NOBLE METALS IN THETFORD MINES OPHIOLITES

THE ABUNDANCES AND GEOCHEMISTRY OF SOME NOBLE METALS IN THETFORD MINES OPHIOLITES, P.Q.

By

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ABSTRACT

Ophiolites are generally regarded as fragments of ancient oceanic crust and upper mantle emplaced on the continents. Thetford Mines ophiolites probably formed in a marginal or back-arc basin by three separate but related igneous events. The first event involved the partial melting of a rising mantle diapir. The melt produced later underwent extensive fractional crystallization involving olivine, spinel, pyroxene and plagioclase to form a layered sequence of dunitic, pyroxenitic and gabbroic cumulate rocks. The residual magma fraction after this extensive fractional crystallization was later erupted as part of hypabyssal rocks and MgO, Cr and Ni poor lavas. During the second and third stages, the residual mantle material from the first episode of melting was remelted to produce melts from which low TiO_2 lavas were formed. The low TiO_2 lavas are also depleted in other incompatible elements such as Zr and Y which presumably were lost into the magma produced by the first stage melting of the mantle. The mantle residue after the multi-stage melting of the mantle is believed to be represented by the harzburgite occurring at the base of the ophiolite suite.

The cumulates display wide variability in their major and trace as well as noble metal contents principally in response to fractional crystallization while the harzburgite displays uniform chemistry, compatible with its origin as a residue of extensive partial melting of the mantle. However, on the average, Thetford Mines plutonic rocks have similar noble metal contents to Mt. Albert pluton, Gaspe, but have higher PGE than the Troodos ophiolites. Thetford Mines rocks are also depleted in the noble metals in comparison to the stratiform layered complexes such as Bushveld and Stillwater. The volcanic rocks can be classified into three groups on the basis of their noble metal contents viz., i) low Ir, low Pd lavas, ii) low Ir, high Pd and iii) high Ir, high Pd lavas. These groups correspond to the lavas produced during the first, second and third igneous events respectively. The noble metal contents of the first group are similar to most ocean floor basalts while the third group lavas are comparable only to oceanic island and intraplate basalts.

During fractional crystallization of the parental magma of the cumulates, Ir was strongly partitioned into early formed rocks such as the olivine-chromite cumulates while Pt and Pd were progressively enriched in the residual magma fraction. Au, however, was less sensitive to fractional crystallization than the PGE.

After the formation of the ophiolites, the lavas and hypabyssal rocks were metamorphosed to greenschist facies by hydrothermal sea water, and the ultramafic rocks were serpentinized, first in the oceanic environment by sea water and later on the continent by meteoric water, Most of the major and trace elements were mobilized during the hydrothermal alteration of the lavas but the PGE were immobile. It is suggested that the redox potential of the hydrothermal solution was not high enough to oxidize the noble metals and so permit mobilization. Au, however, shows some degree of mobilization, and it is believed that some Au occurred along grain boundaries and was carried as particulate material (mechanically) by hydrothermal solution. The noble metals were only slightly mobilized during the continental

serpentinization episode. Their inertness during the oceanic serpentinization episode is attributed to the reducing condition of the oceanic environment which prevented formation of soluble noble metal complex ions.

Unlike many ophiolite occurrences, Thetford Mines rocks appear to have very little economic potential with respect to base and noble metals, principally because of lack of abundant sulfides to act as concentrators of the metals.

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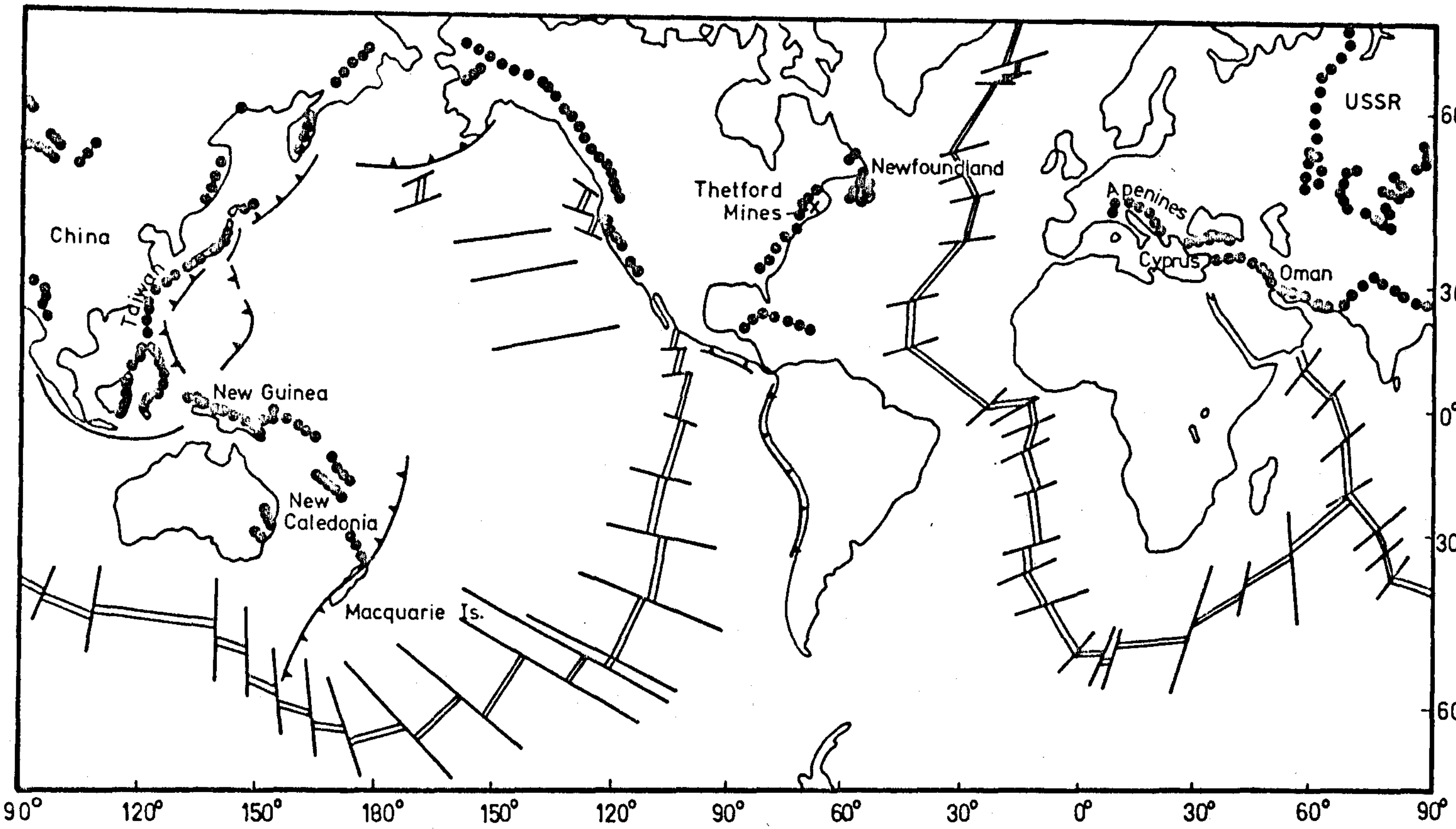
CHAPTER ONE

INTRODUCTION

One of the major concepts in modern geology is the theory of plate tectonics. This theory, developed over a decade ago, suggests that the surface of the earth consists of several thin (100-150 km) but rigid plates. These plates, which may comprise either continental or oceanic crust or both, are in constant motion relative to one another. According to the plate tectonic theory, new oceanic crust is being generated from the mantle at mid-oceanic ridges. From the ridges the newly created crust, with its upper mantle, migrates laterally towards an oceanic trench where it may meet another plate moving in the opposite direction. At the margins where the two approaching plates meet, one plate slips down underneath the other and is consumed. This process is subduction. A postulate of the plate tectonic theory is that under certain circumstances portions of the subducting ocean plate may escape subduction, become detached and eventually incorporated or thrust onto the continental crust. This is obduction. Such obducted fragments of ocean crust and mantle are now called ophiolites (Dewey and Bird, 1970; Bailey *et al.*, 1970; Coleman, 1971).

In current usage, an ophiolite may be defined as an orderly succession of specific ultramafic and mafic igneous rocks, usually with a characteristic pelagic sedimentary associate. Such rock assemblages include peridotite, dunite, pyroxenite, gabbro, pillow basalt and

Figure 1-1. World distribution of ophiolites



World Distribution of Ophiolites

× Study Area

// Mid oceanic ridge

— Transform fault

Subduction zone

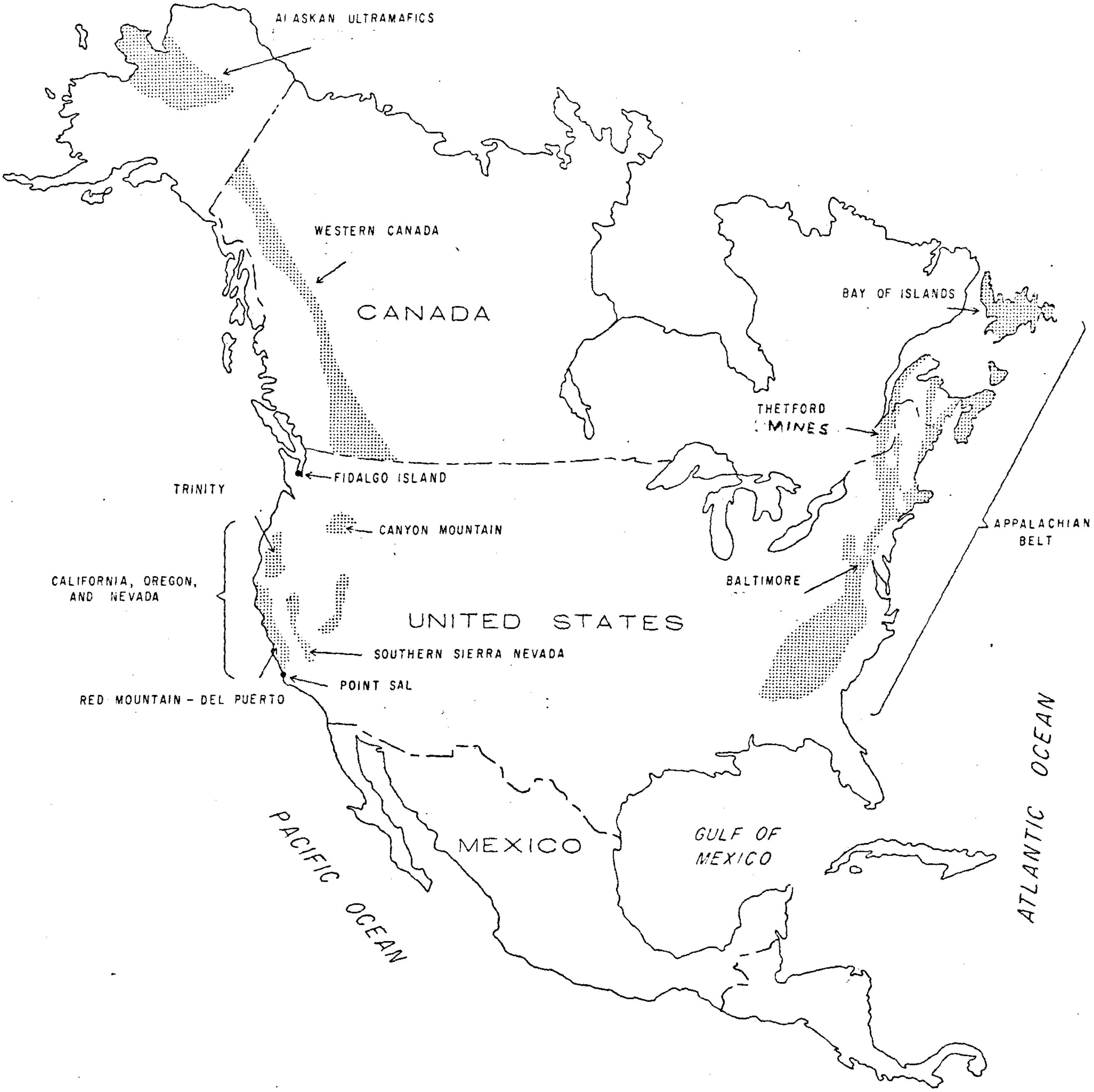
● Ophiolitic occurrence

After Coleman (1972)

argillaceous sediment. Ophiolites generally occur in orogenic zones and island arcs. Figure 1-1 shows the world distribution of ophiolites. In North America ophiolites occur along the western margin of the continent from Alaska to California and along the eastern margin within the Appalachians orogen from Newfoundland in Canada to Alabama in the United States of America (Figure 1-2).

Although rocks now regarded as ophiolites have been studied since the 18th century, for example, Brongniart (1827), Suess (1905), and Steinmann (1906, 1927), a new interest has been generated in the study of ophiolites since they were first conceived as being obducted ancient oceanic crust. Within the last decade an impressively large number of papers have been published on the petrology and geochemistry of ophiolites. The initial interest in ophiolites was a consequence of attempts to test the theory of plate tectonics by comparing ophiolites with modern day oceanic crust. Comparisons have been made of the physical properties, geology, petrology, mineralogy and chemistry for ophiolites with similar properties inferred for oceanic crust from geophysical observations and experimental petrology. Although differences exist between ophiolites and modern day oceanic crust, the similarities between the two are impressive. With the wide but not universal acceptance by earth scientists that ophiolites represent ancient oceanic crust and mantle, studies shifted to the use of features observed in ophiolites to speculate about the geological process that takes place at mid-oceanic ridges and the use of ophiolites to reconstruct zones of ancient lithosphere convergence.

Figure 1-2. Map of North America showing ophiolite occurrences (from North America Ophiolites (1977): R.G. Coleman and W.P. Irwin, eds).


ALASKAN ULTRAMAFICS
WESTERN CANADA
CANADA
BAY OF ISLANDS
THETFORD MINES
FIDALGO ISLAND
TRINITY
CANYON MOUNTAIN
APPALACHIAN BELT
CALIFORNIA, OREGON, AND NEVADA
BALTIMORE
UNITED STATES
SOUTHERN SIERRA NEVADA
POINT SAL
RED MOUNTAIN - DEL PUERTO
MEXICO
GULF OF MEXICO
PACIFIC OCEAN
ATLANTIC OCEAN

However, during the last half of the last decade, samples of the oceanic crust from oceanic ridges and ocean fracture zones have been successfully recovered by both drilling and dredging. Studies on these samples show that although the lithology of ophiolites may not be significantly different from that of the oceanic crust, the chemistry of some ophiolitic rocks are quite different from the chemistry of mid-oceanic ridge rocks. As pointed out by Karig (1971), Dewey and Bird (1971) and Miyashiro (1975) oceanic crust could be generated at other oceanic environments such as marginal basins, island arcs, back-arc basins and inter-arc basins. Consequently, recent studies on ophiolites have been largely concerned with identifying the oceanic environment of formation of the ophiolites by the use of such trace elements as Rb, Sr, REE, Ti, Zr, and Y. Regretably, however, up till now, no suitable geochemical parameters for unequivocal distinction between the various oceanic environments have been found, and the problem of environment of formation is still a subject of debate amongst petrologists. Another aspect of ophiolite studies which has always generated controversy among geologists is the problem of the genetic relationship of the various rock types within an ophiolite suite. Petrological and geochemical consideration have been used for postulating different models to explain the association of ophiolite rocks.

Part of the present study is an attempt to deduce the environment of formation of the Thetford Mines ophiolite and the genetic relationship between the various rock types using their observed noble metal abundances. This is essentially making use of noble metals as geochemical parameters. Similar attempts have been made in using noble metal ratios such as Au/Ir (Greenland et al., 1974), Pd/Pt (Yushko-Zakharova et al., 1967), Pt/Pt+Pd+Ir (Cabri and Harris, 1975), Pt/Pt+Pd (Naldrett and Cabri, 1976) as indicies of magmatic differentiation.

Noble metals are becoming increasingly important both in economics and in industrial use. It is therefore important that the geochemical processes of concentration of these metals and their distribution in rocks be adequately known for exploration purposes. At present the geochemical trends of noble metals in sulfur rich rocks are fairly well known. This is so because the known hosts of noble metal ores, particularly the Pt group metals, are sulfur rich rocks, like the layered igneous complexes of Stillwater and Bushveld and other sulfide bearing rocks such as those found in Sudbury and Kambalda, Australia. On the other hand, the geochemical distribution of the noble metals in sulfur poor rocks have not been well studied despite the fact that some sulfur poor rocks are mineralogically and lithologically similar to the sulfur rich rocks. Ophiolites are one example of such sulfur poor rocks and a study of the distribution of the noble metals in such a suite of rocks will throw some light into the distribution and geochemical behavior of the noble metals in sulfur poor rocks. Although Agiorgitis and Becker (1979), Becker and Agiorgitis (1978) and Agiorgitis et al. (1979) have reported some noble metal values for the Troodos ophiolite, no detailed noble metal geochemical work has been undertaken on any ophiolite.

Mineral deposits of Cu, Zn, and Fe sulfides have been described for many ophiolites, e.g. Constantinou and Govett (1973), Bonatti *et al.* (1976), Duke and Hutchinson (1974). However, no noble metal deposits have been reported in any ophiolite. The sulfide deposits in ophiolites are formed by hot fluid leaching of metals from ophiolitic lavas during hydrothermal alteration with redeposition of the metals as sulfides towards the stratigraphic top of the volcanics. Although no major noble metal has been reported in these deposits, there is speculation that the noble metals, particularly Au and Ag could be mobilized by hydrothermal activity to form ore (Fryer and Hutchinson, 1976; Spooner and Fyfe, 1973). It is therefore of interest to study the effect of hydrothermal alteration of the lavas on the noble metals, and the Thetford Mines ophiolite was chosen for this study with the hope that the findings will shed some light into the behavior of the noble metals in geothermal systems.

1.1 Thesis Objective

The principal objective of this study is to determine the distribution of some noble metals (Au, Ag, Pt, Ir and Pd) in the ophiolites of part of southern Quebec, Canada, for the purposes of:

i) characterizing the ophiolites with respect to their noble metal content,

ii) comparing the Quebec ophiolites with other rocks of similar mineralogy, lithology and chemistry from different tectonic environments, in term of their noble metals, thereby determining their probable environment of formation,

iii) assessing the geochemical and mineralogical factors which control noble metal distribution in sulfur poor rocks,

iv) assessing the effect of secondary geologic processes like serpentinization and hydrothermal alteration on the noble metal distribution in rocks, and

v) evaluating the economic potential of the Quebec ophiolites with respect to their noble metals.

1.2 The Study Area

The study area, situated in southern Quebec, Canada, lies between latitudes 45°55' and 46°05', and longitudes 71°10' and 71°30' (Figure 1-3) and occurs within the northern part of the Appalachian System.

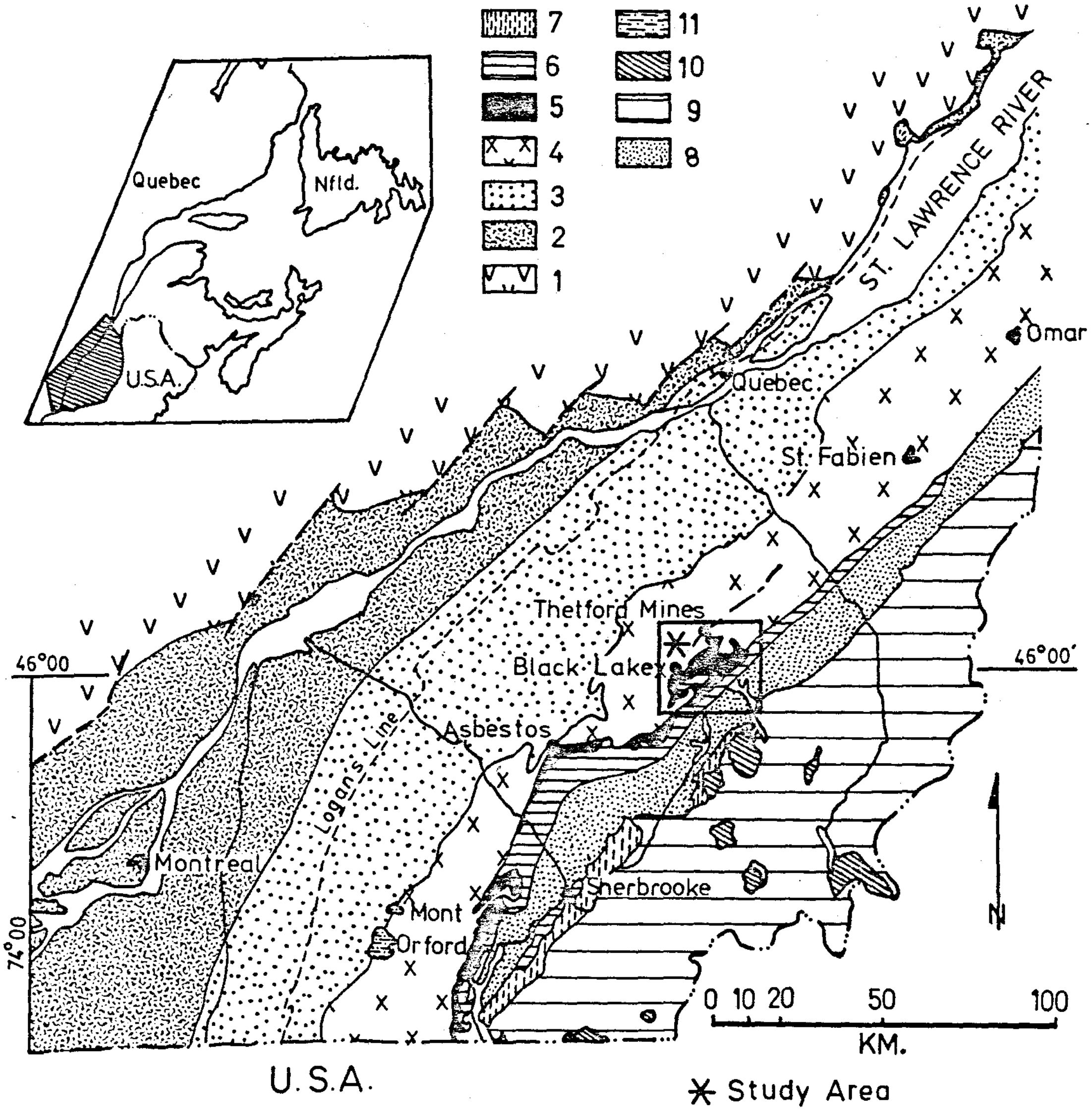
1.2.1 The Geology of Southern Quebec Appalachians

Southern Quebec can be divided into three geological provinces (Poole et al., 1970; St. Julien, 1972; and Laurent, 1975) which, from the northwest to the southeast, are:

i) the Canadian Shield (Grenville Province) with Precambrian metamorphic, igneous and sedimentary rocks,

ii) the St. Lawrence Platform which consists of flat lying lower

Figure 1-3. Map of the Appalachians of southwestern Quebec showing the main structural zones and the major ophiolite localities (after Laurent *et al.*, 1979). 1) Precambrian crystalline basement. 2) Sedimentary cover of the St. Lawrence platform (mainly Ordovician). 3) Cambro-Ordovician outer zone or Appalachian allochthon. 4) Cambro-Ordovician inner zone or Notre Dame schist belt. 5) Ophiolites. 6) Early Ordovician St. Daniel Formation (melanges). 7) Lower to Middle Ordovician Formations of Weedon and Ascot. 8) Middle Ordovician flysch of the Magog Group. 9) Siluro-Devonian belt of the Gaspe-Connecticut Valley synclinorium. 10) Devonian granites. 11) Mesozoic alkaline syenitic and gabbroic intrusive rocks of the Monteregian Hills.


7
6
5
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3
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11
10
9
8
Quebec
Nfld.
U.S.A.
ST. LAWRENCE RIVER
Omar
Quebec
St. Fabien
Thetford Mines
Black Lake
Asbestos
Logan's Line
Montreal
Mont Orford
Sherbrooke
46°00
46°00'
74°00
N
0 10 20 50 100
KM.
U.S.A.
Study Area

Paleozoic sediments (orthoquartzite and carbonate), a flyschoid sequence and some minor occurrences of alkaline igneous rocks,

iii) the Appalachian System which is the host of the ophiolites.

The Appalachian System is an orogen believed to have been developed by the destruction of an ancient continental margin of eastern North America (Wilson, 1966; Williams and Stevens, 1974) and extends from Newfoundland to Alabama.

In southern Quebec, the Appalachians consist of Cambrian-Devonian rocks which have been tectonically deformed. They can be grouped into northeast trending zones (St. Julien, 1972; Laurent, 1975), each zone probably representing rocks formed during different stages of the evolution of the Appalachians. From northwest to southeast, the zones are (Figure 1-3):

a) the External Flysch Trough
b) the Notre Dame Trough
c) the Gaspe-Connecticut Valley Synclinorium.

a) The External Flysch Trough (Outer Zone). This zone, lying southeast of the St. Lawrence platform of flyschoid allochtonous sequences, consists of a series of nappes, imbricated thrust slices and klippen (St. Julien, 1972) emplaced during Cambrordovician times. These rocks include:

i) Cambrian - Lower Ordovician: shale, sandstone, limestone and conglomerate, believed to have been deposited during the initial and main stages of the opening of the proto-Atlantic (Iapetus) Ocean (Windley, 1978) when two sedimentary environments - a continental shelf and a continental rise were formed,

ii) Mid-Ordovician: calcareous wild flysch, representing sediments derived from foundering of the Cambrian carbonate shelf and the redeposition of these sediments on the subsiding shelf. This probably occurred during the main phase of the Taconic orogeny and marked the initiation of the closing of the proto-Atlantic Ocean.

b) The Notre Dame Trough (Inner Zone). This zone comprises formations which probably represent another part of the continental rise and represents a deep sea facies formed during the initial opening of the proto-Atlantic Ocean (Laurent, 1975). Formations include:

i) overturned Cambrian rocks of a) basal quartzite-shale-greywacke assemblage (Rosaire group) and b) an upper impure graded sandstone, quartzite and greywacke (Caldwell group). Associated with these sediments is an igneous complex of mainly mafic-ultramafic rocks with felsic rock which together with the sediments form a belt of about 250 km long. This belt extends throughout the length of the Eastern Townships of Quebec and into the Schikshock mountain of the Gaspe Peninsula. This belt is generally referred to as the Serpentine Belt (Dresser and Denis, 1944; St. Julien, 1972). The mafic-ultramafic rocks of the Serpentine Belt probably represent portions of the oceanic crust formed during the formation of the proto-Atlantic Ocean.

ii) Lower Ordovician rocks of reworked Precambrian rocks (St. Daniel Formation) and calc-alkaline hypabyssal and volcanic rocks (Ascot and Weedon Groups). The calc-alkaline rocks are believed to have formed during the subduction of the proto-Atlantic oceanic crust and therefore represent fossil island arcs. Locally they overlie the mafic rocks of the Serpentine Belt,

iii) Mid-Ordovician flysch sequence of turbidite and black slate (Magog Formation),

iv) Upper-Ordovician conglomerate-slate-sandstone assemblage (Sherbrooke Formation.

c) The Gaspe-Connecticut Valley Synclinorium. This zone consists of mainly post-Taconic orogenic terrigennous rocks, carbonates and volcanics laid down in Early-Mid Silurian and later deformed during the Acadian orogeny in Middle-Late Devonian.

1.2.2 Occurrences of Ophiolites

The Serpentine Belt of the Appalachians in southern Quebec owes its name to the fact that the ultramafic members of the belt have undergone varying degrees of serpentinization and at present these serpentinized rocks are the world's largest producer of asbestos. Ever since the Serpentinite Belt was first mapped and described by Sir William Logan (1863) the mafic-ultramafic rocks have been subjected to a variety of interpretations over the years. The current interpretation is that they represent tectonically emplaced vestiges of ancient oceanic crust and mantle (Laurent, 1975; Seguin and Laurent, 1975): in other words, the mafic-ultramafic rocks are ophiolites. Evidence for their tectonic emplacement include gravity and magnetic data which suggests that the rocks are rootless; lack of extensive metamorphic aureole or chilled margins around the rocks that might suggest intrusion and their fault and thrust plane contacts.

The structural and stratigraphic relationships of the mafic and ultramafic members of the ophiolites are not everywhere the same along the Serpentinite Belt. In some occurrences complete sequence of ultramafic and overlying mafic rocks are observed. Other ophiolites occur as slabs of ultramafic rocks only or dismembered ophiolites while in some cases, the dismembered ophiolites are also fragmented and occur as ultramafic lenses. Some of these incomplete ophiolite suites have locally been interpreted as dykes, intrusive plutons or mantle diapirs. Examples of these are the Mont Albert pluton and the Pennington Dike.

The discontinuous nature of the Serpentinite Belt has resulted in the grouping of the ophiolites in southern Quebec into different complexes. From the south to the north, these complexes are Orford, Asbestos, Thetford mines, East Broughton, St. Fabien and St. Omar (Laurent, 1975) (Figure 1-3). This study is carried out in part of the Thetford Mines Complex principally because it is the most complete and best preserved of the five ophiolite complexes.

1.2.3 Previous Work

The first published geological records of the mafic-ultramafic rocks of southern Quebec are those contained in Sir William Logan and Sterry Hunt's reports for the Geological Survey of Canada (1863) and since then many workers have described these rocks, e.g. Harvie (1911-1916), Cooke (1937), Dresser and Denis (1944) and Riordon (1953). The main objectives of these early workers have been to define and identify the major structural units of the area. However, with the recognition of the mafic-ultramafic rocks as ophiolites or ancient oceanic crust (Lamarche, 1972; Church, 1972, Laurent, 1973) extensive petrological but limited geochemical work has been carried out by St. Julien (1972), Seguin and Laurent (1975), Hebert (1974), Laurent and Hebert (1977), and Laurent (1979). These workers have confirmed the ophiolitic nature of the mafic-ultramafic assemblage. They have also identified the major lithological units of the ophiolite suite and described the main petrological characteristics of the various lithological units. However, geochemical and isotopic studies of the Quebec ophiolites are still lacking and to the best knowledge of the author none of the ophiolite complexes have been studied for noble metal geochemistry until now.

In the present study, no new field mapping was undertaken and rocks which are described and analyzed here have been sampled by the author using maps of earlier workers. Geological description of the rocks is based largely on the limited observations made during sampling and supplemented by literature review.

CHAPTER TWO

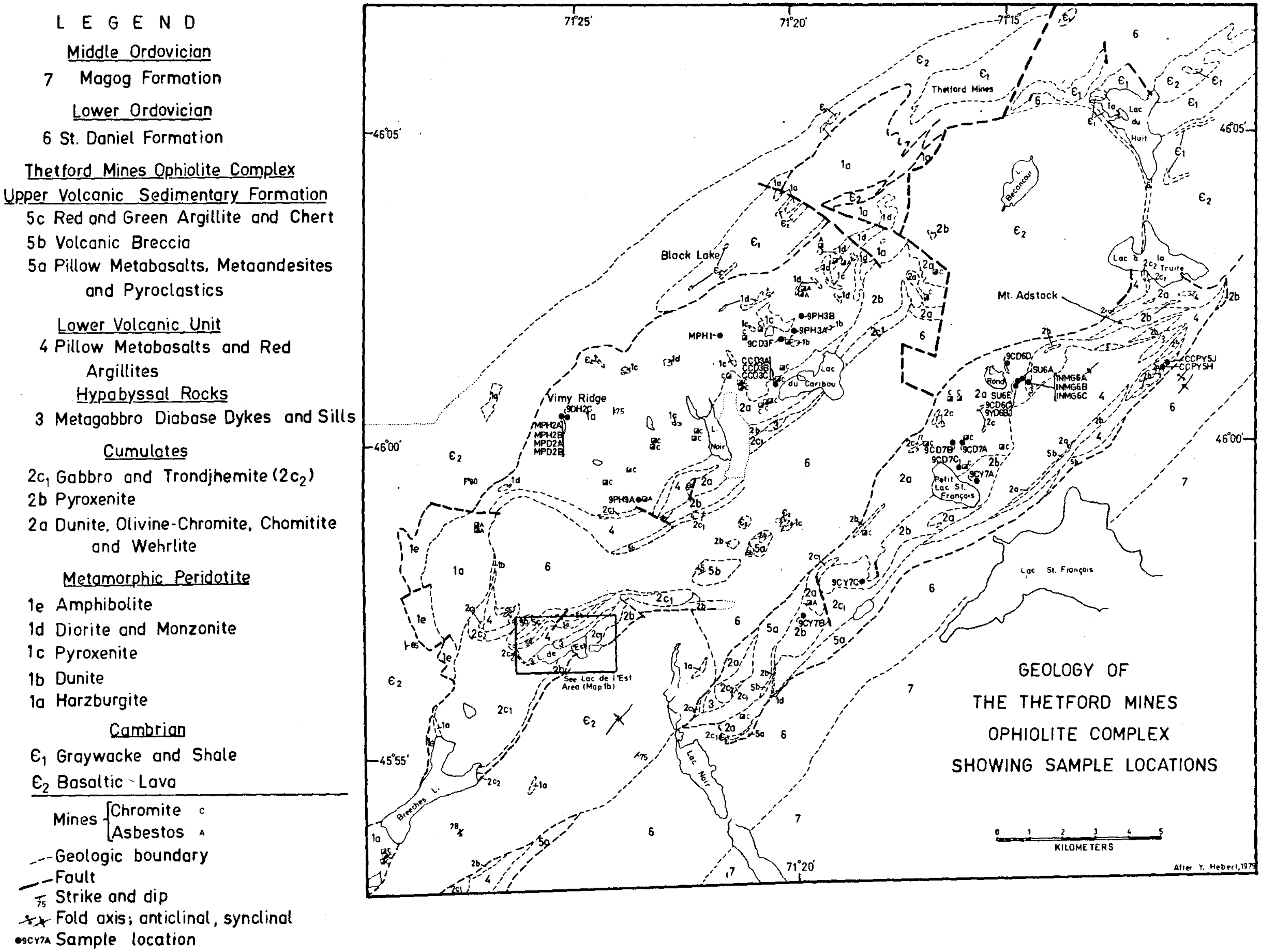
GEOLOGY OF THE THETFORD MINES OPHIOLITE COMPLEX

2.1 Structural Setting

The allochtonous massifs of the ultramafic and mafic rocks together with some felsic rocks occurring in the Eastern Townships of Thetford Mines, Black Lake, Coleraine, St. Daniel, Mt. Adstock and Mt. Ham in the Province of Quebec, constitute what is generally known as the Thetford Mines Ophiolite Complex. The complex is about 48 km long with a maximum width of about 12 km (Hebert and Laurent, 1979) well exposed in most parts and easily accessible.

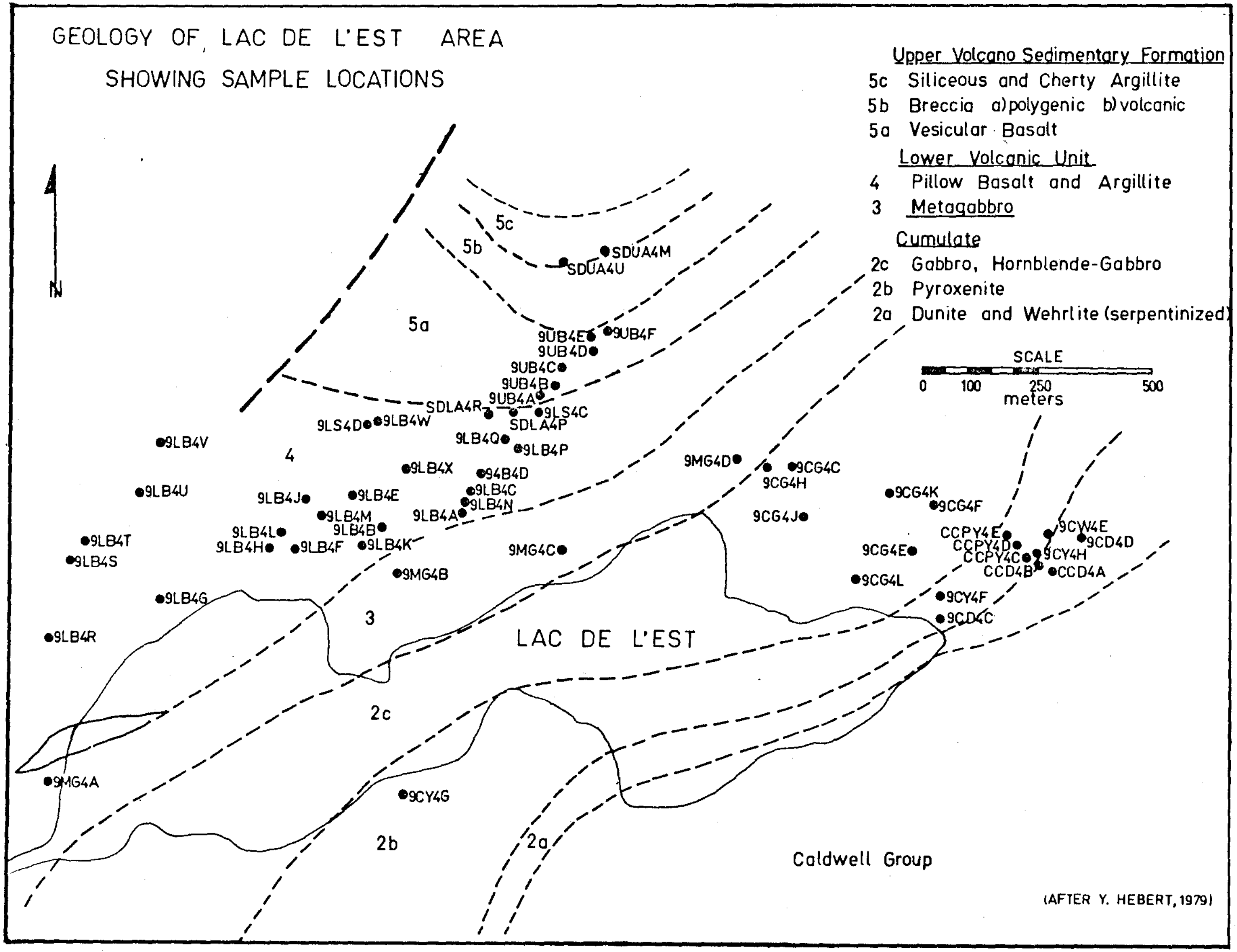
The rocks of the Thetford Mines Complex (TMC) occur in three separate but parallel units, the Black Lake, Mt. Adstock and Mt. Ham massifs, trending NE-SW (Map 1). These massifs have been thrust over the country rocks and contacts of the ophiolite rocks with their country host are invariably sheared and faulted. The Black Lake massif which lies in the NW part of the complex has either been thrust over the Cambrian Caldwell sandstone (Laurent, 1979) or underthrust beneath the Caldwell sandstone (St. Julien, 1972) at its NW margin and is limited on the south by the Mid-Ordovician flysch sequences (Magog Group). The Mt. Adstock massif in the SE part of the complex together with the southeasterly Mt. Ham massif, has been thrust

Map Ia. Map of Geology of the Thetford Mines ophiolite complex showing sample locations (also in back cover)



GEOLOGY OF
THE THETFORD MINES
OPHIOLITE COMPLEX
SHOWING SAMPLE LOCATIONS

Map 1b. Map of Geology of Lac de l'Est area showing sample locations.



GEOLOGY OF LAC DE L'EST AREA
SHOWING SAMPLE LOCATIONS

between the Magog Group and the St. Daniel formation - a melange sequence of black shale, siltstone, phyllites, sandstone, quartzite and mudstone.

2.2 Lithology

Ultramafic rocks make up about 80% by volume of the Thetford Mines Complex. Based on the classification of ultramafic rocks of Streckeisen (1974), these rocks include harzburgite, dunite, wehrlite, ortho- and clino-pyroxenite and websterite. The mafic rocks are mainly gabbro, basaltic and andesitic (?) lavas, diabase dikes and sills. A reconstructed stratigraphy of the Thetford Mines Complex by Laurent (1977) (Table 2-1) is similar to the stratigraphy of other ophiolites, and suggests a stratigraphy consisting of a basal unit of peridotite overlain by an upper unit of layered ultramafic and mafic cumulates which, in turn, are overlain by hypabyssal and volcanic rocks and capped by argillites of probable deep sea origin. Although the Thetford Mines ophiolite is regarded as the most complete of the ophiolite complexes in Quebec, there is no section where the complete sequence from peridotite to volcanics could be traced. The most complete section of the Thetford Mines Complex occurs in the SW part of the Black Lake massif in the vicinity of Lac de L'Est and even here, the ophiolite lacks the peridotite portion. For the purposes of discussion, the ophiolite rocks will be described as metamorphic peridotite, cumulates, hypabyssal rocks and volcanic rocks.

Table 2-1

Rock Units of the Appalachian Ophiolitic Belt of Southern Quebec

Arc island (?) assemblage	(up to 600 m thick)	Pillowed metabasalts, meta-andesites, volcaniclastic tuffs, breccias, and mudstones
UPPER UNIT (up to 2800 m thick)	Extrusives and cover (up to 600 m thick)	B. Red chert and argillite A. Pillowed metabasalts of tholeiitic and picritic composition
	Hypabyssal rocks (up to 700 m thick)	Non-cumulate metagabbro, overlain by meta-diabase and intruded by swarms of aphanitic diabase dikes and stocks of quartzdiorite
	Cumulates (up to 1500 m thick)	C. Gabbroic Zone: Layered gabbro B. Pyroxenitic Zone: Olivine pyroxenites, pyroxenites and plagioclase pyroxenites A. Dunitic Zone: Dunite with wehrlite and chromitite
LOWER UNIT (up to 5000 m thick)	Metamorphic peridotite	Harzburgite ± dunite ± pyroxenite
	Basal sole	Serpentinite and amphibolite

(After Laurent, 1977)

2.3 Igneous Petrology

2.3.1 Metamorphic Peridotite

The base of the Thetford Mines ophiolite is made up essentially of a rather thick (approx. 5 km thick) unit of harzburgitic rocks with minor local occurrences of dunite and pyroxenite. The basal unit is the only member of the Thetford Mines ophiolite sequence that is continuous, extending from Belmina Ridge in the south to Thetford Mines in the north. At Vimy Ridge, a type locality of the unit, the harzburgite outcrop is brownish orange but dark greenish in hand specimen. The rock displays a tectonite fabric with a pronounced planar foliation due to stretched porphyroblasts of pyroxene, leading to the term metamorphic peridotite for the basal unit (Plate 2-1).

Apart from being foliated, the harzburgite also displays layering, commonly in the form of interlayering of harzburgite with pyroxenite and dunite. Such dunite and pyroxenite layers are centimetres to tens of centimetres in width (Laurent, 1977) and may be continuous over a distance of 150 metres like those described by Kacira (1972). This interlayering of ultramafic rocks is believed to be due to the different proportions of orthopyroxene in the different layers.

