Pages: xii, 96

#### ABSTRACT

The Au, Pt, Pd and Ir content of Fred's flow (a layered komatiite flow), Theo's flow (a layered tholeiite flow) and two peridotitic komatiite flows at Pyke Hill, all from Munro Township, were determined using radiochemical neutron activation analysis. In addition, the potential of Pyke Hill peridotitic komatiites as a gold source was evaluated. X-ray fluorescence spectroscopy, atomic absorption spectroscopy and a Leco automatic carbon determinator were used to determine major and trace element content in a total of 43 samples.

Estimates of the PGE content of parental magmas, ppb, are:

	Au	<u>Pt</u>	Pd	Ir
Pyke Hill	1.3	16	10	1.3
Fred's Flow	1.7	7	18	0.20
Theo's Flow	1.9	9	10	0.42

The peridotitic komatiite magma at Pyke Hill has the most mantle like proportions of Pt and Pd. None of the flows studied have been saturated with respect to sulphur. No leaching of siderophile and chalcophile elements has taken place prior to extrusion and cooling.

iii

The low gold content of the unaltered Pyke Hill peridotitic komatiites (average 2.8 ppb) do not make them obvious source rocks for gold deposits. The author wishes to thank Dr. James Crocket who suggested this study and provided valuable guidance during its many years before completion. I also wish to thank my wife, Brenda, for her help, patience and constructive comments in the final preparations.

Thanks are extended to Ms. Laurie Leavitt for typing the bulk of the material and to Mrs. Anne Pickens who typed later chapters.

This research was supported by a N.S.E.R.C. grant to Dr. J. H. Crocket.

v

# TABLE OF CONTENTS

CHAPTER 1	INTRODUCTION	1
	1.1 Purpose of study	1
	1.2 Location and Access	2
	1.3 Previous Work	4
CHAPTER 2	REGIONAL GEOLOGY	6
	2.1 Introduction	6
	2.2 Stoughton - Roquemaure Group	10
	2.3 Structure and Metamorphism	11
CHAPTER 3	GEOLOGY OF MUNRO TOWNSHIP	13
	3.1 General Geology	13
	3.2 Classification of Rock Types	15
	3.3 Distribution of Rock Types	16
CHAPTER 4	DESCRIPTION OF THE VOLCANIC ROCKS	
	IN THE STUDIED AREAS	20
	4.1 Peridotitic Komatiites	20
	4.2 Fred's Flow: A Komatiitic Layered Flow	31
	4.3 Theo's Flow: A Tholeiitic Layered Flow	38
CHAPTER 5	EXPERIMENTAL METHODS	46
	5.1 Field Study	46
	5.2 Analysis of PGE by Radiochemical	
	Neutron Activation Analysis	46
	5.3 Determination of Major and Trace Elements	52

CHAPTER	6	GEOCHEMISTRY	
		6.1 Introduction	54
		6.2 Major Element Variations	54
		6.2.1 Pyke Hill	54
		6.2.2 Fred's Flow	67
		6.2.3 Theo's Flow	71
		6.3 Trace Element Variations	71
		6.3.1 Pyke Hill	71
		6.3.2 Fred's Flow	72
		6.3.3 Theo's Flow	76
		6.4 Discussion	76
CHAPTER	7	DISCUSSION AND CONCLUSIONS	78
		7.1 PGE Content of Parental Peridotite Magma	78
		7.2 Inferences on PGE Content of Mantle Rocks	82
		7.3 Probability of Immiscible Sulfide in	
		Pyke Hill Magma.	86
		7.4 Komatiites as Source Rocks for Gold	÷
		Mineralization	88
REFERE	REFERENCES		90

# LIST OF FIGURES

Figure		Page
1	Geology of the Timmins-Kirkland Lake-	·
	Noranda region	3
2	General stratigraphy and structure of the	
	Timmins-Kirkland Lake area	9
3	Geology of Munro Township	14
4	Stratigraphic sections of the volcanic	
	Succession, Northern Munro Township	17
5	Section through the Munro volcanic pile	
	showing Mg0 variations	18
6	Geological map of Pyke Hill	21
7	Diagrammatic section through three types	,
	of peridotitic lava flows	22
8	Diagrammatic section through Fred's Flow	33
9	Diagrammatic section through Theo's Flow	40
10	Flow chart for radiochemical procedure for	-
	determination of Pd, Ir, Pt and Au	49
11	Major elements versus stratigraphic height,	
	North flow, Pyke Hill	68
12	Major elements versus stratigraphic height,	
	South flow, Pyke Hill	69
13	Al203 versus Fe0/(Fe0 + Mg0)	70

viii

Figure

14	Major elements versus stratigraphic		
	height, Fred's flow	map	pocket
15	Major elements versus stratigraphic		
	height, Theo's flow	map	pocket
16	Trace elements versus stratigraphic heigh	t,	
	North flow, Pyke Hill		73
17	Au, Ir, S, Co and Ni versus stratigraphic		
	height, South flow, Pyke Hill		74
18	Pd, Cr, Cu, Zn and Pt versus stratigraphic	C	
	height, South flow, Pyke Hill		75
19	Ir, Co, Ni and Cr versus stratigraphic		
	height, Fred's flow	map	pocket
20	Pt, Pd, Cu, Au, S, Zn and As versus		
	stratigraphic height, Fred's flow	map	pocket
21	Ir, Co, Ni and Cr versus stratigraphic	••	
	height, Theo's flow	map	pocket
22	Pt, Pd, Cu, Au, S, Zn and As versus		
	stratigraphic height, Theo's flow	map	pocket
23	Pt/(Pt + Pd) versus Cu/(Cu + Ni)		83
24	Ni versus MgO		87

Page

# LIST OF TABLES

Table		Page
Ī	North limb stratigraphy	8
ĪĪ	Average values obtained for USGS standards	52
III	Analytical results of the Pyke Hill samples	55
IV	Analytical results of the Fred's Flow samples	57
<u>v</u>	Analytical results of the Theo's Flow samples	61
VI	PGE content of Pyke Hill samples	64
VII	PGE content of the Fred's Flow samples	65
VIII	PGE content of the Theo's Flow samples	66
IX	Comparison of parental magma compositions	•
	obtained in this study.	79
x	Estimates of the PGE concentrations in the	
	parental magna for the units studied.	81

# LIST OF PLATES

Plate		Page
1	General view of Pyke Hill	23
2	View of a complete flow of Type A at Pyke Hill	23
3	Flow top of a Type A flow, Pyke Hill	25
4	Spinifex zone in a Type A flow, Pyke Hill	25
5	Foliated zone in a Type A flow, Pyke Hill	26
6	Top of cumulate zone in a Type A flow, Pyke Hill	26
7	Knobby peridotite zone in a Type A flow, Pyke Hi	11 27
8	Flow base in a Type A flow, Pyke Hill	27
9	A complete flow of Type C, Pyke Hill	29
10	Schleiren structures in a Type B flow, Pyke Hill	29
11	Flow top breccia, Fred's flow	34
12	Olivine spinifex in Fred's flow	34
13	String beef spinifex in Fred's flow	37
14	Flow base of Fred's flow	37
15	Hyaloclastite of the flow top of Theo's flow	42
16	Hyaloclastite at the flow top of Theo's flow	42
17	Basal peridotite, Theo's flow	44

xi

# LIST OF MAPS

Map

# 1 Areas of study and stratigraphic sample

positions

map pocket

#### CHAPTER 1

#### INTRODUCTION

## 1.1 PURPOSE OF STUDY

In recent years the existence of komatiitic volcanic rocks has been substantiated throughout the Canadian Shield. The best exposed and most pristine examples are located in Munro Township, Northern Ontario. Although the existence of ultramafic flows was recognized and proposed in 1964 by Naldrett (1964), it was in 1973 that Pyke, Naldrett and Eckstrand (1973) documented the existence of ultramafic flows at the base of Center Hill in Munro Township. These flows are referred to here as the Pyke Hill occurrence. Since that time extensive geological and geochemical research has taken place in the area.

This study was undertaken to determine the background concentrations of gold, platinum, palladium and iridium in the komatiitic lavas at Pyke Hill in Munro Township because of the low metamorphic grade and the excellence of bedrock exposure. As the likelihood of metamorphic redistribution of noble metals is minimal, the komatiites of Pyke Hill afford an excellent opportunity to estimate the proportions and

concentrations of PGE\* in magmas derived by high degrees of partial melting of the upper mantle. They are also probably representative of the PGE characteristics of komatiitic magmas which yield Ni-Cu-PGE sulphide ores if subject to saturation with sulphur. It was also shown by Arndt (1975) that other distinctive mafic-ultramafic rock types are present in Munro Township including thick (120 m), layered, differentiated flows of both komatiitic and tholeiitic kindred. These flows provide an opportunity to compare the geochemical behaviour of the PGE in highly differentiated, layered flows of komatiitic and tholeiitic kindred.

It was also recognized that a study of the gold content of the essentially unmetamorphosed ultramafic flows from Munro Township might provide useful data to evaluate the proposed association of gold deposits and ultramafic volcanic rocks in the Abitibi belt (Pyke, 1975).

## 1.2 LOCATION AND ACCESS

Munro Township is situated 13 km southeast of Lake Abitibi and 83 km east of the City of Timmins (Figure 1). Highway 101 follows, approximately, the southern township boundary and a well maintained gravel road provides access

<sup>\*</sup> In this study the abbreviation PGE means platinum group elements plus gold.



Figure 1 Geology of the Timmins-Kirkland Lake-Noranda region (from Goodwin, 1979).

ω

to the central and northern portions of the township.

## 1.3 PREVIOUS WORK

The geology of Munro Township was described by Satterly (1951). Several theses were written on differentiated sills of the area prior to the recognition of extrusive ultramafic lavas. Freeman (1956) described the Munro Sill and Grubb (1962) reported on the sill and associated serpentine and chrysotile formation. MacRae (1963, 1965, 1969) described the Center Hill complex and a number of sills in the area. The first recognition and detailed description of ultramafic lavas in Munro Township was presented by Pyke et al (1973) who described the relatively fresh, well exposed outcrop of ultramafic lavas comprising the Pyke Hill (Spinifex Hill) occurrence in central Munro Township. This paper followed a publication by Viljoen and Viljoen (1969 a,b) alerting geologists to the existence of extrusive Archean ultramafic rocks in the Barberton mountain Land area of South Africa and the recognition by Nesbitt (1971) of skeletal crystal forms in ultramafic rocks of the Yilgarn block, Australia, which he cited as evidence for an Archean ultramafic liquid. Arndt (1975, 1977) and Arndt et al (1977) has presented the most detailed disucssion of the geology, chemistry, and petrology of ultramafic and mafic rocks in several areas of Munro Township, including the komatiite

lavas of Pyke Hill and the mafic-ultramafic rocks in two layered flows. The noble metal geochemistry of these occurrences is the subject of this thesis.

#### CHAPTER 2

#### REGIONAL GEOLOGY

### 2.1 INTRODUCTION

Munro Township is situated just north of center of the Abitibi greenstone belt in the Superior province of the Canadian Precambrian Shield. The regional geology is presented in Figure 1. Goodwin (1968, 1973) describes the Abitibi belt as a crudely S shaped structure approximately 650 km long and 150 km wide which extends in an east northeast direction from Wawa on the northeast shore of Lake Superior to Chibougamau in Quebec. On the north and south the belt is bounded by metasedimentary and gneissic rocks of the Kapuskasing sub-province and the Grenville Province respectively. It is composed of volcanic and sedimentary rocks intruded by granitic plutons. The volcanic rocks range in composition from minor ultramafic lavas to abundant basalt to dacite flows and minor rhyolite lavas and pyroclastic rocks.