Unlike many other ophiolite occurrences, lherzolite is very rare in the Thetford Mines suite and the second dominant rock type of the metamorphic peridotite is dunite. Dunite usually occurs as lenses, dikes and pod-like bodies in the harzburgite (Plate 2-2).

Plate 2-1. Surface of harzburgite showing stretched porphyroblasts of orthopyroxene. Preferred orientation of porphyroblasts impacts a planar foliation in the rock.

(Black Lake)

Plate 2-2. Dunite body (D) in harzburgite (H).

(Vimy Ridge)

Plate 2-1

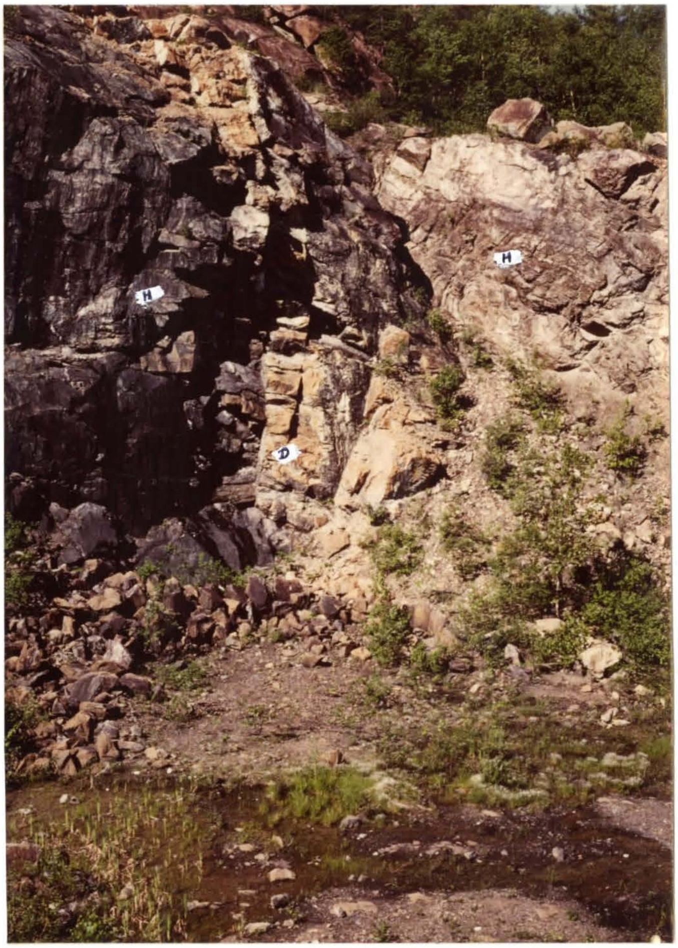


Plate 2-2

Contacts between the dunite bodies and harzburgite are usually sharp and discordant with the foliation of the harzburgite, and unlike the harzburgite, the dunite has a smooth surface due to the absence of porphyroclasts of pyroxene.

The genetic relationship between dunite and harzburgite is not clear. The dunite bodies may be a residue from the partial melting of the harzburgite (Baldwin, 1976; Dick, 1977) or may be a product of the metasomatic alteration of the harzburgite (Dugan and Lallemant, 1977). Kacira (1972), however, suggested that the dunite bodies were xenoliths and injected fragments of the cumulate dunite layer of the ophiolite in the harzburgite and that they were not formed by any secondary process.

The metamorphic peridotite unit has undergone varying degrees of serpentinization and the presence of serpentine minerals gives the rocks their dark greenish colour in hand specimen. Serpentinization is further discussed under the Metamorphic Section.

The essential primary minerals of the harzburgite are olivine and orthopyroxene with chromite and clinopyroxene occurring as accessory minerals. Clinopyroxene is absent in the dunite which consists mainly of olivine with accesory (less than 1%) chromite. Electron microprobe analysis by Kacira (1972) shows that the olivine in the metamorphic unit is forsterite (Fo 89-92) and the orthopyroxene is enstatite (En 92-94).

In the harzburgite, olivine which makes up between 80% and 90% by volume of the rock, is usually unzoned, displays undulatory extinction and usually occurs in two grain sizes. The larger grains of about 0.5 mm - 5 mm (diameter) are usually anhedral, strained and heavily fractured. Crystal edges are either curved or straight and are commonly interlocked with the orthopyroxene edges. On the other hand, the finer olivine grains are mostly polygonal and tend to surround the orthopyroxene grains (Plate 2-3). The setting of the orthopyroxene in the matrix of finer grains gives the rock a blastomylonitic texture. The dunite in the harzburgite does not display the blastomylonitic texture of the harzburgite due to the absence of orthopyroxene. This blastomylonitic texture is believed to be as a result of solid state deformation of the rock during its ascent from the mantle to the upper crust.

Orthopyroxene is mainly enstatite but bronzite has been identified in some samples. Orthopyroxene occurs as elongated or euhedral grains of sizes between 1 and 30 mm in length. In some cases orthopyroxene carries inclusions of olivine and chromite. Extinction is parallel and may be undulatory. A common feature of the orthopyroxene is exsolution lamellae of clinopyroxene. Evidence of deformation of the orthopyroxene in a plastic stage is shown by the occurrence of deformation lamellae in some of the orthopyroxene.

Chromite which normally does not exceed 1% by volume occurs as reddish brown to black anhedral crystals. The mode of occurrence of chromite varies in the rocks. In some cases, usually in the dunite, chromite grains form very thin veins, but otherwise they lie across grain boundaries of olivine or as inclusions in the orthopyroxene. While inclusion of olivine in chromite is common, chromite does not

Plate 2-3. Photomicrograph: Polygonal recrystallized olivine grains (L) surrounding an orthopyroxene porphyroblast (X). This arrangement gives harzburgite a blastomylonitic texture.

Crossed nicols x 63

Sample MPH2A

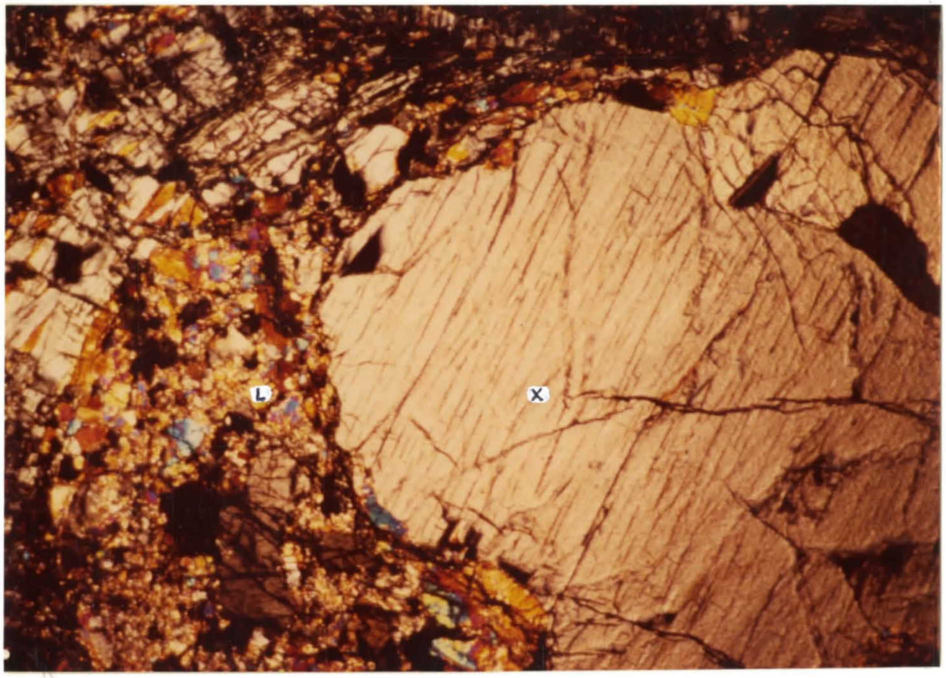


Plate 2-3

occur as inclusions in the olivine.

Clinopyroxene is absent in the metamorphic dunite. In the harzburgite, clinopyroxene occurs mainly as exsolution lamellae in the orthopyroxene. Discrete crystals of clinopyroxene are not common but may occur as diopside in the harzburgite, usually interstitial to the olivine and orthopyroxene grains.

2.3.2 The Cumulates

Lying stratigraphically above the metamorphic periodotite are a group of ultramafic and mafic rocks which display some cumulate textures and rhythmic layering. The contact between the cumulates and the metamorphic peridotite is usually faulted and serpentinized. The cumulates can be divided into three units based on their mineralogy. Starting from the base, these units are: dunite, pyroxenite and gabbro units.

The Dunites. Dunitic rocks are well developed at Lac du Caribou, Mt. Adstock, Lac Rond and Lac de l'Est. They are dark green and usually highly serpentinized. According to Laurent (1977), the dunitic rocks developed in cycles, the lower part consisting of cycles of dunite and chromitite (Plate 2-4) as at Lac du Caribou, while the upper part consists of cycles of dunite and wehrlite. Dunitic rocks are usually layered but locally where cut by dikes of pyroxenite or gabbro, as at Lac Rond, dunites may become brecciated (Plate 2-5)

Plate 2-4. Interlayering of dunite (brown) and chromite band (chromitite) (dark) at the base of the cumulate.

(Lac du Caribou)

Plate 2-5. Brecciated, interlayered dunite (brown) - pyroxenite (dark). Rock layers are discontinuous, of variable thickness and ill defined.

(East of Lac Rond)

Plate 2-4

Plate 2-5

Olivine is the principal mineral of dunitic rocks with chromite and clinopyroxene occurring as accessory minerals. When the proportion of chromite or clinopyroxene is high enough, dunite becomes chromitite or wehrlite. Olivine is usually altered to serpentine minerals but in some cases grain boundaries are preserved, thereby revealing the granoblastic texture of the rock. The cumulate texture of dunite is displayed by the alternation of olivine and chromite bands.

Chromite is usually subhedral to euhedral and may be nodular in some cases. Grain sizes range from 1 mm to 3 mm in diameter and alternation of coarse and fine chromite grains has been observed in some samples. More often than not, chromite grains are fractured and although chromite is not serpentinized, the fractures are usually filled with serpentine minerals. A common feature is the inclusion of olivine in chromite. Such olivine inclusions are usually serpentinized.

The clinopyroxene is diopside and is commonly altered to hydrous minerals such as talc, tremolite or chlorite.

The Pyroxenites. Massive and layered pyroxene rich rocks lie above the dunite unit. The layers result from varying proportions of constituent minerals in the rocks and tend to follow a sequence which varies from place to place. At Lac de l'Est, for example, pyroxenite layers begin with olivine websterite, followed by websterite and terminating with clinopyroxenite with wehrlite occurring irregularly toward the top of the sequence. In other areas such as Mt. Adstock, the pyroxenite layers consist of a basal layer of olivine clinopyroxenite followed by clinopyroxenite and ending in plagioclase clinopyroxenite. In all cases, the transition between dunite and pyroxenite units is wehrlite.

Pyroxenites consist essentially of one or more of three mineral phases: olivine, orthopyroxene and clinopyroxene. Olivine makes its appearance early in the pyroxenite zone as a cumulus phase in olivine websterite and later in wehrlite toward the top of the pyroxenite zone. Olivine is usually serpentinized and its original composition is not known.

Like olivine, orphopyroxene appears early as a cumulus phase in olivine websterite where it may make up to 80% by volume of the rock, with clinopyroxene as both cumulus and intercumulus phases. Unlike the orthopyroxene in the metamorphic peridotite, orthopyroxene in the pyroxenite unit is hypersthene and is commonly altered to bastite.

Clinopyroxene occurs throughout the pyroxenite zone as both a cumulus and a postcumulus phase. In the upper part of the pyroxenite unit only clinopyroxene remains as a cumulus phase to form adcumulate clinopyroxenite. Clinopyroxene is usually diopsidic and is invariably uralitised. Clinopyroxene is frequently fractured (Plate 2-6). These fractures probably occur during the tectonic emplacement of the rocks.

<u>The Gabbros</u>. With the introduction of plagioclase as a cumulus phase, pyroxenite changes into gabbro. At least two groups of rocks form the gabbro zone above the pyroxenite unit. The first group consists of gabbroic rocks which occur in layers, finer grained at the

Plate 2-6. Photomicrograph: Fractures in clinopyroxene. The larger fractures are usually filled with alteration products such as chlorite, epidote and serpentine minerals. This feature is common in the pyroxenites and gabbros.

Crossed nicols x 63

Sample 9CY4F

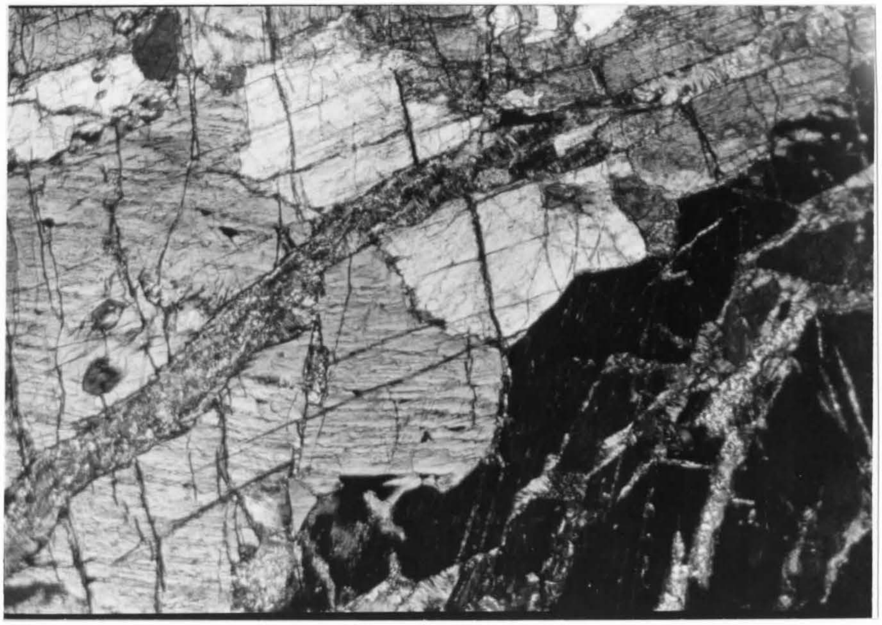


Plate 2-6

base and becoming coarser upwards. At the top, the gabbro become finer again and leucocratic. In the Lac de l'Est area, the second group of rocks consists of patches of pyroxenite and pyroxene and pyroxene-hornblende rich coarse grained gabbro in the middle of the gabbro zone.

Clinopyroxene, plagioclase and hornblende(?) are the main cumulus phases of the gabbros. The clinopyroxene is either diopside or augite. Cores of clinopyroxene rimmed with hornblende is a common feature. Orthopyroxene rarely occurs in the gabbros but when it does, it is hypersthene. Plagioclase is probably labradorite and occurs as tabular crystals, in some cases, together with clinopyroxene. The plagioclase assumes a preferred orientation, thus imparting a laminated structure in the rock. Hornblende occurs in either of two modes, as cumulus and postcumulus phase or as alteration product of pyroxene. As a postcumulus phase, it occurs as poikilitic crystals around plagioclase and pyroxene.

Some of the rocks in the gabbro zone like those in the pyroxenite zone have been cataclastically deformed as revealed by fractures in some of the minerals of the rocks.

2.3.3 Hypabyssal Rocks

Overlying the cumulate gabbro is a complex zone of mafic and felsic rocks which cut and intrude one another. This zone represents the sheeted dike zone of most ophiolites (e.g. Troodos) but is poorly developed here.

The host rocks are melanocratic, fine to medium grained metamorphosed gabbro and diabase with subophitic to ophitic texture. These gabbros have been cut by mafic and silicic dikes which are sometimes sulfide bearing and are also intruded by isolated bodies of quartz diorite and plagioclase bearing granites (plagiogranite). In places like Lac Coulombe, the metagabbro occurs as a swarm of sills.

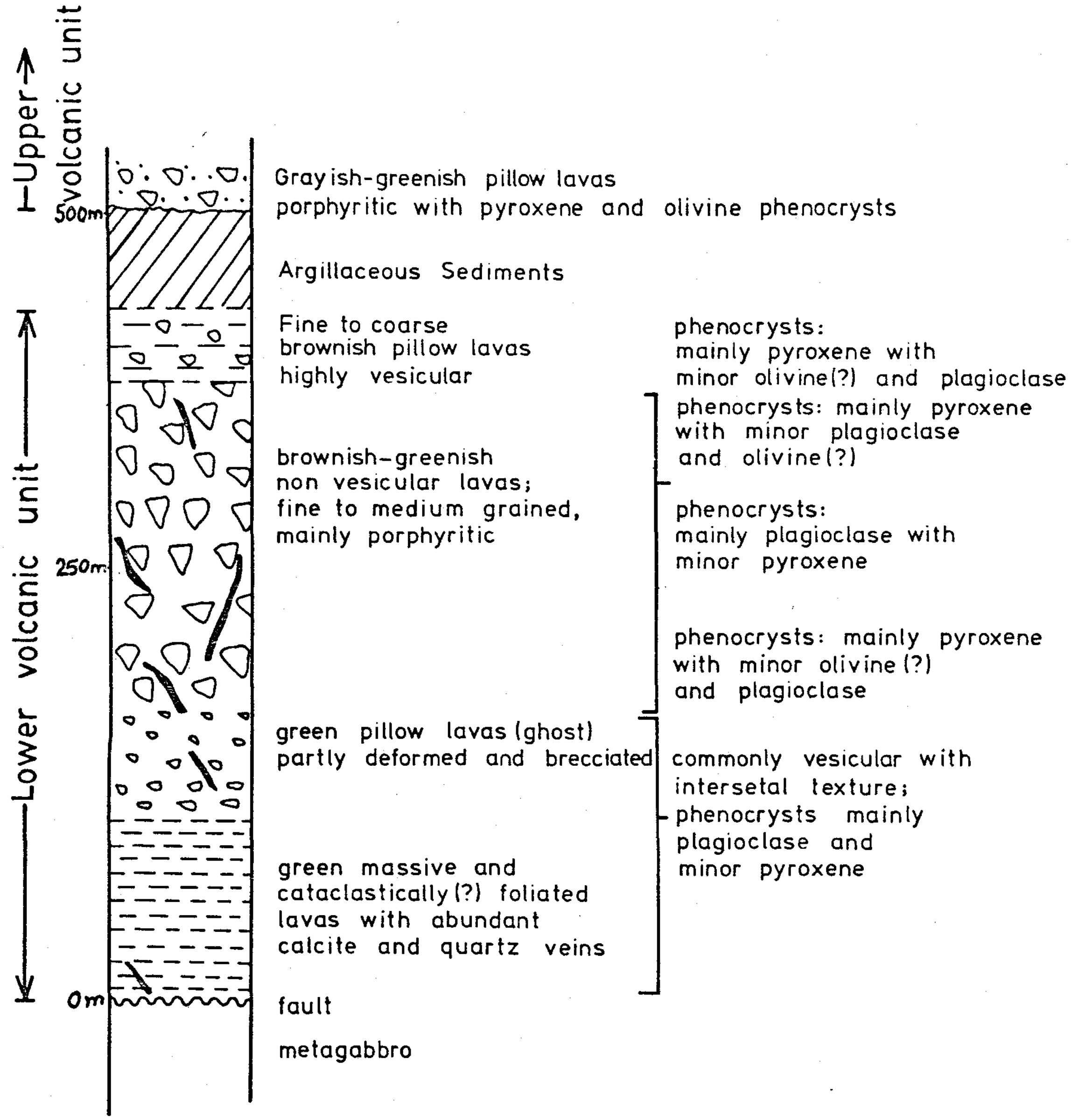
2.3.4 The Volcanic Rocks

Two volcanic units, separated by a thin layer of argillaceous and cherty sediments, lie stratigraphically above the hypabyssal rocks. The boundary between the plutonic and volcanic rocks is believed to be a low angle fault (Laurent and Hebert, 1977). In the Thetford Mines area, exposures of the volcanics occur around Mt. Adstock, Lac Nicolet, Lac Coulombe and Lac de l'Est. It is in Lac de l'Est, however, that the stratigraphic relation of the volcanic units, the sediments and the plutonic rocks are best displayed (see Map1b).

The Volcanic Units at Lac de l'Est. Figure 2-1 is a hypothetical columnar section showing the stratigraphy of the volcanics at Lac de l'Est.

The Lower Volcanic Unit. The lower volcanic rocks lie immediately on the metagabbro. They display a variety of textures.

Figure 2-1. Diagramatic columnar section of the volcanic unit at Lac de l'Est showing textural variation.


Upper volcanic unit
Lower volcanic unit
500m
250m
0m
Grayish-greenish pillow lavas porphyritic with pyroxene and olivine phenocrysts
Argillaceous Sediments
Fine to coarse brownish pillow lavas highly vesicular
phenocrysts: mainly pyroxene with minor olivine(?) and plagioclase
phenocrysts: mainly pyroxene with minor plagioclase and olivine(?)
brownish-greenish non vesicular lavas; fine to medium grained, mainly porphyritic
phenocrysts: mainly plagioclase with minor pyroxene
phenocrysts: mainly pyroxene with minor olivine(?) and plagioclase
green pillow lavas (ghost) partly deformed and brecciated
commonly vesicular with intersetal texture; phenocrysts mainly plagioclase and minor pyroxene
green massive and cataclastically(?) foliated lavas with abundant calcite and quartz veins
fault
metagabbro

In the field, the lowest volcanic lavas are dark green, massive and foliated. They usually carry quartz and calcite veins and locally disseminated pyrite. No pillows have been observed in these rocks. The massive lavas grade stratigraphically into green pillow lavas which have been deformed and in which only ghost pillows are observed. At the base of the unit, lavas are usually brecciated. Veins are common but the lavas may contain vesicles which are filled with quartz and calcite. Upwards, the pillow lavas become lighter and then brownish. The boundary between the lower lavas and the overlying sediments is marked by interfingering of brownish pillow lavas with sediments (Plate 2-7).

The lower volcanic unit is frequently cut by mafic and felsic dikes whose thickness ranges from a few centimetres to hundreds of centimetres. These dikes are probably genetically related to similar dikes in the gabbro but no continuity between the two sets of dikes has been established.

Laurent and Hebert (1977) have classified the rocks of the lower volcanic unit into two types of lava based on mineralogical composition and textural variation within the pillows. The textural variation is well developed in the pillows exposed around Mt. Adstock. The first group of lavas has variolitic margins while the second group is characterized by a globulitic interior. At Lac de l'Est, because of deformation and lack of a well developed pillow structure, textural variation within individual pillows is difficult to observe. However, the author has observed some textural and mineralogical variation as

Plate 2-7. Interlayering of basalt (lower volcanic unit) (dark grey) and argillaceous sediments (dark brown).

(Lac de l'Est)

Plate 2-8. Photomicrograph: Intersetal texture (lower volcanic unit). Plagioclase (pl) ± pyroxene (pseudomorphed by chlorite, ch) set in a groundmass of plagioclase microlites. Vesicles when present usually filled with calcite (c).

Crossed nicols x 63

Sample 9LB4G

Plate 2-7

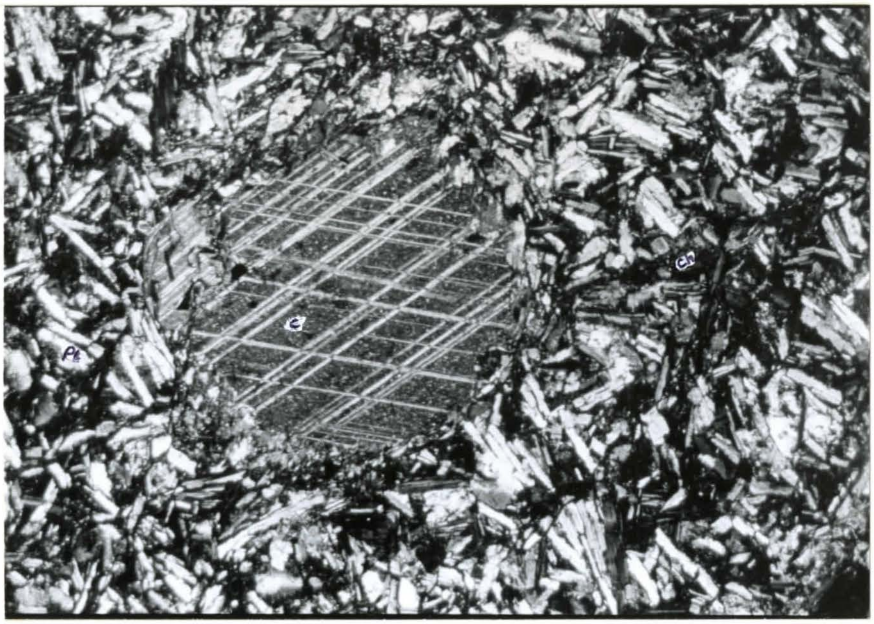


Plate 2-8

described below among the sample studied.

In the lower and middle part of the lava unit, lavas are usually medium grained with an intersetal texture made up of mutually intergrown skeletal plagioclase and pyroxene (Plate 2-8). When phenocrysts are present they are usually plagioclase phenocrysts or microphenocrysts. Vesicles are common and are usually filled with calcite, or less commonly epidote and quartz. The latter type of vesicle is usually difficult to delineate in thin section and probably originates from residual or deuteric fluid which is now altered to epidote and quartz. In this case the vesicles are similar to the segregation vesicle described by Smith (1967). The opaques are ubiquitous and are usually titanomagnetite which is commonly euhedral, but a few samples contain pyrite. A foliation due to parallel arrangement of secondary minerals is occasionally superimposed on the intersetal, porphyritic texture.

Another group of lavas lying stratigraphically over these vesicular basalts is porphyritic with medium to micro-crystalline matrix. The plagioclase in the matrix is stubbier than that of the first group and phenocrysts here are mainly pyroxene and minor olivine(?). No vesicle has been observed in this group. The opaque minerals are hematite(?) and chromite. Chromite, which is observed in one sample only, probably occurred originally as inclusions in olivine, as chromite grains are associated with carbonate which are alteration products of olivine (Plate 2-9). This group occurs stratigraphically above the vesicular lavas.

Plate 2-9. Photomicrograph: Porphyritic texture (lower volcanic unit). Olivine phenocryst, altered to chlorite (c) in a matrix of plagioclase and pyroxene. Other alteration products of olivine include carbonate (c), quartz (q) and Fe-oxides (o).

Crossed nicols x 63

Sample 9LB4M

Plate 2-10. Photomicrograph: Flow texture (lower volcanic unit). Parallel arrangement of pyroxene laths in lavas at the top of the lower volcanic unit.

Crossed nicols x 63

Sample 9LB4U

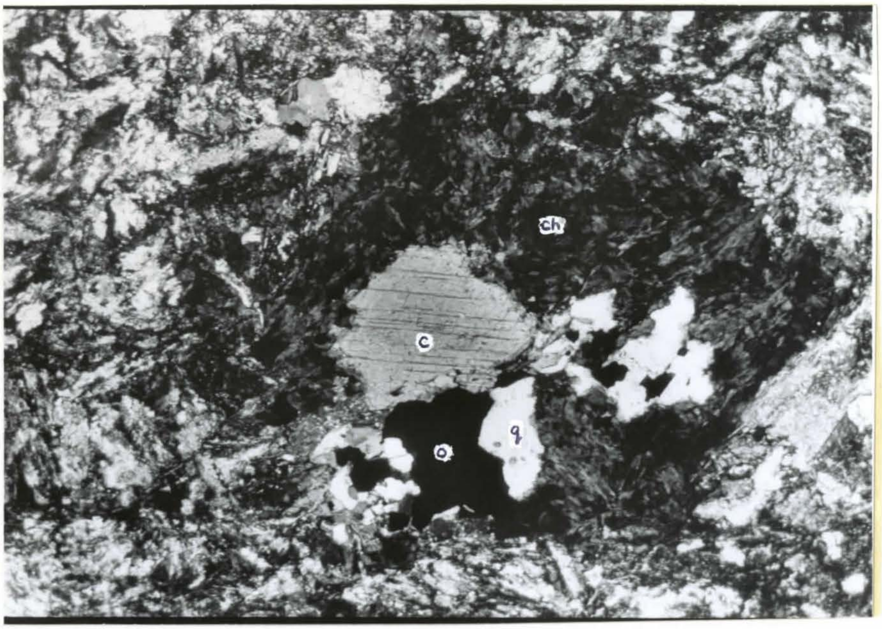


Plate 2-9

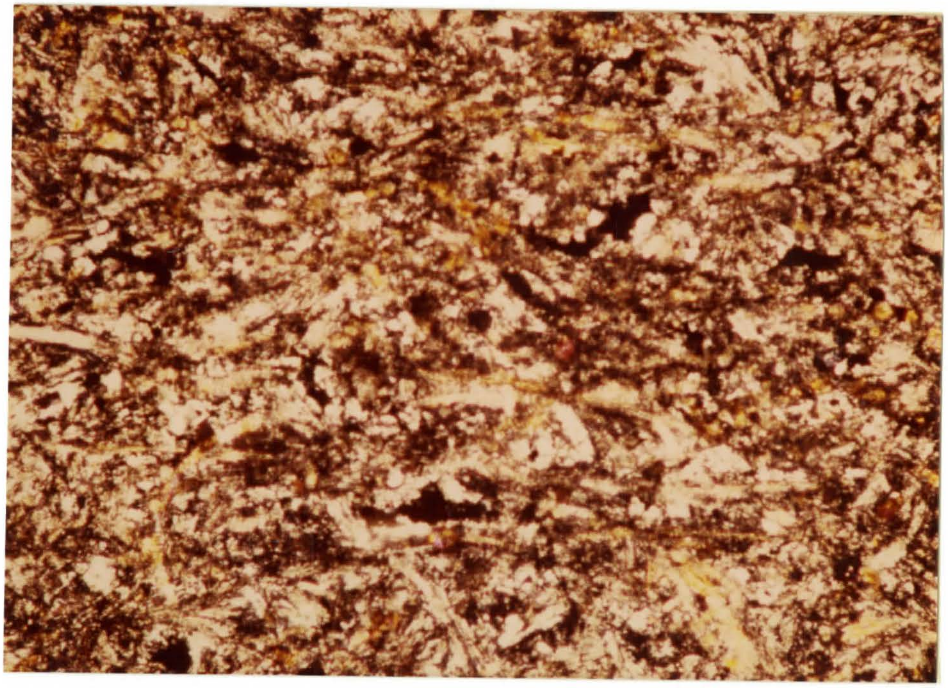


Plate 2-10

Towards the topmost part of the lava unit, the groundmass becomes finer and a flow texture develops in the form of parallel alignment of pyroxene in some samples (Plate 2-10). In the porphyritic variety, phenocrysts are pyroxene, minor olivine and rarely plagioclase. Vesicles filled with calcite quartz and tremolite occur in some samples and many of these vesicles are bounded by laths of pyroxene aligned tangentially to the walls of the vesicles.

The Upper Volcanic Unit. The upper volcanic rocks include a variety of rock types varying from basalt, andesite, pyroclastic agglomerates to acidic tuffs and mudstones (Laurent and Hebert, 1977). In this study only the lower section of the group (approximately 150 m) of mainly basaltic composition was sampled.

The sampled rocks are greenish gray and medium to coarse grained with vesicles which are usually filled with quartz. Like rocks from the lower unit, pillow structure is poorly preserved in these rocks but equivalent rocks elsewhere, for example, at Lac Coulombe, do display well defined pillows.

Under the microscope, the rocks are commonly porphyritic with a groundmass which is essentially pyroxene with phenocrysts and micophenocrysts of pyroxene and olivine(?). No plagioclase has been observed as phenocrysts (Plate 2-11). Opaques are not common and are usually present as fine dust or small veins. These opaques have not been identified but Laurent and Hebert (1977) have indicated that rocks of the upper volcanic unit carry some sulfides, mainly pyrite

Plate 2-11. Photomicrograph: Typical texture in the upper lavas. Pyroxene and olivine phenocrysts (pseudomorphosed by chlorite, ch, and pumpellyite, P) in a subophitic matrix of pyroxene and plagioclase.

Crossed nicols x 25

Sample 9UB4A

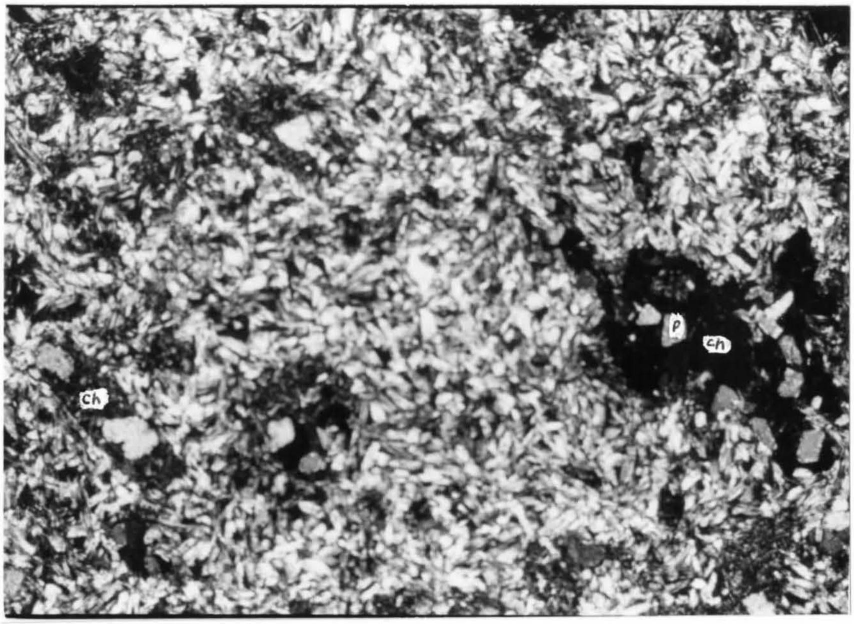


Plate 2-11

and pyrrhotite.

2.4 Metamorphic Petrology

The Thetford Mines ophiolite complex has been recrystallized by metamorphic processes in response to fluid and thermal energy, resulting in the modification of the primary mineralogy and texture of the rocks. Broadly, two types of metamorphism are distinguished: serpentinization and hyrothermal metamorphism.

2.4.1 The Ultramafics

Metamorphism in the ultramafic rocks is in the form of serpentinization. Two episodes of serpentinization have been recognized (Dresser and Denis, 1944; Kacira, 1972; Laurent, 1977). The first serpentinization probably occurred in an oceanic environment (Laurent, 1975) and involved the alteration of olivine to serpentine group minerals including lizardite or chrysotile and the alteration of orthopyroxene to bastite (lizardite). Clinopyroxene is usually preserved but may be altered to tremolite, actinolite or talc. Brucite and magnetite are also produced by the breakdown of olivine during serpentinization and they are usually concentrated along the margins of the newly formed serpentine minerals. Carbonates have been observed in some of the serpentinized rocks.

In the first episode of serpentinization, the harzburgite and the dunite are altered most severely. The pyroxenites are marginally altered unless they contain a high proportion of olivine as in websterite. The original fabric of the rock is destroyed and new textures are formed. In the Thetford Mines area, various textures similar to those described in some Precambrian serpentinized peridotite from Wales by Maltman (1978) and in some serpentinites from ophiolites and ocean floor by Prichard (1979) have been observed in the harburgites and dunitic rocks under the microscope. Such textures include:

i) Mesh texture: mesh texture consists of a network of serpentine (lizardite) cords enclosing polyhedral cores of olivine and orthopyroxene. The cores are either fresh or have undergone various degrees of alteration (Plate 2-12);

ii) Ribbon texture: under shearing stress, the polyhedral mineral core becomes elongated due to the expansion of the cords in one direction so that the mineral cores are now bounded by parallel serpentine cords. The resulting texture is referred to as ribbon texture (Plate 2-13);

iii) Bladed-mat texture: the bladed-mat texture (Plate 2-14) is a less common texture than the mesh and ribbon texture. Here the rock is altered into tiny interlocking blades of antigorite. The antigorite blades may completely replace all pre-existing minerals or may be restricted only to veins which ramify through the rock. The antigorite blades are believed to form from lizardite (Moody, 1976; Prichard, 1979). It is interesting to note that the bladed-mat texture has not been observed in the harzburgite but only in the dunite. Other textures intermediate between these three have also

Plate 2-12. Photomicrograph: Mesh texture (serpentinized ultramafic rocks). Serpentine (lizardite) cords enclose polygonal cores of ferromagnesian minerals.

Crossed nicols x 63

Samples 9DH3F

Plate 2-13. Photomicrograph: Ribbon texture (serpentinized ultramafic rocks). Serpentine (lizardite) cords enclose subparallel elongated cores of ferromagnesian minerals.

Crossed nicols x 63

Sample MPH2B

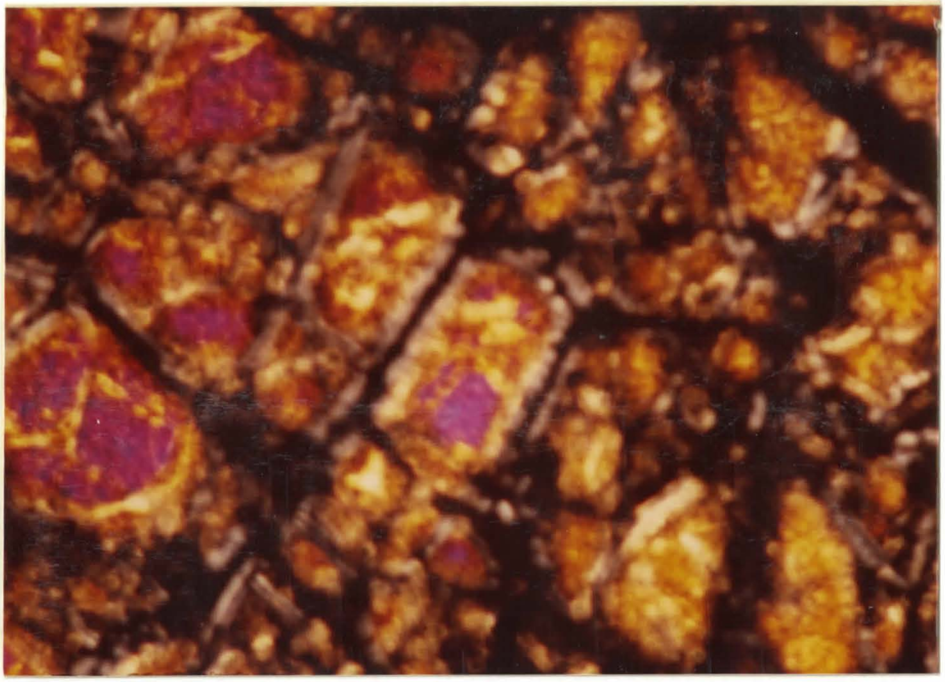


Plate 2-12

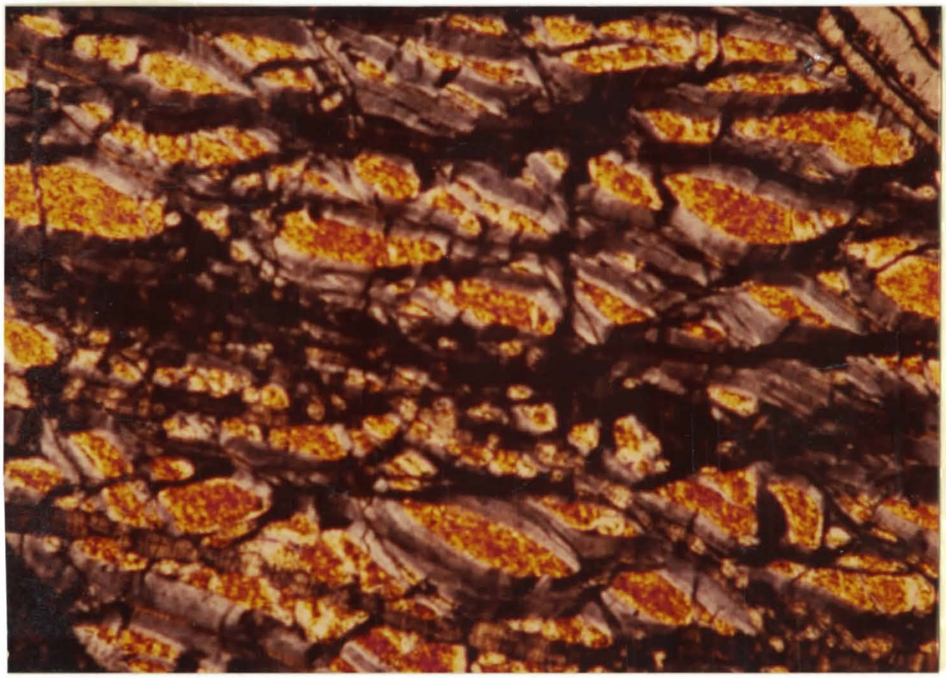


Plate 2-13

Plate 2-14. Bladed-mat texture (seprentinized ultramafic rocks). Ferromagnesian minerals are replaced by interlocking blades of serpentine mineral (antigorite).

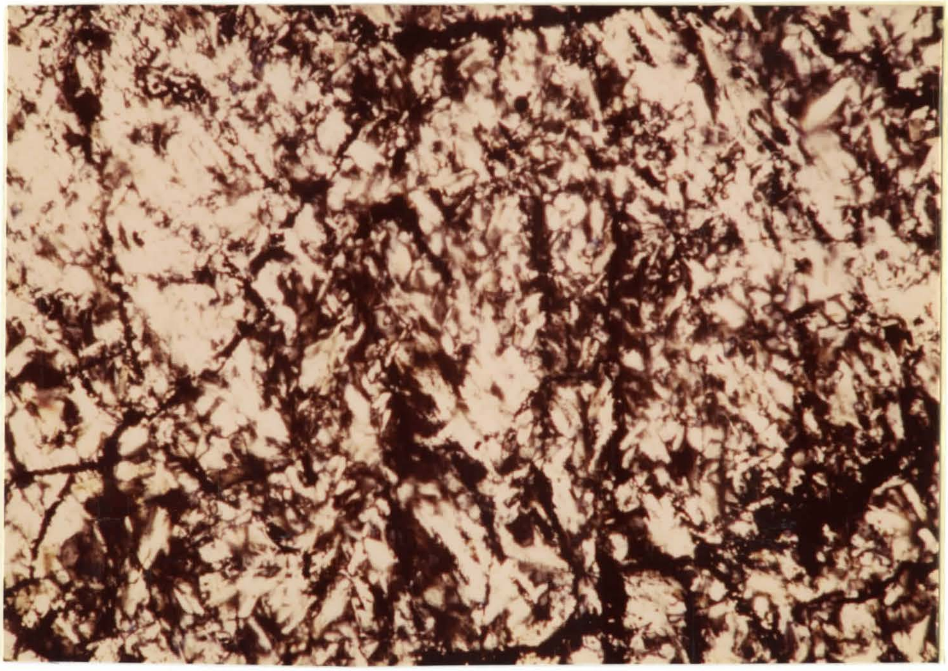


Plate 2-14

been observed.

The second episode of serpentinization is confined to the harzburgite and it involved formation of chrysotile fibers (asbestos) along fractures in the harzburgite. This serpentinization is believed to have occurred during the emplacement of the ophiolites on land (Laurent and Hebert, 1977). The process of serpentinization is further discussed in relation to its effect on noble metal distribution in Chapter Five.

2.4.2 Cumulate Gabbro

In the cumulate gabbro zone the clinopyroxene has been extensively uralitized to fibrous actinolite and talc. In other cases clinopyroxene is feebly altered to a green amphibole with the amphibole forming a rim around the clinopyroxene. The orthopyroxene is altered to bastite while plagioclase is commonly saussurritized into prismatic or spongy crystals of epidote, clinozoisite and albite. Prehnite with chlorite occurs as veins or as partial replacement of plagioclase occassionally. The gabbros show evidence of cataclastic deformation in the form of fractured mineral grains. Such fractures are usually filled with serpentine minerals.

The occurrence of low grade metamorphic minerals like prehnite, chlorite and serpentine as veins together with medium grade metamorphic minerals like amphibole suggests a two stage metamorphism in which the gabbros were amphibolitized during the earlier metamorphism but later suffered a retrograde metamorphism, resulting in the formation of the vein minerals.

2.4.3 Hypabyssal and Volcanic Rocks

Both the hypabyssal and volcanic rocks have been recrystallized under low grade metamorphism. Mineral assemblages of the rocks indicate a progressive increase in intensity of metamorphism downwards from the upper volcanic rocks to the metagabbro. Preservation of igneous textures and abundant calcite and quartz veins suggest that metamorphism in these rocks is principally due to hydrothermal activity similar to that described by Spooner and Fyfe (1973) and Liou and Ernst (1979).

2.4.3.1 The Metagabbro. The metagabbros display the greenschist facies mineral assemblage of albite after plagioclase, actinolite, quartz and calcic amphibole. However, metamorphic mineral assemblage is not uniform. In some sample, chlorite is very rare except for a few veins while chlorite is quite abundant in other samples, being pseudomorphs of plagioclase.

Igneous clinopyroxene is commonly altered to actinolite and chlorite. Epidote seems to be absent in the metagabbro but prehnite and calcite occasionally occur as both vein minerals and alteration products of primary minerals.

2.4.3.2 The Volcanic Rocks. The effect of metamorphism on the volcanic rocks is to recrystallize the primary minerals into minerals of very low to low metamorphic grade with preservation of the igneous textures. The stratigraphic distribution of the major metamorphic minerals produced which include chlorite, actinolite, quartz, calcite, epidote and pumpellyite are shown in Figure 2-2. Accessory minerals are magnetite, hematite and sphene(?).

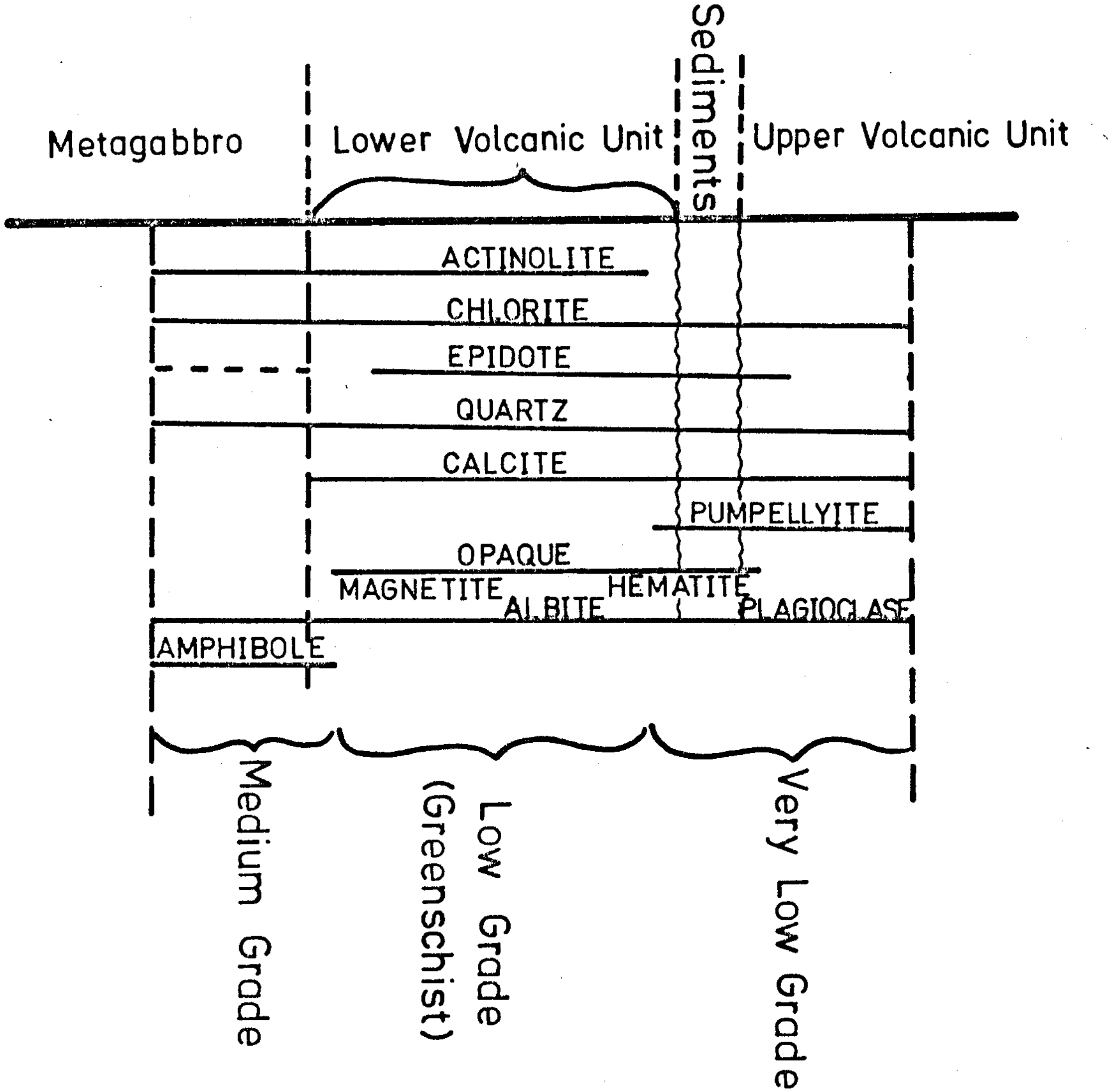
Chlorite replaces olivine and pyroxene phenocrysts and plagioclase. It is greenish in thin section and usually gives anomalous blue interference colour. In foliated samples, chlorite occurs as parallel veins marking the foliation plane.

Actinolite usually occurs in the groundmass and as pseudomorphs of pyroxene phenocrysts. In thin section, optical properties range from colourless to greenish and pleochroic. Crystals are not common; instead, the mineral commonly occurs as fibrous aggregates.

Plagioclase is usually albitized but more calcic plagioclase than albite also occurs as relict of the original plagioclase phenocrysts. Quartz occurs as fine grains but may be coarse when it fills vesicles. In the upper part of the volcanic unit, quartz occurs as part of the groundmass but towards the base it is restricted mainly to veins. Samples near the base of the volcanic unit also show strain with undulatory extinction.

Calcite occurs in the volcanic rocks mainly as fillings in vesicles as veins, but may also form part of the groundmass, particularly in samples with abundant plagioclase phenocrysts, towards the base of the

Figure 2-2 Stratigraphic distribution of metamorphic minerals in volcanic rocks at Lac de l'Est.


Metagabbro
Lower Volcanic Unit
Sediments
Upper Volcanic Unit
ACTINOLITE
CHLORITE
EPIDOTE
QUARTZ
CALCITE
PUMPELLYITE
OPAQUE
MAGNETITE
HEMATITE
ALBITE
PLAGIOCLASE
AMPHIBOLE
Medium Grade
Low Grade (Greenschist)
Very Low Grade

volcanic unit. Epidote occurs as small subrounded crystals with cloudy surfaces usually associated with chlorite and rarely as veins. Pumpellyite, unlike epidote, is euhedral, yellow and pleochroic in thin section. Occasionally irregularly shaped grains of pumpellyite occur with calcite.

Mineral assemblage in the volcanics suggests an increase in degree of metamorphism with depth. In the upper volcanic unit, the mineral assemblage is pumpellyite, epidote, chlorite, quartz, calcite and hematite. This mineral assemblage falls within the lawsonite/ pumpellyite - albite - chlorite zone of very low metamorphic grade as defined by Winkler (1979). In this zone, clinopyroxene is either unaltered or feebly chloritized. Laurent (1979) has indicated that the upper unit contains prehnite, however, the author has not observed prehnite in any of the samples studied from the upper unit.

Below the very low grade metamorphic zone, actinolite appears as pseudomorphs of pyroxene and pumpellyite disappears from the mineral assemblage. Downwards in the volcanic stratigraphy, epidote gradually decreases and hematite is replaced by magnetite as opaque mineral. The disappearance of pumpellyite marks the beginning of the low grade metamorphic zone. The mineral assemblage in this zone is albite, chlorite, epidote, calcite, quartz, hematite and magnetite. This assemblage falls within the clinozoisite-albite-chlorite zone of Winkler (1979) or the greenschist facies.

Laurent (1977) has noted the difference in the relative proportion of actinolite and chlorite in the lower volcanic unit and suggested that the actinolite rich metavolcanics are derived from olivine tholeiite while the chlorite rich rocks are derived from tholeiite. The present author also noted this difference in mineral proportion. However, in the study area (Lac de l'Est), the author is of the opinion that the relative abundance of actinolite and chlorite also depends on the stratigraphic position of the rocks since chlorite tends to decrease while actinolite increases in abundance towards the base of the volcanic unit.

2.5 Discussion

Lamarche (1972) first suggested that the ultramafic-mafic rocks around Thetford Mines originated from an oceanic environment. This view has been taken a step further by Church (1972), Hebert (1974), Laurent (1975) and Seguin and Laurent (1975) in suggesting that the rocks constitute an Ophiolite suite, probably formed originally as an oceanic crust of the Proto-Atlantic Ocean and later emplaced on the western part of the North Atlantic continental margin during the closing of the Proto-Atlantic Ocean. Petrological characteristics of the Thetford Mines complex are similar to those of other ophiolites described elsewhere in some respect but there are also some salient petrological features in the Thetford Mines complex which are not commonly observed in other ophiolites.

The tectonite fabric of the harzburgite suggests that the harzburgite has undergone some subsolidus plastic deformation, probably in a mantle environment (Green and Redcliffe, 1972). The Theford Mines ophiolite differs from most ophiolites such as the Bay of Islands or Troodos in lacking lherzolite. Lherzolite and harzburgite are residues of mantle at about 15% and 25% partial melting. The lack of lherzolite in the Theford Mines complex, therefore, suggests either a large degree of partial melting (greater than 25%) of the mantle during the generation of the Proto-Atlantic oceanic crust, or alternatively, the mantle underwent a two-stage melting. Initially, lherzolite was produced as residue but was later fused to produce a melt and a residue of harzburgite. The dunite and pyroxenite bodies in the harzburgite probably represent crystallized products of such melt at high pressure (e.g. Dickey et al., 1977).

The cumulate rocks have obviously been formed by shallow crustal fractionation of a basic magma. Interlayering of different rock types and lateral pinching of rock layers within the cumulate zone suggest that the magma chamber in which the cumulate rocks formed must have been tectonically active during fractional crystallization. There is no petrological indication of the source of the magma for the cumulates, but the unconformity separating the cumulates and the harzburgite tectonite indicates a non contemporaneous formation of the metamorphic periodotie and the overlying rocks. Lack of primary amphibole and primary magnetite in the cumulates suggest that the magma which gave rise to the cumulates was dry and crystallized at low oxygen fugacity.

Unlike other ophiolites in the Appalachians, for example, the Bay of Islands, Bette Cove and elsewhere, for example, Troodos and Oman, the Thetford Mines complex lacks a sheeted dike zone. In this respect, the Theford Mines complex is similar to Vourinous ophiolites (Laurent, 1975) and the circum-Pacific ophiolites like those in Papua (Coleman, 1977). Since one of the criteria for suggesting that ophiolites are formed at spreading centres is the presence of sheeted dikes in the upper part of ophiolite complexes (Moores and Vine, 1971; Coleman, 1977), the lack of sheeted dikes in the Thetford Mines complex may imply either formation at a fast spreading centre like the East Pacific Rise (Laurent, 1975) or formation at a non spreading centre such as an island arc environment. However, the occurrence of a formation believed to be deep sea pelagic sediments (e.g. Laurent, 1977) within the ophiolites tentatively argues against formation of the Thetford Mines complex at an island arc.

On the basis of textures, the lower volcanic unit could be divided into three groups. However, it is not certain if the textural variation is genetic. Textural variation in the lavas may in part be a reflection of the changing physical conditions during the extrusion of the volcanic rocks. For example, the abundant vesicles in the upper part of the volcanic unit suggests explosive extrusion at a shallow depth (Liou and Ernst, 1979) while the aphyric nature of some of the lava is indicative of rapid chilling.

Mineralogical considerations, however, tend to group the lower volcanic unit into two series: i) those with abundant plagioclase phenocrysts and microphenocrysts - plagioclase phyric, and ii) those with abundant clinopyroxene - pyroxene phyric. It is difficult at this stage, without geochemical considerations, to say categorically whether the relative abundance of plagioclase, pyroxene and olivine in these lavas are due primarily to a continuing crystal fractionation of a common parent magma or due to derivation of lavas from at least two types of magma as suggested by Seguin and Laurent (1975) and Laurent (1977).

On petrological grounds alone, it is more likely that the two lava types are derived from two separate magma sources. Stratigraphically, the plagioclase rich lava usually occurs below the clinopyroxene rich lava. This implies that plagioclase crystallized before clinopyroxene if the lavas were derived from the same magma unless the volcanic unit is overturned. Situations in which plagioclase crystallization preceeds clinopyroxene has been reported in ocean floor basalts (Shido *et al.*, 1971) and in the Western Mediterranean ophiolites (Beccaluva *et al.*, 1977; Venturelli *et al.*, 1979; Lewis and Smewing, 1980). The associated metamorphic peridotite is usually predominantly lherzolite. On the other hand, in situations where clinopyroxene crystallization preceeds plagioclase crystallization such as in Troodos (Smewing *et al.*, 1975) and Oman (Smewing *et al.*, 1975) the associated metamorphic peridotite is mainly harzburgite. According to Venturelli *et al.* (1979) clinopyroxene preceeding plagioclase during fractional crystallization could be explained if the crystallizing magma is clinopyroxene rich, in which case the residue from the mantle after fusion to produce the magma will be clinopyroxene poor, similar to harzburgite.

This view could therefore explain the preponderance of harzburgite in ophiolites in which clinopyroxene is observed to preceed plagioclase during fractional crystallization. In Thetford Mines ophiolites, harzburgite is the dominant mantle residue. This is contrary to what is expected since plagioclase preceeds clinopyroxene during crystallization of the lavas. The only explanation for this observation is that the plagioclase rich rocks were derived from a magma different from that of the clinopyroxene rich lavas. The two lava series could, however, be related via partial melting if their parental magmas were derived from a common mantle source by a two stage partial melting. The first melt produced by such a model would be poor in clinopyroxene and would give rise to plagioclase rich lavas. The mantle residue after the extraction of the first melt would be clinopyroxene rich and remelting of this residue would produce the second melt which would be rich in clinopyroxene. This second melt could give rise to the clinopyroxene rich lavas. The mantle residue, after the extraction of the second melt, would be clinopyroxene poor similar to the harzburgite.

Abundant quartz and calcite veins and infillings of vesicles in the lavas suggest that the lavas were metamorphosed during a sub-sea floor hydrothermal activity. However, evidence of deformation also shows that the rocks have also probably been metamorphosed during a regional metamorphic event. According to Miyashiro (1972) sub-sea floor metamorphism is not attended by shearing. The schistocity in the lower part of the lavas, the mylonitization of the pyroxenite and the cataclastic deformation of the gabbro could therefore not be explained by sub-sea floor metamorphism alone. Fractures in the deformed rocks are usually filled with secondary minerals such as serpentine, prehnite and chlorite, probably as a result of retrograde metamorphism of the already metamorphosed rocks. Such retrograde metamorphism and cataclastic deformation could have taken place along transform faults during ocean floor spreading as suggested by Miyashiro (1972) and Liou and Ernst (1979). However, prehnite and pumpellyite are rare in ocean floor metamorphosed rocks (Lewis and Smewing, 1980). Their abundance in the Thetford Mines ophiolites is therefore suggestive of onland(?) regional burial metamorphism. It is also noted that the Theford Mines ophiolites do not bear any imprint of zeolite facies common in sub-sea floor metamorphosed rocks. Either the physical conditions during the sub-sea floor metamorphism of the Thetford Mines ophiolite was different from that for zeolite facies formation or any original zeolite facies mineral formed during sub-sea floor metamorphism has been erased by later onland regional metamorphism.

It is therefore suggested that the Thetford Mines ophiolites, in addition to sub-sea floor metamorphism involving serpentinization of the ultramafic rocks and the hydrothermal alteration of the lavas and metagabbros, have also been subjected to a regional metamorphism during or after their emplacement on land.

CHAPTER THREE

THE CHEMISTRY OF THE THETFORD MINES COMPLEX

Introduction

The major oxide and some trace element abundances in Thetford Mines rocks have been determined by X-ray flourescence and atomic absorption spectrophotometry. The results are tabulated in the Appendix (Table III-2).

The Thetford Mines ophiolite rocks are characterized by a considerable range of chemical composition in terms of both major and trace elements. The variation in chemistry probably reflects, in part, the variation in mineral modal composition of rocks due to igneous processes such as fractional crystallization and, in part, by mobilization of some of the elements during secondary processes, notably metamorphism. Chemical variation within petrographically related units may be slight, as in the pyroxenites, or significant as in the lavas, and sufficient to warrant a chemical grouping of such units into sub-units.

In spite of the variations in chemistry within the Thetford Mines' rocks, comparison with other ophiolites indicates that the Thetford Mines' ophiolites have similar chemistry with some other ophiolites reported elsewhere.

3.1 Metamorphic Peridotite

3.1.1 Major Element Chemistry

Both the harzburgite and the dunite bodies in the harzburgite are characterized by high MgO and low SiO_2, Al_2O_3, CaO, Na_2O, K_2O and MnO. The metamorphic dunite contains higher MgO and is poorer in other oxides than the harzburgite due to higher proportions of olivine in the dunite.

The harzburgite, and to a lesser extent the dunite, show a rather restricted chemistry. Most of the major oxides show little variation in these rocks. The variation in CaO and Al_2O_3 in the harzburgite is due to the variation in modal diopside and spinel. The uniformity in the chemistry of the harzburgites is reflected in their nearly constant FeO^T/MgO ratio (Figure 3-1) and restricted position on AFM and ACM diagrams (Figures 3-2 and 3-3). The uniform chemistry of the harzburgite, despite varying degrees of serpentinization, indicates that serpentinization causes no significant net gains or losses of major elements and that serpentinization in these rocks is probably isochemical. On the other hand, if the serpentinization of the harzburgite has caused mobility of elements as suggested by Kacira (1972) and Laurent (1975) then the mobilized elements have been redistributed over only a few centimetres of rock. It is also probable that the uniform chemistry of the harzburgites reflects the chemistry of their serpentinized precursor, suggesting that the harzburgites are residual rather than cumulate in origin.

Figure 3-1. Variation of SiO_2 against FeO (total)/MgO in metamorphic peridotite and cumulates in TMC.

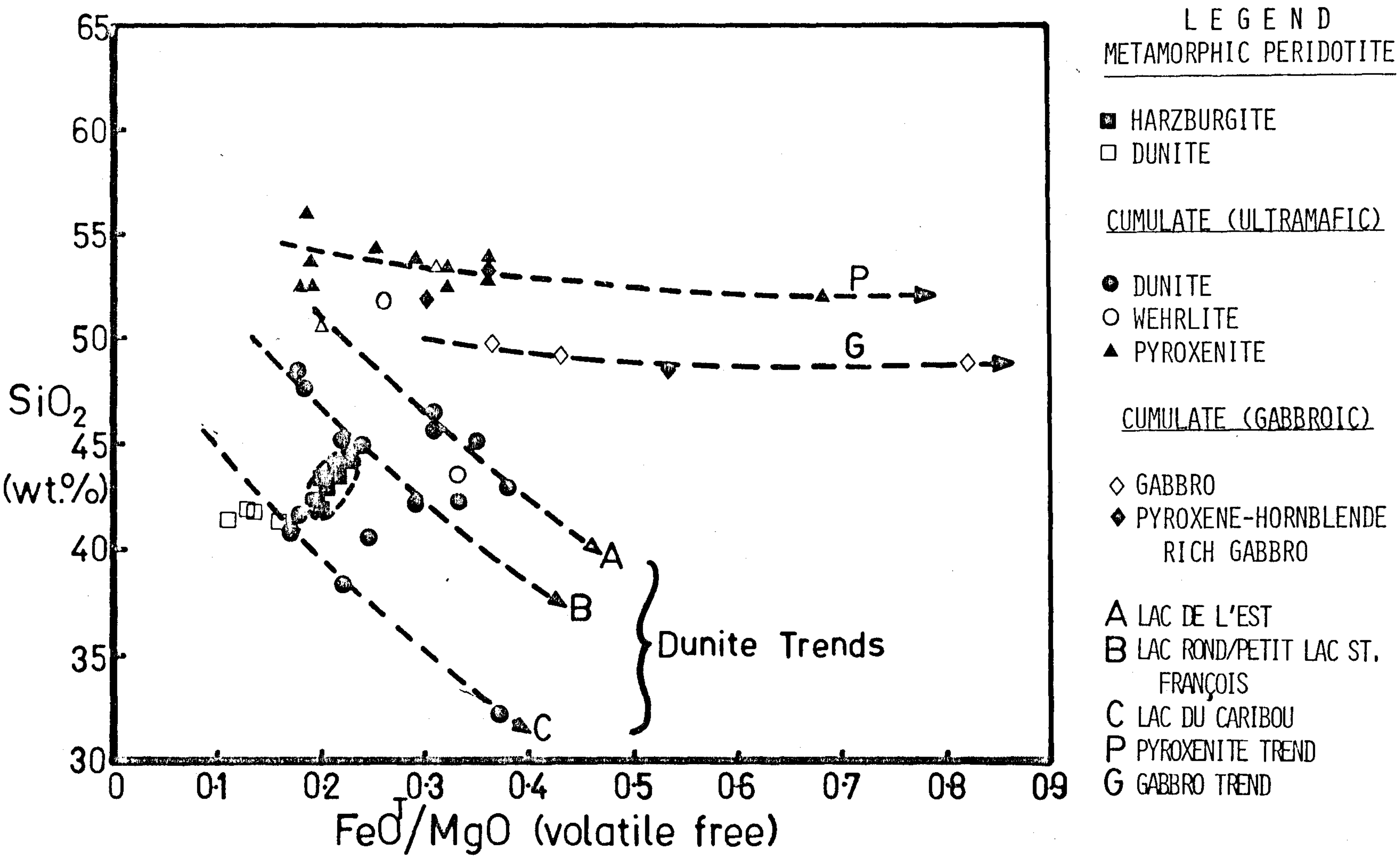

65
60
55
50
45
40
35
30
SiO$_2$ (wt.%)
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
FeO^T/MgO (volatile free)
P
G
A
B
C
Dunite Trends
LEGEND
METAMORPHIC PERIDOTITE
■ HARZBURGITE
□ DUNITE
CUMULATE (ULTRAMAFIC)
● DUNITE
○ WEHRLITE
▲ PYROXENITE
CUMULATE (GABBROIC)
◇ GABBRO
◆ PYROXENE-HORNBLENDE RICH GABBRO
A LAC DE L'EST
B LAC ROND/PETIT LAC ST. FRANÇOIS
C LAC DU CARIBOU
P PYROXENITE TREND
G GABBRO TREND

Figure 3-2. ($Na_2O + K_2O$) - FeO (total) - MgO (AFM) variation diagram for metamorphic peridotite and the cumulate rocks in TMC.

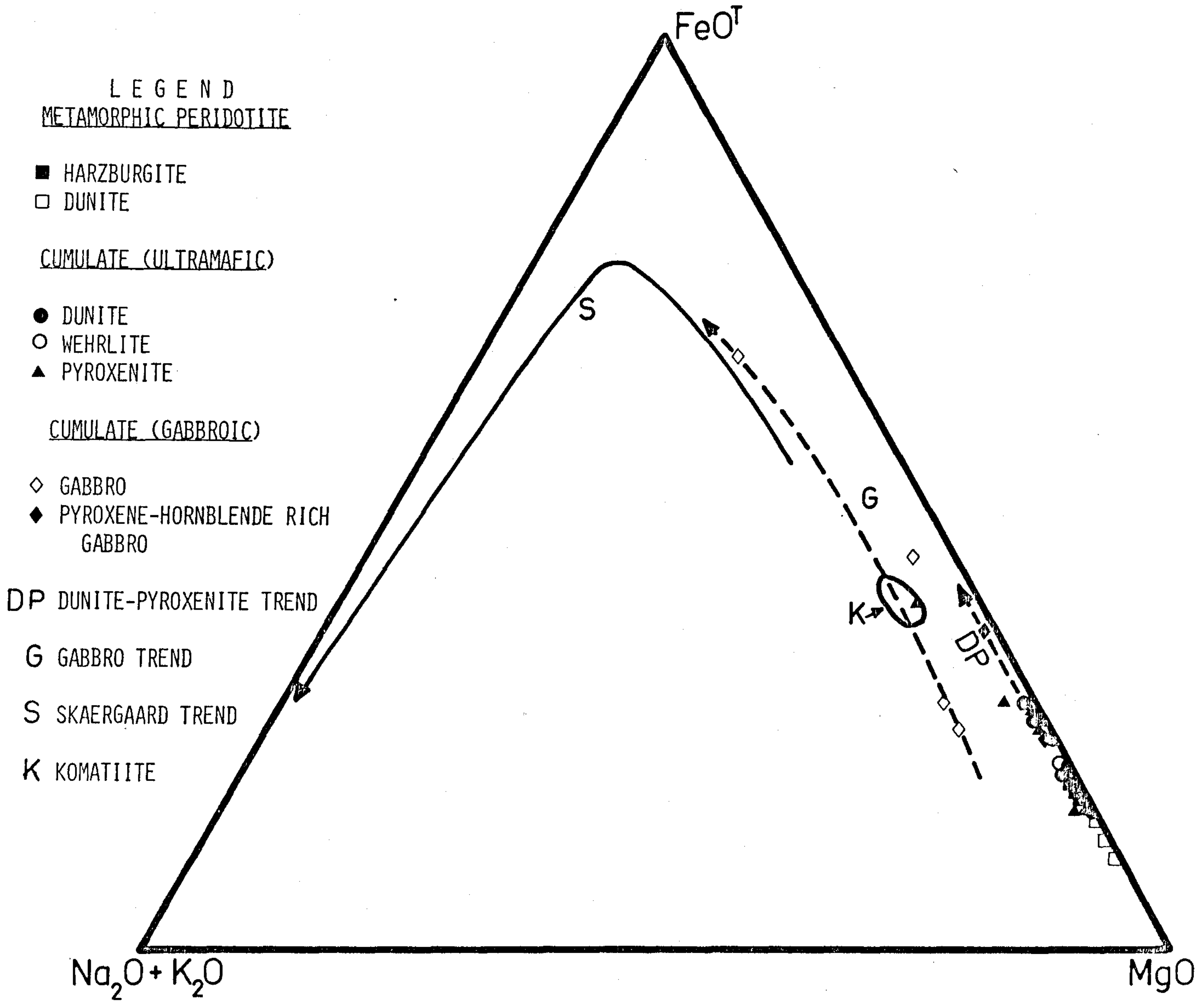
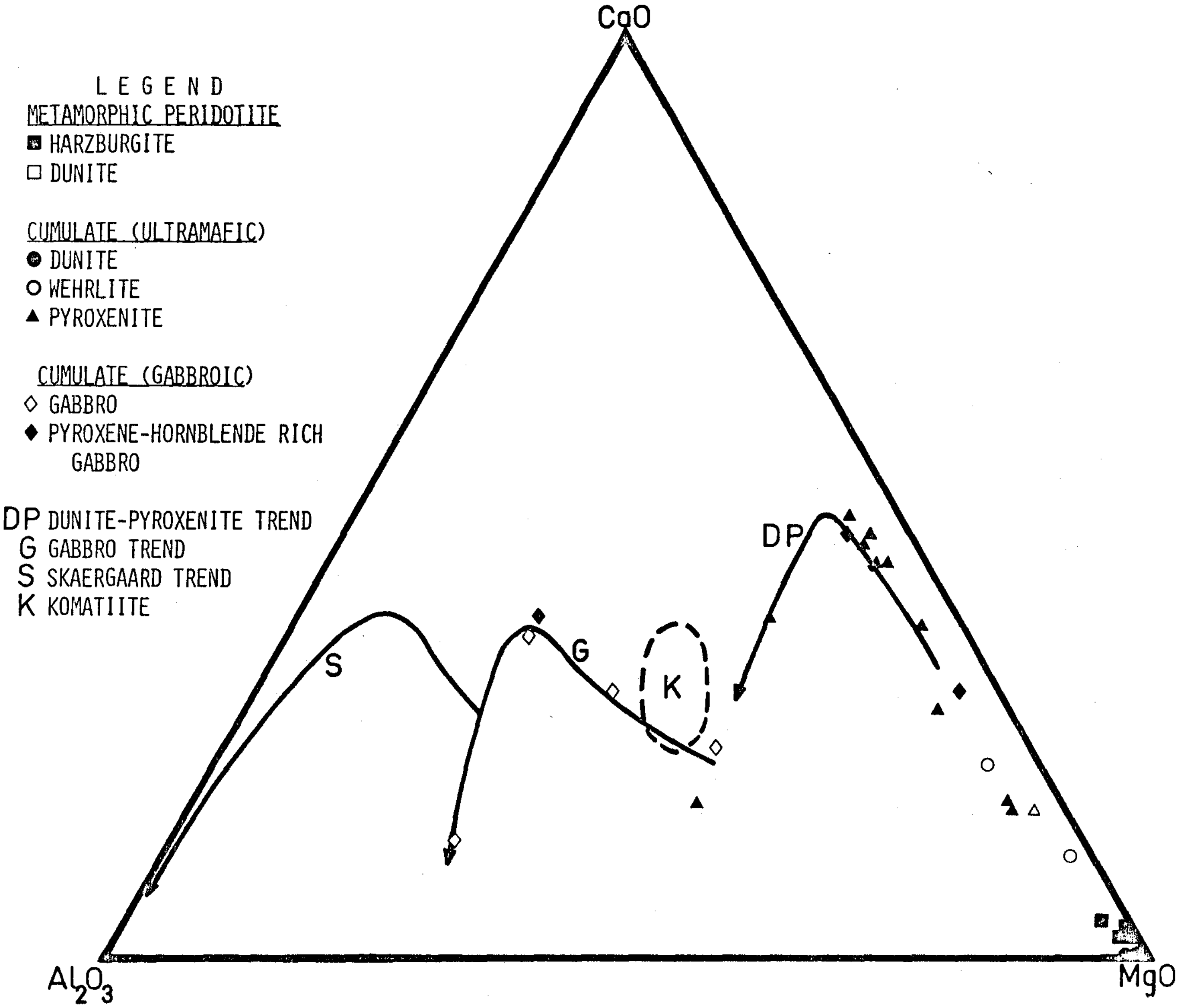

FeO^T
LEGEND
METAMORPHIC PERIDOTITE
■ HARZBURGITE
□ DUNITE
CUMULATE (ULTRAMAFIC)
● DUNITE
○ WEHRLITE
▲ PYROXENITE
CUMULATE (GABBROIC)
◇ GABBRO
◆ PYROXENE-HORNBLENDE RICH GABBRO
DP DUNITE-PYROXENITE TREND
G GABBRO TREND
S SKAERGAARD TREND
K KOMATIITE
S
G
K
DP
Na$_2$O + K$_2$O
MgO

Figure 3-3. Al_2O_3 - CaO - MgO (ACM) variation diagram for metamorphic peridotite and the cumulate rocks in TMC.


CaO
Al2O3
MgO
LEGEND
METAMORPHIC PERIDOTITE
■ HARZBURGITE
□ DUNITE
CUMULATE (ULTRAMAFIC)
● DUNITE
○ WEHRLITE
▲ PYROXENITE
CUMULATE (GABBROIC)
◇ GABBRO
◆ PYROXENE-HORNBLENDE RICH GABBRO
DP DUNITE-PYROXENITE TREND
G GABBRO TREND
S SKAERGAARD TREND
K KOMATIITE
S
G
K
DP

The volatile-free recalculated oxide composition of the metamorphic peridotites is similar to the composition of metamorphic peridotite from other ophiolites such as Troodos and Vourinous (Table 3-1). It is also interesting to note that the Thetford Mines harzburgite is comparable in chemistry to the "pyrolite" mantle model of Ringwood (1975) and other mantle models, e.g. Maalone and Aoki (1977), thereby attesting to the primitive nature of the harzburgite. However, the harzburgite is depleted in SiO_2, Al_2O_3, CaO and TiO_2 (43.36 wt % vs 45.10 wt %; 0.91 wt % vs 4.6 wt %; 1.08 wt % vs 3.10 wt %; 0.02 wt % vs 0.20 wt % respectively) and enriched in FeO and MgO (9.33 wt % vs 7.90 wt % and 44.82 wt % vs 38.10 wt % respectively) when compared with pyrolite. This variation may indicate that the Thetford Mines harzburgite has lost a basaltic(?) fraction containing Al_2O_3, CaO and TiO_2, represented mineralogically by clinopyroxene and feldspar, with respect to its original mantle composition. This would also account for the high MgO content of the harzburgite.

3.1.2 Trace Elements

The metamorphic periodotites are depleted in the incompatible elements Zn, Cu, Y and Zr and their contents of Rb and Sr are below the sensitivity of the analytical method (XRF) used. The rocks are, however, rich in Cr, Ni and Co -- all trace elements accomodated in mineral phases of the rock. Except for Cr which shows a wide range of abundances, the trace element abundances are nearly constant in the

Table 3-1

Comparison of Bulk Rock Chemistry of Thetford Mines Peridotites With Other Peridotites and Mantle Estimates

	1[x]	2[a]	3[a]	4[a]	5[b]	6[x]	7[a]	8[a]	9[a]	10[c]	11[d]
SiO_2	43.36	43.50	39.70	43.50	44.14	41.56	40.00	40.40	40.80	44.71	45.10
Al_2O_3	0.91	0.97	2.40	0.47	2.49	0.20	0.36	0.14	0.54	2.46	4.60
Fe_2O_3		2.60	3.90	5.40			3.60	5.40	2.84		
FeO		5.50	3.90	3.20			3.90	3.90	5.56		
FeO^T	9.93				8.74	6.79				8.15	7.90
MgO	44.82	45.70	48.10	45.70	41.19	50.86	50.90	49.10	49.70	41.00	38.10
CaO	1.08	0.63	1.00	0.77	2.14	0.27	0.05	0.18	0.73	2.42	3.10
Na_2O	0.23	0.58	0.10	0.006	0.09	0.07	0.17	0.005	0.08	0.29	0.40
K_2O	0.07	0.11	-	0.002	0.01	0.07	0.21	0.002	0.03	0.09	0.02
TiO_2	0.02	0.03	-	0.01	0.11	0.02	0.03	0.008	-	0.16	0.20
MnO	0.18	0.11	0.11	0.15	0.13	0.16	0.11	0.17	0.11	0.18	0.10
P_2O_5	-					-					
S				0.019				0.04			
Cr_2O_3		0.35	0.32	0.39	0.38		0.44	0.41		0.42	
NiO		0.29	0.29	0.27	0.25		0.38	0.24		0.26	

Key to Table 3-1 on the next page

Key to Table 3-1

1. Average of 7 harzburgites TMC
2. Average of 3 harzburgites, Vourinos
3. Average of 22 peridotites, Bay of Island
4. Average of 8 harzburgites, Troodos
5. Peridotite, Western Liguria
6. Average of 4 metamorphic dunites, Thetford Mines
7. Average of 2 dunites, Vourinos
8. Average of 10 metamorphic dunites, Troodos
9. Metamorphic dunites, Papua
10. Mantle model, Maalone and Aoki (1977)
11. Mantle model (pyrolite), Ringwood (1975)

Sources of Data

x This study
a Coleman (1977)
b Ernst and Piccardo (1979)
c Maalone and Aoki (1977)
d Ringwood (1975)

harzburgite although they display a wider variation in the metamorphic dunites.

The Ni/Co ratio of the metamorphic peridotites is interesting in comparison with the Ni/Co ratio of the enclosed metamorphic dunite lenses. The Ni/Co ratios of the harzburgite average 19.10 (range 18.41 to 19.79) compared with the chondritic value of 22 while the Ni/Co ratios of the metamorphic dunites range from 21.4 to 33.8. Since the metamorphic dunite is essentially olivine only, such a wide variation of the Ni/Co ratio does not argue in favour of a residual nature for the dunites as suggested by Boudier (1972), Dick (1977) and Baldwin (1976). The variation in Ni/Co is due principally to variation in the Ni content of the constituent olivine of the rock. This is probably caused by crystallization from melts produced by partial melting of a mantle material leaving a solid residue now represented by the harzburgite.

3.2 The Cumulates

Unlike the metamorphic peridotites which show restricted composition, the cumulates display a wide range of chemical composition. Al_2O_3, CaO, Na_2O, K_2O and TiO_2 all increase systematically in abundance from the dunites to the gabbro while MgO decreases. Pyroxenites have intermediate values. SiO_2 increases from about 35-45 wt % in the dunites to higher values in the range of 52-54 wt % in the pyroxenite and then decreases in abundance in the gabbro.

Figure 3-4. Variation of Ni against Cr concentrations in metamorphic peridotite and cumulates.

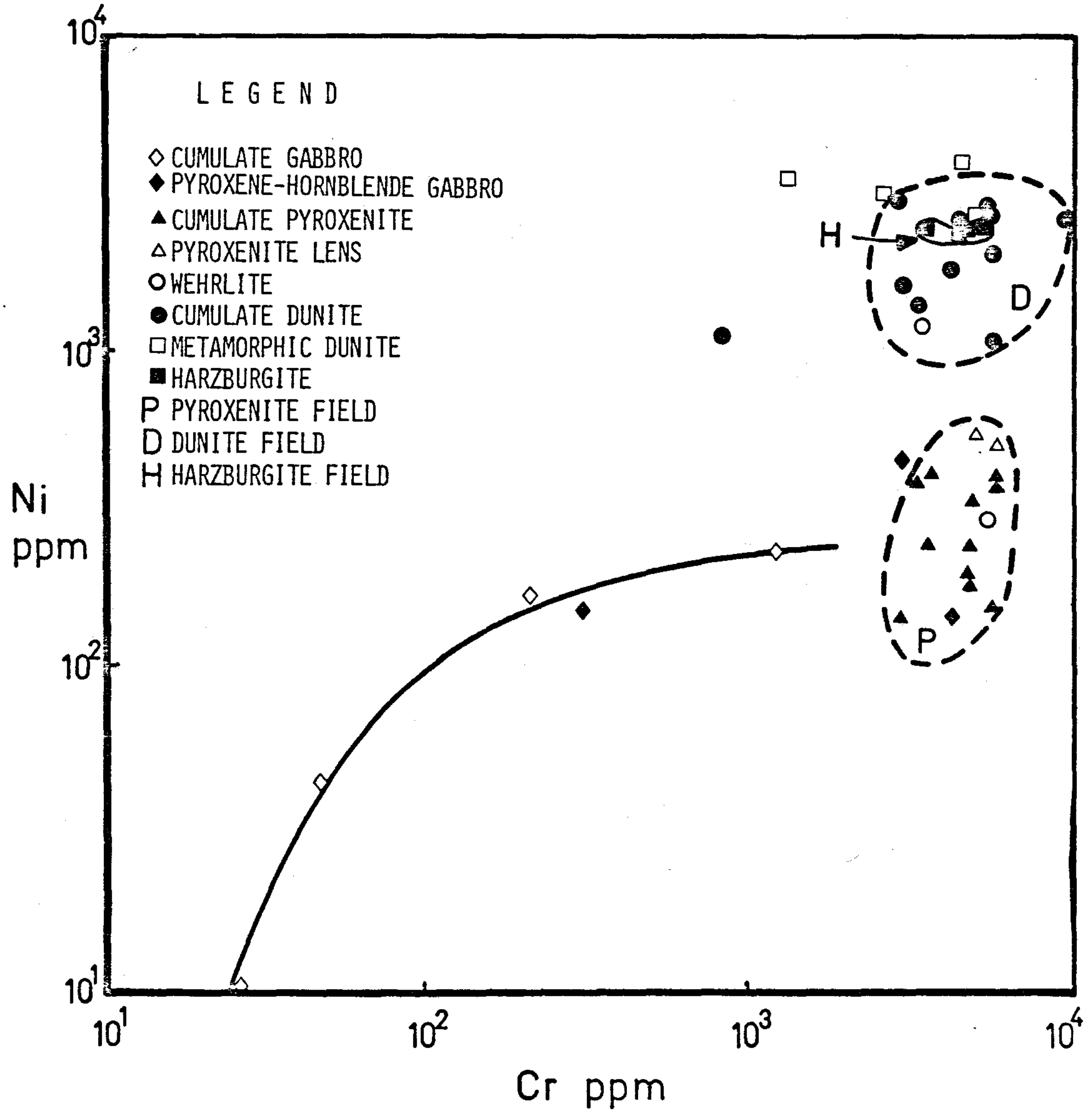
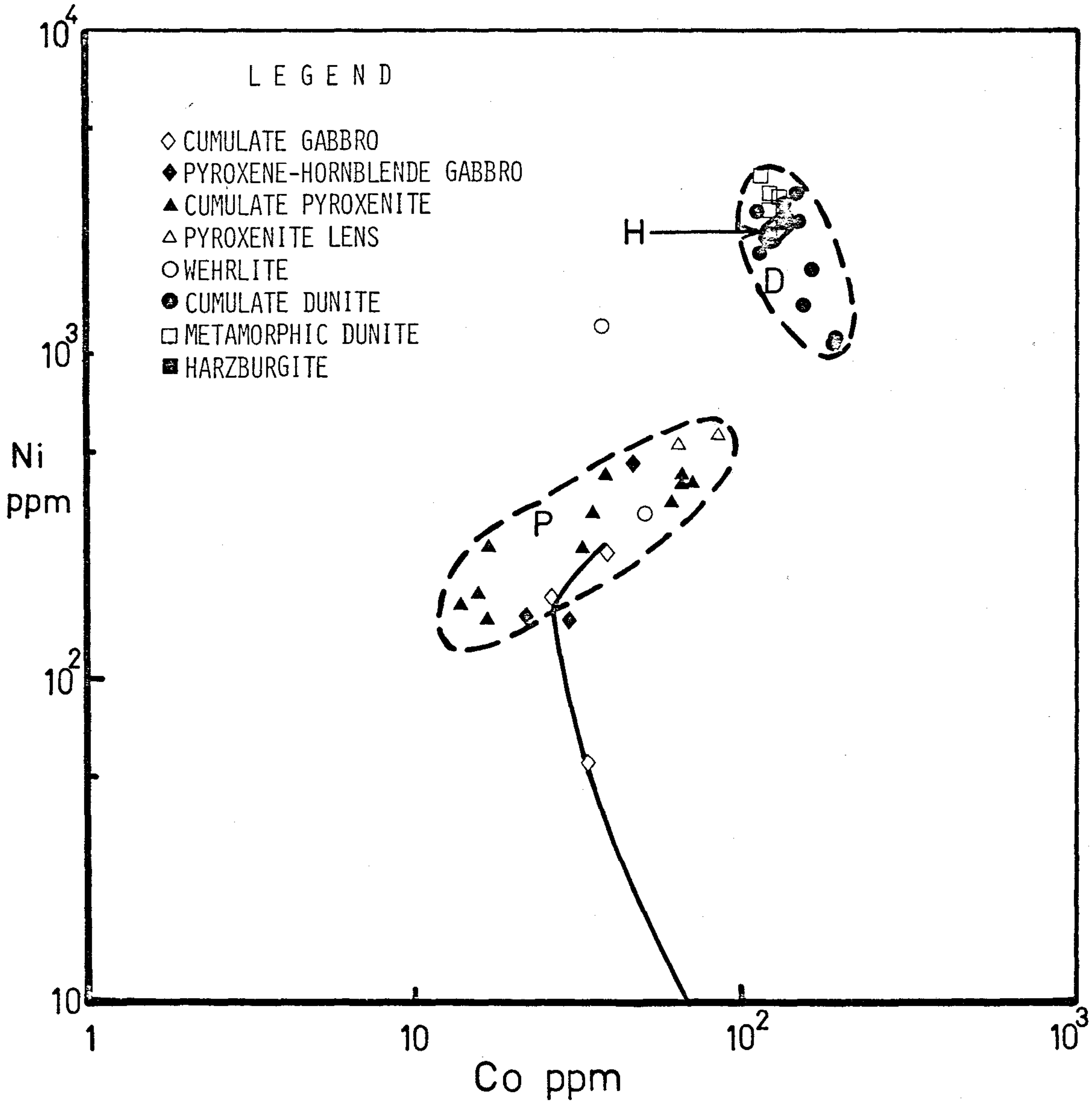

LEGEND
◇ CUMULATE GABBRO
◆ PYROXENE-HORNBLENDE GABBRO
▲ CUMULATE PYROXENITE
△ PYROXENITE LENS
○ WEHRLITE
● CUMULATE DUNITE
□ METAMORPHIC DUNITE
■ HARZBURGITE
P PYROXENITE FIELD
D DUNITE FIELD
H HARZBURGITE FIELD
H
D
P
Ni ppm
Cr ppm
10^1
10^2
10^3
10^4

Figure 3-5. Variation of Ni against Co concentrations in metamorphic peridotites and cumulates in TMC.