There are five volcanic groups ranging chemically from calc-alkaline in the oldest through komatiitic, tholeiitic, calc-alkaline and alkaline in the youngest. Within

each group volcanic cycles vary compositionally from ultramafic and mafic at the base to intermediate and felsic at the top. Sediments, such as argillite, greywacke, conglomerate and banded iron formations are intercalated with volcanics particularly near the tops of cycles. Ultramafic and mafic intrusions such as dykes, sills and small plutons, are present and are more abundant in the lower parts of the cycle.

The general stratigraphy and structure of the Abitibi greenstone belt in the Timmins-Kirkland Lake area, including Munro Township, were recently synthesized by Jensen (1980), Arndt and Jensen (1979, personal communication), Jensen (1979) and Pyke (1978, 1980). Two volcanic cycles or supergroups of rocks are recognized, and their spatial distribution is shown in Figure 2. A major structural element of regional extent is an easterly plunging synclinorium whose axial plane lies roughly midway between the Lake Abitibi and Round Lake batholiths. The Munro Township rocks of interest in this study lie on the north limb of this structure.

A stratigraphic succession applicable to Munro Township is presented in Table I. As indicated in the general stratigraphy of the regional map (Figure 2) the komatiitic rocks of the Munro Township area belong to the Stoughton-Roquemaure Group, the basalt subgroup of the upper volcanic cycle or Supergroup.

Group	Volcanic Rocks	Sediments	Intrusive Rocks	Relationship
Timiskaming Gr. Destor-Porcupine Fault Section 1000 m	Na-rich mafic to felsic alkali volcanic rocks	Turbidites-congl. gwke, argillite iron formation	Mafic to felsic syenodiorites, syenites	Faulted contact with SRG and KG
Blake River Gr. (BRG) 12,000 m	Calcalkalic basalt, andesite, dacite and rhyolite flows and pyroclastic	Volcaniclastic turbidites derived by slumping off volcanic edifices	Gabbro, diorite quartz diorite, and rhyolite domes	Conformably overlies KG
Kinojevis Gr. (KG) 10,000 m	Mg-rich and Fe-rich theoleiitic basalt with minor thol- eiitic andesite, dacite and rhyolite flows	Hyaloclastite and argillite, chert and graphite	Gabbro	Conformably overlies SRG
Stoughton- Roquemaure Gr. (SRG) 10,000 m	Peridotitic and basaltic komatiite and Mg-rich thol- eiitic basalt, Fe-rich tholeiitic basalt at base and top of group	Minor iron form- ation, chert and tuff	Dunite, perid- otite, pyroxen- ite, and gabbro	Disconformably to unconformably overlies HMG or is intruded toward base by Fe-rich thol- eiitic basalt.
Hunter Mine Gr. (HMG) 1,500 m	Calcalkalic basalt, andesite, dacite and rhyolite flows and pyroclastics	Distal tuffs, gwke, argillites, carbonates and iron formation	Rhyolite and dacite breccia dykes and trond- hjemite	Intruded by trondhjemite of Lake Abitibi batholith



Figure 2 General stratigraphy and structure of the Timmins-Kirkland Lake area (from Jensen, 1980)

#### 2.2 STOUGHTON-ROQUEMAURE GROUP

The Stoughton-Roquemaure Group is a komatiitic suite of rocks which overlies the Hunter Mine Group, a calcalkaline suite belonging to the Lower Supergroup. Peridotitic and basaltic komatiites are abundant within the group and are the lithologies that distinguishes it from the overlying tholeiitic volcanics of the Kinojevis Group. The ultramafic komatiites were first recognized by Eakins (1972) in Roquemaure Township, Quebec. The sequence is approximately 10,600 m thick with the lower 4900 m first documented in Roquemaure Township and the upper 5700 m in Stoughton Township, Ontario.

Basaltic rocks comprise the major part of the lower 4900 m of the Stoughton-Roquemaure Group and are massive and pillowed flows. Eakins (1972) describes the volcanic rocks as mafic to ultramafic in composition with coarse grained mafic to ultramafic sills within the basalts. These sills are now recognized as thick differentiated flows. Jensen (1978) describes the upper section of the Stoughton-Roquemaure Group in Stoughton Township as primarily pillowed lavas and thin massive flows of basaltic komatiite and magnesium-rich basalt. A few flows of ultramafic komatiite and iron-rich basalt also occur in this section of the sequence. Cherty iron formation and finely bedded argillaceous tuff are intercalated with some of the lava flows, in particular the ultramafic komatiite and iron-rich basalt flows. The upper 1000 m contain thin massive flows of magnesium-rich and iron-rich tholeiitic basalt with the magnesium-rich basalts dominating near the top. The group is capped by a felsic unit composed of rhyolite tuff and tuff breccia associated with a finely laminated chert.

The Stoughton-Roquemaure Group rocks are conformably overlain by the tholeiitic and calc-alkaline suites of the Kinojevis and Blake River Groups respectively (Jensen, 1979, 1980).

### 2.3 STRUCTURE AND METAMORPHISM

In Munro Township, the volcanic and sedimentary rocks of the Abitibi Belt are tightly folded about east trending axes. Typically the folds are steeply isoclinal and doubly plunging (Goodwin <u>et al</u>. 1970). A later period of more open folding about north trending axes has also affected the area.

Strike slip faulting, in easterly and east southeasterly directions, represents an early, rather inconspicuous event that may be responsible for stratigraphic repetition. The Destor-Porcupine Fault zone in the area is of this type. This early faulting preceeded the intrusion of dykes and related intrusions.

A later period of more obvious, northwesterly and

northerly trending faulting causes displacements in all rock types.

The metamorphic grade in the region is very low and prehnite-pumpellyite facies predominate except in the aureoles of intrusions where grades of upper amphibolite are observed (Jolly, 1974).

#### CHAPTER 3

#### GEOLOGY OF MUNRO TOWNSHIP

### 3.1 GENERAL GEOLOGY

Rock exposed in Munro Township (Figure 3) are part of the upper portion of the Stoughton-Roquemaure Group. They include ultramafic and mafic lavas, peridotite sills, chert, felsic tuff, gabbro and diabase. The major rock types are ultramafic and mafic lavas most of which are thin (2 to 25 m) flows with relatively uniform compositions. Within the thin flows are occasional, thick (100 to 300 m) differentiated flows ranging in composition from peridotite at the base to gabbro at the top. Two such flows in the north central part of the township (see Figure 3), Fred's flow, a differentiated komatiitic flow and Theo's flow, a differentiated tholeiitic flow, were sampled for this study. These units and the geology of the area were mapped at a scale of 1 inch to 400 feet by Arndt (1975). Sills of similar composition and dimension apparently represent comparable magmas intruded into the volcanic pile. Small peridotite sills also occur and thin but laterally extensive beds of chert and felsic tuffaceous rocks are intercalated



Figure 3 Geology of Munro Township (from Arndt, 1977)

.

with the volcanics in the northern part of the township.

Several gabbroic complexes intrude the volcanic rocks and associated sills. These intrusives are concordant to discordant in the volcanic strata. Diabase dykes of both the Matachewan and Nipissing dyke swarms intrude all earlier rock types.

The classic bedrock exposure of thin ultramafic flows at Pyke Hill which was mapped at 1 inch to 10 feet by Pyke <u>et al</u> (1973) was also sampled for this study. Except for the gabbroic complexes and diabase dykes, all rocks are folded about east-west axes. The Pyke Hill area is on the north facing south limb of a west plunging syncline. Fred's and Theo's flows are on the north limb of the same west plunging syncline.

Faulting in northeasterly and east southeasterly directions displaces all rock units. The northeasterly faulting causes mappable horizontal displacements of several hundred metres. The east southeast faults are the most significant and cause large displacements of all early strata.

## 3.2 CLASSIFICATION OF ROCK TYPES

Arndt (1975) divided the volcanic and hypabyssal rocks of Munro Township into the four groups outlined below. Two magmatic associations were recognized including:

1. The komatiitic association of lavas and sills with compositions ranging from peridotite to andesite, and

2. The tholeiitic association of lavas with compositions ranging from pyroxenite to dacite.

The rocks of both magmatic associations were subdivided into two separate groups:

 Discrete, relatively thin (1 m) flows with uniform compositions throughout, (e.g. - flows of the Pyke Hill locality).

 Thick (150 to 500 m), layered flows and sills ranging, in composition, from peridotite at the base to gabbro at the top, (e.g. - Fred's and Theo's flows).

## 3.3 DISTRIBUTION OF ROCK TYPES

Arndt <u>et al</u> (1977) presented three stratigraphic sections (Figure 4) from northern Munro Township and a generalized section (Figure 5) through the volcanic pile which show the stratigraphic setting of Fred's and Theo's flows. Volcanic units thin to the west with an increase in the proportion of komatiitic basalts.

The base of the succession (generalized section, Figure 5) is a sequence of tholeiitic basaltic and andesitic flows and fragmental rocks whereas in the top half, the succession is dominated by komatiitic flows. The top of the basal tholeiitic sequence is marked by a thick



Figure 4 Three stratigraphic sections of the volcanic succession in the northern part of Munro Township (from Arndt et al, 1977)



Figure 5 Detailed but generalized section through the Munro Volcanic Pile showing MgO variations in the Lavas, legend as in Figure 4 (from Arndt <u>et al</u>, 1977) differentiated flow - Theo's flow - or by undifferentiated tholeiitic basalts, all of which are overlain by Fred's flow, a thick differentiated, pyroxenitic komatiite flow. Fred's flow is overlain by thin, komatiite flows. Thick layered sills including the Munro-Warden complex and the Beatty sill (MacRae, 1969), intrude the base of the komatiitic sequence. According to Arndt <u>et al</u> (1977) the ultramafic lavas of Pyke Hill correlate with the lowermost peridotitic komatiites in the succession (Figure 5).

Three volcanic cycles distinguished largely on a basis of varying MgO content are recognized in the komatitic upper half of the section. Lavas gradually become less mafic until a basaltic stage is reached at which point the composition then becomes peridotitic either abruptly, as in cycle 1, or gradually, as in cycle 3 of the succession. Composition and position within the cycle control the size and characteristics of the lava flows. The thinnest flows are the komatiites which initiate a The lower, spinifex bearing flows are only 1 to 2 m cycle. thick. Komatiites higher in the cycle generally are spinifex free, thicker, and of more limited lateral extent. Komatiitic basalt flows are from 3 to 15 m thick low in the komatiitic sequence but thicker, more discrete flows are found in the middle of the sequence.

#### CHAPTER 4

### DESCRIPTION OF THE VOLCANIC ROCKS IN THE STUDIED AREAS

# 4.1 PERIDOTITIC KOMATIITES

The best exposure of peridotitic komatiites is at Pyke Hill (Plate 1). There are approximately sixty-three flows discernable (Figure 6) ranging in thickness from 0.5 to 17 m and in length, from 5 to 200 m. Some but not all flows, exhibit spinifex texture. Spinifex-bearing flows represent an end member of a progression from flows containing no spinifex to flows that contain up to 50% spinifex. The textural variations within spinifex-bearing and spinifexfree flows are shown in Figure 7 from Arndt et al (1977). The flows with well developed spinifex zones (Flow A, Figure 7, Plate 2) have flow tops containing equant olivine phenocrystals and fine grained, randomly oriented, equant skeletal or thin-bladed olivine crystals in a matrix of glass altered to chlorite and serpentine. The flow top has developed polyhedral jointing imparting the appearance of a breccia (Plate 3).

Below the flow top  $(A_1 \text{ zone})$  is a zone  $(A_2)$  containing bladed olivine crystals that increase in size and



Figure 6 Geological map of Pyke Hill showing peridotitic komatiite lava flows (from Pyke et al, 1973)



Figure 7 Diagrammatic section through three types of peridotitic lava flows: A, a flow with an upper spinifex zone; B, a flow with a limited spinifex zone; C, a flow without a spinifex zone (from Arndt <u>et al</u>, 1977) Plate 1. General view of Pyke Hill, looking east (stratigraphic top to left).