LEGEND
◇ CUMULATE GABBRO
◆ PYROXENE-HORNBLENDE GABBRO
▲ CUMULATE PYROXENITE
△ PYROXENITE LENS
○ WEHRLITE
● CUMULATE DUNITE
□ METAMORPHIC DUNITE
■ HARZBURGITE
H
D
P
Ni ppm
Co ppm
10^4
10^3
10^2
10
1
10
10^2
10^3

Within each rock group there are some minor chemical variations. Such variations are best illustrated by variation diagrams and can in general be explained by magmatic differentiation.

3.2.1 SiO_2 vs $Fe\overset{T}{O}/MgO$

A plot of wt % SiO_2 against $Fe\overset{T}{O}/MgO$ (all oxides recalculated on volatile free basis) for the cumulates (Figure 3-1) shows that in the pyroxenites and gabbros, SiO_2 decreases slightly with increases in $Fe\overset{T}{O}/MgO$, that is with differentiation similar to what is observed in some cumulate rocks such as the Skaergaard intrusion (Wager and Deer, 1939) and in early differentiated rocks derived from tholeiitic magmas (Meuller and Saxena, 1977). However, unlike the pyroxenites and gabbros which may be related to one differentiation trend each, the dunites appear to fall on three distinct but parallel trends, each with different $Fe\overset{T}{O}/MgO$ for a given SiO_2 value.

A closer study of Figure 3-1 also show that the dunitic rocks which fall on the same trend are geographically related, and the different $Fe\overset{T}{O}/MgO$ of the trends may suggest that dunites from the different localities were formed from magmas of different bulk composition. Alternatively, it may also indicate that the dunites were formed in cycles by repeated injection of magma, each cycle being represented by a differentiation trend.

The decrease in SiO_2 relative to the increase in $Fe\overset{T}{O}/MgO$ in the dunites is greater than what is expected in a normal tholeiitic differentiation, and is best explained in terms of the amount of the chromite content of the dunites. Chromite carries most of the FeO content of dunites and no SiO_2, and as differentiation proceeds, the amount of chromite in the rock decreases rapidly while the amount of olivine which carries the SiO_2 and MgO contents in the rocks, increases relative to chromite, leading to a rapid increase in SiO_2 with a decrease in FeO^T/MgO (or a decrease in SiO_2 with an increase in FeO^T/MgO).

It is interesting to note that the chromite bearing dunites at Lac du Caribou are closely related to the metamorphic dunites on the SiO_2 vs FeO^T/MgO plot. This may suggest a genetic relationship between the two types of dunites. It is possible that the metamorphic dunites are part of the cumulate chromite bearing dunites that were caught up in the metamorphic peridotite as suggested by Kacira (1972).

3.2.2 AFM and ACM Diagrams

The increase in FeO relative to MgO during differentiation in some of the cumulates is further illustrated on the $(Na_2O + K_2O)$ - FeO^T - MgO diagram (Figure 3-2). During differentiation, there is very little alkali enrichment, On the Al_2O_3 - CaO - MgO plot (Figure 3-3) the cumulates show an increase in CaO relative to MgO with little change in Al_2O_3 during most of the differentiation process but the latest differentiation involves an increase in Al_2O_3. This is a reflection of the importance of plagioclase crystallization towards the end of differentiation.

Both the AFM and ACM diagrams reveal two features of the cumulate rocks:

i) The differentiation trend in the Thetford Mines rocks is generally similar to that of Skaergaard trend although there are differences probably related to the extent of fractionation and to parental magma composition. For example, the Thetford Mines cumulates do not show the rapid increase in FeO and alkalis as do the Skaergaard rocks, and the parental magma of the Thetford Mines cumulates is much more mafic than that of the Skaergaard rocks.

ii) The gabbros do not follow a continuous trend with the dunites and pyroxenites. In fact, there appears to be two distinct but parallel trends, one involving the dunites and the pyroxenites and the other the gabbros. The pyroxenites and pyroxene-rich gabbros in the gabbro zone follow the dunite-pyroxenite trend while the hornblende-rich gabbros follow the gabbro trend.

In both AFM and ACM plots, the gabbro trend crosses the komatiitic field, and the starting material is more mafic than komatiitic.

This "branching off" of the gabbro trend from the dunite-pyroxenite differentiation trend has not been discussed in any other ophiolites and this raises some questions as to whether this branching off is i) due to sampling and analytical error, ii) due to modification of rock chemistry by secondary processes, or iii) real. The observed pattern is probably real since any sampling or analytical error or rock chemistry modification should be reflected in irregular patterns unlike the systematic observed patterns and trends.

Two possible explanations for the "branching off" of the gabbro trend from the dunite-pyroxenite trend are suggested.

i) If all the cumulate rocks were derived from the same magma, then the differentiating magmas must have rapidly basified prior to gabbro formation to account for early gabbros which are more mafic than the last pyroxenites formed. This compositional change could be brought about by mixing of fresh magma with the residual magma.

ii) The gabbro has formed from a different magma than that of the dunite-pyroxenite. One line of evidence for separate parental magmas is the irregular occurrences of pyroxenite and pyroxene-rich rocks within the cumulate gabbro zone. These pyroxene-rich rocks which follow the same differentiation trend as the dunite-pyroxenite trend are probably the last phase of the dunite-pyroxenite crystallization.

It is difficult at present with the limited chemical data to choose between the above alternatives, but it should be noted that the close association of the cumulate gabbro and the dunite-pyroxenite rocks strongly mitigates against the idea of separate magma for the gabbro and the ultramafic cumulates.

3.2.3 Trace Element Variation

The cumulate rocks are very low in trace elements except in Ni, Cr and Co. The cumulate dunites are particularly enriched in

Ni, Cr and Co in that some of the dunites, particularly those at the base of the dunite unit, have higher abundances of Ni, Cr and Co than the harzburgite. Abundances of these elements decrease progressively from the dunites through pyroxenites to gabbro.

Although variation of Ni, Cr and Co within the cumulate rocks is a function of the proportion of ferromagnesian minerals in the rock, there is only a weak inter-element correlation between any pair of the three elements (Figures 3-4 and 3-5). This is probably because more than one mineral phase controls the distribution of these elements. The lack of a continuous trend between the dunite-pyroxenite and the gabbros observed in the major elements is also shown in the trace elements.

The incompatible elements Zr, Y and Sr show a progressive increase in abundance from the dunites through pyroxenite to gabbro but Zn does not appear to change significantly within the cumulate. One major difference between the trace element contents of the Thetford Mines cumulates and layer complexes is the very low Cu content of the Thetford Mines rocks. This may be due to the low sulfur content of the rocks since most of the Cu in the layered complexes is associated with sulfides.

3.3 The Hypabyssal and Volcanic Rocks

As discussed in Section 2.4, the hypabyssal and volcanic rocks have undergone hydrothermal metamorphism which caused alteration of their original mineralogy. Many authors such as Coleman (1977) and Coish (1979) have indicated that along with mineralogy, the original chemistry of hydrothermally altered ophiolite lavas has been modified. The results of element mobility in response to seawater reaction with basalt are inconsistent. This applies to both studies on natural basalt and experimental leaching studies, and is illustrated in Table 3-2. It seems that each case should be treated on its own merit. It is therefore important that any discussion on the chemistry of the Thetford Mines ophiolite hypabyssal and volcanic rocks take into account the effect of hydrothermal alteration.

In order to assess whether the Thetford Mines rocks have been chemically affected by hydrothermal alteration, the observed major oxides and trace element abundances of the volcanic rocks have been plotted against the volatile content which is used as an index of alteration. Total volatile content is used instead of water content only (see Hart, 1973 or Humphris and Thompson, 1978) because CO_2 is an essential component of the alteration products in these lavas.

Inspection of the abundances of major oxides and trace elements in the lower volcanic rocks show that the lavas could be grouped as high TiO_2 lavas (greater than 0.7 wt %) and low TiO_2 (less than 0.35 wt %). Petrographically, the high TiO_2 lavas correspond to the plagioclase phyric lavas while the low TiO_2 lavas are mostly the pyroxene phyric lavas. Because these two groups have some other contrasting chemical characteristic, which are discussed later, they

Table 3-2

Major Elément Trends During Seawater Alteration of Basalt

	Hart and others (1974)	Hekinian (1971)	Shido and others (1974)	Humphris and Thompson (1978)	Coish (1979)
S_1O_2	-	-	±	-	-
T_1O_2	-	-	+	+	n.c.
Al_2O_3	-	-	+	±	n.c.
Fe_2O_3	+	+	+		
FeO	-	-	-		
Total Fe	+	+	+	-	+
MnO	+	+	+	±	?
MgO	±	±	+	+	+
CaO	-	-	-	-	-
Na_2O	±	-	±	±	-
K_2O	+	+	+	±	±
P_2O_5	±	n.c.	+		n.c.
H_2O	+	+	+		

+	increase
-	decrease
±	variable change
n.c.	no significant change

are tentatively regarded as two distinct lava groups.

3.3.1 Mobility of Elements as a Function of Volatile Content

The plots of the major oxides and trace elements against volatile content of each lava sample together with the least square fit and correlation coefficient are shown in Figures 3-6 to 3-9. The direction of movement of the oxides and elements with respect to volatile content is presented in Tables 3-3 and 3-4. Because of the lack of fresh representative rocks for comparison, evaluation of the extent to which the elements and oxides have been mobilized is difficult, and only a qualitative evaluation can be made. An element or oxide is considered to have been mobilized if it shows a systematic variation with volatile content. Where an element or an oxide shows non systematic variation, it is difficult to assign the variability to hydrothermal alteration, fractional crystallization or some combination of the two. However, if an element or an oxide displays a considerable range of values which cannot be explained by fractional crystallization or partial melting, such an element or oxide is considered to have been mobilized.

Using the samples with the lowest volatile content and the least altered mineralogically for comparison, and taking into account the known geochemical behaviour of the elements and oxides during fractional crystallization and partial melting, the extent to which the elements and oxides have been mobilized is summarized in Table 3-5.

Figure 3-6. Variation of loss on ignition (as total volatile content against major element oxides (wt %) for the lower lavas of TMC.

= Type I lava

= Type II lava

a = least square fit line for Type I lava

b = least square fit line for Type II lava

r_a = coefficient of correlation for Type I lava

r_b = coefficient of correlation for Type II lava

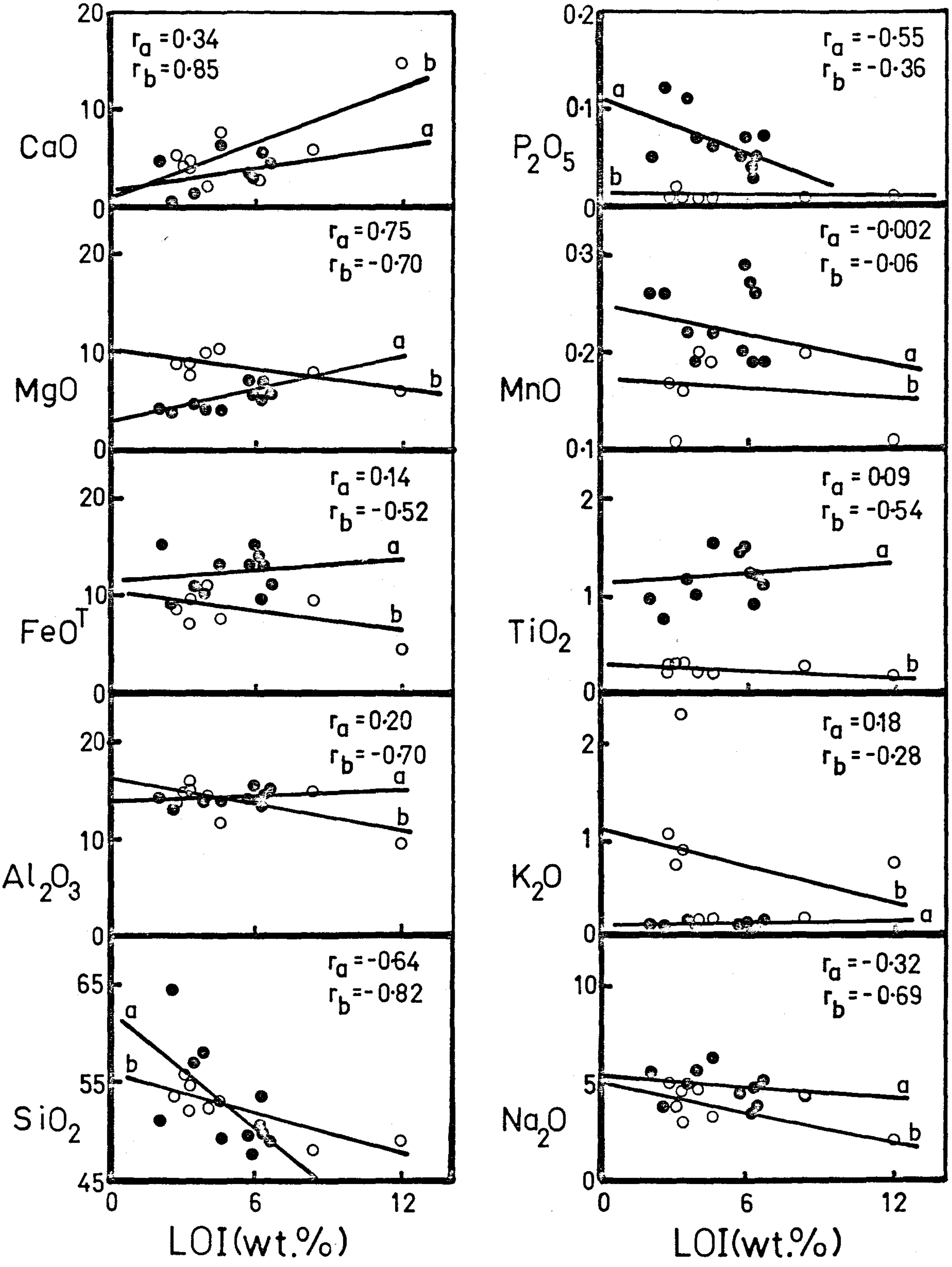

CaO
r_a = 0·34
r_b = 0·85
MgO
r_a = 0·75
r_b = -0·70
FeO^T
r_a = 0·14
r_b = -0·52
Al_2O_3
r_a = 0·20
r_b = -0·70
SiO_2
r_a = -0·64
r_b = -0·82
P_2O_5
r_a = -0·55
r_b = -0·36
MnO
r_a = -0·002
r_b = -0·06
TiO_2
r_a = 0·09
r_b = -0·54
K_2O
r_a = 0·18
r_b = -0·28
Na_2O
r_a = -0·32
r_b = -0·69
a
b
0
6
12
LOI(wt.%)

Figure 3-7. Variation of loss on ignition (as total volatile content) against trace element concentrations (ppm) in the lower lavas of TMC. Symbols the same as Figure 3-6.

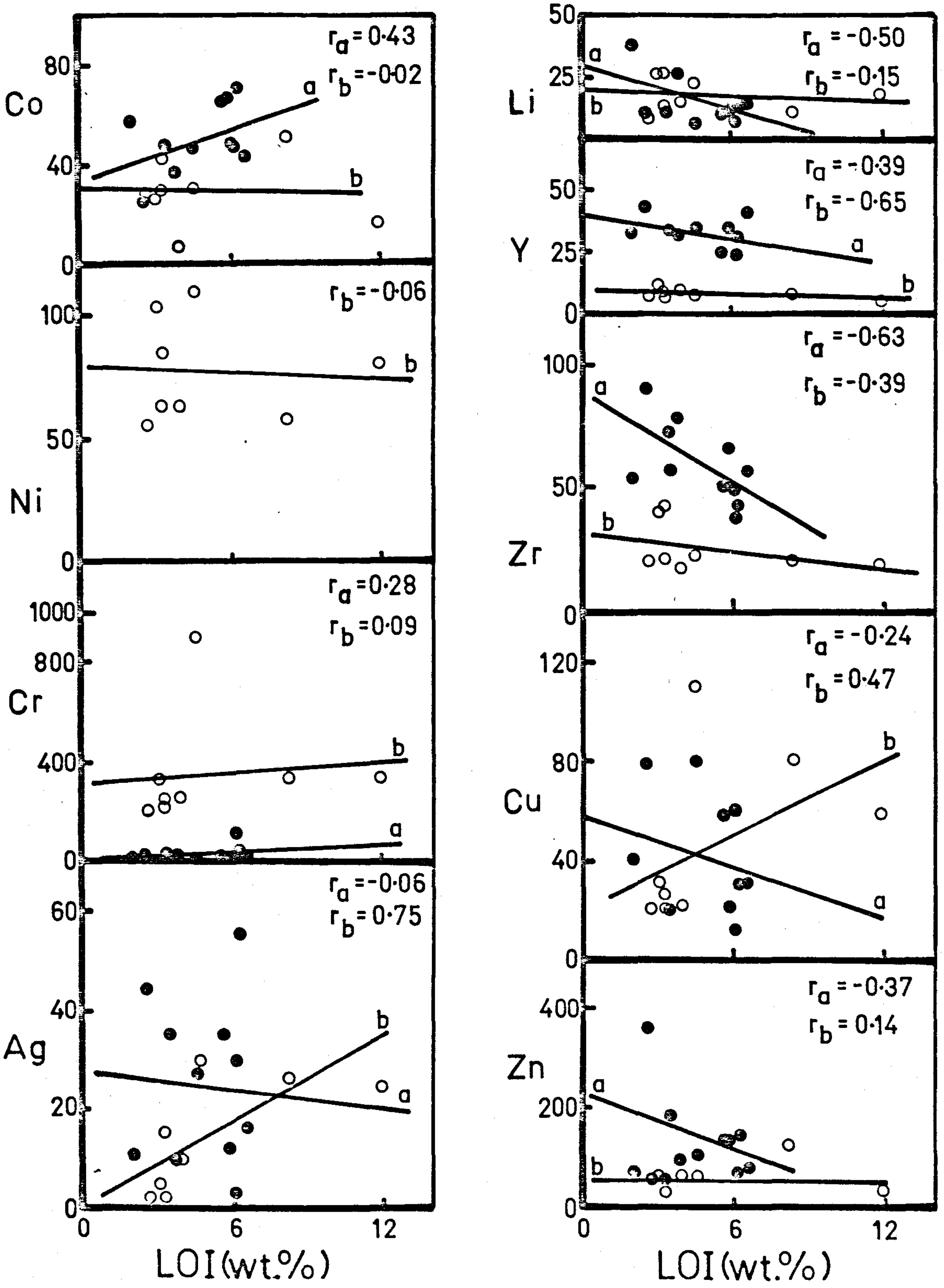

Co
$r_a = 0{\cdot}43$
$r_b = -0{\cdot}02$
80
40
0
a
b
Ni
$r_b = -0{\cdot}06$
100
50
0
b
Cr
$r_a = 0{\cdot}28$
$r_b = 0{\cdot}09$
1000
800
400
0
b
a
Ag
$r_a = -0{\cdot}06$
$r_b = 0{\cdot}75$
60
40
20
0
b
a
0
6
12
LOI(wt.%)
Li
$r_a = -0{\cdot}50$
$r_b = -0{\cdot}15$
50
25
a
b
Y
$r_a = -0{\cdot}39$
$r_b = -0{\cdot}65$
50
25
0
a
b
Zr
$r_a = -0{\cdot}63$
$r_b = -0{\cdot}39$
100
50
0
a
b
Cu
$r_a = -0{\cdot}24$
$r_b = 0{\cdot}47$
120
80
40
0
b
a
Zn
$r_a = -0{\cdot}37$
$r_b = 0{\cdot}14$
400
200
0
a
b
0
6
12
LOI(wt.%)

Figure 3-8. Variation of loss on ignition (as total volatile content) against major element oxides (wt %) for the upper lavas of TMC.

r = coefficient of correlation

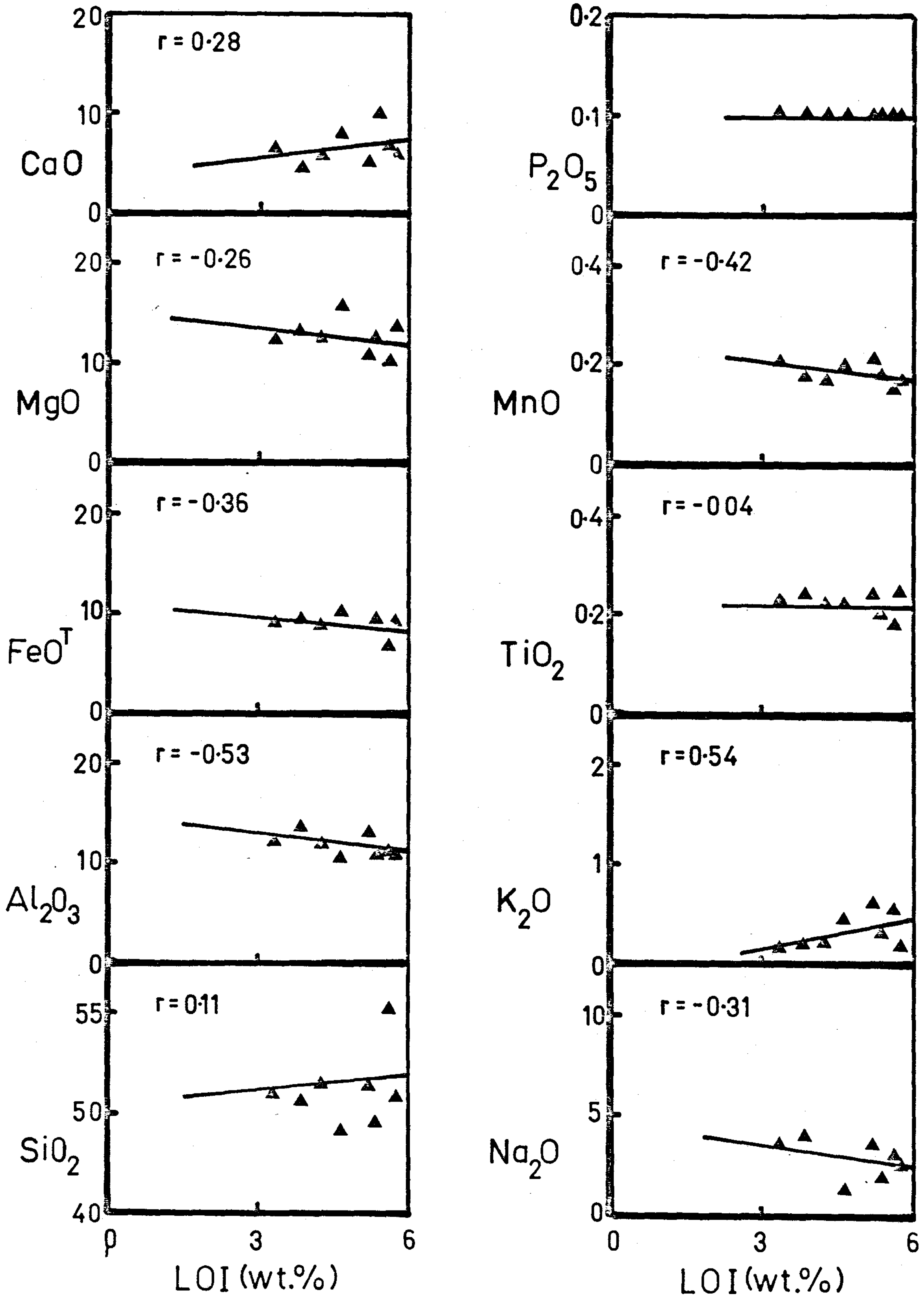

CaO
r = 0·28
MgO
r = -0·26
FeO^T
r = -0·36
Al2O3
r = -0·53
SiO2
r = 0·11
P2O5
MnO
r = -0·42
TiO2
r = -0·04
K2O
r = 0·54
Na2O
r = -0·31
0
10
20
40
50
55
0·1
0·2
0·4
1
2
5
3
6
LOI (wt.%)
LOI (wt.%)

Figure 3-9. Variation of loss on ignition (as total volatile content) against trace element concentrations (ppm) in the upper lavas of TMC. r = coefficient of correlation

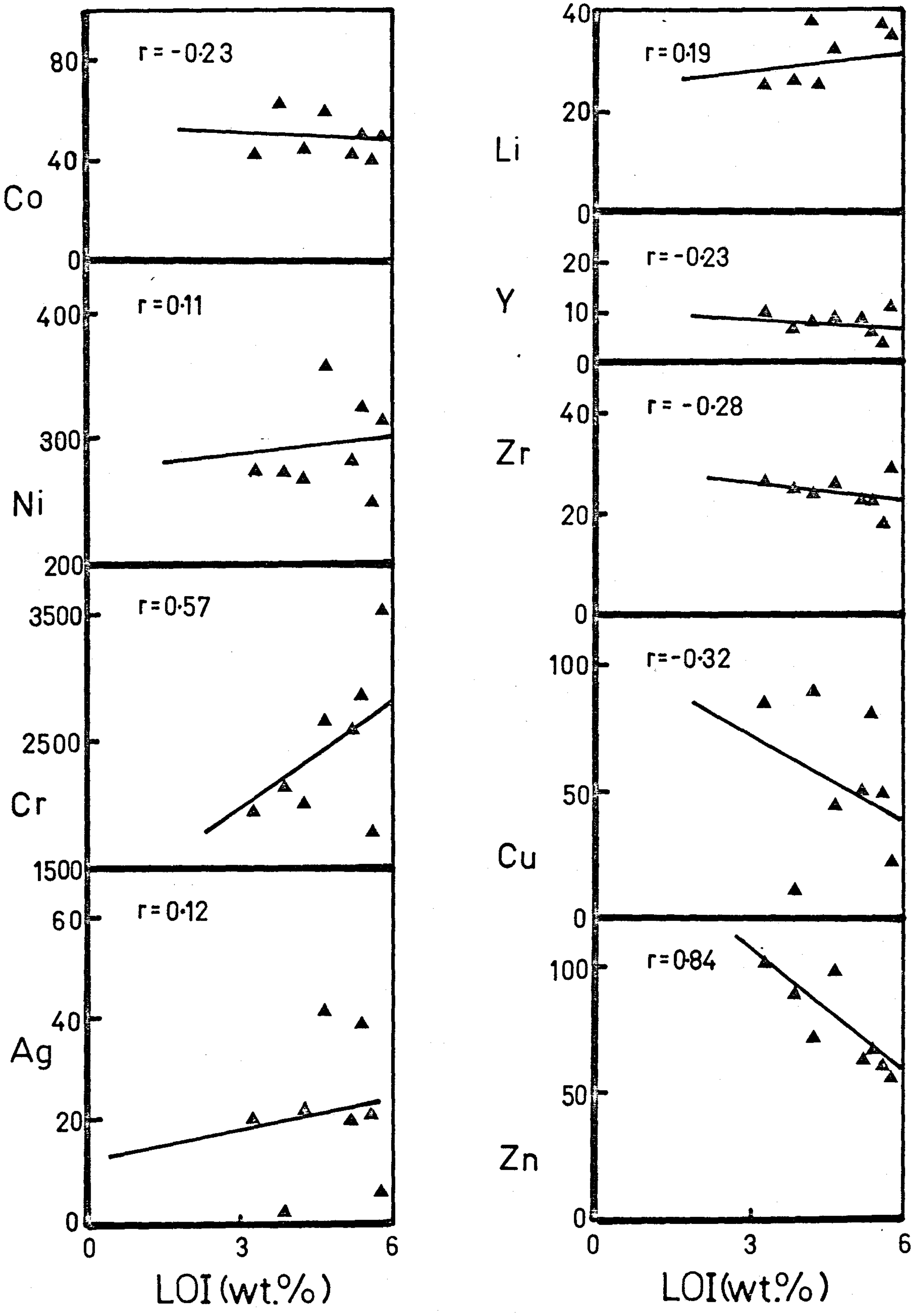

r = -0·23
80
40
Co
0
r = 0·11
400
300
Ni
200
r = 0·57
3500
2500
Cr
1500
r = 0·12
60
40
Ag
20
0
0
3
6
LOI (wt.%)
40
r = 0·19
20
Li
0
r = -0·23
20
Y
10
0
r = -0·28
40
Zr
20
0
r = -0·32
100
50
Cu
0
r = 0·84
100
50
Zn
0
0
3
6
LOI (wt.%)

Table 3-3

Major Element Oxide Trends During Alteration in TMC Lavas

	Systematic Increase	Systematic Decrease	Non Systematic Changes
High TiO_2 (Lower lava) Type I	MgO	SiO_2, P_2O_5	Al_2O_3, FeO^T, CaO, Na_2O, K_2O TiO_2, MnO
Low TiO_2 (Lower lava) Type II	CaO, Na_2O	SiO_2, Al_2O_3, MgO	FeO^T, K_2O, MnO, P_2O_5
Upper lava	K_2O		SiO_2, Al_2O_3, FeO^T, MgO, CaO, Na_2O, TiO_2, MnO, P_2O_5

Table 3-4

Trace Element Trend During Alteration in TMC Lavas

	Systematic Increase	Systematic Decrease	Non Systematic Changes
High TiO_2 (Lower lava) Type I		Zr	Ag, Cr, Co, Zn, Cu, Y, Li
Low TiO_2 (Lower lava) Type II	Ag		Cr, Ni, Co, Zn, Cu, Zr, Y, Li
Upper lava	Cr	Zn	Ag, Ni, Co, Cu Zr, Y, Li

Table 3-5

Degree of Mobilization of Elements and Oxides in TMC Lavas During Alteration

	Extensively Mobilized	Moderately Mobilized	Slightly Mobilized	Immobile
High TiO_2	SiO_2, CaO	FeO^T, MgO	Al_2O_3, TiO_2	K_2O
(Lower lava)	Ag, Zn, Cu	Na_2O, MnO	Zr, Y	
Type I		P_2O_5, Co		
		Li		
Low TiO_2	SiO_2, CaO	Al_2O_3, FeO^T	TiO_2, Zn	P_2O_5
(Lower lava)	MnO, Ag	MgO, K_2O	Zr, Y	
Type II	Cu, Co	Na_2O, Cr		
		Ni, Li		
Upper lava	Ag, Cu	MgO, CaO	Al_2O_3, FeO^T	Zr, Y, TiO_2
		Na_2O, K_2O	TiO_2, P_2O_5,	
		MnO, Cr,	Ni, Co; SiO_2	
		Zn, Li		

In some cases the same element shows an apparently different response to alteration depending on which of the three different lava groups is considered. This may be due to factors such as i) different textures, ii) stratigraphic position, and iii) duration of the contact of lava with sea water.

For the purposes of characterizing the Thetford Mines hypabyssal and volcanic rocks, therefore, only elements which show moderate to insignificant mobility during hydrothermal metamorphism are considered useful.

3.3.2 The Hypabyssal Rocks

One of the four analyzed metagabbros shows different chemical characters from the rest. This sample (9MG4A) is characterized by high MgO, high CaO, low Al_2O_3 and FeO^T/MgO and high Cr and Ni. On the SiO_2 vs FeO^T/MgO and FeO vs FeO^T/MgO plots (Figures 3-10 and 3-11) the sample plots in the calc-alkaline field. The low FeO^T/MgO (0.72) of this sample suggests that the rock may be cumulative although cumulate texture is not recognized in thin section. Alternatively, the gabbro may represent the high level plutonic equivalent of the low TiO_2 lavas of the lower volcanic unit with which it shows some chemical similarities.

The remaining three samples show a rather restricted range of FeO^T/MgO (1.03 - 1.74). The positive correlation between FeO^T and FeO^T/MgO suggests that the three samples are genetically related by magmatic differentiation. Both SiO_2 vs FeO/MgO and FeO vs FeO/MgO indicate that these gabbros are tholeiitic.

3.3.3 The Volcanic Rocks

3.3.3.1 Bulk Chemistry. Chemically, the lower lavas may be considered in terms of two principal types here designated type I and type II for convenience of reference. The feature distinguishing the two lava types is their TiO_2 content. Type I lavas are characterized by relatively high TiO_2 contents (0.75 wt % to 1.55 wt %) while type II lavas have restricted low TiO_2 values (0.18 wt % to 0.31 wt %). Type I lavas are further characterized by having lower MgO but higher FeO^T/MgO than the type II lavas.

The trace element abundances in the lavas also reflect the chemical differences between the lava types. Type I lavas are severely depleted in Ni and Cr but are high in the incompatible elements of Zr and Y. On the other hand, type II lavas are high in Cr and Ni and low in Zr and Y. The type I lavas are plagioclase phyric while the type II lavas are mostly pyroxene phyric. The two lava types might be regarded as cogenetic, related through fractional crystallization. However, the large difference between the TiO_2 values with no intermediate compositions is difficult to explain on the grounds of fractional crystallization.

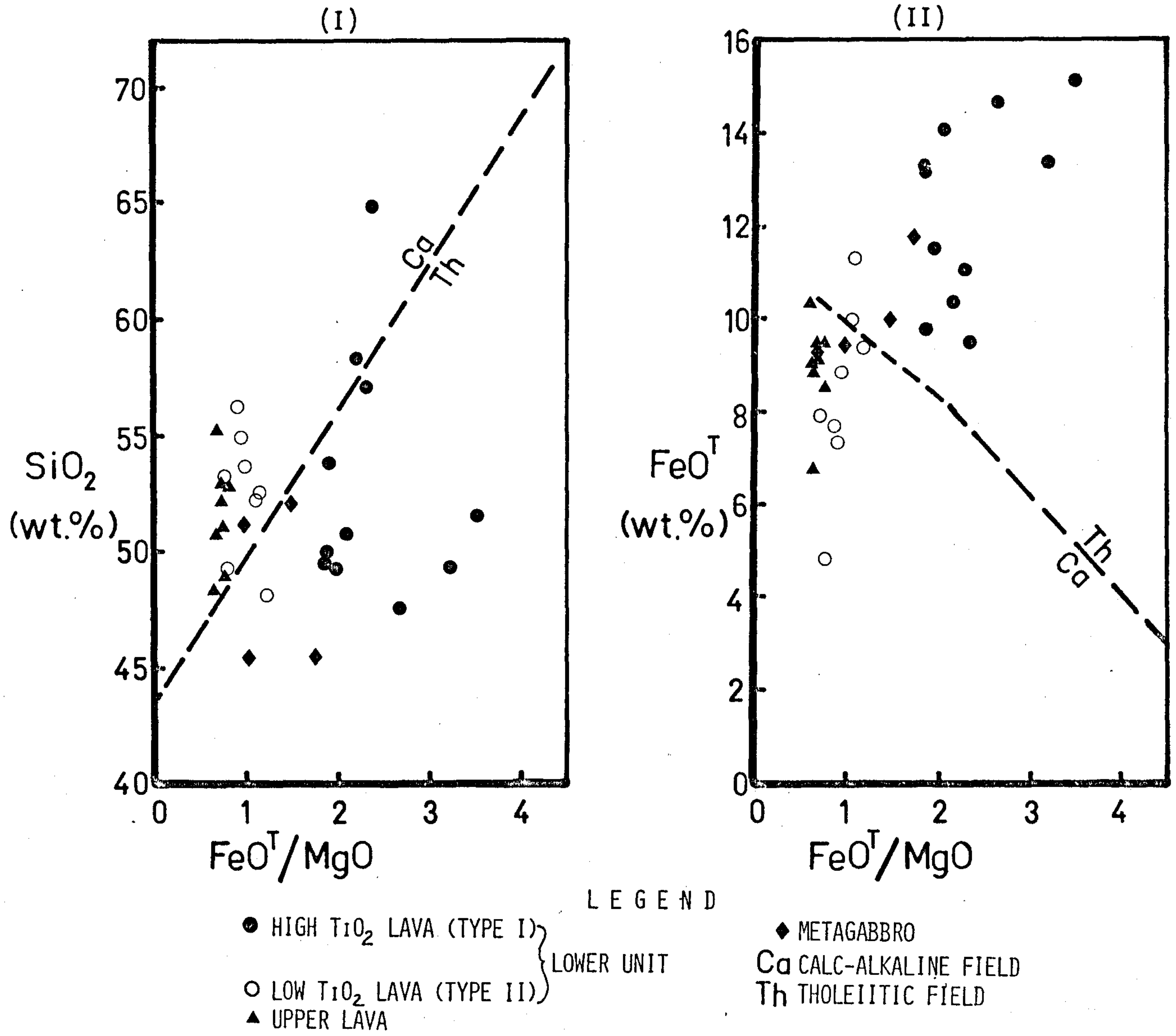
The upper lavas are similar to type II lavas in their TiO_2 and incompatible trace element abundances (P_2O_5, Zr, Y) but have higher MgO but lower Al_2O_3 and K_2O. The upper basalts are also characterized by low FeO/MgO and high Ni and Cr values comparable to values observed in some komatiitic rocks (e.g. Arndt et al., 1977).

All the lavas have normative hyperstene and in addition almost all the lower unit lavas have normative quartz suggesting that they have probably been derived from a tholeiitic magma. Laurent (1977) suggested that some of the lower volcanic unit lavas are derived from olivine tholeiite. However, out of the twenty samples analyzed from the lower unit only two samples have normative olivine. The lack of normative olivine in these rocks may be due to enrichment of SiO_2 by alteration such that hyperstene is formed in excess at the expense of olivine. Alteratively, it may suggest that the lavas are differentiates of a magma by olivine fractionation. The absence of normative diopside in these rocks is attributed to loss of CaO during alteration.

3.3.3.2 Chemical Variation in the Lavas. The chemical variations in the Thetford Mines lavas are shown in the variation diagrams of Figures 3-10 and 3-11. These variation diagrams, SiO_2 vs $\mathrm{FeO}^{T}/\mathrm{MgO}$ and FeO^{T} vs $\mathrm{FeO}^{T}/\mathrm{MgO}$, have been used by Miyashiro (1975) to distinguish theoleiitic and calc-alkaline differentiation trends. Their application to altered rocks has been criticized by many workers, e.g. Moores (1975), Gass et al. (1975) and Coleman (1977). Although the chemistry of Thetford Mines lavas has been modified by alteration as already discussed under Metamorphic Petrology (Section 2.4), the plots of SiO_2 vs $\mathrm{FeO}^{T}/\mathrm{MgO}$ (Figure 3-10) and FeO^{T} vs $\mathrm{FeO}^{T}/\mathrm{MgO}$ (Figure 3-11) effectively distinguish between the type I and type II lavas. On these

Figure 3-10. SiO_2 concentrations against FeO (total)/MgO in hypabyssal and volcanic rocks of TMC

Figure 3-11. Total iron oxide (FeO^T) concentrations against FeO^T/MgO in hypabyssal and volcanic rocks of TMC.


(I)
(II)
SiO$_2$ (wt.%)
FeO^T (wt.%)
FeO^T/MgO
FeO^T/MgO
40
45
50
55
60
65
70
0
2
4
6
8
10
12
14
16
0
1
2
3
4
Ca
Th
LEGEND
● HIGH TiO$_2$ LAVA (TYPE I)
○ LOW TiO$_2$ LAVA (TYPE II)
LOWER UNIT
▲ UPPER LAVA
◆ METAGABBRO
Ca CALC-ALKALINE FIELD
Th THOLEIITIC FIELD

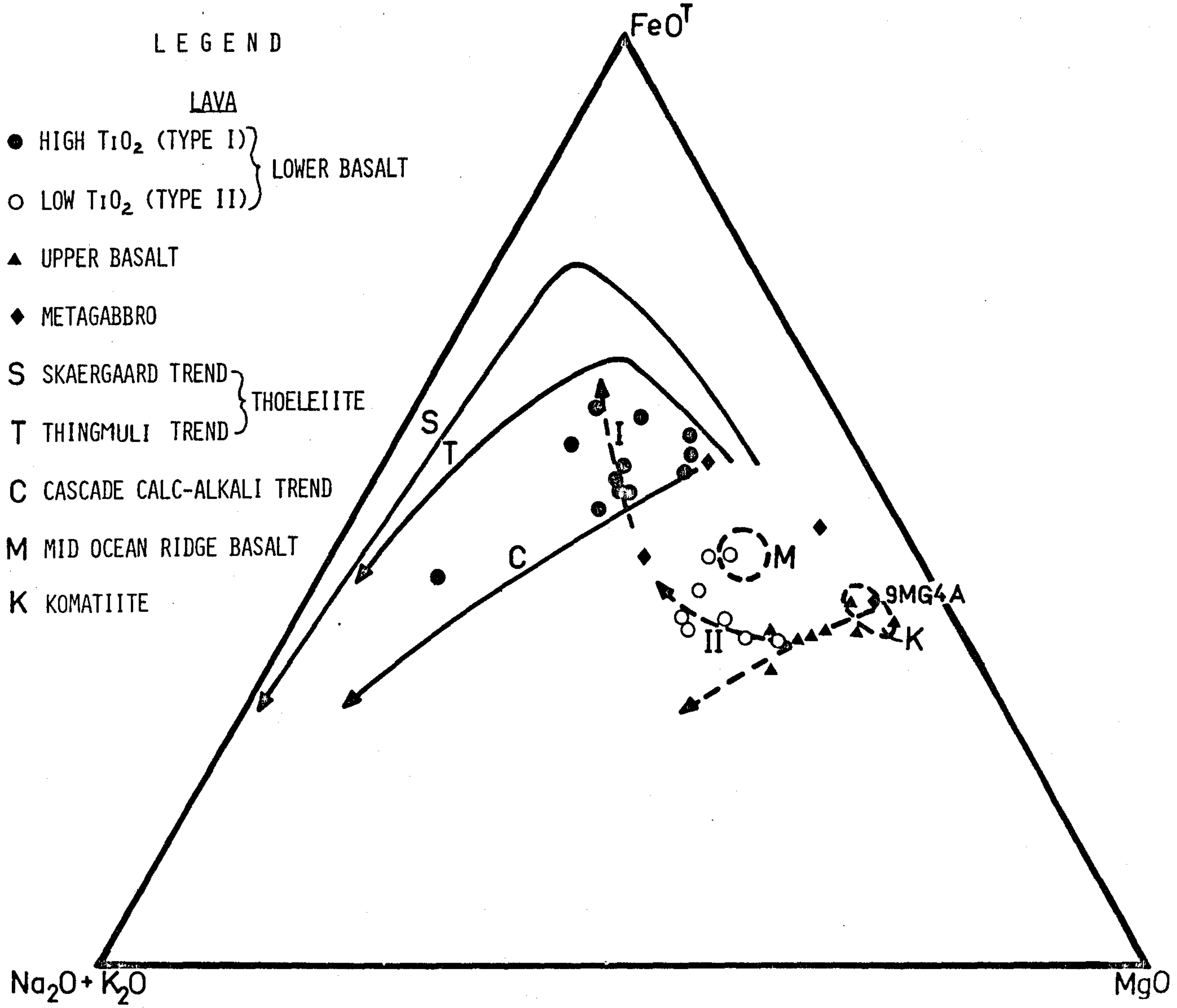
plots, type I lavas are tholeiitic while both type II and the upper lavas are calc-alkaline.

AFM Diagram: Although the type I lavas have $\overset{T}{\text{FeO}}$/MgO ratios ranging from 1.87 to 3.63, on the AFM plot (Figure 3-12) they do not show the strong iron enrichment, followed by alkali enrichment displayed by tholeiites such as the Skaergaard or Thingmuli rocks. Also, the calc-alkali trend suggested for the type II lavas, e.g. in Figure 3-10 and Figure 3-11 is not shown by these rocks on the AFM diagram. Slight FeO enrichment relative to MgO is, however, displayed by the type II lavas in such a way that both type I and type II lavas may be related to a trend shown in Figure 3-12. This trend might imply a genetic linkage between the two lava types. However, in view of the composition gap between the two lava groups, it is doubtful if there is any genetic relationship between the two groups, and the assumed trend may not relate to any igneous process.

The absence of a trend in the lower volcanic unit comparable to any commonly displayed by either theoleiitic magmas or calc-alkalic magmas, is probably due to mobilization of elements during alteration. It therefore appears that the AFM diagram is not diagnostic for the lower volcanic unit lavas with respect to their differentiation trend.

The lavas of the upper unit show a trend which involves an increase in alkali content with very little change in $\overset{T}{\text{FeO}}$/MgO. If the increase in alkali contents is real, then this trend might be interpreted as calc-alkalic. Comparison with other rock types shows that the

Figure 3-12. $(Na_2O + K_2O)$ - $FeO_{(total)}$ - MgO (AFM) variation diagram for hypabyssal and volcanic rocks of TMC.


LEGEND
LAVA
● HIGH TiO_2 (TYPE I)
○ LOW TiO_2 (TYPE II)
LOWER BASALT
▲ UPPER BASALT
◆ METAGABBRO
S SKAERGAARD TREND
T THINGMULI TREND
THOELEIITE
C CASCADE CALC-ALKALI TREND
M MID OCEAN RIDGE BASALT
K KOMATIITE
FeO^T
Na_2O+K_2O
MgO
S
T
C
I
II
M
9MG4A
K

upper lavas are as basic as the komatiites. A calc-alkali trend in which there is very little iron enrichment during differentiation could only be generated from a parental basic magma if earlier formed crystal phases have higher $\mathrm{Fe}\overset{T}{\mathrm{O}}/\mathrm{MgO}$ ratios than olivine and pyroxene, the minerals which control theoleiitic differentiation. However, minerals like plagioclase and spinel which have high FeO/MgO are not observed as phenocrysts in these lavas. It is therefore possible that the lavas were not formed by crystal fractionation, and the increase in their alkali contents is a result of enrichment, particularly in K_2O (Figure 3-7), during alteration.

It is also difficult to relate the relatively uniform FeO/MgO ratios of the upper lavas to formation by accumulation of minerals. This is important in view of their high Ni and Cr contents. A plausible explanation for the observed chemistry and $\mathrm{Fe}\overset{T}{\mathrm{O}}/\mathrm{MgO}$ ratios is that the lavas were formed by varying degrees of partial melting of a source rich in Ni and Cr. A possible candidate for such source material is an already depleted material. For example, harzburgite which is essentially olivine and orthopyroxene with very little clinopyroxene, or lherzolite which is similar to harzburgite but with slightly higher clinopyroxene, could undergo varying small degrees of partial melting and produce melts with similar $\mathrm{Fe}\overset{T}{\mathrm{O}}/\mathrm{MgO}$ ratios. This is because the $\mathrm{Fe}\overset{T}{\mathrm{O}}/\mathrm{MgO}$ ratios of olivine and pyroxenes are almost identical. Melting of these minerals in proportions which differ slightly will not significantly change the $\mathrm{Fe}\overset{T}{\mathrm{O}}/\mathrm{MgO}$ ratio of the melts produced.

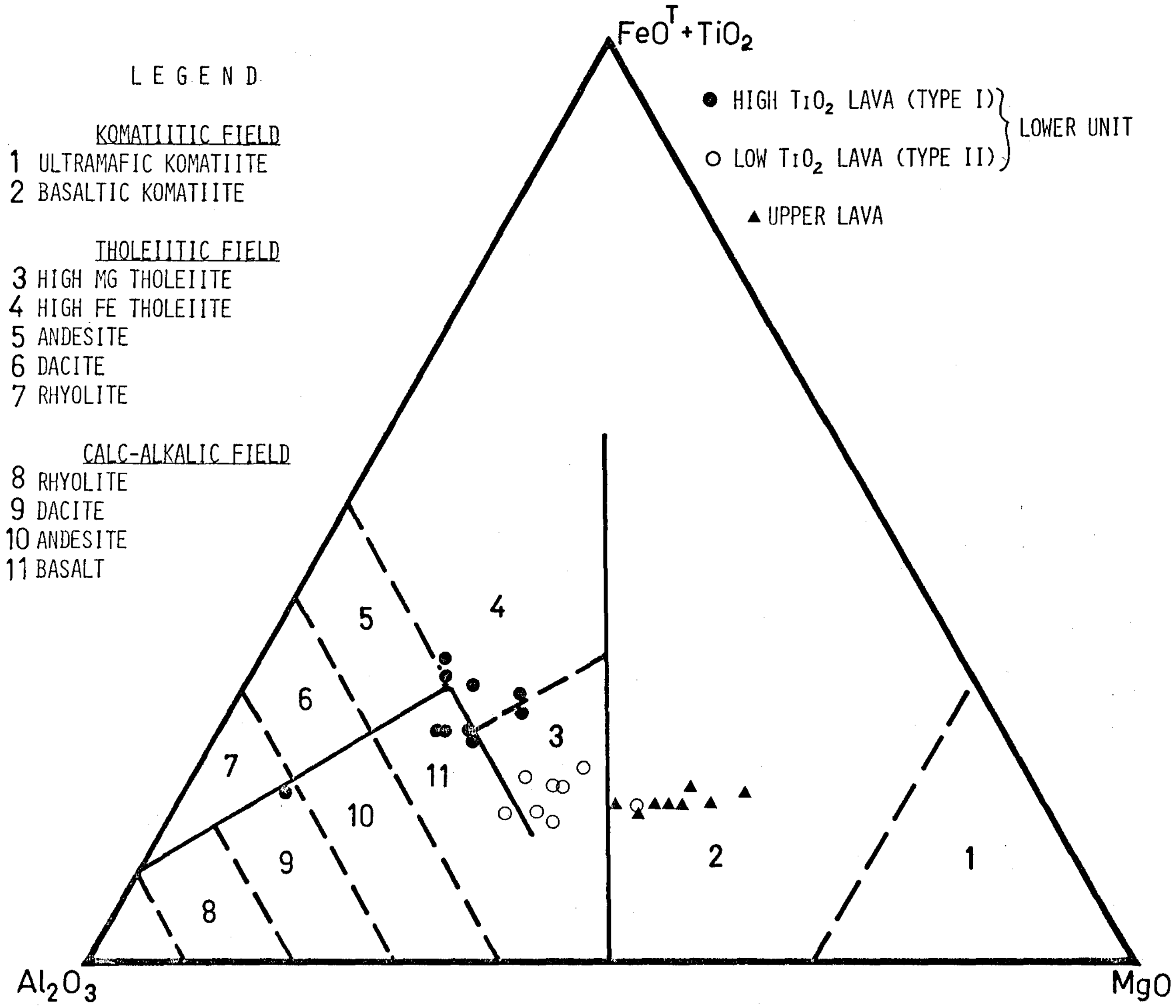
The Jensen Cation Plot: Jensen (1979) has argued that Al_2O_3 should be used instead of (Na_2O + K_2O) in the AFM diagram because of alteration and possible mobilization of the alkalis (Na_2O and K_2O), and that the mole proportion of the cations Al, (Fe + Ti) and Mg should be used instead of the weight per cent of their oxides because of the heavy atom of Fe and Ti relative to Al and Mg, in decribing the variation in chemistry and in classification of basaltic rocks.

Using the Jensen cation plot (Figure 3-13) the Thetford Mines ophiolitic lavas fall into four fields. The type I lavas fall in both high-Fe tholeiite and calc-alkalic fields, type II lavas fall in the high-Mg tholeiite field and the lavas of the upper volcanic unit fall in the basaltic komatiite field.

Some low TiO_2 lavas from other ophiolites have also been described as komatiites; for example, Gale (1973) classified the low Ti Rambler basalts as komatiites on account of their high CaO/Al_2O_3 ratio (1.08), high Mg, Ni and Cr, low Zr, Y and La. Simonian and Gass (1978) used high Mg, Ni and Cr contents of the low TiO_2 basalts of the Troodos ophiolite to classify them as basaltic komatiite. Recently, Upadhyay (1979) described some high magnesian lavas and sills within the low TiO_2 pillow lavas of Betts Cove ophiolites as komatiites using the Jensen cation plot.

Sun and Nesbitt (1978), however, argue that rocks classified as ophiolitic komatiites are formed by remelting of a source rock which is severely depleted compared to the primitive source for the Archean komatiite. They pointed out some geochemical differences

Figure 3-13. Variation of Al_2O_3 - (FeO $_{(total)}$ + TiO_2) - MgO mole proportion (Jensen Cation Plot) for the volcanic rocks of TMC.


LEGEND
KOMATIITIC FIELD
1 ULTRAMAFIC KOMATIITE
2 BASALTIC KOMATIITE
THOLEIITIC FIELD
3 HIGH MG THOLEIITE
4 HIGH FE THOLEIITE
5 ANDESITE
6 DACITE
7 RHYOLITE
CALC-ALKALIC FIELD
8 RHYOLITE
9 DACITE
10 ANDESITE
11 BASALT
$FeO^T + TiO_2$
● HIGH TiO_2 LAVA (TYPE I)
○ LOW TiO_2 LAVA (TYPE II)
LOWER UNIT
▲ UPPER LAVA
Al_2O_3
MgO
1
2
3
4
5
6
7
8
9
10
11

between these ophiolitic komatiites and Archean komatiites, particularly the higher Al_2O_3/TiO_2 ratios in the ophiolites (approx. 60) as compared with Archean komatiites (approx. 20).

The Thetford Mines lavas classified as komatiites also have high Al_2O_3/TiO_2 ratios (average 52) and high CaO/TiO_2 ratios (average 31). Since the absolute Al_2O_3 and CaO contents of these lavas are not significantly different from those of Archean komatiites, their high CaO/TiO_2 and Al_2O_3/TiO_2 ratios reflect their low TiO_2 contents. With the exception of the high CaO/TiO_2 and Al_2O_3/TiO_2 ratios, the lavas have comparable or similar high Ni, Cr and low $\overset{T}{FeO}/MgO$ and similar chondritic TiO_2/Zr (approx. 100) and Zr/Y ratios by comparison with Archean komatiites.

<u>TiO_2 - Zr and Zr/Y - Zr Plots</u>: In recent year, trace elements have become important indicators of the genetic pathway of rocks, particularly basaltic rocks. The incompatible trace elements Zr, Y, Sr, REE and TiO_2 have been used extensively as genetic pathway and tectonic environment discriminants. Pearce and Caan (1973) and Pearce (1979) have used some variation diagrams based on these incompatible elements to distinguish the tectonic regime of the Tethyan ophiolites (Troodos and Oman).

The TiO_2 vs Zr and Zr/Y vs Zr plots after Pearce (1979) are shown in Figures 3-14 and 3-15 for the Thetford Mines lavas. Only the type I lavas fall within the fields occupied by both the mid-ocean ridge basalts and arc lavas. Neither the type II nor the upper

Figure 3-14. Discriminant diagram of TiO_2 against Zr showing the fields occupied by mid-ocean ridge basalts (MORB), island arc tholeiites (arc lavas) and within plate lavas (after Pearce, 1979), and the distribution of TMC lavas.

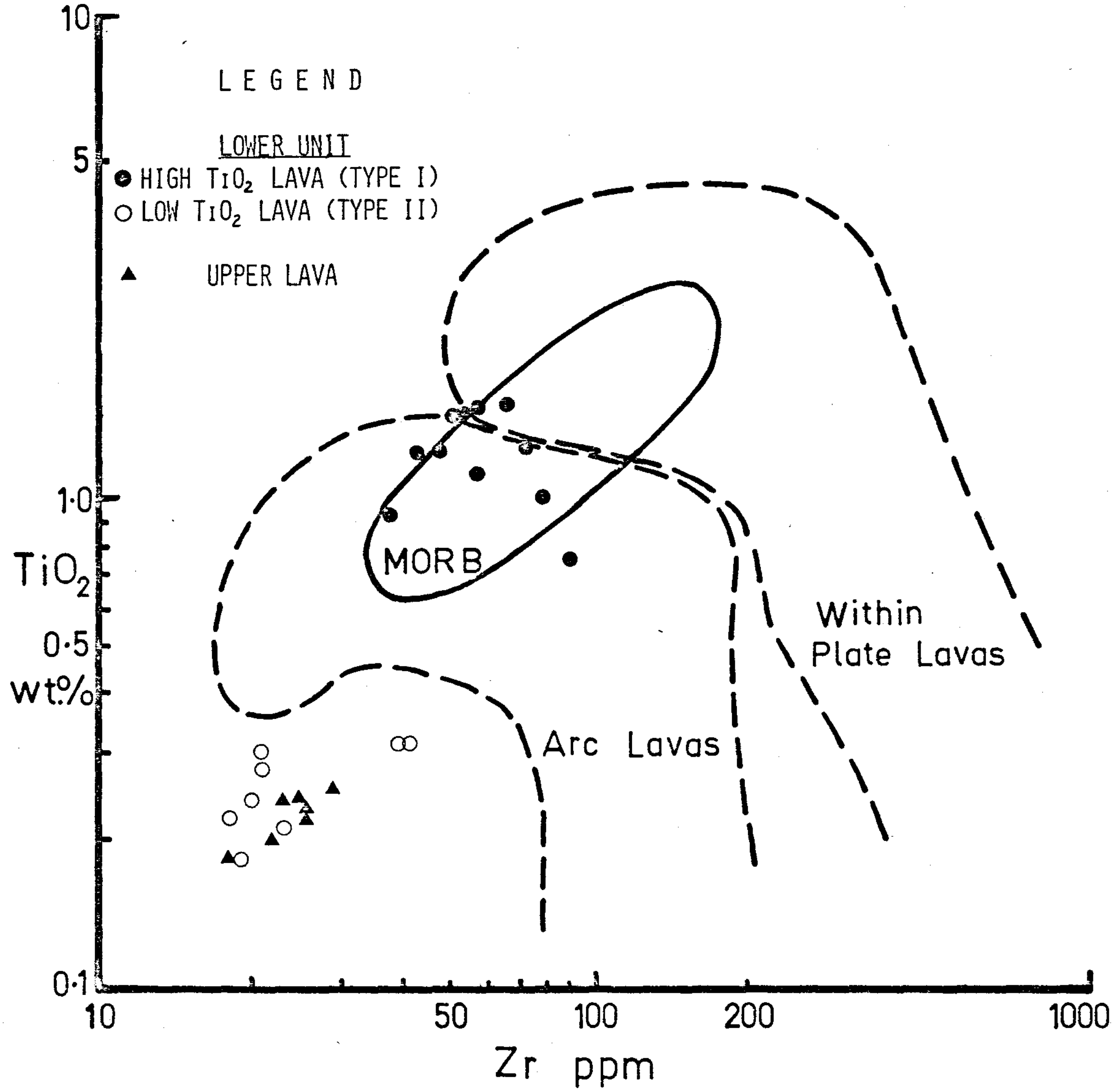
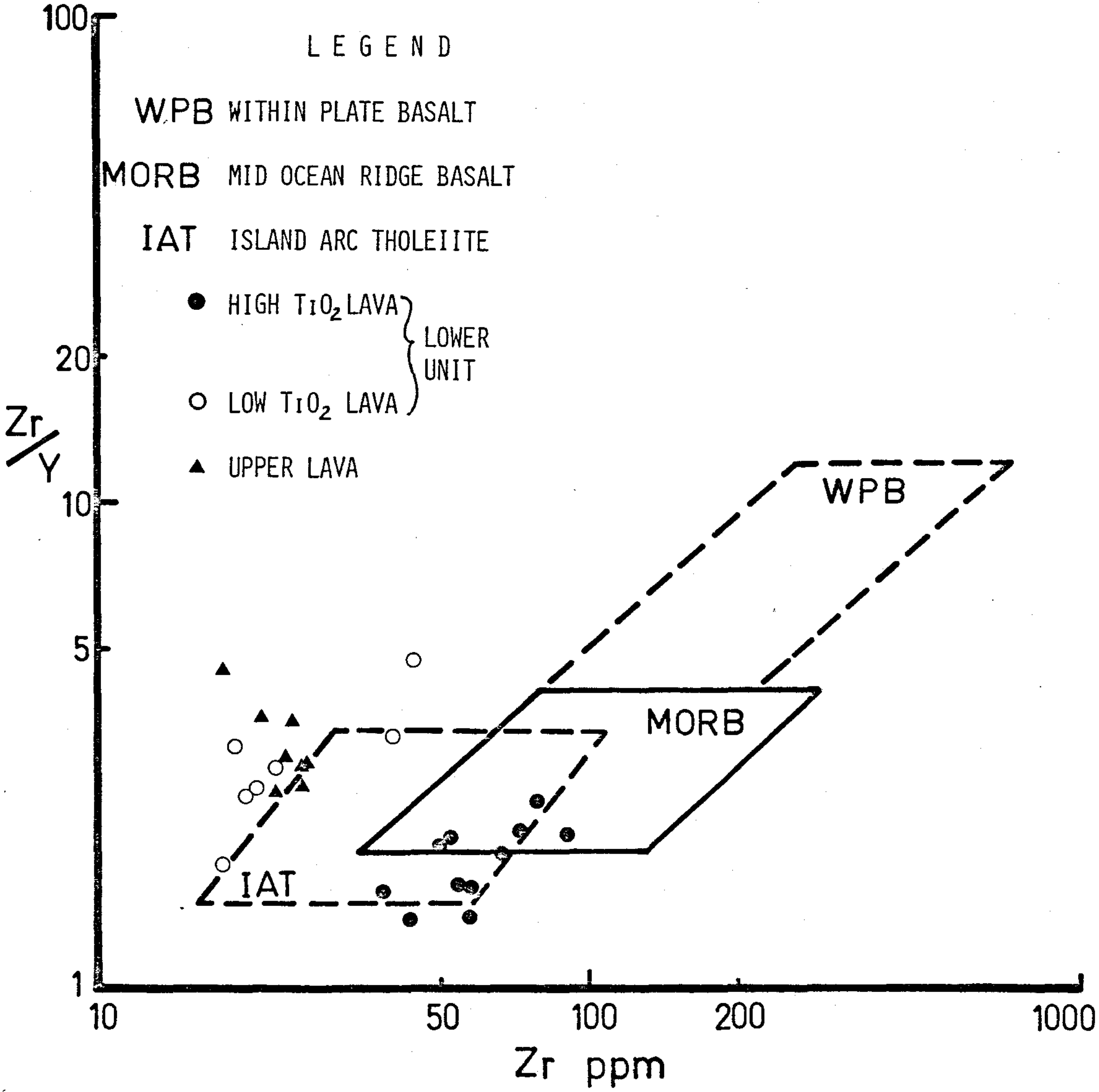

LEGEND
LOWER UNIT
● HIGH TiO2 LAVA (TYPE I)
○ LOW TiO2 LAVA (TYPE II)
▲ UPPER LAVA
MORB
Arc Lavas
Within Plate Lavas
TiO2 wt%
10
5
1·0
0·5
0·1
10
50
100
200
1000
Zr ppm

Figure 3-15. Discriminant diagram of Zr/Y ratio against Zr showing the fields occupied by mid-ocean ridge basalts (MORB), island arc tholeiitic basalts (IAT) and within plate basalt (WPB) (after Pearce, 1979), and the positions occupied by TMC lavas.


LEGEND
WPB WITHIN PLATE BASALT
MORB MID OCEAN RIDGE BASALT
IAT ISLAND ARC THOLEIITE
● HIGH TiO2 LAVA
○ LOW TiO2 LAVA
LOWER UNIT
▲ UPPER LAVA
WPB
MORB
IAT
Zr/Y
100
20
10
5
1
10
50
100
200
1000
Zr ppm

volcanic unit lavas plot in any field. This 'fieldless' situation for the low TiO_2 lavas has also been observed by Coish and Church (1979) for the low TiO_2 basalts of the Betts Cove ophiolites. It appears, therefore, that these discriminant plots are of little use in identifying the tectonic regime of the Thetford Mines lavas.

3.3.4 Discussion

Hydrothermal alteration of the lavas has affected the chemistry of the rocks in such a way that it is difficult to determine the pre-alteration chemical nature of the rocks. Classification based on major element chemistry is susceptible to error and confusion as illustrated by the rather conflicting classification obtained by the different classification schemes as summarized in Table 3-6.

Table 3-6

Summary of Classification of Volcanic Rocks

Scheme	Type I	Type II	Upper Lava
Miyashiro	Tholeiite	Calc-alkalic	Calc-alkalic
AFM	Inconclusive	Inconclusive	Calc-alkalic
Jensen Plot	Fe-Tholeiite Calc-alkalic	Mg-Tholeiite	Kamatiite

In the Thetford Mines lavas, the scheme most susceptible to error is the SiO_2 vs FeO^T/MgO plot because of the extensive mobilization of SiO_2. The Jensen plot is probably superior to the other schemes since it involves at least one element (Al) which has been shown to be relatively unaffected by hydrothermal alteration. However, it is still possible that some samples are mis-classified due to alteration. For example, a tholeiite sample that is enriched in Mg may plot in the calc-alkalic field. The inconclusion of the AFM diagram may also be reflecting the effect of alteration of the lavas. It is also possible that this is due to sampling. Perhaps some rocks which represent some stages of differentiation in the lavas have not been sampled.

The defficiency in the application of discriminant diagrams to ophiolite study is demonstrated by Thetford Mines and Betts Cove ophiolites. It appears that although the incompatible elements used are the least affected by alteration, rocks that have very low contents of the incompatible elements probably as a result of magma generation from an already depleted source, cannot be classified with these diagrams.

The occurrence of high and low TiO_2 lavas in the Thetford Mines complex follows a pattern seen in most ophiolite suites, e.g., Betts Cove (Coish and Church, 1979), Troodos (Smewing, 1975) and Rambler (Gale, 1973). However, the disposition of the lavas in Thetford Mines, at least in Lac de l'Est area, differs from that of Betts Cove and Troodos. In Betts Cove, the high and how TiO_2 lavas occupy juxtapositions (Church, 1972) while in Troodos, the high TiO_2 lavas lie stratigraphically on top of the low TiO_2 lavas. In Lac de l'Est (Thetford Mines) the low TiO_2 lavas overlie the high TiO_2 lavas. The

Table 3-7

Comparison of Major Element Chemistry of TMC Lavas with Basalts from Different Tectonic Settings

	Ophiolites								Island Arcs			Marginal Basins			Ocean Basin				
	Thetford Mines			Betts Cove		Cyprus													
	(1)	(2)	(3)	(4)	(5)	(6)*	(7)*	(8)	(9)	(10)*	(11)*	(12)	(13)*	(14)*	(15)	(16)	(17)	(18)	(19)
				5298	18	243AL	6aXT			482/12	331/450			95-1		JCS18			
	High Ti(I)	Low Ti(II)	Upp. Bas.	High Ti	Low Ti	High Ti	Low Ti	High Ti	High Ti	Low Ti	Low Ti	High Ti	High Ti	Low Ti					
SiO_2	52.88	52.49	51.68	50.54	46.66	49.84	53.85	50.37	49.41	57.42	55.22	50.34	48.8	47.70	50.15	50.66	50.28	49.21	49.11
Al_2O_3	14.45	13.98	11.69	15.39	12.66	16.17	11.55	14.65	16.78	10.73	7.90	16.45	16.4	15.88	15.57	15.26	14.88	15.81	15.85
Fe_2O_3					3.07	7.48	1.70	2.19						2.19					
FeO					5.77	2.86	6.34	9.24						7.03					
FeO^T	12.43	8.44	8.93	11.31					9.54	9.17	11.49	9.06	9.7		10.28	8.32	11.35	10.20	11.38
MgO	5.43	8.59	12.64	6.20	14.36	9.23	12.92	7.13	6.67	13.82	19.01	7.32	8.6	10.98	7.51	7.89	7.11	8.53	7.76
CaO	3.47	6.18	6.58	9.54	13.17	9.67	9.01	11.74	11.32	5.63	4.75	10.85	12.6	13.71	11.85	13.05	11.46	11.14	11.21
Na_2O	4.81	3.94	2.96	4.89	0.17	2.53	1.29	1.88	3.19	1.70	0.36	3.34	2.4	1.02	2.77	2.04	2.66	2.71	2.73
K_2O	0.14	0.79	0.31	0.16	0.04	0.29	0.16	0.31	0.47	0.80	0.48	0.43	0.18	0.03	0.20	0.16	0.16	0.26	0.22
TiO_2	1.23	0.25	0.22	1.45	0.19	0.76	0.31	1.75	1.51	0.10	0.24	1.45	1.2	0.37	1.35	0.75	1.77	1.39	1.42
MnO	0.23	0.18	0.18	-	-	0.12	0.16	-	0.14	0.18	0.20	0.16	0.2	0.16	0.16	0.16	0.18	0.16	0.18
P_2O_5	0.15	0.01	0.01	0.12	0.01	0.20	0.03	0.17	-	0.03	0.04	0.20	0.08	0.01	0.16	0.06	0.17	0.15	0.14

Key to Table 3-7

1. Average high TiO_2 basalts (TMC)(11); this study
2. Average low TiO_2 basalt (lower unit, TMC)(8); this study
3. Average low TiO_2 basalt (upper unit, TMC)(8); this study
4. Upper lava, Betts Cove; Coish and Church, 1979
5. Lower lava, Betts Cove; Coish and Church, 1979
6. Upper pillow lava, Troodos*
7. Lower pillow lava, Troodos*
8. Olivine-basalt lava, Tonga arc; Carmichael et al., 1974
9. Average basalt dredged from behind Mariana Island arc (5); Hart et al., 1972
10. High Mg andesite, Mariana trench*
11. High Mg andesite, Papua*
12. Average basalt from South Sandwich spreading center (back arc) east Scotia Sea (23); Tarney et al., 1977
13. Average of least altered basalt (11) Lau Basin; Hawkins, 1976

14 Basalt, Lau Interarc basin*

15. Mid Indian Ocean ridge basalt (68); Massey, 1980
16. Plagioclase phyric basalt, Leg 37 Hole 334 DSDP; Blanchard et al., 1976

17 East Pacific Rise basalt glass (38); Melson et al., 1976

18. Average mid-oceanic ridge basalt; Sanders et al., 1979
19. Average ocean-floor basalt (94); Caan, 1971

* Data from Sun and Nesbitt (1978)

boundary between the two lava types is not defined at Lac de l'Est and both low and high TiO_2 lavas are interlayed in the stratigraphic middle of the lava unit. This interdigitation of lava types may be due to extrusion or eruption of different lavas from adjacent vent systems. Alternatively, it may arise from cyclic generation of different but closely related magmas.

Comparison of the Thetford Mines lavas with other basalts (Table 3-7) shows that the type I lavas (high TiO_2 lavas of lower unit) are similar to both ocean basin and island arc high TiO_2 lavas but are depleted in CaO, MgO and enriched in Na_2O relative to the ocean basin and island arc lavas. On the other hand, the low TiO_2 lavas (type II) are more similar to the island arc low TiO_2 lavas such as those from Mariana and Papua than lavas from marginal basins. In comparison to other ophiolites, the Thetford Mines lavas are very similar to the Betts Cove lavas.

In conclusion, because of the uncertainty in the classification of the Thetford Mines, lavas, principally due to mobilization of the elements during alteration, for the purposes of further discussion, the lavas will be referred to as: high TiO_2 lavas (type I), low TiO_2 lavas (type II) of the lower volcanic unit and upper lavas.

CHAPTER FOUR

DISTRIBUTION OF NOBLE METALS IN THE THETFORD MINES COMPLEX

The abundance of the noble metals Au, Ir, Pt and Pd in TMC rocks and some mineral separates were determined using radiochemical neutron activation procedures. The details and accuracy of the analytical procedures are given in Appendix II. The mineral separates are chromite, olivine and orthopyroxene from a harzburgite sample, chromite from a cumulus dunite, orthopyroxene and clinopyroxene from a websterite. The methods of separation and purity of the minerals are described in Appendix IV.

The results of all analyses are presented together with the mean values and standard errors for each rock type in Table 4-3. Likely sources of errors are also discussed in Appendix II. For some rock types where there is a wide variation in noble metal contents, only samples whose metal values lie between $\overline{X}-2\sigma$ and $\overline{X}+2\sigma$ are used in mean and standard error calculations, where $\overline{X}$ and σ are the mean and standard deviation of all analyzed samples in the rock type considered. Samples with noble metal values outside $\overline{X}-2\sigma$ and $\overline{X}+2\sigma$ are regarded as anomalous with respect to other samples. These anomalous samples have probably lost or gained noble metals by secondary processes. Those with very high noble metal contents may also be carrying anomalous concentrations of noble metal bearing phases. Where a given rock type shows geographic variation in its noble metal contents, the mean values are initially calculated for each locality. These mean values are then used to calculate the overall mean for the rock type, based on the number of samples from each locality.

Some samples have been analyzed in duplicate and results range from good agreement to variation by a factor of more than two between duplicates. There are very small variations in the replicate analyses of the rock standard USGS W-1 (Appendix II) using similar analytical procedures as for the samples. The samples were also usually determined together with the rock standard. One can then conclude that any large difference in duplicate analyses of the samples is due to sample inhomogeneity.

4.1 Distrubtion of Noble Metals in Minerals

It is usually useful to know the abundances of elements, particularly trace elements, in rock forming minerals in order to adequately understand the distribution of the elements in rocks. For economic elements such as the noble metals, the knowledge of mineral affinities for them is very important for the modelling of their ore formation. Because noble metals are commonly associated with sulfide bearing rocks, many sulfide minerals have been analyzed for noble metals, particularly the PGE, e.g. Keays (1968), Chyi and Crocket (1976), Crocket *et al.* (1976) and Page *et al.* (1976). The fractionation trend of the noble metals in the sulfide minerals is therefore fairly well known.

Available data on sulfur poor rocks indicate that rocks rich in oxide phases, particularly chromite, have higher PGE than rocks that are predominantly silicate minerals, see for example, Page et al. (1976) and Khvostova et al. (1976). However, the role of chromite as a collector of noble metals is still not clear. For example, noble metal abundances do not always correlate with Cr abundances (see Keays and Davidson, 1976) and even when high PGE abundances have been reported in chromite separates or in chromite bearing rocks, the chromite involved has been observed to contain either sulfide inclusions or discrete platinum minerals.

Of the major silicate minerals which form sulfur poor rocks, only olivine is thought to concentrate some noble metals, particularly Ir. This is borne from the apparent fractionation of Ir into early formed rocks in differentiated rock suites, e.g. Gottfried and Greenland (1972). Also some high Ir values have been reported for olivine mineral separates. Ross and Keays (1979) reported that olivine separates from the ultramafic host rocks of some Ni-sulfides in Western Australia are enriched in Ir but depleted in Pd and Au relative to their co-existing liquid. Razin et al. (1965) also found that among the essential minerals in the ultramafic rocks of the Inaglinsh massif, USSR, olivine contains the highest contents of Pt metals. There are, however, some doubts as to whether the high PGE in olivine is due to solid solution of PGE or sulfide and chromite inclusions in the mineral. For example, Gijbels et al. (1976) found a strong positive correlation of Ir with Cr with the observed high

Ir in olivine. In a recent review of the role of olivine in concentrating Ir, Keays (1980) has suggested that fractionation of Ir in olivine may be a function of factors like pressure, temperature and sulfur saturation of the magma from which the olivine is crystallizing.

The initial objective of this part of the study was to determine the relative abundance of the noble metals in co-existing minerals in the various rock types of the Thetford Mines ophiolite. This was an attempt to asses the role of each important rock forming mineral in concentrating the noble metals. However, during the course of the study, it became apparent that this goal could not be achieved fully, for the following reasons:

i) most of the rocks have been severely altered such that fresh minerals are scarce,

ii) because of alteration, separation of minerals of high purity was difficult and time consuming such that only a few samples could be separated,

iii) most of the cumulate rocks are either formed by adcumulus growth of their constituent minerals or have abundant post-cumulus materials; at present the role of post-cumulus material or adcumulus process in concentrating metals in minerals is not fully understood and this could lead to misinterpretation of data,

iv) although Thetford Mines ophiolites are, in general, sulfur poor when compared with rocks such as the layered complexes, samples from Lac de l'Est area are enriched in sulfur relative to samples from other localities; if the relatively high S in the Lac de l'Est samples indicates sulfide inclusions in minerals, the observed noble metal could be misinterpreted.

One ofthe samples (9PH3A) from which minerals have been separated contains no post cumulus material, is sulfur poor and little altered. Data obtained from the mineral separates from this sample should therefore give a reliable estimate of the relative importance of the different minerals in concentrating the noble metals. The only disadvantage of this sample is that it is a harzburgite which probably represents a mantle residue. The observed noble metal fractionation among its minerals may not necessarily hold for cumulate rocks or any other rock type which are formed at higher crustal levels.

4.1.1 Abundance of Noble Metals in TMC Minerals

Table 4-1 summarizes the abundances of Au, Ir, Pt and Pd in the mineral separates from a harzburgite sample (9PH3A), and olivine-chromite cumulate (CCD3A) and a cumulate pyroxenite (CCPY4C). Comparison of the abundances of noble metals in the minerals shows that in the harzburgite the noble metals follow the relationship chromite: olivine:orthopyroxene: = 2.2 : 1.0 : 1.0 (Au); 4050 : 3.5 : 1.0 (Ir), 39 : 1.0 : 1.0 (Pt) and 142 : 1.0 : 1.5 (Pd).

The data for Au clearly shows that Au does not differentially fractionate into any of the mineral phases. Similar results have been reported by Agioritis and Becker (1979) for chromite, olivine and

Table 4-1

Abundances of Au, Ir, Pt and Pd in Mineral Separates from TMC (ppb)

	Au	Ir	Pt	Pd
Untreated chromite (harzb)	1.45	446.0	301.0	107.0
Chromite treated with acid (harzb)	1.51	3.50	22.0	18.30
Olivine (harzb)	0.67	0.38	7.80	0.75
Orthopyroxene (harzb)	0.70	0.11	7.74	1.15
Untreated chromite (ol-ch cumulate)	3.29	158.0	22.47	6.89
Chromite treated with acid (ol-ch cumulate)	5.71	110.1	13.26	7.74
Orthopyroxene (websterite)	2.43	0.31	29.55	1.57
Clinopyroxene (websterite)	3.10	0.16	36.91	0.90

orthopyroxene from an enstatite periodotite from the Troodos ophiolites. Agioritis and Becker (1979) obtained the Au ratio of 4.52 : 1.33 : 1.0 for chromite : olivine : orthopyroxene. In contrast to Au, the PGE, particularly Ir, are significantly fractionated into the chromite. This is similar to the results of many workers such as Razin _et al._ (1965), Razin and Khomenko (1969), Page _et al._ (1976) and Gijbels _et al._ (1974) who found enrichment of platinum metals in chromite over all co-existing silicate minerals in different rocks.

The high Ir contents in chromite might be attributed to ionic substitution of Ir for Cr in the chromite lattice as suggested by Agioritis and Wolf (1978) who found a logarithmic correlation of Ir with Cr in the chromites from the Greek alpine complexes. Substitution is possible between Ir^{+4} (ionic radius = 0.68 Å) and Cr^{+3} (ionic radius = 0.63 Å). The high Pt and Pd values in the chromite are more difficult to account for in terms of ionic substitution of either Pt or Pd for Cr. Both Pt^{+2} (ionic radius = 0.80 Å) and Pd^{+2} (ionic radius = 0.80 Å) which are the common ionic forms of Pt and Pd respectively are too large to allow substitution for Cr^{+3}. It is, however, possible that some substitution of Pt^{+4} (ionic radius = 0.65 Å) for Cr^{+3} (0.63 Å) might occur (Grimaldi and Schnepfe, 1969) but this will only account for a small percentage of the Pt in the chromite.

The chromite from the olivine-chromite cumulate (or chromite rich dunite) is considerably depleted in the PGE, particularly Pt and Pd but is richer in Au relative to the chromite from the metamorphic peridotite. The difference in the abundance levels of the noble metals in the different chromite may reflect the noble metal abundances of the source materials for the chromites. The difference may also be a result of the different physico-chemical conditions of formation of the chromites. The harzburgite (metamorphic peridotite) is believed to be mantle residue, so its chromite has crystallized under higher temperature and pressure than the cumulus chromite which crystallized at crustal level. If the PGE are more soluble in chromite at higher temperatures (Hagen, 1954 and Gijbels *et al*., 1974) then the metamorphic chromite formed under mantle conditions may have incorporated more PGE than the cumulus chromite due to higher temperatures of formation. There is, however, a possibility that the noble metal values for the metamorphic chromite are too high. These 'high' values may be due to analytical error associated with the small weight of the sample analyzed. However, such error will probably not change the reported values by more than a factor of 2. This will not change the interpretation that the metamorphic chromite concentrates the PGE more efficiently than the cumulus chromite.

In the websterite (CCPY4C) the noble metals follow the relationship orthopyroxene : clinopyroxene 1.0 : 1.3 (Au); 1.9 : 1.0 (Ir); 1.0 : 1.3 (Pt) and 1.7 : 1.0 (Pd). Thus, there is little differential partitioning of the noble metals into either of the two pyroxenes. The slight enrichment of Ir in the orthopyroxene over the clinopyroxene may be due to earlier crystallization of orthopyroxene in the host rock. This may also explain the enrichment of olivine in Ir over orthopyroxene in the harzburgite assuming prior crystallization of olivine. The enrichment of Pd of orthopyroxene relative to clinopyroxene in the websterite and similar enrichment of Pd in orthopyroxene relative to olivine suggest that orthopyroxene has a higher affinity for Pd than the other two ferromagnesian minerals.

4.1.2 Comparison of Noble Metals Abundance in Thetford Mines Mineral and Minerals from Other Rocks

There are very few data on the noble metal contents of minerals from sulfur poor rocks. Available data (Tables 4-1 and 4-2) show that the metamorphic chromite from Thetford Mines is depleted in Au but enriched in the PGE relative to chromites from Mt. Albert pluton and the Bushveld complex. Comparison with the Greek chromites is more difficult in that the Greek chromites display a considerable range of PGE contents. The data of Agiorgitis and Wolf (1977, 1978), however, suggest that Thetford Mines metamorphic chromites are comparable to only the Skyros chromites with PGE contents of 705-1065 ppb Ir; 185-265 ppb Pt and 25-43.5 ppb Pd. On the other hand, the cumulus chromite is comparable in Ir contents but is depleted in Pt and Pd compared to the Greek chromites. In comparison with Mt. Albert chromites, the cumulus chromites are characterized by very high Ir and low Pd contents.