Plate 2. View of a complete flow of Type A at Pyke Hill The flow is 3.25 metres thick with the flow top to the left.


decrease in randomness of orientation from top to bottom of the zone (Plate 4). As the olivine blades increase in size and become oriented sub-perpendicular to the flow direction they are arranged in books or sheaths. The spinifex zone shows a sharp contact with the underlying B<sub>1</sub> zone.

The B, or "foliated zone" contains tabular olivine grains aligned parallel to the flow direction (Plate 5). The foliated zone may or may not be present but if present may be up to 30 cm thick. The contact between the foliated zone and the underlying cumulate zone  $(B_2)$  is gradational (Plate 6). The cumulate zone is characterized by equant olivine grains in a matrix of skeletal subcalcic clinopyroxene, cruciform, dendritic or euhedral chromite and altered glass. Olivine grain size increases toward the zone base. The B<sub>3</sub> zone or the "knobby peridotite zone" (Pyke et al, 1973) is present at Pyke Hill but is not known to occur elsewhere in the township. It is characterized by a rough weathering surface produced by rounded accumulations of matrix material (Plate 7). The  $B_A$  zone is a basal peridotite, actually a continuation of the B<sub>2</sub> zone interrupted by the B3 zone. At the base of the flow there is a thin zone of chilling with minor polyhedra (Plate 8).

Over half of the exposed flows contain no spinifex textures and are considered Type C as in Figure 7. Polyhedral jointing is present throughout Type C flows (Plate 9).

Plate 3. Flow top of a Type A flow, Pyke Hill (contact below camera lens cap).

Plate 4. Spinifex zone in a Type A flow, Pyke Hill (top to the left).



Plate 5. Foliated zone in a Type A flow, Pyke Hill. The bottom of the spinifex zone is visible at the top of the photo.

Plate 6. Top of cumulate zone in a Type A flow, Pyke Hill. The top of the knobby peridotite zone can be seen at the bottom of the photo.



Plate 7. Knobby peridotite zone in a Type A flow, Pyke Hill.

Plate 8. Flow base in a Type A flow, Pyke Hill. Also present is the base of the cumulate zone and part of the knobby peridotite zone.



The joints are close spaced and rectangular near the top and become longer, thicker, more widely spaced and gently curved towards the center of the flow. Such flows contain 45 to 55% equant olivine crystals with over-growths of skeletal olivine. In Type C flows the size and habit of olivine grains are similar to the grains in the B<sub>3</sub> zone of spinifex bearing flows but are less abundant. The matrix is composed of altered glass and skeletal, dendritic, radiating and plumose growths of clinopyroxene. Chromite occurs as dendritic and cruciform crystals and, occasionally, as euhedral cube shaped grains. Flows that contain only a limited spinifex zone (Type B, Figure 7) have a polyhedrally jointed A, zone and a thin spinifex-textured The spinifex-textured zone is underlain by the A, zone. B zone which contains equant olivine grains that have some skeletal olivine overgrowths. In a zone 1 to 2 m thick just below the spinifex-textured region is a zone that may contain crescent shaped, concave upward bodies called These schleiren are from 2 to 10 cm thick and schleiren. from 0.5 to several m long (Plate 10). They can be isolated bodies or they may be connected to the spinifex-textured A<sub>2</sub> zone by small cross-cutting veins. The proportion of olivine grains increases down section until a maximum of 60 to 70% olivine is reached three-quarters of the way through a flow. Olivine then decreases towards the bottom.

Plate 9. A complete flow of Type C, Pyke Hill. The flow is 1 metre thick (top at top of photo).

Plate 10. Schleiren structures in a Type B flow, Pyke Hill.

.

•

,





An interpretation of the Pyke Hill flows was offered by Pyke et al (1973) and additional comment was given by Arndt et al (1977). Further comment on their mode of formation is noted here. Peridotite flows, containing between 10% and 15% olivine phenocrysts, are extruded onto the sea floor. Within an hour horizontal movement ceases and a thin chilled crust forms on the flow top. The original (telluric) olivine phenocrysts begin settling and crystallization of additional olivine phenocrysts begins. As the phenocrysts settle a crystalfree zone forms under the chilled crust that is thickening at a rate of 1 to 3 cm per hour during the first 10 hours (Bickel, 1979, personal communication). The crystal free zone contains no nucleui greater than 100  $\stackrel{0}{A}$  and cools at a rate less than  $\frac{1}{2}^{O}C$  per hour (Lofgren, 1979, personal communication). Skeletal olivine begins to form in the crystal-free zone next to the thickening flow top. The crystal free zone continues to widen but at a progressively slower rate due to the greater abundance of phenocrysts. In the crystal free zone skeletal olivine continues to grow increasing in size and decreasing in randomness of orientation with the blades of olivine aligning perpendicular to the thermal gradient and original flow direction. A foliated zone may form by the accumulation of early skeletal olivine that is detached from the flow top by

minor convection currents or seismic shocks, and settles to the bottom of the crystal free zone. Eventually, depending on factors such as flow thickness and extrusion temperature, the flow will cool to a point where no further settling of olivine phenocrysts occurs and the skeletal olivine fills the available crystal-free space.

The pertinent points relevant to textural development are:

1. The flow must cease all lateral movement before spinifex can form.

 Thicker and/or hotter flows will develop larger spinifex zones.

3. Spinifex develops in a peridotitic liquid with 0no nucliation centers larger than 100 A and with cooling rates of less than  $\frac{1}{2}^{O}C$  per hour, and

4. The most important consideration is that the Type C and Type A flows are the end members of a continuous process.

4.2 FRED'S FLOW: A KOMATIITIC LAYERED FLOW

This flow was named after Frederick John Wicks who first found the clinopyroxene spinifex. Fred's flow has been traced along strike for 6 km and reaches a maximum thickness of 160 m near its eastern end of exposure (Arndt, 1975, 1977). To the west, however, it thins markedly. Figure 8 is a diagrammatic cross-section through Fred's flow showing the major units. The units are very persistent laterally, and as the flow thins, each unit also becomes proportionally thinner.

The brecciated flow top (Plate 11) is pyroxenitic komatiite in composition (16-20% MgO) and the breccia is foliated with crude cross and graded bedding. Fragments near the top of the flow are small (1 mm to 1 cm) and angular, and are either amygdaloidal or porphyritic. The porphyritic types contain microphenocrysts of olivine, that have been serpentinized and replaced by chlorite, quartz, or carbonate. The matrix is devitrified mafic glass.

Fragment size increases to about 10 cm towards the base of the breccia zone where fragments are sub-rounded to rounded. The larger fragments contain equant grains altered solid or skeletal olivine in a groundmass of fine grained skeletal and acicular augite and devitrified glass. The matrix between the fragments is similar in composition and texture to that in the fragments but is richer in relict glass.

The breccia grades downwards into the spinifextexture zone and microspinifex develops in the fragments and matrix. The upper portion of the spinifex zone contains randomly oriented, bladed olivine grains (Plate 12) in a matrix of acicular, skeletal clinopyroxene in devitrified



Flowtop breccia Fragments composed of 30% equant olivine phenocrysts in a matrix of clinopyroxene and devitrified glass.

Olivine spinifex textured lava 5% randomly oriented olivine wafers in a clinopyroxene-rich matrix.

<u>Clinopyroxene spinifex textured lava</u> Large needles of clinopyroxene with orthopyroxene or pigeonite cores oriented perpendicular to the flowtop, in a matrix of plagioclase and fine acicular pyroxene.

<u>Transition zone</u> Isolated large clinopyroxene grains in a basaltic matrix.

<u>Medium-grained gabbro</u> Discrete coarse grains of clinopyroxene and plagioclase. Up to 10% quartz in the groundmass.

Pyroxene cumulate Subhedral cumulate grains of clinopyroxene and lesser orthopyroxene.

Olivine cumulate Close-packed, equant, euhedral grains of olivine, minor anhedral and acicular clinopyroxene in a glassy groundmass.

Border zone 30% olivine, 30% orthopyroxene, 30% clinopyroxene; subhedral equant grains.

Figure 8 Diagrammatic section through Fred's Flow, a Komatiitic layered flow (from Arndt <u>et al</u>, 1977) Plate 11. Flow top breccia, Fred's flow.

Plate 12. Olivine spinifex in Fred's flow (top to the right in the photo).





glass. The olivine spinifex occurs only in the upper 0.3 to 2 m of the spinifex zone with clinopyroxene spinifex comprising most of the spinifex zone. The olivine content decreases as the clinopyroxene forms long, thin needles perpendicular to the flow top (Plate 13). The clinopyroxene needles are up to 3 cm long and 0.7 mm wide and are set in a matrix of fine augite, plagioclase and minor quartz and chlorite. The needles consist of a discontinuous chlorite core probably after pigeonite (Arndt, 1975, 1977) and a rim of augite. The clinopyroxene mantles are highly zoned from magnesium rich at the inner contact to iron rich at the margin (Arndt, 1975 1977).

Near the bottom of the spinifex-texture zone, the pyroxene needles become less abundant, shorter, thicker, and stubbier while the plagioclase and pyroxene grains in the matrix increases in size.

The gabbro unit consists of intergrowths, or less commonly, subhedral discrete grains of clinopyroxene and plagioclase. The pyroxene grains have colourless cores rimmed by brownish pyroxene which in turn are mantled by pleochroic green amphibole. Small euhedral grains of quartz make up to 15% of the gabbro.

The occurrence of coarse patches of chlorite (7 mm in diameter) marks the base of the gabbro unit and the top of the cumulate unit. The chlorite patches increase in frequency with increasing clinopyroxene and decreasing plagioclase. The original subhedral orthopyroxene grains poikilitically enclose smaller grains of plagioclase and clinopyroxene. In the upper part of the cumulate zone there is a progression in rock type from websterite to clinopyroxenite to peridotite but this progression is often disrupted by rhythmic banding and layering. The pyroxenite zone is only 20 m thick with olivine becoming the dominant cumulus mineral in the underlying zone. Orthopyroxene is generally completely altered to chlorite or serpentine except when it occurs as small intercumulus grains in the peridotite zone.

In the peridotite zone olivine usually occurs as equant, solid, euhedral grains but sometimes as elongate prismatic grains. The olivine grain size of both habits is larger in the peridotite zone than in peridotitic komatiite flows. Equant grains are from 0.5 to 1.5 mm and prismatic grains from 0.7 to 3 mm in length (Arndt, 1975, 1977). The olivine grains are in a groundmass of clinopyroxene and/or orthopyroxene and plagioclase. Cubes and octahedra of chromite were noted in all cumulates, but were most common in the peridotite zone.

The border zone occupies the lower 10 m of the flow (Plate 14), euhedral grains of orthopyroxene and clinopyroxene gradually replaced the olivine. This zone contains

Plate 13. String beef spinifex in Fred's Flow (top of flow toward top of photo).

Plate 14. Flow base of Fred's Flow. The contact is just above the lens cap with dark brown weathering peridotite at the top and gray weathering basalt at the bottom.



approximately equal amounts of orthopyroxene, clinopyroxene and olivine, with minor amounts of brown hornblende and chromite. The lower contact is a 15 cm chilled zone composed entirely of hydrous minerals. Small euhedral phenocrysts of green-brown amphibole (0.2 mm) are enclosed in a matrix of very fine needles of the same mineral and minor chlorite.

Arndt (1975, 1977) gives the following sequence of events for the formation of Fred's flow. A lava of pyroxenitic komatiite composition containing 10-20% olivine phenocrysts was erupted very rapidly to produce a thick, extensive lava flow. The basal border zone formed from a phenocryst-depleted liquid due to flowage differentation which kept the olivine phenocrysts suspended above the base of the flow. As movement ceased telluric olivine phenocrysts and cumulus olivine accumulated at the base to form the peridotite zone. Simultaneously large skeletal crystals grew downward from a chilled flow top breccia to form the spinifex zone. The olivine depleted liquid crystallized pigeonite and augite in the spinifex zones and orthopyroxene and augite in the cumulate zones. The residual fractinated liquid crystallized as gabbro.

## 4.3 THEO'S FLOW: A THOLEIITIC LAYERED FLOW

This flow was named after the discoverer of the

hyaloclastite flow top, Nicholas Theodore Arndt. Figure 9 from Arndt et al (1977 ) is a diagrammatic section through Theo's flow which immediately underlies Fred's flow and has many characteristics in common with it. For example, Theo's flow is as thick as Fred's flow, although not as laterally extensive, and both are differentiated. To the east Theo's flow gradually divides into a number of thinner flows that are gradational into or have sharp intrusive contacts with aphanitic pyroxenite and tholeiitic basalt To the west the flow is terminated by a zone of flows. northeast faulting. The stratigraphic position of Theo's flow west of the faulting is occupied by a band of mafic hyaloclastites and volcanic breccias (Arndt, 1975, 1977). In the area studied Theo's flow is 180 m thick and 500 m long.

Although Fred's and Theo's flow have some similarities, their flow top zones are strikingly different. Theo's flow has no spinifex and the flow top breccia is composed of hyaloclastite while the top of Fred's flow was partially formed as a friction breccia (Arndt, 1977). In Theo's flow pea-sized fragments occur at the top of the hyaloclastite zone in which there may be angular and shardshaped or sphericle to subrounded globules (Plate 15). Preserved in some of the fragments are basaltic textures with relect phenocrysts of plagioclase, clinopyroxene and



<u>Hyaloclastite</u> Well-sorted, pea-sized fragments, or larger angular fragments and globules of glassy pyroxenitic material.

Aphanitic pyroxenite Fine pyroxene grains mantled by brown amphibole.

<u>Pegmatoid gebbro</u> Patchy distribution of coarse to very coarse (3 cm) subhedral grains of clinopyrexene and plagioclase.

Normal gabbro Medium grained clinopyroxene and plagioclase.

Noritic gabbro 10% orthopyroxene grains, now altered to chlorite, within a normal gabbroic rock.

Pyroxene cumulate Subhedral grains of clinipyroxene and lesser, (10%) orthopyroxene.

<u>Olivine cumulate</u> 70% equant subhedral grains of olivine, 20% anhedral grains of clinopyroxene and orthopyroxene in a glassy matrix.

Figure 9 Diagrammatic section through Theo's Flow, a Tholeiitic layered flow (from Arndt et al, 1977) olivine but most fragments are composed of sideromelane (Arndt, 1975, 1977). The matrix is chloritized glass shards and fine grained detritus.

Near the base of the hyaloclastite zone the fragments are up to 20 cm in diameter and have cores with a basaltic texture and rims of altered glassy material (Plate 16). The larger fragments may be angular or be highly irregular and ameboid in shape.

Underlying the hyaloclastite zone is a fine grained, gray, aphanitic pyroxenite. The pyroxenite is composed of subhedral augite grains (0.5 to 1 mm) rimmed by fibrous green amphibole. Minor constituents are chlorite and oxides. A breccia less mafic in composition than the flow top, forms veins and dykes intruding the hyaloclastite, aphanitic pyroxenite and sometimes the underlying gabbro. Theo's breccia veins probably formed at a late stage in the cooling of the flow due to entrance of sea water into the semi-solid rock or molten lava along cooling cracks. Reaction with the rock produced a hyaloclastic type breccia.

The aphanitic pyroxenite zone is 3 to 12 m in thickness and appears to vary inversely with the thickness of the hyaloclastite zone. Polyhedral jointing is common in this zone.

Aphanitic pyroxenite grades gradually into the gabbro zone. The contact is defined by grain size and mineralogical

Plate 15. Hyaloclastite at the flow top of Theo's flow.

Plate 16. Hyaloclastite at the flow top of Theo's flow.



variations. Generally the gabbro is a medium grained, equigranular rock composed of plagioclase, clinopyroxene and iron oxides. Near the base of the gabbro zone chloritized orthopyroxene grains appear. The lower contact of the gabbro zone is defined by the disappearance of cumulate plagioclase.

In Theo's flow, unlike Fred's flow, clinopyroxene is the dominant cumulus mineral. Olivine forms only a 2 to 10 m thick unit at the base of the ultramafic cumulate zone. In the basal peridotite (Plate 17) the cumulus minerals include approximately 30% olivine, about 30% clinopyroxene and 15% orthopyroxene. Minor amounts of brown hornblende and plagioclase are also found. In general the olivine has been serpentinized and the orthopyroxene altered to chlorite.

The pyroxene cumulate is a medium grained rock composed primarily of colourless augite (60-80%) which is often twinned and exhibits diallage structure. The pyroxene cumulate also contains minor orthopyroxene which forms euhedral prismatic grains that are highly chloritized. The intercumulus material is an acicular intergrowth of clinopyroxene and plagioclase and fine opaque minerals.

The boundary area between the clinopyroxenite and peridotite units often contains rhythmic layering of peridotite, clinopyroxenite, and/or websterite. The basal zone,

Plate 17. The basal peridotite (reddish brown portion of outcrop at top of photo) of Theo's flow. Photo taken from the pyroxene cumulate zone.



underlying the ultramafic cumulate zone, is aphanitic pyroxenite and hyaloclastite similar to the flow top but with highly variable thickness. The hyaloclastite varies from 0.5 to 5 m in thickness.

Arndt (1975, 1977) proposed that Theo's flow formed from a magma of piciitic composition containing 15% to 20% olivine and pyroxene phenocrysts. The magma erupted in a submarine environment producing large quantities of hyaloclastite breccia which formed a thick insulating blanket under which the lava differentiated to form the ultramafic cumulate rocks and a basaltic residual liquid. The residual liquid crystallized to form the gabbroic zone.

#### CHAPTER 5

### EXPERIMENTAL METHODS

### 5.1 FIELD STUDY

The excellent detailed maps of Pyke Hill (Figure 6) and Fred's and Theo's flows provided by Pyke <u>et al</u> (1973) and Arndt (1975) respectively were used as the basis for sampling each of the areas studied. The studied areas are outlined on Map 1. The samples from Pyke Hill were taken from two flows that were well defined as discrete spinifex bearing flows (Figure 6). Fred's flow was sampled in two localities, the first exposed the upper portion of the flow from the flow top breccia to the gabbroic unit and the second locality exposed the cumulate units and basal contact. Theo's flow was exposed as a single outcrop and was sampled at approximately equal spaced intervals throughout the flow. The samples were taken from only fresh unweathered material and were at least 2 kg in weight.

# 5.2 ANALYSIS OF PGE BY RADIOCHEMICAL NEUTRON ACTIVATION ANALYSIS

The samples were crushed to pea sized chips and then an aliquot powdered to 200 mesh and 200 to 250 mg

was accurately weighed ( $^{\pm}$  0.001 mg) into a labelled quartz ampoule of 2 mm inside diameter. The ampoules were sealed with a gas-oxygen flame or aluminum foil and fibreglass tape.

Standard hydrochloric acid solutions of Pt, Pd, Ir and Au were prepared from Johnson Matthey "Specpure" Pt, Pd, and Au sponge and ammonium chloroiridate. Au and Pd were combined into a single solution in 2M HCl while Pt and Ir were prepared as a separate solution (Crocket <u>et al</u>, 1968). Approximate solution concentrations were : Au, 10 ppb; Pd, 80 ppb; Ir, 0.25 ppb and Pt, 500 ppb.

The standards were prepared for irradiation by accurately weighing a quantity of solution into quartz ampoules with a capillary glass pipette. Approximately 50 mg of 100-200 mesh fused quartz powder was then added to absorb the solution. The ampoules were put in a drying oven at 70°-75°C overnight. Irradiation units consisted of 8 to 10 samples and 4 standards (2 containing Au and Pd and 2 containing Pt and Ir) packaged in an aluminum radiation can.

The samples and standards were irradiated in the McMaster pool type research reactor at an average total neutron flux of  $2 \times 10^{13} n/cm^2/sec$ . Variation of the neutron flux with position in the reactor requires that the same loading position (7E) or one adjacent be used for all

irradiations. The samples were irradiated for 36 to 40 megawatt hrs. and cooled for 72 hrs. A second 6 to 9 megawatt hr. irradiation was carried out after 72 hrs. to induce sufficient 13.5 hr 109Pd activity as that generated during the first irradiation decays significantly during the first 72 hr. cooling period. After a final 9 hr. cooling period the radiochemistry was started.

As sensitivity is dependant upon induced activity, the nuclide with highest yield is generally counted. For this reason <sup>109</sup>Pd, <sup>198</sup>Au and <sup>199</sup>Au (from <sup>199</sup>Pt by a beta decay) were used for the respective elements. Despite the somewhat higher yield of <sup>194</sup>Ir, <sup>192</sup>Ir is preferred because of the convenience of the 74 day half-life and the diagnostic gamma spectrum. The pertinent nuclear reactions are:

26.7% <sup>108</sup>Pd (n, 𝔅) 13.46 hr. <sup>109</sup>Pd (𝔅 only), 37.3% <sup>191</sup>Ir (n, 𝔅) 74.3 day <sup>192</sup>Ir (𝔅: 290, 308, 316, 470 Kev), 7.21% <sup>198</sup>Pt (n, 𝔅) 0.5 hr <sup>199</sup>Pt𝔅....> 3.12 day <sup>199</sup>Au (𝔅: 158 Kev),

100% <sup>197</sup>Au (n, **%**) 2.695 day <sup>198</sup>Au (**%**: 412 Kev).

The analytical procedures used were those described by Crocket <u>et al</u> (1968) and Keays (1968) with modifications developed by Teruta (1974). A detailed discussion of these procedures is not undertaken here but a flow chart is present in Figure 10.

<sup>109</sup> Pd betas were counted with a Nuclear Chicago beta

Figure 10 FLOW CHART FOR RADIOCHEMICAL PROCEDURE FOR DETERMINATION OF Pd, Ir, Pt and Au Na<sub>2</sub>O<sub>2</sub> - NaOH Fusion of Samples + Carriers Leach with 2M HNO, Convert to Chlorides with Aqua regia Adsorb on Dowex I Anion Resin in presence of Ce<sup>IV</sup> Adsorbed Not Adsorbed Pd, Ir, Au, Pt Alkalis, Alkaline Earths, Rare Earths, Other Elute Resin with Transition Elements 0.1M HCl - 0.1 M Thiourea Solution Eluted Retained I Pd, Au Ir Elute Ir with 6M HCl Evaporate solution to 75 ml and precipitate sulphides by adding conc. NH<sub>4</sub>OH Fe(OH); and Cr(OH); Centrifuge precipitate, dissolve in Aqua regia, convert to chlorides scavenge and take up to 15 ml of 6M HCl Precipitate Ir<sup>o</sup> with Zn<sup>o</sup> Ethyl Acetate Extraction HCl Phase Organic Phase Pd Au Precipitate Au<sup>O</sup> Fe(OH) , scavenge with Hydroquinone Precipitate Pd<sup>II</sup> with DMG

counter, consisting of a scaler-timer, an automatic sample changer and a proportional gas flow Geiger-Mueller counting tube with coincidence shielding. The detector had an average background of 3.0 counts per minute. Electronic drift was monitered by an Uranium standard source.