Available data on other minerals are limited to Au, Ir and Pd abundances. The Ir contents of olivine from TMC harzburgite are similar

Table 4-2A

Comparison of Noble Metal Abundances in Minerals of TMC and Other Rock Suites (ppb)

Source of Minerals	Chromite				Olivine				Orthopyroxene				Clinopyroxene				Ref.
	Au	Ir	Pt	Pd	Au	Ir	Pt	Pd	Au	Ir	Pt	Pd	Au	Ir	Pt	Pd	
<u>Layered Complexes</u>																	
Critical, transitional and lower zones, Bushveld		77								0.35							1
Rhum						0.35								0.075			1
<u>Alpine Complexes and Ophiolites</u>																	
Chromites from Greek alpine complexes	0.48-10.8	1.2-1065	<15-265	<0.3-43.5													
Average	2.8	170.6	220	34.5													2
Mt. Albert pluton	3.4	4.3		24													
Enstatite peridotite	0.9-6.03																3
Troodos	2.71				0.80				0.6								4

Table 4-2A (continued)

Source of Material	Chromite				Olivine				Orthopyroxene				Clinopyroxene				Ref.
	Au	Ir	Pt	Pd	Au	Ir	Pt	Pd	Au	Ir	Pt	Pd	Au	Ir	Pt	Pd	
Mantle material																	
Spinel lherzolite nodule, Australia						0.3		0.7									5
Garnet lherzolite nodule, Lesotho						0.47		0.30									5
Host of sulfide ores (komatiite?)																	
Meta-olivine peridotite (Australia)						5.68		0.22									5

Key to Table 4-2A

1. Data from Crocket, 1979
2. Gijbels et al., 1974, 1976
3. Crocket and Chyi, 1972
4. Agiorgitis and Wolf, 1977, 1978
5. Keays, 1980

Table 4-2B

Comparison of Noble Metal Ratios in Minerals

	Au/Ir	Pt/Ir	Pd/Ir
Chromites			
Greek alpine complexes	0.016	1.29	0.20
Mt. Albert pluton	0.79	-	5.58
Thetford Mines, harzburgite	0.003	0.67	0.24
Thetford Mines, olivine-chromite cumulate	0.02	0.14	0.14
Olivines			
Spinel lherzolite, Australia			2.33
Garnet lherzolite, Lesotho			0.63
Meta olivine peridotite, Australia			0.04
Thetford Mines, harzburgite			1.97

to the Ir contents in olivine from Rhum complex and lherzolite nodules from Australia and Lesotho but considerably lower than the Ir contents in meta-olivine peridotite from Australia. Both the orthopyroxene and the clinopyroxene from Thetford Mines websterite have similar Ir contents as the pyroxene from the layered complexes.

Perhaps of more importance than comparison of absolute abundances of noble metals is the comparison of metal ratios. The absolute noble metal abundances probably reflect the abundance of the metals in the parental magmas or sources of the host rocks for the minerals. On the other hand, noble metal ratios indicate the fractionation of the noble metals with respect to one another in response to the stage of evolution of the minerals or rocks compared, e.g. low Pd/Ir denotes primitiveness (Pd/Ir for chondrites $\simeq 1$, also see Keays, 1980). Thetford Mines chromites and the Greek chromites have similar Pd/Ir ratios and so do olivine minerals from Thetford Mines and the spinel lherzolite from Australia. These minerals and their host rocks must be comparable in primitiveness. In comparison, Mt. Albert chromites with high Pd/Ir is probably less primitive than any of these rocks.

4.1.3 Mode of Occurrence of Noble Metals in the Chromites

A portion of the chromite separates was treated with HF and then with hot concentrated H_2SO_4. This was to remove any trace of silicate material that might adhere to the chromite, thereby destroying any chromite-silicate boundary and removing any noble metal that might be residing at the chromite-silicate boundary.

Comparison of noble metal contents of the treated and untreated chromite (Table 4-1) shows that Au is not affected by the acid treatment. The variation in Au contents is probably due to minor inhomogeneous distribution of Au in the chromites. On the other hand, the PGE are depleted in the treated, relative to the untreated samples. Depletion is only slight in the cumulus chromite but is significant in the metamorphic chromite.

In the metamorphic chromite, the treated fraction is depleted by a factor of 14 in Pt, a factor of 6 in Pd and almost all its Ir is lost relative to the untreated sample. In the cumulus chromite the PGE abundance ratios of untreated : treated chromite are 1.4 : 1 (Ir); 1.7 : 1 (Pt); and 0.89 : 1 (Pd). The difference in the proportion of PGE lost from the treated metamorphic chromite and cumulus chromite suggests different siting of the PGE in the two chromites. It is believed that only silicate inclusions and silicate-chromite boundary were removed from the chromite treated with acid. Since the silicates do not host any appreciable amount of PGE, it follows that the bulk of the PGE in the metamorphic chromite occurs along the chromite-silicate boundary. By contrast, most of the PGE in the cumulus chromite occurs within the chromite.

It is difficult to know if the PGE in the metamorphic chromite occupied grain boundaries during rock formation or migrated to grain boundaries as a result of post igneous processes. Hagen (1954) and Gijbels *et al.* (1974) have suggested that chromite might expel some of its PGE during cooling. If this is true for the Thetford Mines chromites, one may suggest the following hypothesis for the mode of occurrence of PGE in the metamorphic chromite:

> If the harzburgite is formed under mantle conditions (Boyd and MacGregor, 1968; Sobolev et al., 1975; Menzies, 1976), then under the prevailing high temperatures, chromite might incorporate substantial amounts of the PGE. During cooling, or most probably, during plastic deformation of the mantle material as it rose upwards to the crust, the PGE exsolved and migrated outwards to occupy the boundaries between chromite and silicate minerals.

It is doubtful if the PGE were originally incorporated into the metamorphic chromite in solid solution (that is, that they occupy lattice sites) as they would be difficult to exsolve in that condition. Rather, they probably occur as uncharged atoms, discrete platinum minerals or native alloys or as ions in defect sites or ion vacancies in the minerals structure. The latter type of control may be particularly important as a high degree of lattice disorder is expected in response to high temperature. At any temperature, it is expected that the amount of PGE incorporated will depend on their atomic or ionic size and that the element with the smallest radius would be preferentially taken up. In six-fold co-ordination, ionic radii for Ir^{+4}, Pt^{+2}, and Pd^{+2} are 0.68 Å, 0.80 Å and 0.80 Å respectively. The order of abundance of the noble metals should be Ir > Pt = Pd if ionic radius is a significant factor controlling substitution. The observed abundances are Ir > Pt > Pd. The dominance of Pt over Pd probably reflects the abundance of the metals in the source area.

Because of the lower temperature of formation of the cumulus chromite, significant disorder in the chromite lattice is not expected, hence, the PGE will form solid solution with suitable elements like Cr and Fe rather than fill defect lattices. Consequently, extensive exsolution of the PGE does not occur in the cumulus chromite.

4.2 Abundances of Noble Metals in Rocks of TMC

Results of analyses on whole rocks are presented in Table 4-3. The ranges and mean values of noble metal contents in individual rock types are also shown in Figure 4-1.

4.2.1 Metamorphic Peridotite

The harzburgite unit of the metamorphic peridotite has a relatively uniform Ir content but more variable Au, Pd and Pt contents with average values of 1.26 ppb, 3.55 ppb, 9.48 ppb and 4.44 ppb for Au, Ir, Pt and Pd respectively. Samples from Black Lake area are low in Pd (0.82 ppb for an average of 5 samples). Since the samples from Black Lake are collected from an open pit mine, it is possible that their low Pd content is due to removal of Pd by surface water although there is no evidence of weathering of these samples from thin section studies. The consistency in the low Pd values for individual samples also suggests that the low Pd values may be real. These Black Lake samples may be lacking in a phase which concentrates Pd.

On the other hand, variation in Au content is erratic and this may be due to secondary processes. Although there is no conclusive evidence yet that alteration enriches the rocks in Au, it is observed that samples 9PH3A and 9PH3B from Lac du Caribou which are the least altered rocks have the lowest Au contents. The effect of alteration on the noble metal concentration is further discussed in Section 5.2.

The uniformity in Ir in the harzburgite suggests that Ir is probably hosted by a phase which occurs in constant proportion in the harzburgite. Keays (1980) indicated that Ir could be strongly partitioned in the olivine of some peridotites. However, in the Thetford Mines rocks chromite is probably the host of most of the Ir (see Section 4.1) and since chromite occurs in a relatively constant proportion in the harzburgite (approximately 1% by volume) this would explain the uniform Ir contents in the rocks.

The dunite bodies in the harzburgite have restricted but low noble metal contents. The average noble metal contents are 0.27 ppb, 3.57 ppb, 2.42 ppb and 0.29 ppb for Au, Ir, Pt and Pd respectively. Except for Ir, the dunites have lower noble metal contents than the harzburgite. The rather high Ir content of sample 9DH2C from Vimy Ridge is probably a reflection of the high chromite content of this sample. The genetic implication of the low noble metal contents of the metamorphic dunites will be discussed later.

Table 4-3A

Noble Metal Concentrations (ppb) in Metamorphic Peridotite (TMC)

Sample	Au	Ir	Pt	Pd
Harzburgite				
+MPH1	1.28	3.93	7.36	0.82
*MPH1A	3.43	2.86	0.58	0.68
*MPH1C	0.76	2.14	18.40	0.45
MPH2A	1.09	3.11	4.55	5.24
MPH2B	1.50	3.27	14.47	10.22
9PH3A	0.24, 0.19	4.49, 5.94	12.92, 21.24	2.54, 4.40
9PH3B	0.17	3.43	3.94	4.56
9PH9A	3.27	2.32	nd	2.32
Average	1.26±0.42	3.55±0.40	9.48±2.38	4.44±1.21
Dunite				
MPD2A	0.22	1.87	4.22	0.53
MPD2B	0.33	1.07	nd	0.09
9DH2C	0.33	8.90	0.06	0.12
9DH3F	0.20	2.43	2.97	0.43
Average	0.27±0.03	3.57±1.56	2.42±1.10	0.29±0.10

\+ composite of 5 samples from the same locality

* not included in calculation of average - forms part of MPH1

nd not detected

Table 4-3B

Noble Metal Concentrations (ppb) in Cumulate Dunite (TMC)

Sample	Au	Ir	Pt	Pd
Dunite with chromite band (Lac du Caribou)				
CCD3A	0.34	39.0	1.66	0.28
CCD3B	0.21	21.65	1.41	0.38
Dunite with abundant disseminated chromite (Lac due Caribou)				
CCD3C	0.21	5.46	1.17	0.23
CCD3D	0.27	0.75	0.57	0.16
Dunite (Lac Rond)				
CCD6C	0.19	2.30	9.77	1.88
9CD6D	0.47	1.94	3.02	0.18
SU6A	*6.42	4.47	1.46	2.45
SU6E	0.37	1.51	7.93	4.02
Lac St. Francois/ Bisby Lake				
9CD7A	1.34	5.45	11.07	1.14
9CD7B	4.89	1.32	11.35	8.54
9CD7C	0.94	1.27	30.48	11.76
Lac de l'Est				
CCD4A	0.39	1.34	43.41	77.08
CCD4B	0.33	0.58	10.39	33.33
CCD4C	0.68	1.18	53.69	39.29
CCD4D	0.55,0.56	3.71,2.77	171.6,196.2	87.70,83.77
Average for dunite without chromite band	0.89	2.37	28.32	20.45

* Not included in calculation of average

Table 4-3C

Noble Metal Concentrations (ppb) in Pyroxenites (TMC)

Sample	Type	Au	Ir	Pt	Pd
<u>Lac de l'Est</u>					
9CW4E	wehrlite	2.82	0.33	3.33	6.94
CCPY4B		0.67	0.02	nd	6.16
CCPY4C		0.66	0.23	9.37	14.67
CCPY4D		1.84	0.24,0.35	25.36,23.86	67.79,63.96
CCPY4E		0.40	0.36,0.40	40.49,47.11	75.02,74.59
9CY4F		3.93*	0.14	33.35	66.60
9CY4G		0.93,0.68	0.17,0.11	15.15,9.50	30.38,26.34
9CY4H		2.07	0.83	102.3	133.2
<u>Mt. Adstock</u>					
CCPY5H		0.84	0.07,0.08	4.07,7.80	14.87,13.55
CCPY5J		1.23	0.21,0.20	17.83,10.68	17.24,18.81
<u>Lac Rond</u>					
9YD6B		0.26	0.01	7.70	3.23
CCPY6F		0.31	0.14,0.16	27.07	31.80,22.51
<u>Petit Lac St. Francois</u>					
9CY7A		103.5*,107.5*	0.07	nd	36.24
9CY7B		0.53	0.90	14.92	3.88
9CY7C		1.88	0.11	7.30	15.12
Average for pyroxenite		1.10	0.28	27.22	39.76

* Not included in calculation of average

nd Not detected

Table 4-3D

Noble Metal Concentrations (ppb) in Gabbro (TMC)

Sample	Au	Ir	Pt	Pd
Cumulate gabbro				
9CG4E	0.92	0.033	nd	10.57
CCG4F	0.46	0.013	9.59	0.46
CCG4G	4.91	0.012	1.77	0.50
CCG4H	0.56	0.008	2.13	0.21
Average for cumulate gabbro	1.71±0.92	0.017±0.005	4.50±2.08	2.94±2.20
Pyroxene-hornblende rich gabbro				
9CG4J	2.46	0.030	18.36	27.50
9CG4K	32.49	0.220	5.44	74.50
9CG4L	0.94	0.140	5.95	9.50
Metagabbro				
9MG4A*	10.51	0.033	9.44	45.79
9MG4B	0.36	0.052	12.03	0.77
9MG4C	0.66	0.010	nd	0.38
9MG4D	0.71	0.013	3.35	0.12
INMG5B	0.56	0.030	4.22	1.61
INMG5D	2.49	0.020	3.36	2.41
Average for metagabbro	0.96±0.35	0.025±0.007	5.74±1.82	1.06±0.38
Diabase dikes				
INMG5C	3.17	0.09	10.84	9.71
9DB4M	2.18	0.22	7.35	7.67

* Not included in calculation of average

Table 4-3E

Noble Metal Concentrations (ppb) in Lavas (TMC)

Sample	Au	Ir	Pt	Pd	Ag
Type I lavas					
9LB4A	4.82	0.018	3.53	<0.38	10.5
9LB4B	1.10	0.039	10.15	0.48	28.7
9LB4C	3.87	0.032	3.65	<0.24	43.5
9LB4D	9.16*	0.008	nd	<0.40	35.1
9LB4E	3.13	0.041	nd	<0.24	55.2
9LB4G	0.91	0.019	14.06	<0.20	9.7
9LB4H	1.18	0.109*	nd	<0.32	29.3
9LB4J	1.71	0.012	2.71	<0.48	30.4
9LB4K	0.42	0.007	nd	<0.15	10.9
9LB4L	13.40*	0.009	nd	<0.16	11.8
9LB4X	2.14	0.006	2.95	<1.6*	2.9
Average	2.14±0.47	0.019±0.004	6.18±1.78	<0.31±0.04	
9LB4F (Dacite)	0.77	0.018	1.29	<0.40	14.3
Type II lavas					
9LB4M	2.84	0.042	8.97	15.23	26.2
9LB4N	3.11	0.056	11.19	12.97	10.3
9LB4P	1.32	0.027	19.93	12.35	2.3
9LB4Q	1.49	0.027	nd	10.76	2.0
9LB4R	0.85	0.047	3.83	7.69	15.7
9LB4U	0.81	0.111	9.71	3.28	5.1
9LB4V	1.10	0.087	30.76*	7.61	29.5
9LB4W	9.48*	0.054	nd	7.90	29.8
Average	1.65±0.33	0.056±0.010	9.15±2.42	9.72±1.26	

Table 4-3E (continued)

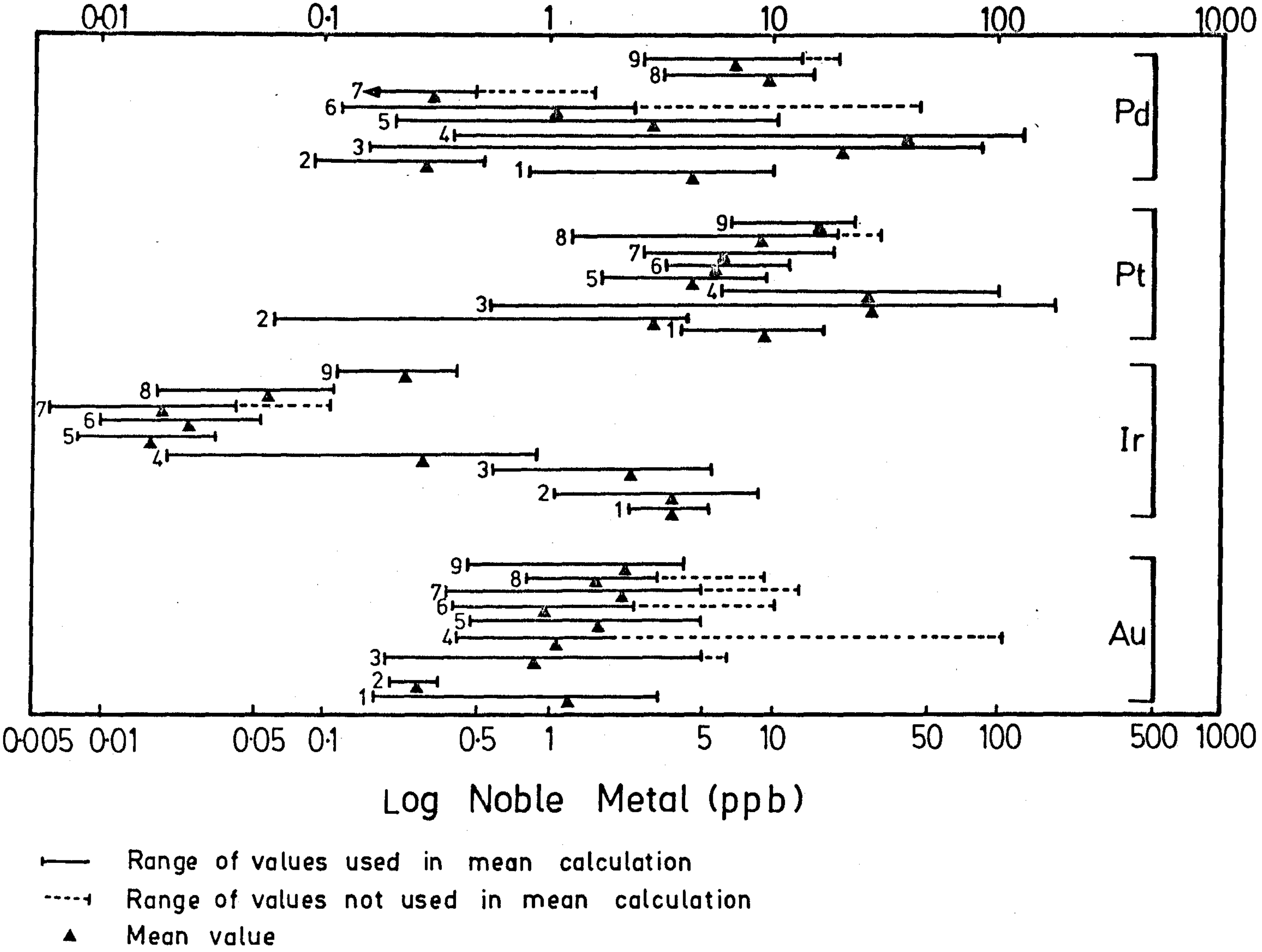
Sample	Au	Ir	Pt	Pd	Ag
Upper lavas					
9UB4A	1.79	0.178	6.75	2.68	20.0
9UB4B	0.45	0.117	20.94	2.85	2.0
9UB4C	2.14	0.154	nd	6.29	23.8
9UB4D	2.70	0.238	17.88	8.73	38.8
9UB4E	3.80	0.334	nd	5.62	6.3
9UB4F	4.01	0.396	23.68	13.61	21.0
9LB4S	1.00	0.261	10.97	19.73*	43.7
9LB4T	1.78	0.194	nd	7.91	20.2
Average	2.21±0.41	0.234±0.031	16.04±2.81	6.81±1.32	

* Not included in calculation of average

nd Not detected

Figure 4-1. Range and mean values of Au, Ir, Pt and Pd in the different rock types of TMC.

1 = harzburgite
2 = metamorphic dunite
3 = cumulate dunite
4 = pyroxenite
5 = cumulate gabbro
6 = hypabyssal rocks (intrusive gabbro)
7 = type I lava
8 = type II lava
9 = upper lava


0·01
0·1
1
10
100
1000
Pd
Pt
Ir
Au
1
2
3
4
5
6
7
8
9
0·005
0·01
0·05
0·1
0·5
1
5
10
50
100
500
1000
Log Noble Metal (ppb)
Range of values used in mean calculation
Range of values not used in mean calculation
Mean value

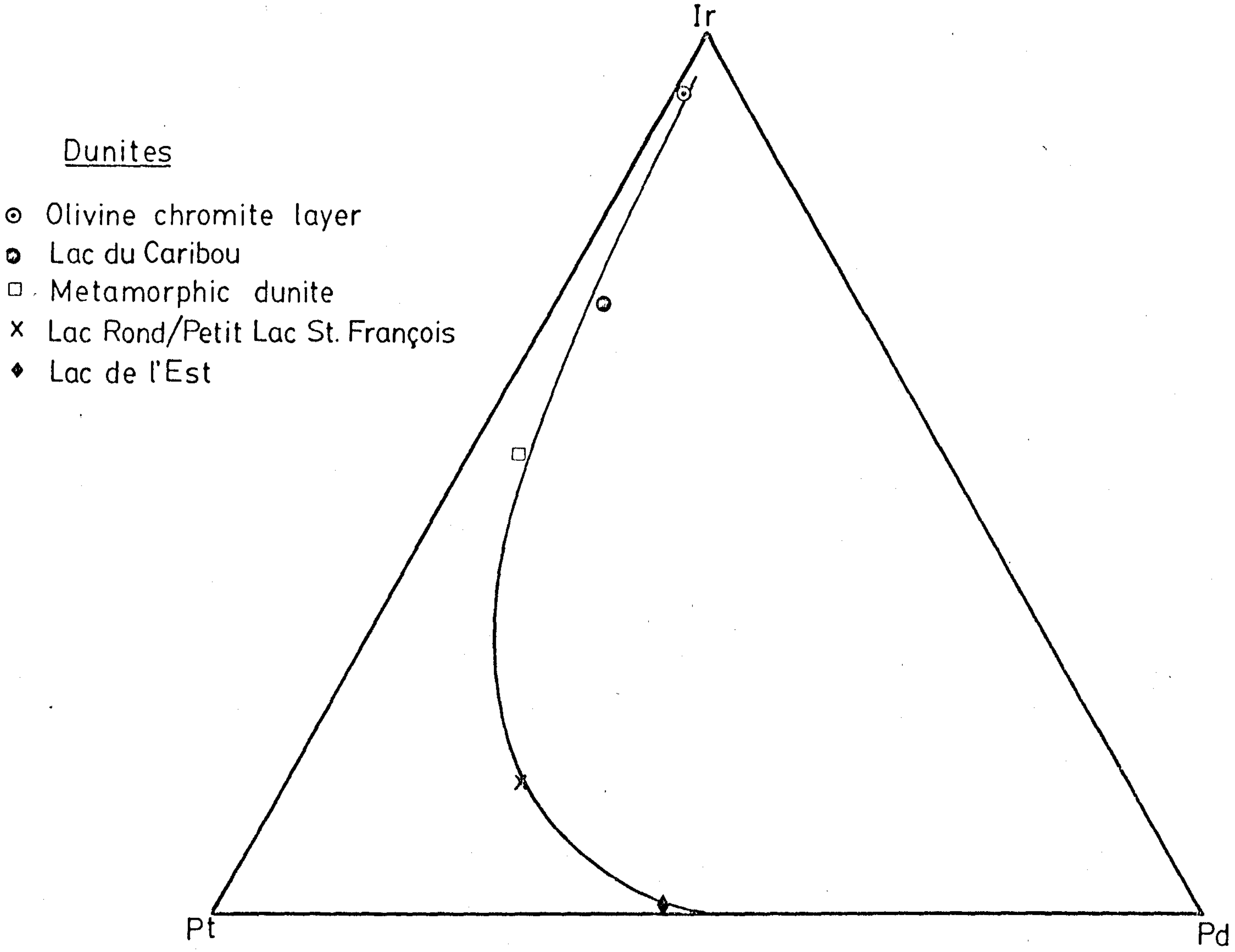
4.2.2 The Cumulates

The cumulate rocks are characterized by wide variation in the abundances of platinoid metals but very little variation in Au contents. More than any rock type, the dunites display the greatest variation in noble metals, particularly in Pd and Pt.

From major element considerations (Section 3.2) it was pointed out that the SiO_2 vs FeO^T/MgO plot of the dunites suggests that the dunites are probably formed in cycles with those at Lac du Caribou as the most primitive, or alternatively, the dunites have been derived from different magma sources. The variation in the noble metals also appears to be related to geographic localities and possibly to stratigraphic position. Averages for PGE contents for each locality have been plotted on Ir-Pt-Pd triangular diagrams in order to assess the degree of variation of the three platinum group elements. The Ir-Pt-Pd plot (Figure 4-2) shows a trend of continuously decreasing Ir and a general increase in Pd/Ir ratio from Lac du Caribou through Lac Rond to Lac de l'Est. If the Pd/Ir ratio of silicate melts increase with magmatic differentiation as suggested by authors such as Keays and Davidson (1976) and Keays (1980), then the PGE trend observed in the dunites can be related to magmatic differentiation.

It is interesting to note that the metamorphic dunites in the harzburgite plot on the same trend as the cumulate dunites. Whether this is suggestive of a genetic relationship between the metamorphic dunites and the cumulate dunites will be discussed later.

Figure 4-2. Ir - Pt - Pd variation diagram for the dunites of TMC.


Ir
Dunites
⊙ Olivine chromite layer
● Lac du Caribou
□ Metamorphic dunite
x Lac Rond/Petit Lac St. François
◆ Lac de l'Est
Pt
Pd

With the exception of samples from Lac Rond and Petit Lac St. Francois, the dunites are low in Au. It is not known whether the higher values from these two localities reflect enrichment by secondary processes such as serpentinization.

The pyroxenites have more restricted ranges of noble metal values than the dunites, but like the dunites, variation in PGE contents can also be related to geographic locations as may be seen by comparing the average noble metal contents from the different locations (Table 4-3).

Au values are relatively uniform for the cumulate pyroxenites regardless of locality. However, one sample (9CY7A) from Petit Lac St. Francois is exceptionally high in Au. Separate duplicate analyses of this sample gave values of 108 ppb and 104 ppb with an average of 106 ppb and a percentage difference of only 3.8%. Since this percentage difference is less than the estimated error of 5% for Au analysis, contamination of the sample is ruled out and the high value is real. Since this sample is not significantly different either in mineralogy or alteration state or in PGE contents from other samples from the same locality or elsehwere, its high Au value is puzzling. Occurrence of Au in discrete phases such as alloys or sulfide inclusions would probably not give the small percentage difference between duplicate analyses observed. If the high Au content is due to alteration such as serpentinization then the sample must have been preferentially and thoroughly soaked in a fluid of high Au contents.

The pyroxenites include a variety of mineralogically different rocks ranging from websterite to clinopyroxenite. Variation in noble metal contents, particularly the PGE, appear to be related more to rock composition than stratigraphic position. However, there is a crude trend of decreasing Ir from the bottom to the top of the pyroxenite unit. The clinopyroxenite rocks have higher PGE contents than either the websterite or wehrlite. It is not clear at present why this is so since there is no evidence that clinopyroxene concentrates PGE. For example, analysis on the minerals from a websterite from the study area by the author (Section 4.1) does not show any enrichment of PGE in clinopyroxene over the whole rock. Since clinopyroxenites are monomineral1ic and are formed mostly by adcumulate processes, the high PGE in the clinopyroxenites may be due to diffusion of noble metals from the interprecipitate magma to minerals (mainly clinopyroxene) during adcumulus growth.

Despite a trend towards a decrease in the PGE contents upwards stratigraphically, variation in noble metal contents in the cumulate gabbro is restricted. However, the pyroxene-hornblende rich gabbroic rocks within the cumulate zone have considerably higher noble metal contents than the main cumulate gabbro but comparable with the noble metal contents of the main pyroxenite rocks. The hornblende-rich gabbro (sample 9CG4K) is particularly rich in noble metals. Laurent (pers. comm.) has indicated that the hornblende in the sample is primary, indicating that the magma from which the rock was derived was very hydrous. Such a hydrous magma should be residual in nature, and pegmatoid texture suggests a slow cooling history. The noble metals may have been concentrated in this residual slowly cooled magma by diffusion. The high Cu contents (581 ppm Cu) of sample 9CG4K also suggests that the residual magma was rich in Cu. A similar noble metal-Cu rich residual liquid has been suggested by Keays and Crocket (1970) for the enrichment of Au and Pd in chalcopyrite from the ore zone of Strathcona Mine, Sudbury.

4.2.3 The Hypabyssal and Volcanic Rocks

Except for an amphibolitized metagabbro, the metagabbros have low noble metal contents and probably crystallized from a magma low in noble metals. The amphibolitized metagabbro, however, is more than ten times and forty times richer in Au and Pd respectively than the average for the other metagabbros. Since the amphibolitized metagabbro is also chemically different from other metagabbros in some major and trace elements, it is possible that the amphibolitized gabbro was derived from a different magma with higher noble metals.

The abundances of the PGE, Ir, Pt and Pd in the volcanic rocks show marked variations. Pd values range from less than 0.15 ppb to 15 ppb. Ir values range from 0.006 ppb to 0.40 ppb while Pt contents range below the sensitivity limit of the analytical procedure up to 30 ppb. Samples with low Pd contents have low Ir contents and those with high Pd have high Ir values. Variation in Pt abundances, however, appears to have no trend and this may be partly due to poorer analytical precision or greater heterogeneity of Pt in the volcanic rocks.

The variations in the PGE abundances in the volcanic rocks appear to be more related to rock composition rather than stratigraphic position as each of the three chemically different lava types is characterized by different ranges of PGE abundances. The high TiO_2 lavas of the lower volcanic unit (type I) are characterized by very low Pd contents (0.15-1.6 ppb, average 0.31 ppb) and low Ir contents (0.006-0.11 ppb, average 0.019 ppb). One sample (9LB4H) in this group with Ir contents of 0.11 ppb but low Pd contents (0.32 ppb) is considered anomalous with respect to Ir. This sample has higher Cr contents than other samples in the group. Either its high Ir content is due to contamination or chromite inclusions which concentrate Ir. The low TiO_2 lavas of the lower volcanic unit (type II) are characterized by high Pd contents (3.3 ppb - 15 ppb, average 9.7 ppb) and high Ir contents 0.027-0.11 ppb, average 0.056 ppb). The lavas of the upper volcanic unit have a similar range of Pd values as the type II lavas but much higher Ir contents (0.12-0.40 ppb, average 0.23 ppb).

On account of the low Pd/Ir ratio (16) of the type I lavas as compared to the Pd/Ir ratio (174) of the type II lavas and the upper lavas (29) one is tempted to regard the type I lavas as the most primitive of the three lava types. However, their very low Ir contents suggest that the low Pd/Ir ratio of the type I lavas is a reflection of low Pd contents rather than primitive nature. In fact, for the type I lavas to be so depleted in both Ir and Pd, their genesis must have involved a magma severely depleted in both Ir and Pd by an earlier crystallization event which removed the noble metals. Alternatively, the source magma was saturated in sulfur and a separation of an immiscible sulfide-rich fraction from the magma scavenged the noble metals.

With the exception of three samples (9LB4D, 9LB4L and 9LB4W) with high Au values (9.2, 13 and 9.5 ppb respectively), there is little variation in the Au contents (0.42-4.8 ppb) of the three lava types. The samples with the high Au contents have probably been enriched in Au during hydrothermal alteration of the lavas.

4.3 Geographic Variation in Noble Metal Abundances

The geographical variation in the noble metal contents, particularly the PGE, of the dunites has earlier been attributed to magmatic differentiation. Since similar variation in noble metal abundances is also observed in the pyroxenites it is necessary to review other possible explanations for these geographic variations. Unfortunately, gabbroic and lava samples from different localities have not been analyzed, so possible geographic variation in noble metals for these rock types is unknown.

Besides magmatic differentiation, four other possible explanations may be suggested for the observed variations in noble metal contents in the dunites and pyroxenites:

i) Different magma sources: Kacira (1972) grouped the rocks of Thetford Mines into: a) a northern assemblage, comprising rocks around Thetford

Mines, Lac du Caribou and Lac de l'Est, and b) a southern assemblage, comprising rocks from Mt. Adstock, Lac Rond, Petit Lac St. Francois and Bisby Lake. Kacira suggested on the grounds of different types of metamorphic textures, that the two assemblages were derived from different magma sources and that the southern assemblage was emplaced first. Comparison of the mean values of noble metals in the dunites and pyroxenites (Table 4-4) shows that the dunites and pyroxenites from Mt. Adstock, Lac Rond, Petit Lac St. Francois and Bisby Lake (southern assemblage) are similar in noble metals but have lower Pt and Pd contents than equivalent rocks from Lac de l'Est and higher Pt and Pd contents than rocks from Lac du Caribou. Similarity in the noble metal contents of the constituent rocks of the southern assemblage, therefore, supports the suggestion of Kacira that the southern assemblage rocks were derived from a separate magma from the northern assemblage. The geographic variation in noble metal abundances may, therefore, be a reflection of the difference in the noble metal contents of the magma sources for the two rock assemblages.

ii) Sulfide inclusions: The higher Pt and Pd contents of Lac de l'Est rocks in comparison with rocks from other localities may be due to Pt and Pd bearing sulfides in the Lac de l'Est rocks. Alternatively, the lower PGE contents of rocks at Lac du Caribou, Lac Rond and Petit Lac St. Francois may result from sulfur saturation of their magma at some stage prior to emplacement of the magma in its present structural setting. The sulfur would have scavenged the PGE from the magma and sulfides may have been lost during intrusion and prior to crystallization.

Table 4-4

Comparison of Mean Values (ppb) of Noble Metals in Different Localities of TMC

Locality	Dunites				Pyroxenites			
	Au	Ir	Pt	Pd	Au	Ir	Pt	Pd
Lac du Caribou	0.24	3.11	0.87	0.20				
Lac Rond	0.34	2.56	5.55	2.13				
Petite lac St Fracois	2.39	2.68	17.6	7.15	1.21	0.36	11.1	18.4
Lac de l'Est	0.49	1.59	72.8	58.9	1.08	0.29	38.3	55.7
Mt Adstock					1.04	0.14	10.1	16.1

Such a mechanism has been suggested to explain the low Ir contents of komatiitic ultramafic flows from Mt. Clifford in Australia (Keays, 1980). Although no sulfide phase has been identified in Lac de l'Est rocks, this explanation is supported by the relatively higher sulfur contents of the Lac de l'Est rocks (Table III-3). One problem with this hypothesis, however, is that Ir is fractionated from both Pt and Pd despite the chalcophilic nature of all the three PGE. With this mechanism one would expect rocks to be either depleted or enriched in all three platinum elements.

iii) Variable amount of postcumulus material in rocks: Another possible explanation for the observed noble metal variations may be related to the amount of trapped postcumulus material in rocks at different localities. Why rocks from different localities have different amounts of postcumulus material is not known. Because of serpentinization, most of the primary texture of the dunitic rocks has been obliterated. However, the dunitic rocks at Lac du Caribou are observed to have little or no postcumulus material while most of the pyroxenites from Lac de l'Est have appreciable amount of postcumulus material as intercumulus minerals. It is possible that the dunites from Lac de l'Est also have significant postcumulus material. If the noble metals, with the exception of Ir, are rejected by earlier formed minerals and concentrated in residual magmas, then rocks with large amount of trapped postcumulus material would be enriched in Pt, Pd and Au. However, the rocks are not enriched in Au. Perhaps the source magma is originally low in Au. Alternatively, it is possible that crystal/magma partition coefficient for Au is quite different from that of Pt or Pd, hence Au does not follow Pt and Pd.

iv) Post-igneous remobilization of noble metals: Variation in noble metals in rocks and ores have been attributed in part to post-emplacement remobilization of noble metals by late stage hydrothermal fluid, serpentinization or diffusion down a thermal gradient in the presence of an aqueous fluid phase. Thus Hoffman *et al*. (1979) suggested that the variation in the PGE contents in the Levack West Mine, Sudbury, is due to diffusion of the PGE under a decreasing thermal gradient from the hanging wall to the footwall of the mine through an intergranular water-rich phase. There are no heat flow data to confirm or disprove the existence of any thermal gradient over the various localities in the Thetford Mines area. However, the metamorphic mineralogy of Lac de l'Est rocks is not significantly different from rocks in other localities. This argues against any thermal gradient. It is also doubtful if remobilization of elements under any of the above conditions would affect only Pt and Pd.

Any of the above hypothesis could be responsible for the observed variation in the PGE in the dunites and pyroxenites. It is also possible that more than one mechanism was involved. However, any plausible mechanism must take into account: 1) the very high Ir content of the chromite-bearing dunite at Lac du Caribou, 2) the apparent differentiation trend within the dunites, and 3) the high sulfur contents of Lac de l'Est rocks.

Taking all available data into consideration, two alternative hypotheses are tentatively suggested to account for the geographic variation in PGE contents of the cumulate ultramafic rocks:

1) The cumulate rocks are derived from three or two magma sources (Mt. Adstock, Lac Rond, Petit Lac St. François and Bisby Lake), Lac du Caribou and Lac de l'Est or southern assemblage and northern assemblage.

2) The cumulate rocks formed from a single magma source. In this case, the sequence of events is envisaged as follows: the parental magma contains a small amount of dissolved sulfur under relatively high oxygen fugacity such that no immiscible sulfide melt can form. The magma undergoes fractionation beginning with chromite and olivine crystallization to form olivine-chromite cumulate and chromite rich dunites such as those at Lac du Caribou. FeO and Ir are concentrated in the chromite (see Section 4.1.1). The residual magma will, therefore, become depleted in FeO and Ir but enriched in Pt and Pd as these metals are not taken up by the early formed minerals. A decrease in the FeO content of the residual magma causes a decrease in oxygen fugacity which along with decreasing temperature and pressure will result in a decrease in the amount of sulfur that can be held in solution (Haughton et al., 1974; Buchanan and Nolan, 1979) such that sulfur will exsolve as immiscible sulfide droplets. These sulfide droplets may scavenge the Pd and Pt of the magma. Either the amount of Au in the magma is low originally or the sulfide does not scavenge Au. If the sulfide droplets are too small to form a separate melt or sink to the bottom of the magma chamber, they are probably suspended or dispersed

within the residual magma, although there is no reason to believe that they will be homogeneously distributed within the residual magma. Continuation of fractional crystallization of this residual magma would lead to formation of the chromite poor dunites and pyroxenites. The fraction which forms the Lac de l'Est dunites and pyroxenites might contain the sulfide droplets with the scavenged Pt and Pd. During metamorphism, the noble metals in the sulfide may have been released and equilibrated with the minerals of the rocks leading to high abundance of Pt and Pd in the Lac de l'Est rocks.

4.4 Fractionation of Noble Metal

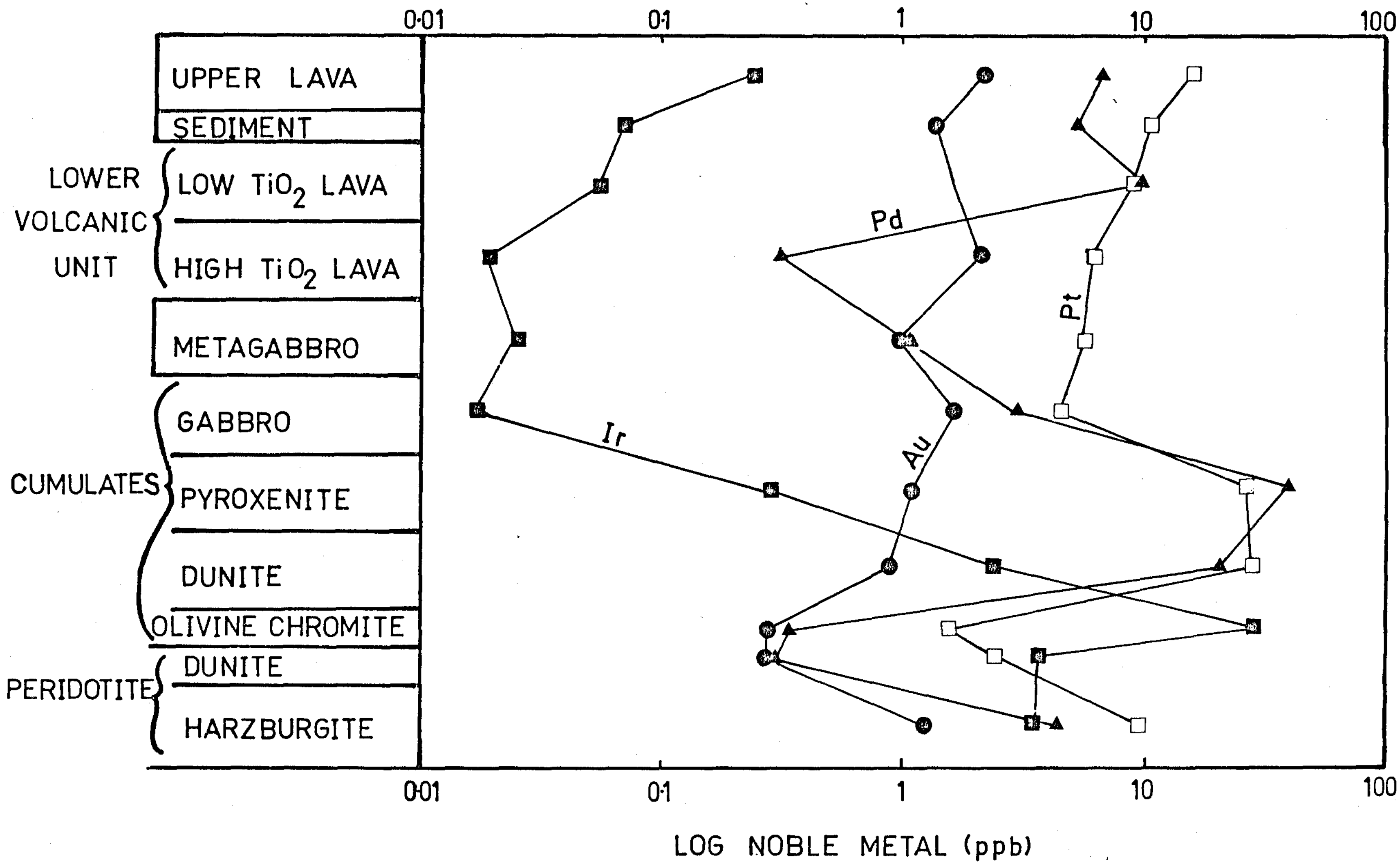
Fractionation of the noble metals in response to rock composition is shown in a vertical profile in Figure 4-3. Here, the calculated overall averages of the noble metals in each rock type are taken as representative of the noble metal contents of the magma or magma fractions which gave rise to the rock types. This is in accordance with the idea that rocks of each rock type have the same parental magma irrespective of geographic location.