For the gamma counting a model 4410 Nuclear Data system employing a 50 mH<sub>z</sub> analog to digital converter and an 8K. computer for data processing and storage was employed. The capacity of the system was 3000 channels after the various control programs were loaded into the memory. Output was to a TC 33 ASR teletype. The 8K computer was programmed to subtract backgrounds and integrate photopeak areas so that net photopeak counts could be obtained directly in the readout. The detector used was an Ortec, Li drifted Ge crystal having an active volume of 30 cm<sup>3</sup> and a resolution of 2.0 Kev at 662 Kev (<sup>137</sup>Cs) with a peak to background ratio of 15 to 1.

Both Pt and Au were measured in the Au gamma spectrum using the 158 Kev of <sup>199</sup>Au and the 412 Kev of <sup>198</sup>Au respectively. There is a competing <sup>199</sup>Au contribution from Au via the reaction <sup>197</sup>Au  $(2n, \sigma)$  <sup>199</sup>Au. This contribution was evaluated by counting an Au standard source in each experiment from which the ratio of 158 to 412 Kev radiation was determined. The correction procedure is described in detail by Teruta (1974).

The 316 Kev photopeak of <sup>192</sup>Ir was used for measure-
ment of this element. However in some samples the 316 Kev photopeak was overlapped by the 320 Kev photopeak of  $^{51}$ Cr. For these cases the 470 Kev photopeak of  $^{192}$ Ir was used for measurement although this peak has poor counting statistics. To test for  $^{51}$ Cr contamination of the 316 Kev photopeak of  $^{192}$ Ir, the ratio of the 316 Kev to the 470 Kev photopeaks of  $^{192}$ Ir in samples was always compared with the ratio for the standards.

The activity of <sup>109</sup>Pd was determined by graphical analysis of a decay curve. Pd samples were usually counted for 3 to 4 weeks after the end of the irradiation in order to subtract activities due to long-lived contaminants. The long-lived activities were extrapolated back graphically to  $t_0$  (reference time for the calculation of Pd) and subtracted from the total sample activity at  $t_0$ , resulting in the activity of <sup>109</sup>Pd alone (see Teruta, 1974, for detailed example).

Concentrations were calculated by comparing specific activity of the element in the samples with that in the standards. The equation used for the calculations is:

٠

$$Mx = Ms \frac{Ix}{Is_{O}} \frac{Ys}{Yx}$$

where Mx = weight of the element in the sample (gm) Ms = weight of the element in the standard (gm)  $Ix_0$  = count rate for the sample at  $t_0$  $Is_0$  = count rate for the standard at  $t_0$  Yx = radiochemical yield in the sample

Yx = radiochemical yield in the standard.

Precision and accuracy were evaluated by including two samples of USGS standard sample PCC-1 with each of the last four irradiations and one or two samples of W-1 with all of the other irradiations. Table II indicates the average values obtained for PCC-1 and W-1 and the standard deviations for each element.

Table II Average values obtained for USGS standards PCC-1 and W-1

<u>Au(ppb)</u> s.d. <u>Pt(ppb)</u> s.d. <u>Pd(ppb)</u> s.d. <u>Ir(ppb)</u> s.d. PCC-1 0.85(8)\* .18 4.3(7) 1.9 6.32(7) 3.6 2.3(7) .9 W-1 4.1(8) 2.1 10.2(2) 2.0 10.0(4) 0.8 0.40(4) .9 \* number of analysis used for average.

The PGE content of PCC-1 and W-1 in Table II compare well with the published values except for Ir in PCC-1. The Ir appears to be significantly lower than the published values but no value over 3.33 ppb was obtained. There may be a larger variation of Ir in PCC-1 that was not detected with the small sample population used in this study.

5.3 DETERMINATION OF MAJOR AND TRACE ELEMENTS

The major and trace elements, except PGE, and CO2, were determined in fusion pellets (Norrish <u>et al</u>, 1969) on a model PW1450 Philips, automatic, sequential spectrometer.

The trace elements were determined by XRF using a powder pellet procedure described by Marchand (1973). Standards used were GSP-1, MRG-1, NIM-N, BCR-1, SY-2 and UG-1. The Cu and Ni values for the Pyke Hill samples were also determined using atomic adsorbtion spectroscopy. The AAS values were determined using a Perkin Elmer Model 603.

The CO2 values were determined with a model WR-12 Leco automatic carbon determinator (infrared cell adsorption of CO2).

#### CHAPTER 6

#### GEOCHEMISTRY

#### 6.1 INTRODUCTION

Tables  $\overline{III}$ ,  $\overline{IV}$  and  $\overline{V}$  list the major and trace elements and tables  $\overline{VI}$ ,  $\overline{VII}$  and  $\overline{VIII}$  list the PGE for Pyke Hill, Fred's flow and Theo's flow samples respectively.

- 6.2 MAJOR ELEMENT VARIATIONS
- 6.2.1 PYKE HILL

The unusual character of komatiitic volcanic rocks is that they include rocks derived from parental magmas that are ultramafic in composition. The most ultramafic compositions listed in Table  $\overline{III}$  are the olivine cumulates of spinifex bearing flows. These compositions do not represent parental magmas. The exact composition of the parental magma is difficult to determine due to the presence of up to 5% (Pyke <u>et al</u>, 1973) telluric olivine in the magma upon eruption. A best estimate of the parental magma composition is probably the composition of the chilled margins of the flow.

A plot of oxides versus stratigraphic height of some of the major elements for the North (Figure 11) and South

## TABLE III

### ANALYTICAL RESULTS OF THE PYKE HILL SAMPLES

SOUTH FLOW

Oxides, wt. %; traces (S-As), ppm Tables III, IV and V

	JHC-5 Flow Top	JHC-6 Fine Spinifex	JHC-7 Coarse Spinifex	JHC-8 Foliated Zone	JHC-9 Cumulate Zone	JHC-10 Knobby Perid.
SiO2	41.42	44.17	45.16	39.68	39.84	40.74
A1203	7.00	8.04	9.32	4.46	4.93	4.94
TiO2	0.33	0.38	0.42	0.22	0.24	0.25
Fe0 <sub>T</sub>	11.80	11.58	11.69	11.01	10.11	10.40
MnO	0.14	0.14	0.15	0.14	0.14	0.13
MgO	26.38	22.44	18.96	31.96	30.84	31.87
CaO	5.35	7.19	8.59	3.19	4.47	4.98
Na2O	0.17	0.58	0.87	0.12	0.50	0.27
K20	0.06	0.15	0.13	0.04	0.13	0.17
P205	0.05	0.05	0.05	0.05	0.05	0.05
LOI	7.30	5.28	4.66	9.14	8.76	6.20
CO2	0.29	0.42	0.42	0.33	0.43	0.33
S	385	345	172	428	318	289
Ni	1350	940	650	1860	1690	1720
Cu	75	26	40	25	22	- 20
Zn	53	76	79	58	66	62
Cr	2470	2590	2680	1730	2070	1990
Со	105	97	85	111	97	102
Pb	6	6	8	7	· 5	7
As	37	<1	16	15	30	0

# TABLE III

## (Cont)

### NORTH FLOW

	JHC-11 Flow Top	JHC-12 Coarse Spinifex	JHC-13 Cumulate Zone	JHC-14 Cumulate Zone	JHC-15 Flow Base
Si02	41.25	43.48	41.51	42.70	42.26
A1203	6.66	6.81	7.09	6.35	5.86
TiO2	0.30	0.32	0.29	0.32	0.28
FeO <sub>T</sub>	11.19	11.91	10.36	11.40	10.64
MnO	0.13	0.14	0.14	0.14	0.14
MgO	26.52	25.29	28.53	25.55	28.82
CaO	5.74	6.51	5.44	6.18	5.81
Na2O	0.19	0.56	0.26	0.12	0.25
к <b>2</b> 0	0.09	0.23	0.20	0.18	0.14
P205	0.05	0.05	0.05	0.05	0.05
LOI	7.88	4.70	6.14	7.02	5.75
CO2	0.34	0.35	0.37	0.31	0.30
S	191	344	300	329	169
Ni	1460	1290	1210	1340	1510
Cu	20	35	33	26	35
Zn	62	62	72	72	69
Cr	2440	1790	2540	2600	2170
Со	103	95	105	102	102
Pb	7	8	6	6`	6
As	17	0	29	5	3

•

.

# TABLE $\overline{IV}$

ANALYTICAL RESULTS OF THE FRED'S FLOW SAMPLES

	070876-1 Flow Top	070876-2 Olivine Spinifex	070876-3 Olivine Spinifex	070876-17 Flow Top	070876-18 Olivine Spinifex
SiO2	48.64	49.35	46.63	48.37	48.77
A1203	12.06	12.05	10.65	11.11	9.64
TiO2	0.68	0.58	0.53	0.55	0.41
FeO <sub>T</sub>	13.65	12.38	13.27	12.46	10.47
Mn0	0.14	0.14	0.16	0.14	0.14
Mg0	11.33	10.93	15.39	13.74	14.17
Ca0	8.94	9.73	9.14	9.23	11.65
Na20	1.33	1.23	0.75	1.60	0.13
K20	0.16	0.16	0.11	0.08	0.04
P205	0.04	0.04	0.05	0.04	0.04
LOI	3.03	3.42	3.32	2.67	4.52
CO2	0.21	0.14	0.15	0.13	0.51
S	457	479	491	138	164
Ni	143	109	515	249	350
Cu	92	124	55	52	36
Zn	94	83	89	81	86
Cr	490	605	1560	1490	1150
Co	78	68	94	76	66
Pb	6	5	5	6	7
As	15	25	14	8	7 ∘

# TABLE $\overline{IV}$

## (Cont)

	070876-19 Pyroxene Spinifex	070876-20 Pyroxene Spinifex	070876-21 Gabbro	070876-22 Gabbro	080876-17 Pyroxenit(
SiO2	48.01	51.08	49.92	49.69	34.24
A1203	11.01	12.55	13.20	10.88	3.57
Ti02	0.55	0.57	0.65	0.55	0.18
FeO <sub>T</sub>	14.02	11.00	13.50	12.54	13.37
Mn 0	0.16	.0.14	0.14	0.16	0.15
Mg0	13.60	8.20	7.18	13.13	35.14
Ca0	8.16	10.31	8.98	8.87	2.37
Na20	0.85	3.18	3.42	1.25	0.02
K20	0.18	0.08	0.12	0.45	0.04
P205	0.04	0.04	0.04	0.04	0.05
FOI	3.42	2.86	2.85	2.44	10.87
C02	0.34	0.165	0.30	nd*	0.14
S	882	277	881	352	281
Ni	304	84	47	182	2196
Cu	48	5	50	40	1
Zn	107	51	84	86	71
Cr	1160	373	90	1010	6680
Со	87	55	64	77	136
Pb	7	6	5	6	6
As	<1	22	<1	<1	32

nd\* - not detected

	080876-18 Peridotite	080876-19 Peridotite	080876-20 Peridotite	080876-21 Border Zone	080876-24 Gabbro
SiO2	37.65	40.68	41.16	40.79	50.12
A1203	3.61	9.10	6.80	11.86	13.25
Ti02	0.19	0.50	0.32	0.73	0.67
Fe0 <sub>T</sub>	9.63	13.37	11.29	13.58	13.09
Mn0	0.13	0.16	0.13	0.23	0.14
MgO	34.99	20.26	23.45	18.50	7.40
Ca0	2.78	9.15	9.02	6.61	10.01
Na20	0.07	0.13	nd*	1.27	1.89
K20	0.04	0.05	0.04	0.32	0.08
P205	0.05	0.04	0.05	0.05	0.04
LOI	10.85	6.56	7.75	6.06	3.29
CO2	0.17	0.21	2.37	0.26	nd*
S	368	248	2350	175	534
Ni	2469	856	1284	101	67
Cu	3	54	34	nd*	115
Zn	61	124	84	111	66
Cr	4390	2510	3760	291	132
Co	116	100	90	69	68
Pb	7	8	7	5	6
As	<1	23	<b>∠</b> 1	27	14

۰.

•

.

# TABLE $\overline{IV}$

## (Cont)

	080876-25 Pyroxene Spinifex	080876-26 Pyroxene Spinifex	080876-27 Pyroxene Spinifex	080876-28 Flow Top
SiO2	49.86	50.10	49.25	47.83
A1203	13.25	13.05	11.19	10.92
TiO2	0.66	0.62	0.53	0.52
FeO <sub>T</sub>	13.00	12.77	12.02	14.11
Mn0	0.15	0.15	0.14	0.14
Mg0	7.34	7.23	12.15	15.38
Ca0	9.52	10.11	9.43	7.20
Na20	2.57	2.78	1.72	0.53
K20	0.20	0.05	0.06	0.11
P205	0.04	0.04	0.04	0.04
LOI	3.39	3.10	3.46	3.21
CO 2	0.59	nd*	0.019	nd*
S	521	514	534	769
Ni	52	58	141	257
Cu	50	54	40	41
Zn	84	77	60	78
Cr	129	142	835	1140
Со	66	67	67	83
РЬ	8	7	6	6
As	18	<۱	49	4

•

# TĄBLE $\overline{\underline{V}}$

## ANALYTICAL RESULTS OF THE THEO'S FLOW SAMPLES

	080876-1 Peridotite	080876-2 Peridotite	080876-3 Pyroxenite	080876-4 Pyroxenite	080876-5 Pyroxenite
SiO2	38.06	46.48	51.53	49.74	50.68
A1203	3.46	7.77	5.78	6.43	8.43
TiO2	0.42	0.44	0.66	0.70	0.89
FeO <sub>T</sub>	17.39	11.30	9.51	11.46	12.96
Mn 0	0.19	0.17	0.14	0.14	0.15
Mg0	25.44	18.42	14.70	14.66	10.45
Ca0	4.21	11.78	14.99	13.54	12.75
Na20	0.03	0.59	1.13	0.66	2.03
K20	0.06	0.09	0.08	0.13	0.09
P205	0.04	0.05	0.04	0.04	0.04
LOI	10.70	2.92	1.44	2.50	1.54
C02	1.11	0.11	1.12	0.40	0.27
S	359	162	3640	131	344
Ni	1739	383	211	328	163
Cu	16	29	38	38	175
Zn	90	91	76	74	86
Cr	2830	1750	1890	1160	201
Со	162	65	46	75	57
Pb	5	7	5	5	5
As	26	2	87	< 1	13

•

# TABLE $\overline{\underline{v}}$

2

.

# (Cont)

	080876-6 Pyroxenite	080876-7 Gabbro	080876-9 Aphanetic Pyroxenite	080876-10 Hyalo- clastite	080876-11 Gabbro
Si02	51.89	51.35	50.61	49.42	51.43
A1203	5.80	13.93	9.85	10.15	9.25
TiO2	0.65	1.22	1.11	1.16	0.98
${ m FeO}_{{f T}}$	10.50	14.59	14.67	15.36	11.99
Mn0	0.14	0.16	0.16	0.15	0.13
Mg0	13.73	4.47	9.62	10.00	10.24
Ca0	15.06	9.52	10.24	7.51	12.33
Na20	0.68	2.58	2.16	3.34	1.58
К20	0.06	0.62	0.08	0.09	0.20
P205	0.04	0.05	0.05	0.05	0.05
LOI	1.45	1.51	1.45	2.76	1.83
C02	0.21	0.36	0.93	3.19?	1.59
S	284	1050	2420	7800	2790
Ni	235	52	114	197	136
Cu	43	83	152	159	84
Zn	71	124	97	158	94
Cr	780	15	269	760	429
Со	55	70	71	81	51
Pb	6	5	5	6	5
As	16	39	20	18	16

# TABLE $\overline{\underline{v}}$

## (Cont)

	080876-12 Pyroxenite	080876-13 Gabbro	080876-14 Haloclastite
Si02	51.89	51.38	43.74
A1203	6.77	10.05	10.19
Ti02	0.78	1.09	1.27
FeO <sub>T</sub>	10.85	13.23	18.04
Mn0	0.14	0.15	0.17
Mg0	12.66	8.38	11.20
Ca0	13.89	12.11	10.55
Na20	1.45	1.44	0.97
К20	0.10	0.26	0.47
P205	0.05	0.05	0.06
LOI	1.67	1.87	3.34
C02	0.66	1.16	0.99
S	1210	1230	1870
Ni	191	120	110
Cu	79	97	115
Zn	85	104	220
Cr	1260	237	130
Со	53	59	83
Pb	5	5	20
As	47	3	12

## TABLE $\overline{VI}$

PGE CONTENT OF PYKE HILL SAMPLES (ppb)

		North	Flow	
SAMPLE #	Au	Pt	Pd	Ir
JHC-11	2.25(5)*	16(2)	10.1(1)	1.22(3)
JHC-12	2.59(3)	16(2)	10.4(1)	0.92(2)
JHC-13	2.14(4)	10(2)	8.1(1)	0.90(3)
JHC-14	3.47(5)	10(3)	5.2(1)	0.91(3)
JHC-15	2.04(3)	13(2)	7.8(1)	1.21(3)
Average	2.50	13	8.32	1.03

## South Flow

JHC-5	1.31(3)	14(1)	8.80(1)	1.11(2)
JHC-6	2.16(3)	18(2)	10.37(1)	0.83(2)
JHC-7	2.19(3)	28(1)	11.30(1)	0.62(2)
JHC-8	3.10(5)	9(2)	7.52(2)	0.36(4)
JHC-9	6.63(5)	16(3)	5.64(1)	2.09(3)
JHC-10	2.53(5)	7(2)	6.14(2)	1.68(4)
Average	2.99	15	8.30	1.12

Average for north and south flows

.

2.8 14 8.3 1.08

\* Number of replicate assays for each sample

## TABLE $\overline{\text{VII}}$

## PGE CONTENT OF FRED'S FLOW SAMPLES(ppb)

SAMPLE #	Au	Pt	Pd	Ir
070876-1	2.95	13.1	16.9	0.16
070876-2	5.74	16.6	21.9	0.24
070876-3	2.29	7.23	20.3	0.24
070876-17	1.68	6.73	17.8	0.19
070276-18	2.06	4.31	11.7	0.31
070876-19	0.77	6.72	17.2	0.25
070876-20	0.43	5.55	5.14	0.09
070876-21	1.17	0.10?	nd*	0.04
070876-22	1.12	22.7	19.4	0.64
080876-17	0.83	4.09	3.74	1.24
080876-18	1.39	3.95	4.13	1.50
080876-19	2.92	12.5	9.97	0.72
080876-20	1.16	15.7	6.53	1.15
080276-21	0.84	3.20	1.48	0.08
080876-24	3.84	15.8	7.92	0.12
080876-25	1.65	13.4	7.17	0.17
080876-26	3.74	2.11	0.35	0.04
080876-27	1.76	20.9	10.4	0.65
0808-76-28	1.82	17.9	12.4	0.66

nd\* - not detected

.

## TABLE VIII

PGE CONTENT OF THEO'S FLOW SAMPLES (ppb)

SAMPLE #	Au	Pt	Pd	Ir
080876-1	0.53	nd*	5.23	0.33
080876-2	0.50	13.0	7.54	0.35
080876-3	0.43	8.64	5.68	0.46
080276-4	0.53	16.0	14.6	0.62
080876-5	3.93	67.8	37.2	1.53
080876-6	1.02	23.0	15.8	0.75
080876-7	0.51	nd*	nd*	0.05
080876-9	2.34	5.74	10.0	0.40
080876-10	1.44	11.6	10.2	0.41
<b>080876-11</b>	2.88	3.33	6.01	0.17
080876-12	0.58	7.13	5.40	0.23
080876-13	4.14	9.54	9.31	0.29
080876-14	1.71	5.21	3.77	0.18

•

nd\* - not detected

(Figure 12) flows indicates that the major elements in the North flow are not as distinctly fractionated between spinifex and cumulate zones. Two recognizable major element patterns appear in the South flow. One group of elements, including SiO2, Al2O3, TiO2,  $FeO_T$ , CaO and Na2O shows a higher concentration in the spinifex zone than the cumulate zone. MgO, on the other hand, is higher in the cumulate zone than in the spinifex zone. These variations are thought to result from the higher proportion of olivine in the cumulate zone as compared with the spinifex zone.

Arndt <u>et al</u> (1977) demonstrated distinct differentiation of komatilitic and tholeilitic rocks of Munro Township when Al203 is plotted against Fe0/Fe0 + Mg0. On such a plot all samples from Pyke Hill clearly lie in the komatiltic field (Figure 13).

6.2.2 FRED'S FLOW

The chemical variation within the flow are presented in Figure 14, where the weight percent oxide is plotted against sample stratigraphic position. Fred's flow shows a grouping of elements similar to the Pyke Hill South flow when the variation between cumulate and spinifex zones is considered.



Figure 11 Selected major elements versus stratigraphic height, North flow, Pyke Hill.



Figure 12 Selected major elements versus stratigraphic height, South flow, Pyke Hill.



Figure 13 Al2O3 versus FeO/(FeO+MgO) for Pyke Hill, Fred's flow and Theo's flow with a proposed line dividing Komatiites from Tholeiites.

The Si02 content in the upper part (breccia to gabbro) of the flow is higher than in the cumulate zones. The reverse is true for Mg0. As in the Pyke Hill case, Al203, Ti02,  $FeO_T$ , Ca0 and Na20 vary in the same manner as the Si02 content. Mg0 is the only major element exhibiting a higher concentration in the cumulate zone probably due to the higher olivine content in that zone. In figure 13 samples from Fred's flow plot in the komatiite field as defined by Arndt et al (1977).

#### 6.2.3 THEO'S FLOW

Theo's flow is clearly of tholeiitic affinity as indicated by its high TiO2 content and high FeO/FeO+MgO ratios. Figure 13 shows the distinctly different trend of the samples from Theo's flow when compared to Fred's flow and Pyke Hill. A plot of the weight percent oxides versus stratigraphic position within the flow is shown in Figure 15. There is a marked depletion in SiO2 and an increase of MgO and FeO<sub>T</sub> in the basal peridotite which is seen as a reflection of the increasing olivine content in the cumulate zone. Throughout the rest of the flow the variation of the major elements is relatively small.

#### 6.3 TRACE ELEMENT VARIATIONS

#### 6.3.1 PYKE HILL

The trace element values presented in Tables  $\overline{III}$ and  $\overline{VI}$  for Pyke Hill follow trends similar to the major. elements. Little trace element variation was found within the North Flow (Figure 16). The South flow best illustrates the trends as in the major elements (Figure 17 and 18). Au, Ir, S, Co and Ni generally decrease in concentration from flow top to coarse spinifex and increase sharply in the cumulate zone (Figure 17). Pd, Cr, Cu, Zn and, to a lesser extent, Pt follow a trend similar to Si02 with concentrations increasing to a high in the coarse spinifex and decreasing from spinifex zone to cumulate zone (Figure 18).

#### 6.3.2 FRED'S FLOW

The variations in the trace elements (Tables  $\overline{IV}$  $\overline{VII}$ ) for Fred's flow follow trends exhibited by the major elements. Trace elements having a trend similar to Mg0 are Ir, Co, Ni and Cr (Figure 19). The peridotite zone contains higher concentrations of these elements than either the gabbro or spinifex zones. The spinifex zone shows erratic values compared to the gabbro zone. The Ir concentration similarly decreases from the middle of the peridotite zone to nearly the top of the gabbro zone. Concentrations of Pt, Pd, Cu and Au are lower in the cumulate zones with respect to the gabbro and spinifex zones (Figure 20). All of the above elements reach their highest concentrations in the gabbro zone. S, Zn and As are relatively evenly distributed through the different zones of the flow.