Gold: Au values vary little between the different rock types, with averages ranging from 0.27 ppb to 2.2 ppb. If the metamorphic dunites and the olivine-chromite cumulates are neglected, the averages for Au contents in the major rock types range only from 0.89 - 2.2 ppb. This lack of control by rock composition on the distribution of Au has also been shown elsewhere (Moisenko and Fatyanov, 1972; Gottfried et al., 1972; Crocket, 1974; and Agiorgitis and Becker, 1979). For example, Crocket (1974, Table 79-E-3) shows that the average Au contents of most silicate rocks vary by only a factor of 2 and Agiorgitis and Becker (1979) reported a restricted range (0.08-3.7 ppb Au) in the rocks of Troodos ophiolite complex. Despite the lack of strong fractionation of Au between rock types, the average Au content of the mafic rocks (1.82 ppb Au) is higher than that for the ultramafic rocks (0.92 ppb Au).

The distribution of Au in differentiated rocks has been studied by many workers such as Vincent and Crocket (1960), Rowe (1969) and Agiorgitis and Becker (1979). These workers conclude that Au shows an indifferent behavior and does not follow any particular phase during magmatic differentiation. The cumulate section of the ophiolite is believed to have been formed by magmatic differentiation. A closer look at the distribution of Au in the Thetford Mines ophiolite shows that Au values increase from 0.28 ppb in the olivine-chromite cumulate, the earliest formed rock type (stratigraphic bottom) to 1.7 ppb in the gabbro, the last formed rock type (stratigraphic top). Thus, the ratio of the average Au content in the most fractionated rock type to the average Au content in the least fractionated rock type in Thetford Mines ophiolites in 6 : 1 as compared to 3 : 1 for the Skaergaard rocks and about 4 : 1 for the differentiated dolerite sheet of Great Lake, Tasmania.

The variations in the Au contents observed in the cumulate rocks of Theford Mines ophiolites, albeit small, do suggest that the distribut-

Figure 4-3. Variation of noble metal concentrations with rock types of TMC.


0·01
0·1
1
10
100
UPPER LAVA
SEDIMENT
LOWER VOLCANIC UNIT
LOW TiO_2 LAVA
HIGH TiO_2 LAVA
METAGABBRO
CUMULATES
GABBRO
PYROXENITE
DUNITE
OLIVINE CHROMITE
PERIDOTITE
DUNITE
HARZBURGITE
Pd
Pt
Ir
Au
0·01
0·1
1
10
100
LOG NOBLE METAL (ppb)

ion of the Au may partly be controlled by magmatic differentiation.

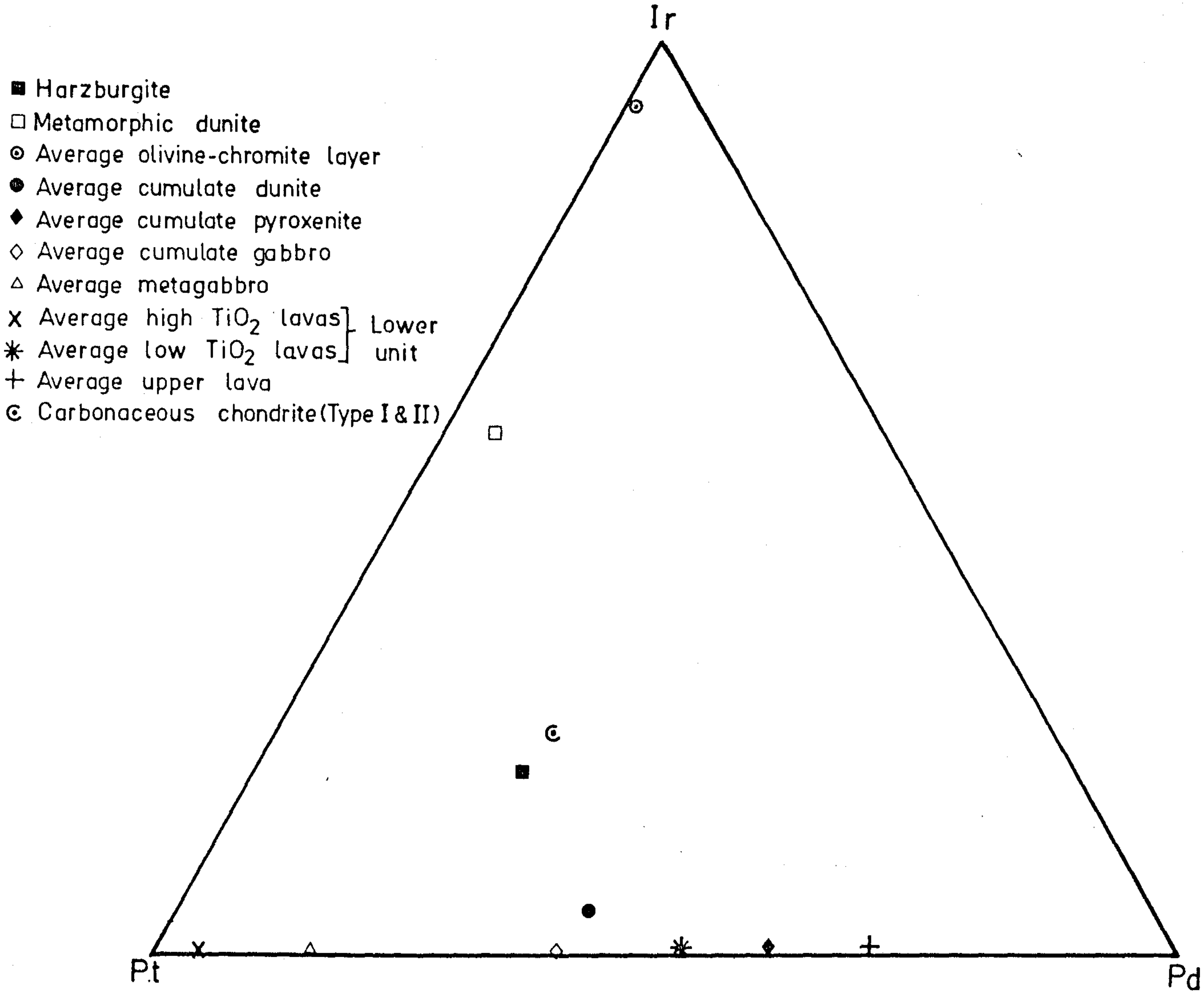
The Platinum Group Elements (PGE): In contrast to Au, the PGE show marked fractionation between the various rock types. The abundance levels in the ultramafic rocks are significantly higher than those of the mafic rocks. Including the metamorphic peridotite, the weighted average PGE contents of the ultramafic rocks are 3.5 ppb Ir, 20.5 ppb Pt and 20.4 ppb Pd as compared to 0.077 ppb Ir, 8.1 ppb Pt and 4.3 ppb Pd for the mafic rocks. Thus, the ultramafic ; mafic PGE ratios of 45.7 (Ir), 2.53 (Pt) and 4.77 (Pd) show that Ir is more fractionated between ultramafic and mafic rocks than either Pt or Pd.

Besides fractionation of the PGE between ultramafic and mafic rocks, PGE fractionation occurs within both the mafic and ultramafic rocks although in the mafics it is not as marked as in the ultramafic rocks. However, the fractionation trend in the mafic rocks is not clear enough to be diagnostic of any genetic process as variation in the PGE within the non-cumulate mafic rocks may reflect the PGE contents of the sources of the rocks. Comparison of the average PGE contents of individual rock types within the cumulate section shows that Ir systematically decreases, stratigraphically upwards, from 30 ppb in the olivine-chromite cumulate to 0.27 ppb in the pyroxenites and 0.017 ppb in the gabbro. This is similar to the observation of Greenland (1971) in the Great Lake dolerite sill, Tasmania, where Ir contents systematically decrease from 0.25 ppb at the base to 0.006 ppb at the top. This observation is explained by the strong partitioning of Ir into early formed minerals. The very high Ir contents (30 ppb) in the olivine-chromite cumulate as opposed to only 2.4 ppb Ir in the chromite poor dunite is a result of a much higher fractionation of Ir into chromite than olivine.

Fractionation of Pt and Pd is almost the reverse of that of Ir. Both Pd and Pt increase in abundance from the olivine-chromite cumulate to a maximum value in the dunite and pyroxenite and then decrease in the gabbro. If the gabbro is genetically related to the ultramafic cumulates by magmatic differentiation then the observed fractionation trend of Pt and Pd is in contrast to the suggestion that residual magma is enriched in Pd and Pt during magmatic differentiation (e.g. Naldrett and Cabri, 1976). If residual magma is enriched in Pt and Pd one would expect the cumulate gabbro to have the highest Pt and Pd contents.

The fractionation of the PGE amongst themselves is shown graphically in Figure 4-4. In all the rock types, except in the metamorphic peridotite, Ir is well fractionated from both Pt and Pd. Ir abundance accounts for more than 90% of the total PGE contents of olivine-chromite cumulate but less than one per cent in each of the other rock types. Except in the metagabbros and the type I lavas, Pt and Pd are not significantly fractionated from one another. Usually the abundance of one metal is less than a factor of 3 of the abundance of the other metal. The coherence of Pt and Pd in the ophiolites further attests to the view that Pt and Pd have similar geochemical affinity which differs from that of Ir (e.g. Cousins, 1973).

Figure 4-4. Fractionation of the PGE in rocks of TMC. Data on the carbonaceous chondrites which represent unfractionated material is shown for comparison with rocks of TMC. PGE values used for the chondrites are from the data of Crocket (1979) -- 518 ppb (Ir), 1050 ppb (Pt) and 575 ppb (Pd).


Ir
Pt
Pd
■ Harzburgite
□ Metamorphic dunite
⊙ Average olivine-chromite layer
● Average cumulate dunite
♦ Average cumulate pyroxenite
◇ Average cumulate gabbro
△ Average metagabbro
X Average high TiO_2 lavas
✳ Average low TiO_2 lavas
Lower unit
+ Average upper lava
ϲ Carbonaceous chondrite (Type I & II)

Compared with the chondrites only the harzburgite displays unfractionated PGE (see Figure 4-4). The chondrite-like relationship of the PGE in the harzburgite is compatible with its primitive nature as suggested by major element geochemistry.

4.5 Comparison with Other Rocks

Comparison of noble metal abundances of Thetford Mines ophiolites with other rocks is limited by the following major problems:

1) Thetford Mines ophiolites consist of many rock types, each of which has a range of noble metal abundances. Because the genetic relationship of many of these rock types are not fully established, the noble metal content of the ophiolites cannot be represented by a single average value.

2) The bulk of the existing noble metal abundance data pertains to rocks associated with sulfide ores. Sulfides might have scavenged the noble metals from the magmas of these rocks, or alternatively, the rocks might have been enriched in noble metals by sulfide inclusions.

3) Most reported data on other rocks are limited to one or two of the noble metals determined in this study. This, therefore, limits the scope of comparison.

4) A significant percentage of the existing noble metal data has been obtained by analytical methods which differ from the procedure used in this study. Systematic differences in accuracy and sensitivity in these methods could grossly exaggerate or diminish the differences in

the compared data.

In order to minimize the effects of these problems, comparisons are made only between rocks of similar chemistry, petrography or mode of genesis. The rocks compared include ophiolites, Alpine complexes, Alaska or Urals type complexes, layered stratiform complexes, komatiites, and rocks of basaltic composition. Where possible, only data obtained by neutron activation procedure on unmineralized or sulfur-poor rocks are compared. Noble metal abundances in these rocks are presented in Table 4-5 to Table 4-10. Because of the importance of the volcanic rocks of the ophiolites in relation to their environment of formation, comparison with rocks of basaltic composition is deferred until Chapter Six.

4.5.1 Ophiolites

In spite of all the geochemical interests in ophiolites, they are one of the least studied ultramafic-mafic rock associations with respect to the noble metals. The only data on ophiolites reported in the literature are those on the Troodos complex (Agiorgitis and Wolf, 1977, 1978; Agiorgitis and Becker, 1979; Becker and Agiorgitis, 1978). Page *et al.* (1979) also reported some noble metal abundances in chromites from the Oman complex. The average noble metal contents of the Troodos suite are listed in Table 4-5. It should be pointed out, however, that the listed averages may be biased in view of the small number of sample analyzed.

Table 4-5

Noble Metal Contents (ppb) in Troodos Ophiolites, Cyprus

Rock Type	Au	Ir	Pd	Pd/Ir
Peridotite (2)	1.39	4.84	9.58	1.98
Dunite (1)	0.52	0.4	0.33	0.83
Pyroxenite	2.16	0.05	13.36	267.2
Gabbro	1.07	0.033(6)	3.14(2)	95
Lower Basalt	0.08	0.24	0.42	17.5
Upper Basalt	3.24	0.022	0.47	21.4

Sources

Au: Agiorgitis and Becker, 1979

Ir, Pd: Becker and Agiorgitis, 1978

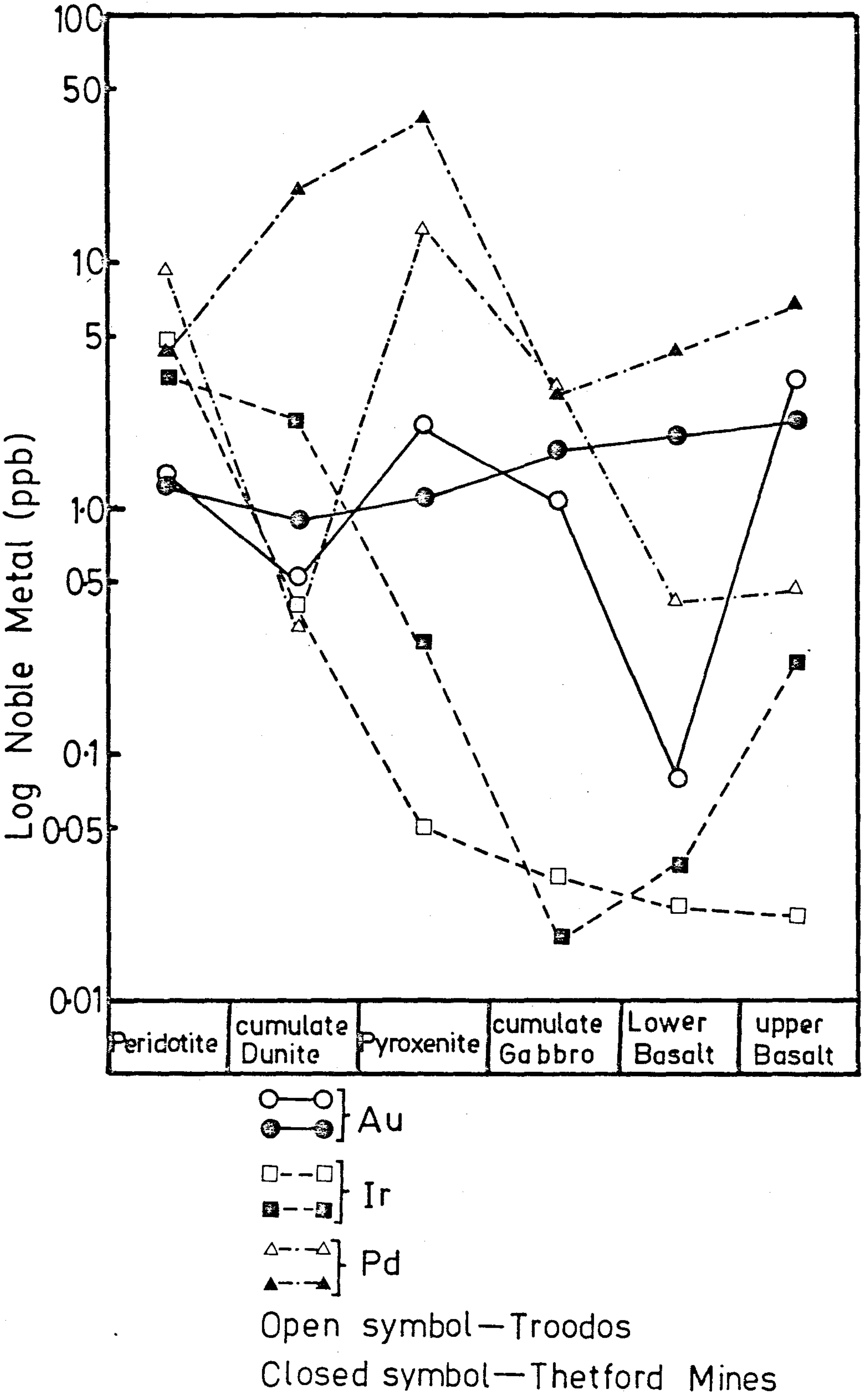
When the averages of absolute noble metal abundances are compared, only the gabbros of the two ophiolite suites are comparable in that their noble metal abundances differ by less than a factor of 2. The peridotites also have comparable Ir and Au values but the Troodos peridotite is enriched in Pd by more than a factor of 2 relative to Thetford Mines. The most pronounced difference in the noble metal abundances in the two ophiolite suites is observed in the cumulate ultramafic rocks. Both the dunites and pyroxenites in Troodos are significantly depleted in Ir and Pd relative to Thetford Mines. Ir is depleted by a factor of about 6 in both the pyroxenite and dunite while Pd is depleted by a factor of 3 in the pyroxenite and by as much as a factor of 62 in the dunite. Although certain dunitic samples in Thetford Mines have similar low Pd values as in Troodos, these samples with low Pd contents are usually characterized by much higher Ir contents than their Troodos equivalents. The Pd/Ir ratios (average 0.01) of these samples are much lower than the Pd/Ir ratios (average 0.8) for the Troodos rocks.

One possible reason for the low PGE in the cumulates of Troodos may be that the magma from which they crystallized was saturated in sulfur prior to crystallization. Separation of sulfides might have scavenged the PGE in the magma. One line of evidence in support of a possible sulfur saturation of Troodos magma is the abundant occurrence of sulfide ores within the Troodos suite. If the Troodos magma was saturated in sulfur, then the conditions under which it was crystallizing must have been quite different from those in Thetford

Mines. High Ir contents of the early formed rocks in Thetford Mines would suggest that the magma in Thetford Mines was not saturated in sulfur at the onset of crystallization; otherwise, sulfur could have removed the Ir in the magma. The low Ir in Troodos on the other hand, suggests removal of Ir from the magma before crystallization started. This would imply different physico-chemical conditions from those operating in Thetford Mines, such as lower temperature, lower oxygen fugacity or higher sulfur fugacity, all conditions which will decrease the solubility of sulfur in magma and cause an early separation of sulfide from the magma.

The fractionation trend of the noble metals in the two ophiolite suites are compared in Figure 4-5. In Thetford Mines, Au is relatively uniformly distributed in contrast to Troodos where the rocks display a wide variability in their Au contents. The lower basalt is depleted in Au relative to other rock types. Agiorgitis and Becker (1979) suggested that the low Au contents in the lower basalt is due to hydrothermal leaching of Au from the lavas with a concommitant enrichment of Au in the upper basalt. If this is true, then hydrothermal leaching of Au from the lavas must have been less effective in Thetford Mines as the lower lavas are similar in their Au contents to the upper lavas. However, the author disagrees with Agiorgitis and Becker (1978) in respect of the Troodos upper lavas. There is evidence that the upper lavas in Troodos were emplaced after the hydrothermal alteration of the lower lavas (e.g. Gass, 1967; Constantinou and Govett, 1971; and Smewing et al., 1975). If Au has been leached from the lower lavas, it

Figure 4-5. Comparison of noble metal trends in Troodos and Thetford Mines ophiolites. The data used for Troodos are from Becker and Agiorgitis (1978) and Agiorgitis and Becker (1979).


100
50
10
5
1·0
0·5
0·1
0·05
0·01
Log Noble Metal (ppb)
Peridotite
cumulate Dunite
Pyroxenite
cumulate Gabbro
Lower Basalt
upper Basalt
Au
Ir
Pd
Open symbol—Troodos
Closed symbol—Thetford Mines

should be enriched in the sulfide bodies or the metalliferous sediments which were formed during hydrothermal activity (Govett and Pantazis, 1971) and now lie between the lower and upper lavas in many localities. This is supported by the data of Fryer and Hutchinson (1976) on the iron rich sediments overlying the sulfide ore bodies in Troodos complex. Fryer and Hutchinson (1976) reported Au values of 18 ppb to 857 ppb in these sediments.

Fractionation trends of the platinum elements, Ir and Pd in the two ophiolites are similar in certain respects. In the cumulate section, Pd contents increase from the dunite to the highest values in the pyroxenite and decrease in the gabbro. Ir, on the other hand, decreases systematically from the dunite through the pyroxenite to low values in the gabbro. The difference in trend is observed in the basalts. In Troodos, the systematic decrease in Ir continues from the gabbro through the lower basalt to lowest in the upper basalt. This would tend to support a genetic linkage of the lavas and the cumulates via magmatic differentiation. On the other hand, in Thetford Mines, some of the lavas are much higher in Ir than the stratigraphically underlying cumulate gabbro, and a genetic relationship between these lavas and the cumulates by magmatic differentiation is difficult to explain.

Another contrasting feature in the two ophiolite suites is the comparison of Ir and Pd values in the lower and upper lavas. In Thetford Mines, the upper and lower lavas are characterized by significantly different contents of both Ir and Pd. This difference in noble metal values may relate to mode of genesis or differing tectonic environments of formation of these lavas. No such distinction in noble metal contents is observed between the upper and lower lavas in Troodos. This is surprising in view of the different tectonic settings that have been postulated for the Troodos lavas viz; ocean ridge environment for the lower lavas and off ridge or island arc environment for the upper lavas (see Pearce, 1975).

4.5.2 Alpine-Type Complex

Alpine-type complexes are large ultramafic-mafic bodies found in orogenic zones. They are characterized by harzburgite or lherzolite, dunite and gabbroic rocks. Early interpretation of these rocks was that they were formed either as high temperature intrusions (Green, 1967) or as cumulate rocks (Thayer, 1967, 1969). Later, with better understanding of these rocks, Alpine-type complexes were regarded as basal zones of ophiolite complexes, e.g. Bailey et al. (1970), Coleman (1971, 1977) and Ringwood (1975). But in contrast to the layered sequence of ophiolite complexes, Alpine-type complexes occur commonly as isolated blocks.

Like the ophiolites, noble metal data on Alpine-type complexes (Table 4-6) are scanty and most data come from the USSR. The bulk of the existing data pertains to harzburgite-dunite association and therefore only the metamorphic peridotite in Thetford Mines are compared with the Alpine-type complexes. For the purposes of comparison, the weighted noble metal averages of the harzburgite and dunite are used, but this does not at present imply any genetic relationship between the dunite and the harzburgite.

By comparison, Alpine-type rocks from the Urals are significantly enriched in Pt and Pd relative to those from Thetford Mines and other localities but Ir contents are comparable. The reasons for the high Pt and Pd values in the Urals are not known. Although different analytical procedures from the one used for Thetford Mines rocks may be a factor, it is also possible that the high values may reflect differences in geographic localities.

Pt and Pd contents of the metamorphic peridotite from Thetford Mines are similar to those from Burro Mtn., USA and the averages compiled by Crocket (1979) for several localities in the USA. The USGS rock standard PCC-1 which is also an alpine peridotite (Coleman, 1977) also has similar noble metal contents to the Thetford Mines rocks.

The data of Crocket and Chyi (1972) and the Pt analysis by the author indicate that the average Au, Ir and Pt contents of the Mt. Albert pluton are similar to the metamorphic peridotite in Thetford Mines. Mt. Albert is, however, enriched in Pd. This comparison is important in view of the suggestion by Laurent (1975) that Mt. Albert pluton may be genetically related to the ophiolites of southern Quebec in contrast to the view of MacGregor (1964) that Mt. Albert pluton is an intrusion. Although similarities in Au, Ir and Pt contents would suggest a possible genetic linkage, the high Pd contents in Mt Albert, which is reflected in high Pd/Ir (3.3) and low Pt/(Pt+Pd)

Key for Table 4-6

I = Neutron Activation analysis

II = Acid decomposition or fusion - spectrophotometric

III = Fire-assay or chemical dissolution - emission spectroscopy

* = Analysis by the author

Table 4-6

Comparison of Noble Metal Contents of TMC and Alpine Complexes

Rock Type and Locality	No. of Samples	Analytical Method	Noble Metal Contents in ppb						Reference
			Au	Ir	Pt	Pd	Pd/Ir	$\mathrm{Pt}_{/\mathrm{Pt+Pd}}$	
Dunite and peridotite, Urals	8	II		5.7	73	18	3.16	0.8	Naldrett and Cabri, 1976
Dunite, Ray-Iz massif, Polar Urals	4	II			112	15		0.88	Khovastova *et al*., 1976
Harzburgite, Ray-Iz massif, Polar Urals	4	II			26	4		0.87	Khovostova *et al* , 1976
Dunite, Nuralinsky, Urals	1	II		4.1	8.2	2.0	0.49	0.67	Forminykh and Khovostova, 1970
Peridotite, Burro Mtn., USA	18	III			<10	<4		0.71	Crocket, 1979
Dunite, peridotite, Red Mtn., Cypress Island, Twin Sisters, U A	4	III			<10	<4		0.71	Crocket, 1979
PCC-1 (Peridotite, Sonoma County, Calif.) USGS Rock Std.	14, 14 15, 15	I	0.73	5.0	6.3	4.0	0.80	0.61	This study (see Appendix II)
Harzburgite dunite, Mt. Albert, Que	13, 13 5, 13	I	1.9	2.2	9.9*	9.5	4.3	0.51	Crocket and Chyi, 1972
Harzburgite, TMC	7	I	1.26	3.6	9.5	4.4	1.2	0.68	This study
Metamorphic dunite, TMC	4	I	0.27	3.6	2.4	0.3	0.01	0.88	This study
Average for metamorphic peridotite, TMC	11	I	0.9	3.6	7.4	2.9	0.82	0.71	This study

(0.55) as compared to Pd/Ir (0.82) and Pt/(Pt+Pd) (0.71) for the Thetford Mines suggest, however, that Mt. Albert pluton is more differentiated than the ophiolitic peridotite.

4.5.3 Alaskan-Type or Urals-Type Complexes

Alaskan-type complexes are ultramafic and gabbroic rocks which occur in orogenic areas such as Alaksa, the Urals and British Columbia, Canada, as small concentrically zoned intrusions. When well developed, each intrusion consists of a dunitic core surrounded in succession by olivine peridotite, olivine pyroxenite, magnetite pyroxenite and finally hornblende pyroxenite or hornblendite. The Alaskan-type complexes are compared with the cumulate rocks of Thetford Mines due to 1) their similar mode of formation, that is fractional crystallization of a magma, 2) the similarity in rock types - association of dunite and pyroxenite, 3) their overall low sulfur contents, and 4) the similarity in tectonic environment of emplacement, that is, orogenic zone.

Alaskan-type complexes, however, differ from the ophiolites in that they are alkalic, and the abundance of primary hornblende in some of their rocks indicates that they are much more strongly differentiated than the ophiolites.

Noble metal data on the Alaskan-type complexes are mostly on the Urals and in most cases are limited only to Pt and Pd. The data presented in Table 4-7 show that there is no significant difference in the noble metal contents in rocks from the Urals and Alaska. The chrome-poor cumulte rocks from Thetford Mines are depleted in Au, Ir and Pt but are comparable in Pd relative to the Alaskan-type complexes. Consequently the Alaskan-type ultramafics have higher Pt/Pd ratio (1.7) and lower Pd/Ir (3.3) than the ophiolitic ultramafic rocks (Pt/Pd = 0.95, Pd/Ir = 21). The Alaskan-type chromite-rich dunites, such as those in the Urals, are considerably enriched in all the PGE in comparison to the chromite rich olivine-chromite cumulates in Thetford Mines. This difference is probably the result of secondary processes in the Ural dunites. Fominykh and Khovostova (1970) indicated that the chromites are cemented to the minerals of the dunites by platinoid minerals probably brought by solution.

The dominance of Pt over Pd in the Alaskan-type complex in contrast to similar abundances of Pt and Pd in the ophiolites may be explained in terms of the mode of genesis of the rocks. Taylor (1967) has argued that Alaskan-type rocks are derived from ultramafic magmas. On the other hand, the ophiolites might have crystallized from a less mafic magma. A higher degree of partial melting of the mantle would therefore be needed to produce the Alaskan-type magma than the ophiolite magma. Since Pt is more siderophilic than Pd (e.g. Cousins, 1973), it is believed that Pt is more residual than Pd. High degrees of melting of a magma source will be required to produce a melt enriched in Pt relative to Pd. The higher Pt/Pd in the Alaskan-type rocks is, therefore, probably due to the higher degree of melting of the mantle to produce the Alaskan-type rocks than the ophiolites.

Table 4-7

Comparison of Noble Metal Contents of TMC Ultramafic Cumulates and Alaskan Type Complexes

Rock Type and Locality	No. of Samples	Analytical Method	Noble Metal Contents in ppb						Reference
			Au	Ir	Pt	Pd	Pd/Ir	$Pt_{/Pt+Pd}$	
USSR									
Dunite, peridotite, Urals	4, 2 10, 10	I, II	1.2	7.2	57	21	2.9	0.71	Averages calculated from the data of Fominykh and Khovostova, 1970, & Sobolev *et al*., 1973
Pyroxenite, Urals	12, 6 6	I	2.6		38	25		0.73	
Dunite, various localities, Urals	4	II		9.6	82	32	3.3	0.72	Recalculated from Crocket, 1979
Alkali ultramafic complex mainly pyroxenite, Donbas-Azov	7, 11	?			25	36		0.41	Crocket, 1979
Weighted average for above			2.3	8.8	48	29	3.3	0.62	
Dunite with chromite Schlieren, Nizhni Tagil	1	II		320	3900	4600	14.4	0.46	Fominykh and Khovostova, 1970
Dunite with chromite schlieren, Kayrlyn, Urals	1	II		62	560	330	5.3	0.63	Fominykh and Khovostova, 1970
Weighted average of above (chromite rich rocks)				190	2230	2465	13	0.48	
Alaska									
Average for Alaska complexes excluding sulfide rich Salt Chuck	64, 73				54	32		0.63	Crocket, 1979

Table 4-7 (Continued)

Rock Type and Locality	No. of Samples	Analytical Method	Noble Metal Contents in ppb						Reference
			Au	Ir	Pt	Pd	Pd/Ir	$Pt_{/Pt+Pd}$	
<u>TMC</u>									
Chromite poor ultramafic cumulates (dunites + pyroxenites)	21, 24, 23, 24	I	0.98	1.4	28	29	20.8	0.49	This study
Chromite-rich dunites	2	I	0.22	30.3	1.5	0.33	0.01	0.82	This study

I = Neutron activation analyses

II = Acid decomposition or fusion - spectrophotometric

It is also possible that the dominance of Pt over Pd in the Alaskan-type complexes is related to abundant oxide phases such as chromite and magnetite in rocks of the complexes. If the higher concentration of Pt than Pd in chromites (see Section 4.1) suggests that oxide phases have a higher affinity for Pt than Pd, then the higher Pt/Pd ratios in the Alaskan-type complexes than the ophiolites may be explained in terms of the higher proportion of oxide phases in the Alaskan-type complexes.

4.5.4 Komatiites

In some Archean terrains of the world such as the greenstone belts of Canada, the Eastern Goldfields of Australia, South Africa and Zimbabwe, there are ultramafic-mafic volcanic and hypabyssal rocks described as komatiites. These rocks are hosts of some of the world's Ni-Cu sulfide ores. Komatiites usually occur in stratigraphic sequences characterized by highly magnesian basal ultramafic flows succeeded upwards by less magneian mafic lava (Ardnt et al., 1979). The base of the sequence may be peridotite cumulates rich in forsterite olivine as in Munro Township, Canada, or massive dunitic flows. The stratigraphy of komatiites, in general, has a crude resemblance to that of ophiolites. Also, some chemical characteristics, for example, high MgO, Ni and Cr, low TiO_2, low FeO/FeO MgO (Arndt et al., 1977) are shared by some rocks of the two igneous suites.

Komatiites are formed by very high degrees of partial melting of the mantle (Ringwood, 1975) probably up to 70% melting (Green, 1970).

Table 4-8

Comparison of Noble Metal Contents of TMC and Komatiites

Rock Type and Locality	No. of Samples	Noble Metal Contents in ppb				Pd/Ir	$Pt_{/Pt+Pd}$	Reference
		Au	Ir	Pt	Pd			
Australia								
Spinifex textured flow B, Mt. Clifford	9		2.68		9.1	3.40		Keays, 1980
Cumulate textured flow B, Mt. Clifford	5		1.88		7.1	3.78		Keays, 1980
Canada								
Average, spinifex textures, Munro Twp.	5	2.10	0.94	18.4	10.2	10.85	0.64	MacRae and Crocket, 1979
Average, cumulate textures, Munro Twp.	6	3.32	1.19	10.83	6.73	5.66	0.67	MacRae and Crocket, 1979
Weighted average for komatiite, Munro Twp.	11	2.8	1.08	14	8.3	7.69	0.62	
TMC, ultramafic cumulates	23, 26, 25, 26	0.92	3.63	25.7	27.1	7.46	0.49	This study

The ophiolites are more likely to be formed by a smaller degree of partial melting (see Coleman, 1977). Also, komatiite magma may have been equilibrated with a sulfide melt in the source region (Naldrett and Cabri, 1976). In contrast, it is quite unlikely that the Thetford Mines ophiolites have undergone such a process although the ophiolite magmas may contain some sulfur, as in Lac de l'Est (see Section 4.3).

It is therefore of interest to compare noble metal distribution in the komatiites and the ophiolites in view of their similarities in stratigraphy and chemistry and their differences in regards to their initial magmas.

Some noble metal values of komatiitic rocks from Canada and Australia are presented in Table 4-8 for comparison with Thetford Mines ophiolitic rocks. The average Au content for komatiites is about three times that of ophiolitic ultramafic cumulates. However, komatiites are lower in the PGE, perhaps due to equilibration of their metals with immiscible sulfides in the source region (Naldrett and Cabri, 1976). In such a case most of the PGE of the source region would partition into the sulfide melt leaving the komatiite magma impoverished in the PGE. On the other hand, the komatiite magma might have become saturated in sulfur after generation (Keays, 1979), in which case, later separation of sulfides from the melt could have scavenged the PGE from the magma.

An interesting aspect of the PGE abundances in the komatiites is their Pt/Pd ratios. The data on Munro Township rocks(MacRae and Crocket, 1979) show that Pt predominates over Pd. Their average Pt/Pd ratio of 1.7 is much higher than the average value of 0.95 for the ophiolitic ultramafic cumulates. As suggested for the Alakan-type rocks, the dominance of Pt over Pd in the komatiites is probably a reflection of the production of komatiitic melts by high degree of partial melting of the mantle.

4.5.5 Ultrabasic-Basic Layered Complexes

Some of the large ultrabasic-basic layered complexes which occur in the cratonic areas of the world, such as South Africa (Bushveld complex) and USA (Stillwater complex) have similar stratigraphy and internal structure as the cumulate section of the ophiolites. In both cases cumulate processes are the dominant mode of formation of rocks from a mafic magma. Comparison of noble metal contents in the two types of rock suites is therefore interesting with respect to assessing the importance of cumulate processes in controlling the distribution of the noble metals in rocks.

Noble metal contents in the Bushveld and Stillwater complexes (Table 4-9) are highly variable, with the chromite and sulfide horizons having economic Pt and Pd contents. By contrast, the chromite bearing horizons in the ophiolites are extremely low in Pt and Pd. It is not clear why this is so, but two factors may be responsible for the high platinum metals in the chromite horizon in layered complexes. One factor is the close association of sulfides with the chromites in the layered complexes. If sulfides are the main PGE carriers in the layered complexes,

Table 4-9

Comparison of Noble Metal contents of TMC and Layered Complexes

Rock Type and Locality	No. of Samples	Analytical Method	Noble Metal Contents in ppb						Reference
			Au	Ir	Pt	Pd	Pd/Ir	Pt$_{/Pt+Pd}$	
Layered Complex Mineralized									
Merensky Reef, Bushveld		II	310	74	3740	1530	20.7	0.71	Hiemstra, 1979
UG-2 Reef, Bushveld		II	50	50	3200	1960	39.2	0.62	Hiemstra, 1979
Banded Zone, Bushveld		II			3268	11438		0.22	Naldrett and Cabri, 1976
Non-mineralized									
Ultramafic zone, peridotite member, Stillwater Complex	27	II			26	49		0.34	Crocket, 1979
Ultramafic zone, bronzite member, Stillwater Complex	67	II			21	12		0.64	Crocket, 1979
Average ultramafic zone, Stillwater Complex					25	42		0.37	
Banded and upper gabbro zone, Stillwater Complex	27				5	11		0.31	Crocket, 1979

Table 4-9 (continued)

Rock Type and Locality	No. of Samples	Analytical Method	Noble Metal Contents in ppb						Reference
			Au	Ir	Pt	Pd	Pd/Ir	$Pt_{/Pt+Pd}$	
<u>Thetford Mines Complex (TMC)</u>									
Average ultramafic cumultes	23, 26, 25, 26	I	0.92	3.63	25.7	27.1	7.5	0.49	This study
Average cumulate gabbro	4	I	1.71	0.017	4.5	2.92	173	0.61	This study

I = Neutron activation analysis

II = Fire assay

then the high Pt and Pd in the chromite layer is easily explained. Another factor is that PGE minerals are also important PGE carriers in many cases - certainly in the Merensky Horizon of the Bushveld complex. This suggests that the magma becomes supersaturated with respect to PGE. The crystallization of chromite must have coincided with that of the PGE minerals. In Thetford Mines, the chromite layer forms very early in magma crystallization history - long before the magma can become saturated in the PGE. The high PGE level in the layered complexes is not attained in Thetford Mines ophiolites probably because of low PGE in the magma or different physico-chemical conditions of magma crystallization from those of the layered complexes.

In contrast to the chromite-rich layers, the chromite-poor sections of the ophiolites are comparable in noble metal contents to the non-minerallized sections of the layered complexes. For example, the average Pt and Pd contents in ophiolitic ultramafics are less than a factor of 2 lower than the corresponding averages for the ultramafic rocks in the Bushveld. Also, the Pt contents in the gabbroic rocks are similar in the two rock suites but the Pd values in Bushveld are almost three times those of the ophiolites.

Of more significance than the comparison of absolute PGE contents is the comparison of noble metal ratios. Both in the ophiolite and the layered complexes the Pt/Pd ratio is less than unity. The average Pt/Pd ratio of the unmineralized ultramafic zone in Stillwater complex is 0.60, not significantly different from the Pt/Pd ratio (0.95) of the ophiolitic cumulus ultramafic rocks. These ratios are significantly lower than the

Pt/Pd ratios in Alaskan-type rocks (average Pt/Pd = 1.7) and in the komatiites (average Pt/Pd = 1.7). Both the layered complexes and the ophiolites are derived from tholeiitic magmas which require moderate degrees of partial melting of the mantle. Their similar Pt/Pd ratios are compatible with the earlier suggestion that the Pt/Pd ratios of the rocks may reflect the degree of partial melting required for the generation of their parental magmas. It appears, however, from their lower Pt/Pd ratio, that the layered complexes are derived from a less mafic magma (smaller degree of partial melting) than the ophiolites.

Cousins and Vermaak (1976) indicated that in the Bushveld complex the Pt/(Pt + Pd) ratio increases stratigraphically upwards, although this view is considered controversial (Naldrett and Cabri, 1976). Superficially, the Pt/(Pt + Pd) ratio trend in the Thetford Mines ophiolites appears to be similar to that indicated for the layered by Cousins and Vermaak (1976) in that the ophiolitic dunites have a marginally lower ratio (0.58) than the overlying pyroxenite (average ratio = 0.59) which in turn has a lower average than the overlying gabbro (average ratio = 0.60). In detail, however, this trend is not consistent, probably as a result of continuously changing physico-chemical conditions of the crystallizing ophiolite magma.

4.5.6 Mantle Materials

Ultrabasic nodules such as garnet peridotite carried as xenoliths in kimberlites, and spinel lherzolite in some alkali basalts are

Table 4-10

Comparison of Noble Metal Contents of TMC and Upper Mantle Derived Materials

Material Source	No. of Samples	Analytical Method	Noble Metal Contents in ppb						Reference
			Au	Ir	Pt	Pd	Pd/Ir	$\mathrm{Pt}_{/\mathrm{Pt+Pd}}$	
Kimberlites, Yakutia, USSR	10	II		7.6	187	53	6.97	0.78	Crocket, 1979
Ultrabasic nodules in kimberlite, Yakutia, USSR	2	II		18	35	80	4.44	0.30	Crocket, 1979
Kimberlite (India, South Africa)	11	I	12	3.0		8.1	2.7		Paul *et al.*, 1977
Nodules in kimberlites (India, South Africa)	10	I	6.2	18		3.8	0.21		Paul *et al.*, 1977
Ultramafic nodules from alkali basalt (various localities)	6, 6, 3	I	0.5	3.5		<10.3	<2.95		Jagoultz *et al.*, 1979
Spinel lherzolite nodules (various localities)	13, 7, 13	I	0.7	3.4		4.6	1.36		Morgan and Wandless, 1979
Garnet lherzolite nodules (various localities)	4, 2, 4	I	1.2	6.8		5.1	0.75		Morgan and Wandless, 1979

Table 4-10 (Continued)

Material Source	No. of Samples	Analytical Method	Noble Metal Contents in ppb						Reference
			Au	Ir	Pt	Pd	Pd/Ir	$\mathrm{Pt}_{/\mathrm{Pt+Pd}}$	
Thetford Mines Complex									
Harzburgite	7	I	1.26	3.6	9.5	4.4	1.2	0.68	This study
Metamorphic dunite	4	I	0.27	3.6	2.4	0.3	0.01	0.88	This study

I = Neutron activation analysis

II = Fusion or acid decomposition - spectrophotometric interpreted as possible undepleted upper mantle materials (Ringwood, 1975; Jagoutz, 1979). The kimberlites and alkali basalts are also believed to be products of small degrees of partial melting of rocks similar to the nodules. On the other hand, the metamorphic peridotite of ophiolites may represent a residue of the mantle after extensive partial melting, in two or more stages (Ringwood, 1975; Coleman, 1977; Menzies, 1977). It is of interest, therefore, to compare the noble metal contents in the ultramafic nodules and the ophiolitic metamorphic peridotite from Thetford Mines in order to assess how 'primitive' the ophiolitic metamorphic peridotites actually are.