Figure 16 Trace elements versus stratigraphic height, North flow, Pyke Hill.



South flow, Pyke Hill.

.



#### 6.3.3 THEO'S FLOW

The trace element concentrations for Theo's flow are found in Tables  $\overline{V}$  and  $\overline{VIII}$ . The trace elements behave similar to the major elements with variations in the hyaloclastite and basal peridotite zones but relatively small variations throughout the rest of the flow (Figure 21 and 22) except in the following instances. In the center of the pyroxene cumulate a sample is low in Cr but high in Au, Pt, Pd, Ir, and Cu. Adjacent samples support the observed low Cr and high Pt and Pd values. S does not correlate with high siderphile element concentrations.

#### 6.4 DISCUSSION

In all of the study areas the major and trace elements behave as would be expected in magmas subject to fractional crystallization of olivine (Arndt, 1975). The strongest compositional control is exhibited by olivine because of its simple chemical composition and its relatively significant concentration in all of the rocks involved. The olivine cumulate zones are enriched in MgO and depleted in SiO2 with respect to the assumed parental magma compositions.

The PGE do not behave as a single group but fractionate into the melt or cumulus phases. Ir fractionates into the solid phase in all flows while Pt and Pd fractionate into the melt. In Fred's flow , the residual liquid is progressively depleted in Ir as the cumulus zone builds up, reaching a very low Ir concentration by the time gabbro forms (Figure 19). The reverse is true for Pt, Pd and, to a lesser extent, Au. The highest Ir value in Fred's flow is near the center of the peridotite probably due to the fact that the flow was extruded containing 10% to 20% telluric olivine (Arndt, 1977) which settled before olivine started precipitating from the melt. In Theo's flow the center of the clinopyroxenite zone contains a high concentration of PGE (Figure 21). This may be due to the trapping of magma during rapid accumulations of clinopyroxene grains. As the trapped liquid forms adcumulus growth onto the cumulus clinopyroxenes, observed to some extent in thin sections, an intercumulus liquid is fractionated out enriched in PGE and other trace elements. The intercumulus liquid would be most enriched in the center of the clinopyroxenite, being the last section of the flow to crystallize due to insulation. In the South Flow at Pyke Hill the cumulate zone is enriched in Ir and Au and depleted in Pt and Pd while the reverse is true for the spinifex zone.

#### CHAPTER 7

#### DISCUSSION AND CONCLUSIONS

#### 7.1 PGE CONTENT OF PARENTAL PERIDOTITE MAGMAS

The parental magma composition for the rocks included in this study were chosen from the flow top and near flow top zones. The flow top samples were selected because they are most likely to represent the magmatic composition before fractionation began. The calculated parental magma compositions agree with the best estimates of other researchers (Arndt, 1975; Arndt, 1977, and Arndt et al, 1977) as shown in Table  $\overline{IX}$ .

No one unit of a typical thin ultramafic flow (Pyke Hill type) is ideal for estimation of initial magma composition but flow boundary rocks, either top or bottom, are probably best because they represent chilled liquids. The cumulate zone may well contain olivine that is essentially xenocrystic; that is, material not precipitated from the magma but rather derived from the source region. The spinifex zone is probably a better representative of initial liquid composition, but may be subject to some olivine fractionation prior to crystallization. While the flow

Table  $\overline{IX}$ 

Comparison of parental magma compositions obtained in this study with the average values reported by other researchers

	<u>Peridotitic Komatiite</u>		Fred's Flow		Theo's Flow	
	This * Study	Arndt <u>et al</u> 1977	This Study <sup>O</sup>	Arndt 1977	This + Study	Arndt 1977
SiO2	44.75	46.0	49.72	47.9	51.11	49.9
TiO2	0.35	0.32	0.57	0.42	1.16	0.90
A1203	7.40	7.40	11.42	9.40	10.22	8.10
Fe0 <sub>m</sub>	12.44	11.5	12.81	12.2	15.34	12.5
MnO	0.15	0.22	0.14	0.21	0.16	0.21
MgO	28.63	26.5	14.12	21.1	10.03	14.7
Ca0	6.00	7.40	9.49	7.60	9.07	11.80
Na2O	0.20	0.45	1.64	0.90	2.82	1.86
к20	0.08	0.10	0.08	0.19	0.09	0.07

All values calculated anhydrous

\* average of samples JHC-5 and JHC-11 ( flow tops for North and South Flows )

- o sample 070876-17 (flow top breccia)
- + average of samples 080876-9 and 080876-10 ( aphanitic pyroxenite and hyaloclastite respectively )

contacts represent quenched liquids caution is necessary because the contact zones are probably more subject to contamination and alteration than the flow interiors and may trap some xenocrystic material. Nevertheless, to the extent that any unit from an ultramafic flow represents the parental magma, the flow contact rocks are considered the best units for this purpose.

An estimate of the noble metal concentrations in the parental magma for Pyke Hill, Fred's Flow and Theo's Flow are given in Table  $\overline{X}$ . Some support for choosing flow boundary samples (i.e. flowtop,  $A_1$ , or flow base,  $B_A$ ) as representative of parental magma compositions is obtained from the North Flow unit at Pyke Hill. This thin flow (3.24 m) should have cooled relatively fast with minimal opportunity for fractionation so that little variation in PGE content of any facies in the flow is to be expected. This is precisely the case, at least if PGE variation in different units of the North Flow is compared with that in the thicker South Flow. Ideally identical PGE values in the flow top and flow bottom samples might be expected if these units represent rapidly quenched magmas and are not subject to metal losses or gains during or after lithifi-Inspection of the PGE data indicates identical Au cation. and Ir values within experimental error in the flow top and flow base units of the North Flow. There is a difference of 20% in Pd and Pt in these units. It is interesting to

note that S, Ni, Zn, Cr, Co and Pb differ by only 11% or less in these units in the North Flow. These observations suggest that the flow top (or flow base) has effectively quenched in the original magma composition. It seems most unlikely that such a diverse suite of elements would be so consistent in flow top and base if sea water leaching or other alteration had removed or added metals. The presence of xenocrystic or telluric olivine from the source rock cannot be ruled out although there are no features of the PGE data suggesting its presence.

## TABLE X

Estimates of the PGE concentrations in the parental magma for the units studied, ppb

	<u>Au</u>	Pt	Pd	Ir
Pyke Hill <sup>*</sup>	1.9	16	10	1.3
Fred's Flow <sup>O</sup>	1.7	7	18	0.20
Theo's Flow <sup>+</sup>	1.9	9	10	0.42

all values calculated anhydrous

- averaged of samples JHC-5 and JHC-11 (flow tops for North and South Flows)
- o sample 7-17 (flow top breccia)
- + average of samples 8-10 and 8-9 (hyaloclastite and aphanitic pyroxenite respectively)

#### 7.2 INFERENCES ON PGE CONTENT OF MANTLE ROCKS

Naldrett and Cabri (1976) showed that komatiitic and tholeiitic hosted sulfide ores were clearly differentiated in a plot of Pt/(Pt+Pd) versus Cu/(Cu+Ni). Figure 23 shows the compositions of the magmas investigated here plotted in Pt/Pd and Cu/Ni coordinates. The Pyke Hill magma plots near Cl, C2 chondrites suggesting that the Pyke Hill komatiites have mantle-like proportions of Pt, Pd, Cu and Ni. Fred's Flow plots very near the komatiite field while Theo's Flow plots on the tholeiitic trend.

If the arguments of Chou (1978) and Morgan and Wandless (1979) that siderophile elements in the upper mantle are in chondritic proportions are accepted, it is probable that magmas generated by high percentage partial melting such as peridotitic komatiites would inherit metals like Pt and Pd in roughly their source rock proportions. The siting of PGE in mantle rocks such as garnet or spinel lherzolite is poorly known but Mitchell and Keays (1981) present evidence that sulfide and discrete platinum group minerals may be important hosts. Oshin and Crocket (in press, Econ. Geol.) conclude from studies of ophiolites that chromite may also be an important PGE host in the case of Ir. Thus. in the case of Pt and Pd the metals may be regarded to a first approximation as incompatible elements in the mantle source rock environment which probably fractionate moderately



Figure 23 Correlations of Cu-Ni and Pt-Pd ratios in sulfide ores of Komatiitic and Tholeiitic magmas with Munro Township and carbonaceous chondrites data. Tholeiitic trend line and Komatiite field from Naldret<sup>t</sup> and Cabri (1976).

to strongly toward the melt. In cases where up to 70% melting of source rock is involved it is perhaps not surprising to obtain such metals in their source rock, that is in chondritic proportions.

These arguments, however, are not true in the case of Ir because the Pyke Hill rocks yield Pd/Ir ratios of approximately 8 in comparison with a chondritic value of about 1 (Paul et al, 1979). If the preceding arguments that Pd is strongly fractionated towards the melt are correct then presumably the reverse applies to Ir. Apprentaly Ir must be hosted by some mantle mineral which is highly refractory and not completely melted even at very high percentage partial melting. Chromite is probably a major host of Ir but relatively small degrees of partial melting should eliminate spinel from a source rock of lherzolite composition (Ringwood, 1975). The probable residual phases after extensive partial melting are olivine and orthopyroxene. There are not data which suggest an association of Ir with orthopyroxene. Ross and Keays (1979) cite some evidence from Kambalda that olivine may host Ir. In the South Flow Pyke Hill rocks, Ir is lower in the spinifex-bearing facies than the cumulate facies which carries the higher model olivine content, but the differences are small. Spinifex samples average 0.6 ppb Ir compared with 1.89 ppb in cumulus samples, a difference of a factor of 3. However in

the weakly differentiated North Flow the cumulus and spinifex zone Ir contents are essentially the same. Thus, although the data are by no means convincing, they are at least compatible with the suggestion that Ir may be hosted by olivine in mantle source rocks and thereby be retained in the residue. An alternative possibility is that Ir is hosted by a discrete platinum group element mineral whose melting temperature significantly exceeds the source rock liquidus. A possible candidate is an iridium-osmium alloy with melting temperature on the order of 2300<sup>o</sup>C. Whatever the reason, the Pyke Hill magmas are certainly not chondritic with respect to PGE ratios involving Ir. This does not imply a non-chondritic mantle with respect to PGE but is probably more readily explained in terms of PGE fractionation between melt and residue during magma generation at source.

A further aspect of the Pt/Pd-Cu/Ni plot is significant. The Pt/(Pt+Pd) ratio of komatiite-hosted sulfide ores is lower, by approximately two, than the ratio in Pyke Hill magmas. If a magma carrying Pt and Pd in Pyke Hill proportions becomes saturated with sulfur which draws these metals into an immiscible sulfide fluid, then the partition of Pt and Pd between sulfide and silicate liquids must favor Pd over Pt if the resulting Pt/(Pt+Pd) ratio of the sulfide is less than that of the silicate magma. Distribution coefficients for partition of Pt and Pd between sulfide and silicate melts are not known with much certainty. However, both the experimental data of Rajamani <u>et al</u> (1978) and the calculated values of Ross and Keays (1979) indicate that Pd partitions more strongly into a sulfide liquid than does Pt. Thus, the formation of an immiscible sulfide liquid in a magma with Pt-Pd proportions as in Pyke Hill peridotitic komatiite would yield sulfides with Pt/(Pt+Pd) ratios trending towards the ratios actually observed for komatiitic sulfide. This observation supports the arguments to follow that the Pyke Hill magma was not saturated with sulfur prior to eruption.

### 7.3 PROBABILITY OF IMMISCIBLE SULFIDE IN PYKE HILL MAGMAS

It can be shown that the Pyke Hill magmas were not saturated in sulfur and therefore that scavenging of PGE's did not take place. Using a plot of Ni verses MgO, Duke and Naldrett (1978) proposed two trends of Ni concentrations: the upper line for a sulfide-undersaturated system and the lower line for a sulfide-saturated system (Figure 24). The spinifex values for the non-cumulate phases can be used as a rough estimate of the derived liquids (Naldrett, personal communication, 1981). The Pyke Hill spinifex samples plot above the sulfide-undersaturated line clearly showing that the magma was not scavenged for siderophile elements prior to extrusion and cooling.

The approximate derived liquid composition for


Figure 24 A plot of the approximate derived liquids for Pyke Hill, Fred's flow and Theo's flow confirming that all systems are sulphide - undersaturated. Curve a is for a sulfide - undersaturated model using the preferred valves of  $D_{Ni}^{0/L}$ with curves b and c  $\frac{+}{2}$  25%. Curve d is for a sulfide - saturated model using the preferred values of sulfide solubility with curves e and f  $\frac{+}{2}$  25%.

Fred's Flow plots near the line for sulfide-undersaturation. Theo's Flow approximate derived liquid composition plots just below the line for sulfide undersaturated systems. None of the volcanic units analyzed in this study have been scavenged for siderophile elements before extrusion; therefore, the estimates of the PGE content of the parental magmas are valid.

### 7.4 KOMATIITES AS SOURCE ROCKS FOR GOLD MINERALIZATION

It has been suggested that komatiitic volcanic rocks are a source rock for Archean gold deposits. Viljoen et al (1970) proposed that the Komatii formation in the Barberton Mountain Land region of South Africa was the source of the gold for the small Steynsdorp Goldfield on the basis of a gold content of 5 to 20 ppb (determined by fire assay) and a proximity to known gold deposits. Anhaeusser et al (1975) cast doubt on the high gold content of the Komatii formation reporting values of only 1 to 1.5 ppb Au using neutron activation analysis. Pyke (1975) proposed komatiitic volcanic rocks as the source rock for gold deposits in the Porcupine Gold Camp, of the Abitibi Belt because of their proximity to ultramafic flows using the Viljoen et al (1970) analytical data as support. Pyke's case was weakened by Karvinen (1980), who proposed that the gold deposits were associated with a regional carbonate horizon and concomitant carbonatization. Fyon (1980) demonstrated than an association of felsic

porphyry-carbonate alteration-ultramafic flows were more closely associated with gold deposits in Timmins than proximity to komatiitic volcanic rocks. Fyon also showed that the mafic and ultramafic volcanic rocks in the Porcupine Gold Camp have similar gold concentrations.

The results from this study show that the gold content of the komatiites at Pyke Hill average 2.8 ppb with a parental magma content estimated at 1.9 ppb. These values are not anomalous and would rule out komatiites as the single source for gold deposits. The Pyke Hill komatiites are very pristine in appearance in the field and appear microscopically and chemically unaltered. The possibility exists that very mild alteration due to sea water at the time of extrusion has removed some of the gold but to date no evidence has been put forward to substantiate this possibility.

#### REFERENCES

Anhaeusser, C. R., Fritze, K., Fyfe, W. S. and Gill, R. C. D. (1975) Gold in "primitive" Archaean volcanics. Chem. Geol., 16, 129-135.

- Arndt, N.T. (1975) Ultramafic rocks of Munro Township and their volcanic setting. Unpub. Ph.D. thesis, Univ. Toronto, Toronto, Ont., 297 p.
- (1977) Thick, layered peridotite-gabbro lava flows in Munro Township, Ontario. Can. J. Earth Sci., 14, 2620-2637
- Arndt, N.T., Naldrett, A. J. and Pyke, D. R. (1977)
  Komatiitic and iron-rich tholeiitic lavas of
  Munro Township, Northeast Ontario. Jour. Petrol.,
  18, 319-369
- Chou, C-L. (1978) Fractionation of siderophile elements in the earth's upper mantle. Proc. Lunar Planet. Sci., 9th, 219-230.
- Crocket, J. H., Keays, R. R. and Hsieh S. (1968) Determination of some precious metals by neutron activation analysis. J. Radioanalyt. Chem., <u>1</u>, 487-507.
- Eakins, P. R. (1972) Roquemaure Township, Abitibi-West County, Quebec. Que. Dep. Nat. Resour., Geol. Rep. 150, 69 p.

- Freeman, P. (1956) The petrology of the Beatty-Munro sill, Matheson. Unpub. M.Sc. thesis, McGill Univ., Montreal, P.Q.
- Fyon, J. A. (1980) Seawater alteration of early Precambrian (Archean) volcanic rock and exploration criteria for stratiform gold deposits, Porcupine Camp, Abitibi Greenstone Belt, Northeastern Ontario. Unpub. M.Sc. thesis, McMaster University, Hamilton, Ontario, 238 p.
- Goodwin, A. M. (1968) Evolution of the Canadian Shield. Proc. Geol. Assoc. Can., <u>19</u>, 1-14.  $\checkmark$
- (1973) Petrochemical trends in Archean volcanic assemblages, Abitibi Belt, Ontario and Quebec, Canada. Geol. Soc. Amer., Abst. programs, <u>5</u>,
- \_\_\_\_\_ (1979) Archean volcanic studies in the Timmins-Kirkland Lake-Noranda Region of Ontario and Quebec. Geological Survey of Canada, Bulletin 278, 51 p. <
- Goodwin, A. M. and Ridler, R. H. (1970) The Abitibi Orogenic Belt, <u>in</u> Basins and geosynclines of the Canadian Shield, Geol. Surv. Can., Pap. 70-40, 1-30.
- Grubb, P. I. C. (1962) Serpentine and chrysotile formation in the Matheson ultrabasic belt, Northern Ontario. Econ. Geol., <u>57</u>, 1228-1246.

- Jensen, L. S. (1978) Geology of Stoughton and Marriott Townships, District of Cochrane. Ont. Geol. Survey, Rept. 173, 72 p.
- (1979) Larder Lake Synoptic Mapping Project, District of Cochrane and Timiskaming; p 64-69 in Summary of Field Work, 1979, by the Ontario Geological Survey, edited by V. G. Milne,
  O. L. White, R. B. Barlow and C. R. Kustra,
  Ontario Geological Survey, MP 82, 235 p.
  (1980) Kirkland Lake-Larder Lake Synoptic Mapping Project, Districts of Cochrane and Timiskaming; p 55-60 <u>in</u> Summary of Field Work, 1980, by the
  Ontario Geological Survey, edited by V. G. Milne,
  O. L. White, R. B. Barlow, J. A. Robertson and
  A. C. Colvine, Ontario Geological Survey, MP 96, 201 p.
- Jolly, W. T. (1974) Regional metamorphic zonation as an aid in study of Archean terrains; Abitibi Region, Ontario. Can. Min., <u>12</u>, 499-508.
- Keays, R. (1968) A neutron activation analysis technique for determination of the precious metals and its application to a study of their geochemistry. Unpub. Ph.D. thesis, McMaster Univ., Hamilton, Ontario.

- MacRae, N. D. (1963) Petrology of the Centre Hill complex, northern Ontario. Unpub. M.Sc. thesis, McMaster Univ., Hamilton, Ont.
- (1965) Petrology and geochemistry of ultramafic gabbroic intrusions in the Abitibi area, Ontario. Unpub. Ph.D. thesis, McMaster Univ., Hamilton, Ont.
- (1969) Ultramafic intrusions of the Abitibi Area, Ontario. Can. J. Earth Sci., <u>6</u>, 281-303.
- Marchand, M. (1973) Determination of Rb, Sr, and Rb/Sr by XRF. Tech. Memo 73-2, Dept. Geology, McMaster Univ., Hamilton, Ontario, Canada

Mitchell, R. H. and Keays, R. R. (1981)

Abundance and distribtuion of gold, palladium and iridium in some spinel and garnet lherzolites: implications for the nature and origin of precious metal-rich intergranular components in

the Upper Mantle. Geochim. Cosmochim. Acta, <u>45</u>, 2425-2442. Morgan, J. W. and Wandless, G. A. (1979)

Terrestrial upper mantle: siderophile and volatile trace element abundances. Abstract. Lunar and Planetary Science,  $\overline{X}$ , 855-857.

Naldrett, A. J. (1964) Ultrabasic rocks of the Porcupine and related nickel deposits. Unpub. Ph.D. thesis, Queen's Univ., Kingston, Ont.

- Nesbitt, P. W. (1971) Skeletal crystal forms in the ultramafic rocks of the Yilgarn Block, Western Australia: Evidence for an Archean ultramafic melt. Geol. Soc. Aust. Spec. Publ. 3, 331-348.
- Norrish, K. and Hutton, J. T. (1969) An accurate X-ray spectographic method for the analysis of a wide range of geological samples. Geochim. Cosmochim. Acta, 33, 431-453.
- Oshin, I. O. and Crocket, J. H. (in press) Noble metals in Thetford Mines ophiolites, Quebec, Canada. Part 1. Distribution of Au, Ir, Pt and Pd in the ultramafic and gabbroic rocks. Econ. Geol.
- Paul, D. K., Crocket, J. H. and Nixon, P. H. (1979) Abundances of palladium, iridium and gold in Rimberlites and associated nodules <u>in</u> Kimberlites, Diatremes, and Diamonds: Their Geology, Petrology, and Geochemistry. Proc. 2nd International Kimberlite Conference, vol. 1, 272-279 (edited by F. R. Boyd and H. O. A. Meyer). American Geophysical Union, 1979.
- Pyke D. R. (1975) On the relationship of gold mineralization and ultramafic volcanic rocks in the Timmins area. Ont. Div. Mines, MP 62, 23 p.

- (1980) Geology of the Timmins Area, District of Cochrane. Ontario Geological Survey Open File Report 5281, 369 p.
- Pyke, D. R., Naldrett, A. J. and Eckstrand, O. R. (1973) Archean ultramafic flows in Munro Township, Ontario. Geol. Soc. Amer. Bull., <u>84</u>, 955-978.
- Rajamani, V., Chou, C.-L., and Naldret, A. J. (1978) Partition of Pt-Group elements between sulfide and basaltic melts. Econ. Geol., <u>73</u>, p 313.
- Ringwood, A. E. (1975) Composition and Petrology of the Earth's Mantle. McGraw-Hill, New York, 618 p.
- Ross, J. R. and Keays, R. R. (1979) Precious metals in volcanic-type nickel sulfide deposits in Western Australia. I. Relationship with the composition of the ores and their host rocks. Can. Min., <u>17</u>, 417-436.
- Satterly, J. (1951) Geology of Munro Township. Ann. Rept. Ont. Dept. Mines, <u>60</u>, pt. 8, 60 p.
- Teruta, Y. (1974) A study of the Distribution of some Noble Metals in the Merensky Horizon, Bushveld Igneous Complex. Unpub M.Sc. thesis McMaster Univ. Hamilton, Ont. 137 p.

- Vilgoen, M. J. and Vilgoen, R. P. (1969a). Evidence for the existence of a mobile extrusive peridotite magma from the Komatii Formation of the Onverwacht Group. <u>in</u> Upper Mantle Project, Spec. Publ. Geol. Soc. S. Afr., <u>2</u>, 87-112.
  - (1969b) The geology and geochemistry of the lower ultramafic unit of the Onverwacht Group and a proposed new class of igneous rock. <u>in</u> Upper Mantle Project, Spec. Publ. Geol. Soc. S. Afr., 2, 55-85.







Figure 14: Selected major element oxides versus stratigraphic position, Fred's flow.



# 0 10 20 30 40 50 60 Weight Percent

### Figure 15: Selected major element oxides versus stratigraphic position, Theo's flow.







## Figure 21 - Ir, Co, Ni and Cr versus stratigraphic height, Theo's flow.