Data available on the kimberlites and nodules are presented in Table 4-10. The data from the Soviet Union are significantly higher than those from other localities. This raises some questions as to whether these high values are real, due to sample contamination (kimberlites and nodules are known to be contaminated by crustal materials, e.g. Ringwood, 1975; Paul et al., 1977) or whether they are due to analytical procedures.

However, in comparison to data from other localities the noble metal contents in ophiolitic harzburgites from Thetford Mines are more similar to those of the spinel lherzolite nodules than the other mantle materials. For example, compared with the garnet peridotite nodules, the harzburgite are strongly depleted in Ir although they have comparable Au and Pd contents.

The similarities in the noble metal contents and metal ratios such as Pd/Ir of the spinel lherzolite nodules and the ophiolitic harzburgite and the low Pd contents in the garnet peridotite nodules, strongly suggest that the ophiolitic harzburgite are not the residue of partial melting of a mantle source similar to these nodules; otherwise, the harzburgite would have been more depleted in Pd than the nodules. This may imply that these nodules are not as undepleted as previously thought. It is, however, possible that the harzburgite is derived from a more primitive source with respect to noble metals, than these nodules. On the other hand, the low Au and Pd contents of the metamorphic dunite are compatible with the interpretation of the dunites as a residue from extensive melting of a source similar to the nodules, especially the spinel lherzolite.

4.6 Summary

The main points about the distribution of noble metals in the Thetford Mines ophiolites are summarized as follows:

1) The noble metals do not seem to have preferential affinity for any of the ferromagnesian minerals such as olivine, orthopyroxene, and clinopyroxene. They are, however, fractionated into chromite. Of all the noble metals studied, Ir has the highest affinity for chromite.

2) In the harzburgite, the noble metals were probably incorporated into vacancies in the chromite lattice at a high temperature but were exsolved to grain boundaries during cooling or plastic deformation. In the cumulates the noble metals are probably in solid solution in the minerals.

3) The different rock types of the ophiolites are characterized by different noble metal abundances which may be genetic. Noble metal contents in the dunites and pyroxenites also vary according to geographic locations. This geographic variation in noble metal abundances may be due to: i) magmatic differentiation, ii) sulfide inclusions or sulfur saturation of parental magma, iii) different source magmas, iv) variable amounts of postcumulus material in rocks, v) post-igneous remobilization, or vi) a combination of any of the above.

4) Comparison of average noble metal contents in the different rock types indicates that Au is uniformly distributed through the ophiolite but the PGE are fractionated. Ir is concentrated in the olivine-chromite cumulate or chromite-rich dunite, which may represent the oldest or first formed cumulate while Pt and Pd are concentrated in the later formed dunite and pyroxenite, respectively.

5) Differences in the noble metal contents and metal ratios between ophiolites and other suites such as Alaskan-type complexes, komatiites and layered complexes may be attributed to the different degrees of partial melting involved in the generation of the respective parental magma.

6) The ophiolitic harzburgite closely resembles spinel lherzolite nodules in its noble metal contents and metal ratios, indicating that the harzburgite is primitive or is derived from a very primitive source.

CHAPTER FIVE

GEOCHEMICAL BEHAVIOR OF NOBLE METALS IN THETFORD MINES COMPLEX

The various rock types of the Thetford Mines ophiolite suite were formed by igneous processes of which the most important is fractional crystallization. Some of the lavas were probably formed by varying degrees of partial melting (e.g. Sun and Nesbitt, 1978) of mantle source rocks. Although it was suggested in Chapter Four that magmatic differentiation was a possible factor in the fractionation of the noble metals, the extent to which fractional crystallization as a type of magmatic differentiation controls the distribution of the noble metals in the rocks, is not yet known. There is also the possiblity that secondary processes such as hydrothermal activity and serpentinization have modified the distribution of these noble metals. It is, therefore, necessary to evaluate the relative roles of both igneous and secondary processes in controlling the distribution of noble metals. Such as exercise is useful in the modelling of metal ore genesis.

5.1 Behavior of Noble Metals during Igneous Processes

5.1.1 Geochemical Background

The noble metals are predominantly siderophiles and chalcophiles with little lithophile tendency. Theoretically, they should be rejected by silicate minerals. However, their detection in rocks indicates that at least some of the noble metals in magmas have been incorporated into rocks. Whether such incorporation is by sulfide mineral inclusion, metal alloys or by ionic substitution of noble metals for other elements in silicate mineral lattices is a matter of considerable uncertainty. Many workers, e.g. Keays (1968), Chyi (1968), Vincent and Crocket (1960), Mantei and Brownlow (1967),have suggested that the noble metals, particularly Au, exist predominantly as uncharged atoms or metal alloys in rocks. However, some authors report strong correlations between noble metals, including Au, and the more abundant elements in minerals, for example, Ir with Cr and V (Razin et al., 1965), Ir with Ni (Agiorgitis and Becker, 1978), Pt and Pd with Ni (O. Ye Yushko-Zakharova et al., 1967),Pt and Pd with Fe, V, Ni and Cr (Clark and Greenwood, 1972), Au with Mg and Cr (Keays and Scott, 1976). These correlations indicate some limited substitution of elements by the noble metals in rock-forming minerals. If ionic substitution has played a major part in the distribution of the noble metals in rocks, then one should expect the noble metals to display regular or systematic variation in their abundances with differentiation in differentiated rock series.

It is pertinent at this stage to summarize the geochemical parameters which might influence the distribution of the noble metals in rocks if they substitute for other elements in the crystallizing magma. These parameters are listed in Tables 5-1 to 5-3.

Table 5-1

Electronic Configuration and Oxidation States of Pd, Ir, Pt and Au

	At. No.	Elect. Configuration	Oxidation States		
Pd	46	$4d^{10}5s^{0}$	+4	II, IV	
Ir	77	$5d^{7}6s^{2}$	+6	III, IV	+3 = highest oxidation state
Pt	78	$5d^{9}6s^{1}$	+6	II, IV	II = most common oxidation state
Au	79	$5d^{10}6s^{1}$	+3	I, III	

Source: Larsen, 1965

Table 5-2

Metallic, Covalent and Ionic Radii of Pd, Ir, Pt and Au

	Metallic radius (A°)	Covalent radius (A°)	Co-ord No. 6 Ionic Radius (A°)
Pd	1.37	IV, 1.31 (Oct)	II, 0.80 IV, 0.65
Ir	1.36	III, 1.32 (Oct)	IV, 0.68
Pt	1.39	IV, 1.31 (Oct)	II, 0.80 IV, 0.65
Au	1.44	I, 1.50 (Tet)	I, 1.37 III, 0.85

Sources: Larsen, 1965; Mason, 1966

Table 5-3

Ionization Potential, Electronegativity and Electrode Potential of Pd, Ir, Pt and Au

	Inonization Potential				Electro-negativity	Standard Electrode Potential E°(volts)	
	I	II	III	IV			
Pd	8.33	19.42	32.92	(49)	2.4	$Pd \rightleftharpoons Pd^{++} + 2e^-$	0.92
Ir	9.1	-	-		2.2	$Ir \rightleftharpoons Ir^{++} + 2e^-$	1.1
						$Ir \rightleftharpoons Ir^{+++} + 3e^-$	1.15
Pt	8.96	18.56	(29)	(41)	2.2	$Pt \rightleftharpoons Pt^{++} + 2e^-$	1.2
						$Au \rightleftharpoons Au^{+++} + 3e^-$	1.50
Au	9.22	20.05	(30)	(44)	2.4	$Au \rightleftharpoons Au^{+} + 1e^-$	1.68

Sources: Ahrens, 1953; Larsen, 1965; Krauskopf, 1979

Ionic Size and Charge. On the basis of Goldschmidt's rules on trace element distribution (Goldschmidt, 1937), the platinum metals, Ir, Pt and Pd, could theoretically substitute for elements whose ionic radii are within 15% of the ionic radii of the PGE (Table 5-2). Such elements include Fe, Ni, Co, Mn, Zr and Cu (divalent state) which may be substituted by Pt and Pd in the divalent state, and Cr, Fe, Co (trivalent state) and Ti (tetravalent state) which may be replaced by Pt and Ir in the tetravalent state. Au (monovalent state) may also substitute for Ag, Cu and K (monovalent state). Of these elements, only Fe, Ti and K occur as major elements in rock-forming minerals. Cr may also concentrate as chromitite. The other elements are essentially trace elements which, with the exception of Ni and Co, occur in late forming minerals.

Whether the noble metals substitute for these elements depends on factors such as ionization potential, oxidation potential, electronegativity (bonding energy factors) and crystal field stabilization energy.

Bonding Factors. Radius and charge have been demonstrated not to be the dominant factors in the substitution of certain trace elements for major elements. Ahrens (1953) and Ringwood (1955) have proposed that ionization potential and electronegativity of elements may be important since both parameters influence the type of bond formed by elements. Whether the noble metals will enter a silicate phase in a magma depends on whether they can form strong bonds with

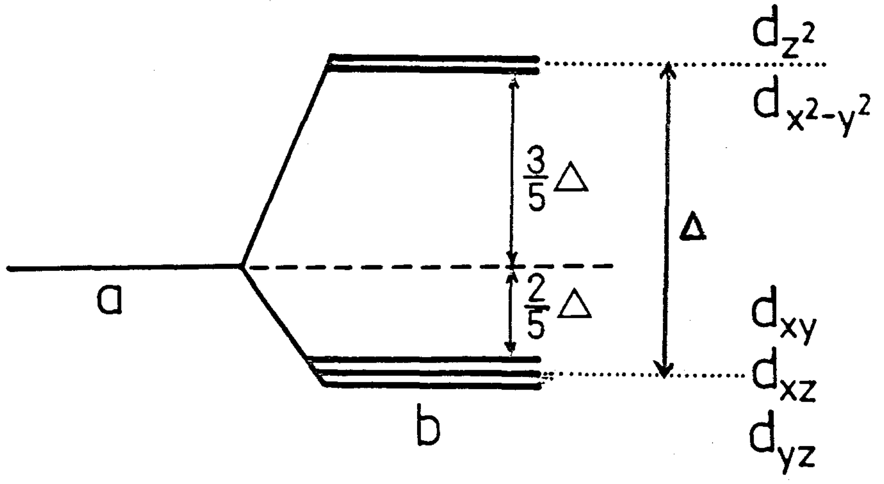
O^{2-} in the magma. Ionization potential is a measure of the power of a cation to attract anions. Cations with low ionization potential form ionic bonds while those with high ionization potential tend to deform the anions with which they combine. Because of their high ionization potential, the noble metals' anions, e.g. Pd^{+2}, Pt^{+2} and Au will deform the O_2^- of a magma to such an extent that only weak or unstable bonds will be formed. Thus on the basis of their high ionization potentials, the noble metals will not be expected to enter the silicate lattice appreciably. If they do, the order of entry will be Pt, Pd, Ir and Au.

The electronegativity of a cation is defined as its tendency to form covalent bonds. Cations with large electronegativity values will have greater tendencies to form covalent bonds. Ringwood (1955) stated that if two ions can occupy the same position in a crystal lattice, the one with the lower electromegativity will be preferentially incorporated because it will form stronger and more ionic bonds than the other. Thus Pt^{+2} will be preferentially taken in the crystal lattice relative to Pd^{+2}. In comparison with both Fe^{+2} (electronegativity 1.65) or Cr^{+3} (electronegativity 1.6) the noble metals will be rejected from the silicate structure, that is, on the basis of electronegativity, the noble metals will not substitute for the elements they would otherwise replace on the basis of ionic size and charge.

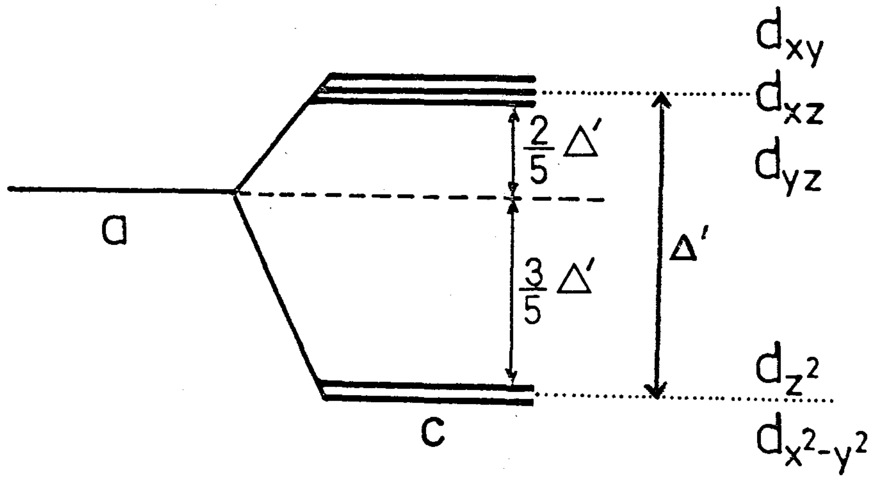
Crystal Field Stabilization Energy. On the basis of their high ionization potentials and electronegativity values, the noble metals will be rejected from the silicate structure. If they are incorporated due to their favorable sizes and charges, they will concentrate in the late formed minerals except Ir which may be incorporated in early formed chromite. It has, however, been shown that these parameters do not always control the distribution of trace elements in rocks. The distribution of transition elements, in particular, has been difficult to interpret on the basis of parameters such as ionic size, ionization potential, electronegativity, etc. However, the crystal field theory has been successfully applied to the study of the distribution of transition elements such as Ni, Co, Cu, V, etc. (Curtis, 1964; Burns, 1964; Burns and Fyfe, 1967).

The crystal field theory, developed by Orgel (1952) and later introduced into Geochemistry by Williams (1959), Dunitz and Orgel (1957) and Burns (1964), could be summarized as follows: in rock forming minerals, ions occur in specific coordination sites (octahedral and tetrahedral for oxides and ferromagnesian minerals). Transition elements are characterized by five d orbitals. In a coordination site, the energy of the five d orbitals are split into two energy groups: a doublet (in octahedral field)or triplet (in tetrahedral field) of higher energy than the unresolved d orbitals, and a second triplet (in octahedral) or doublet (in tetrahedral) of lower energy than the unresolved d orbitals (Figure 5-1). The total energy difference between a situation in which the d electrons of a system have been resolved and that in which the d electrons of a system are unresolved is known

Figure 5-1. Energy splitting of d electron orbitals in octahedral and tetrahedral fields. Δ and Δ' (crystal stabilization energy) are the differences in the energies of the two orbital sub-groups in octahedral and tetrahedral fields respectively.



a = free ion, b = ion in octahedral field



a = free ion, c = ion in tetrahedral field as the crystal field stabilization energy (Δ). An ion will enter either the octahedral site or the tetrahedral site depending on which site has the higher crystal field stabilization energy. Put in other words, when two ions compete for a site, the ion which has a higher preferred crystal field stabilization energy will occupy the site first.

The theoretical crystal field stabilization energies of the common noble metal ions in octahedral (Δ) and tetrahedral (Δ') fields are listed in Table 5-4. Although the absolute crystal field stabilization energies are not known, qualitative prediction about which ion will preferentially enter the coordination sites can be made.

In a magma ions could either partition into the octahedral sites in the crystallizing mineral or into the tetrahedral sites of the

Table 5-4

Crystal Field Stabilization Energy for Noble Metals

Ion	No. of d electrons	Octahedral stabilization energy (Δ)	Tetrahedral stabilization energy (Δ' = 4/9Δ)	Octahedral preference energy (Δ - Δ')
Pd^{+2}	8	6/5	4/5	38/45
Pd^{+4}	6	2/5	3/5	6/45
Ir^{+3}	6	2/5	3/5	6/45
Ir^{+4}	5	0	0	0
Pt^{+2}	8	6/5	4/5	38/45
Pt^{+4}	6	2/5	3/5	6/45
Au^{+1}	10	0	0	0
Au^{+3}	9	3/5	2/5	19/45

magma. It can be seen from Table 5-4 that ions like Pd^{+4}, Pt^{+4}, Ir^{+3}, Ir^{+4} and Au^{+1} have low octahedral preference energy. That is, these ions will not have any tendency to enter the octahedral sites. Consequently they will be rejected by the silicate mineral octahedral sites. Pd^{+2}, Pt^{+2} and Au^{+3}, however, have high octahedral preference energy. These ions, particularly Pd^{+2} and Pt^{+2}, will preferentially enter the octahedral sites in silicate lattice. However, since these ions have 8 or 9 electrons, i.e. unfilled d orbital, they are prone to distortion in the octahedral site. Such distortion will result in a negative octahedral field stabilization energy. In addition, with 8 or 9 d electrons, these ions will have a greater tendency to form square planar complexes than octahedral complexes (Larsen, 1965). In other words, they will not enter the octahedral sites of the silicates and consequently will remain in the magma.

In summary, from theoretical points of view, the noble metals should not enter the silicate structure extensively. They may, however, be concentrated in residual magmas where they may form minerals with sulfur, arsenic, tellurium or alloys with one another. From electronegativity and crystal field considerations, the order of abundance of the noble metals in early formed minerals is Pt > Pd > Ir > Au.

5.1.2 Geochemical Behavior of the Noble Metals during Fractional Crystallization

The geochemical behavior of the noble metals during fractional crystallization is best evaluated by comparing variations in their concentration with variations in the abundance of an element which is known to vary with fractional crystallization. One may also compare noble metal concentration with stratigraphic position. However, due to crosscutting of rock types and lack of stratigraphic continuity in the cumulate section it is not possible to correctly determine the relative stratigraphic position of the cumulate rocks in the Thetford Mines ophiolites.

Major element oxides have been variously used as indicies of fractional crystallization. Such oxides include SiO_2 (Harker, 1909), MgO (Wright and Fiske, 1971) and $MgO/(MgO + FeO^T)$ (Wager and Deer, 1939). However, it is believed that the formation of chromite in the early part of magma crystallization history in Thetford Mines cumulate rocks has considerably altered the normal SiO_2, FeO^T and MgO trends, at least in the dunitic rocks (see Section 3.2). Of the trace elements, Ni values decrease while Co values increase with increases in fractional crystallization, i.e., the ratio of Ni/Co decreases with fractional crystallization. This has been well demonstrated for the Skaergaard intrusion by Wager and Brown (1968).

Therefore, to evaluate the behavior of the noble metals during fractional crystallization, the concentration of the noble metals in the cumulate rocks are plotted against Ni/Co ratios as in Figure 5-2. In the following text, the assumption is made that all the cumulate rocks are formed by fractional crystallization of a common parental magma. It is, however, possible that the parental magma was being replenished during crystallization, in view of the overlapping of the Ni/Co ratios of the youngest dunites and the oldest pyroxenites on the one hand and the youngest pyroxenites and the oldest cumulate gabbros on the other.

Gold. The variation of Au as a function of Ni/Co is shown in Figure 5-2a. The Au content in the crystallizing solids remains constant at about 0.25 ppb for most of the early stages of magma fractionation, but towards the end of crystallization of dunitic rocks, begins to increase. Variation in Au contents becomes irregular when pyroxenites begin to crystallize in the middle part of magma crystallization. The abrupt increase in Au content at the top of the gabbro layer suggests a possible enrichment of Au in the late fraction of the magma.

The uniform Au content in the early-formed rocks suggests that the crystal-liquid partitioning of Au is near unity and remains constant. The early rocks consist predominantly of olivine with varying proportions of chromite. The uniform Au contents in these rocks over a long period of magma crystallization indicates that the partitioning of Au into chromite and olivine is similar. The slight increase in Au contents of the late dunites may be viewed in terms of effect of an increase in intercumulus material in the rocks coupled with a slight decrease in crystal-liquid partition coefficient of Au as the magma became less basic.

The irregular behavior of Au in the middle and later parts of of the cooling history of the magma (late pyroxenite and gabbro zone) cannot be interpreted in terms of fractional crystallization alone. Three explanations are suggested for the observed irregular distribution of Au:

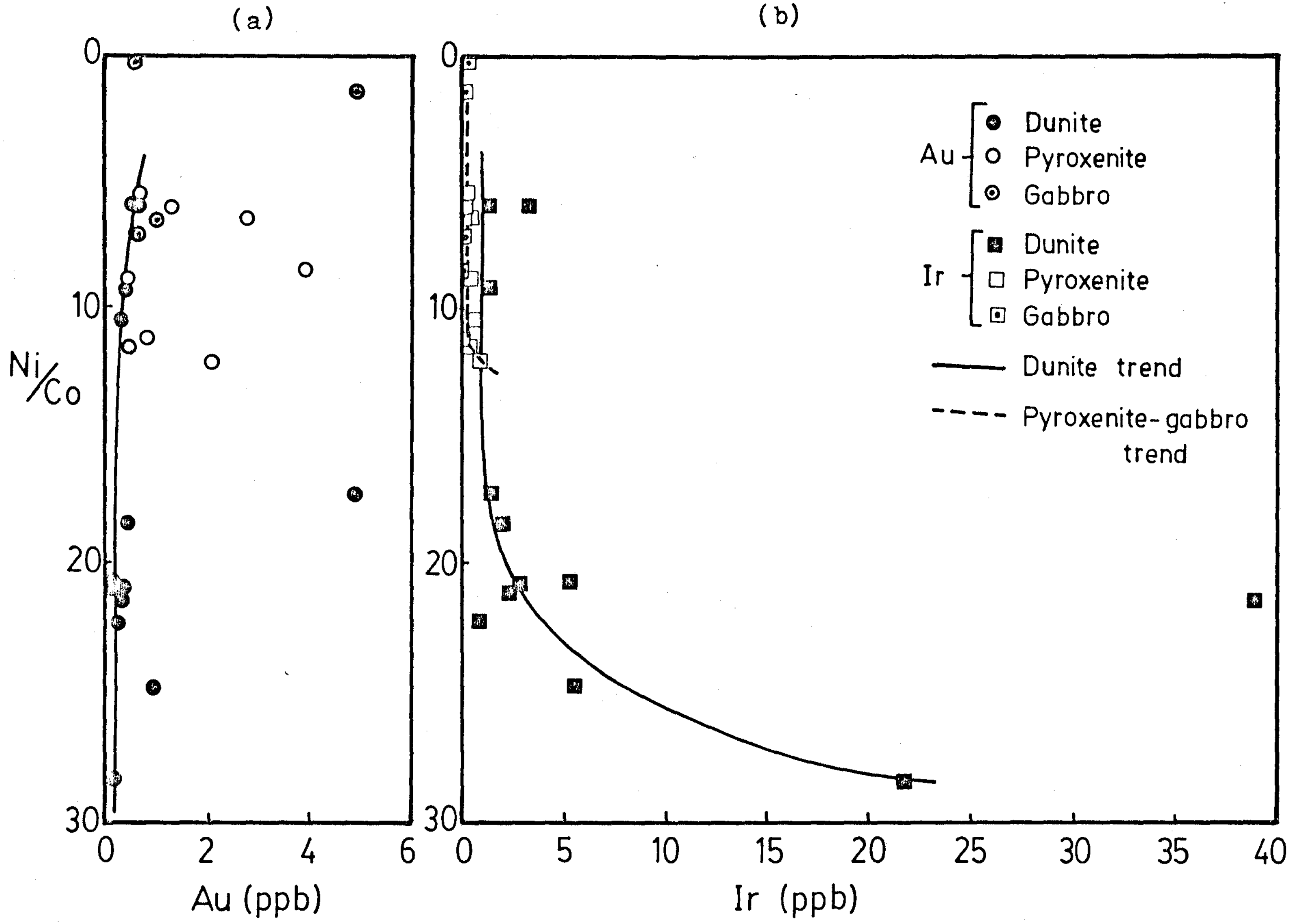
1) Irregular occurrence of a Au bearing phase: During the middle part of magma cooling history, a phase, probably a sulfide, which concentrates Au may start to crystallize. If this phase occurs sporadically in the crystallized rocks, then Au values in the rocks will follow no trend and tend to be irregular as observed.

2) Varying amounts of postcumulus material: If Au is concentrated in residual magma, then the Au content of a rock will be essentially controlled by the amount of residual magma trapped in the rock as postcumulus material. Different amounts of postcumulus material in the pyroxenites and gabbros may, therefore, be responsible for the irregular distribution of Au in these rocks.

3) Post-igneous mobilization of Au: If Au is mobilized by post-igneous activities, then different degrees of mobilization of Au in the rocks may produce irregular distribution of Au in the rocks.

It is difficult to say which of these three possibilities is most likely. However, in view of the non-uniform distribution of sulfur, and different cumulate textures in the pyroxenites and gabbros, the first and second explanations are probably more important than the last.

Figure 5-2. Variation in Ni/Co against Au and Ir concentrations in cumulate rocks of TMC.


(a)
(b)
Ni/Co
0
10
20
30
0
2
4
6
Au (ppb)
0
10
20
30
0
5
10
15
20
25
30
35
40
Ir (ppb)
Au
● Dunite
○ Pyroxenite
⊙ Gabbro
Ir
■ Dunite
□ Pyroxenite
⊡ Gabbro
Dunite trend
Pyroxenite-gabbro trend

Iridium. Figure 5-2b shows the variation of Ir with fractional crystallization. The highest concentrations of Ir occur in the most primitive rocks, that is, rocks with the highest Ni/Co ratios. Ir concentration tends to fall off very rapidly during the course of magma crystallization such that by the time pyroxenites begin to form the concentration of Ir in the rocks has decreased by about a factor of 48. During these early stages of magma crystallization, the amount of Ir appears to correlate with the amount of chromite in the rocks which suggests that chromite may be the host for Ir. Decreases in Ir values continue with differentiation during the crystallization of the pyroxenites and gabbro but rather slowly. Before the end of crystallization, Ir has almost been entirely removed from the magma.

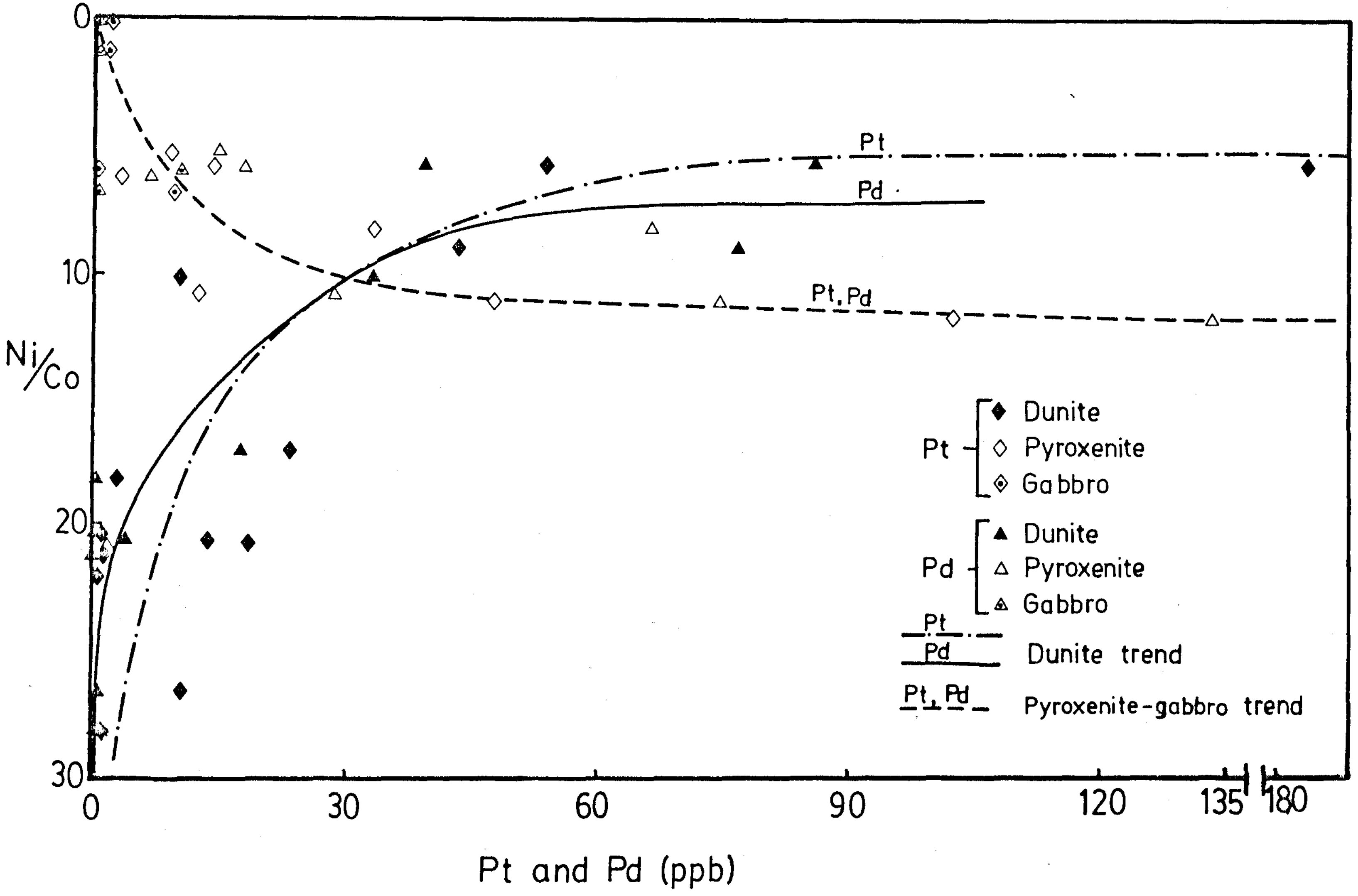
The initial rapid depletion of Ir attests to the general idea that Ir is residual and has a high crystal-liquid partition coefficient. However, the less rapid depletion of Ir from the magma during pyroxenite-gabbro crystallization, that is when no significant amounts of chromite or olivine is crystallizing, suggests that the high crystal-liquid partition coefficient of Ir is only applicable to chromite and probably olivine. Ir will probably remain in the magma if chromite or olivine is not crystallizing.

Platinum and Palladium. Pt and Pd behave coherently during the course of crystallization. As can be seen from Figure 5-3 the geochemical behavior of both Pt and Pd is almost the reverse of Ir. During the early stages of magma crystallization Pt and Pd contents are low in the rocks, that is, they are preferentially partitioned into the residual liquid. However, it appears that Pt partitions more strongly into the solid than Pd as the Pt content shows a greater increase in rocks than Pd as crystallization progresses. Towards the beginning of the middle part of the crystallization history (that is during the crystallization of the youngest dunites), Pt and Pd contents in rocks increase rather drastically. This increase in Pt and Pd contents appear to peak in the latest dunites and the earliest pyroxenites. Thereafter, Pt and Pd contents decrease rather slowly at first and then rapidly towards the end of pyroxenite formation and the beginning of crystallization of the gabbros.

The rapid increase in Pt and Pd in the late dunites probably signals the appearance of a major Pt and Pd bearing phase in the rocks. Removal of such a phase from the magma is marked by a rapid decrease in the Pt and Pd contents in the late pyroxenites and the gabbros. It is observed that the late dunites have higher sulfur contents than other rocks. It is, therefore, possible that the Pt-Pd bearing phase is a sulfide. However, some of the pyroxenites that have high Pt and Pd contents do not have significantly high sulfur contents. Perhaps in addition to a sulfide phase, the noble metals occur as alloys, native metals or as complexes with elements such as Bi, Te, As and Sb. Unfortunately, the abundance of these elements were not determined.

The geochemical behavior of Pt and Pd is, therefore, that of gradual concentration in the residual magma fraction until such a time that they are incorporated into a non-silicate phase.

Figure 5-3. Variation in Ni/Co against Pt and Pd concentrations in cumulate rocks of TMC.



0
10
20
30
Ni/Co
0
30
60
90
120
135
180
Pt and Pd (ppb)
Pt
Pd
Pt, Pd
Pt ♦ Dunite
◇ Pyroxenite
◈ Gabbro
Pd ▲ Dunite
△ Pyroxenite
⟁ Gabbro
Pt
Pd
Dunite trend
Pt, Pd
Pyroxenite-gabbro trend

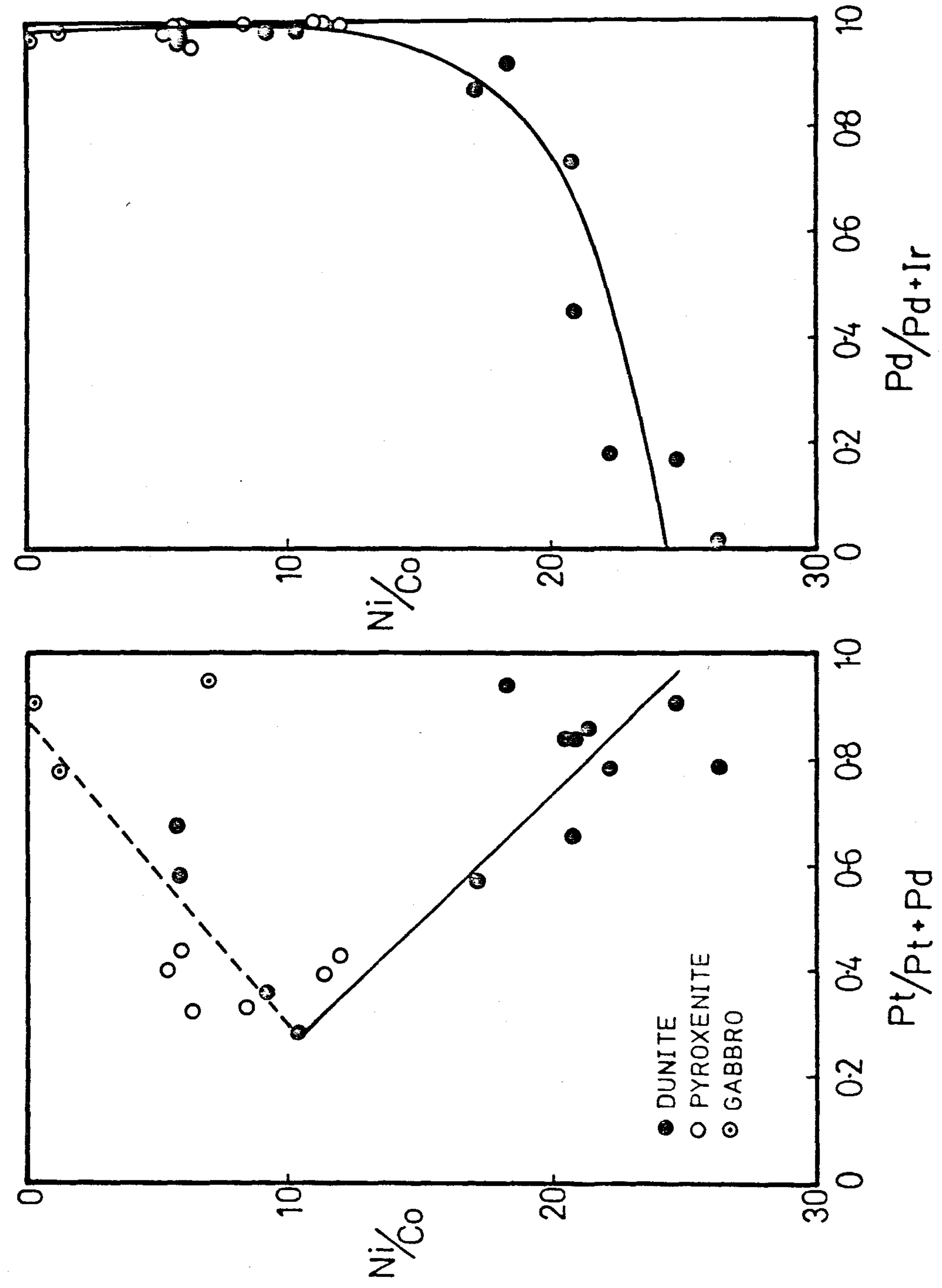
5.1.3 Use of Noble Metal Ratios as Indicies of Magmatic Differentiation

Various workers have suggested that certain noble metal ratios vary with magmatic differentiation. For example, Yushko-Zakharova et al. (1967), Naldrett and Cabri (1976) indicate that Pd/Pt ratios increase while Pt/(Pt + Pd) ratios decrease with differentiation. The data of Ross and Keays (1979) show an increase in Pt/(Pt + Pd) with differentiation for komatiites. Other metal ratios believed to increase with differentiation of basic magma include Pt/(Pt + Ir + Os) (Cabri and Harris, 1975), Pt/(Pt + Ir + Pd + Au), Pd/(Pt + Ir + Pd + Au) (Gijbels et al. (1976), Pt/Σ noble metal, Pd/Σ noble metal (Page et al., 1976).

From the variation of the noble metals with differentiation in Thetford Mines as shown in Figures 5-2 and 5-3, it is suggested that the following metal ratios will increase with increasing differentiation: Pt/(Pt + Pd + Ir), Pd/(Pt + Pd + Ir), Pt/(Pt + Ir), Pd/(Pd + Ir), Pt/Ir, Pd/Ir. The ratios Pt/Pd and Pt/(Pt + Pd) are more difficult to predict because of the coherence of Pt and Pd.

In Figure 5-4a Pt/Pt + Pd ratios are plotted against Ni/Co as an index of magmatic differentiation. Two separate and opposite trends are indicated by the data. In the less differentiated rocks which generally include the earlier cumulate, the Pt/Pt + Pd ratio decreases with increasing degree of magmatic differentiation (decreasing Ni/Co ratios). There is then a reversal of slope with later cumulates being characterized by increasing Pt/Pt + Pd with increasing fractionation.

Figure 5-4. Variation in Ni/Co against Pt/Pt + Pd and Pd/Pd + Ir in cumulate rocks of TMC.


Ni/Co
0
10
20
30
Pd/Pd+Ir
0
0·2
0·4
0·6
0·8
1·0
(b)
Ni/Co
0
10
20
30
Pt/Pt+Pd
0
0·2
0·4
0·6
0·8
1·0
(a)
● DUNITE
○ PYROXENITE
⊙ GABBRO

The trend with the negative slope includes the dunites from Lac du Caribou, Lac Rond and Petit Lac St. François. The abrupt change in slope coincides with an increase in absolute concentrations of Pt and Pd in the rocks and the formation of the dunites at Lac de l'Est. The dunites at Lac de l'Est are believed to be the youngest of the dunites in Thetford Mines ophiolite complex.

As discussed earlier (Section 5.1.2), the dunites at Lac de l'Est have higher sulfur contents than other rocks which probably account for their higher Pt and Pd contents. It was also suggested that these dunites and some of the pyroxenites might contain, in addition to sulfide phases, some other Pt-Pd bearing phases such as metal alloys, complexes of other elements or native metals. It appears, therefore, that the change from the trend with negative slope to that of positive slope also marks the beginning of the crystallization of sulfides and possibly other Pt-Pd bearing phases during magmatic differentiation.

As the formation of the dunites at Lac du Caribou, Lac Rond and Petit Lac St. Francois involved fractional crystallization of olivine and chromite only, the trend of decrease in Pt/Pt + Pd ratios with decreasing Ni/Co ratios or increasing magmatic differentiation, implies that Pt partitions more strongly into olivine and chromite, and probably into silicates and oxides in general than Pd. As the abrupt reversal in the trend of Pt/Pt + Pd ratio coincides with an increase in sulfur contents in the rocks, it is logical to conclude that the reversal in trend of Pt/Pt + Pd ratio during magmatic differentiation is a result of the crystallization of sulfide or some non-silicate phases and that the increase in the Pt/Pt + Pd ratio during the formation of these rocks is due to a tendency for Pd to partition into sulfide phases more readily than Pt.

The variation of the Pt/Pt + Pd ratio in the Thetford Mines ophiolites may be compared with those of other rock suites. The data of Ross and Keays (1979) suggest that Pt/Pt + Pd ratios increase with differentiation in komatiites. Cousins and Vermaak (1976) also suggest that the Pt/Pt + Pd ratio in the Bushveld complex increases stratigraphically upwards, although the data of von Gruenewalt (1976) are inconsistent with the suggestion of Cousins and Vermaak (1976). An increase in Pt/Pt + Pd ratio with increasing differentiation is also implied from the data of Page et al. (1972, 1976) for the Stillwater complex, and from the data of Page et al. (1980) for the Fiskenaesset complex, Greenland. These suggested trends of increase in the Pt/Pt + Pd ratio with differentiation are similar to the trend in the cumulate rocks of Lac de l'Est where the concentrations of Pt and Pd in the rocks are believed to be controlled by sulfide crystallization. These trends are at variance with the hypothesis of Naldrett and Cabri (1976) that the Pt/Pt + Pd ratio should decrease with differentiation of the host rocks of ores derived from theoleiitic magmas. Naldrett and Carbri's (1976) hypothesis is, however, consistent with the observed trend of decreasing Pt/Pt + Pd ratios with differentiation in the early formed cumulate rocks (dunites at Lac Caribou, Lac Rond and Petit Lac St. Francois) of the Thetford Mines complex where the concentrations of

Pt and Pd in rocks are believed to be controlled by silicate and oxide crystallization.

The trend of Pd/Pd + Ir (Figure 5-4b) is that of an increase in the ratio with increasing differentiation. The increase, however, is exponential in that the ratio initially increases gradually and then rapidly before levelling off.

Because of the rapid depletion of Ir from a crystallizing magma, noble metal ratios involving Ir, such as Pd/Ir, Pd/Pd + Ir, etc., may not be suitable as a sensitive index of fractionation. For example, it is difficult to distinguish between rocks formed during the middle part of the crystallization of the magma at Thetford Mines (pyroxenites) and the later rocks (gabbro) on the basis of Pd/Ir or Pd/Pd + Ir. Similarly, the use of ratios like Pt/Pd, Pd/Pt + Pd or Pt/Pt + Pd may be limited severely if the crystallizing magma is saturated with sulfur.

5.1.4 Correlation of Noble Metals with Other Elements

The correlation matrix for each rock type was calculated using a computer program written by Mr. A. Kabir of the Department of Geology, McMaster University and the data are presented in Table 5-5 for the elements which show significant correlation (significant at 95% level) with the noble metals.

Gold. In general Au does not show any consistent correlation with any element and where positive correlation is established, it is with elements of large ionic radius wuch as Na, K and Cu. This may suggest some ionic substitution of these metals by Au, but it may also reflect the tendency of these metals, like Au, to be partitioned into the residual fraction of a differentiating magma. In the type II lavas, Au correlates positively with Cr, Ni and MgO. This might imply partitioning of Au into early formed phase like olivine as suggested for a similar observation on the MAR basalt by Keays and Scott (1976). However, as Au is considerably larger than Ni, Mg or Cr it is doubtful if the correlation is due to any ionic substitution.

The lack of correlation between Au and the PGE in almost every rock type of the Thetford Mines ophiolites (except the upper lavas) is expected as Au has different geochemical characteristics from the PGE, particularly the tendency of Au not to partition into the solid phase during magmatic crystallization (see Section 5.1.2). The strong positive correlation of Au with Ir in the upper lavas is, however, surprising. This may, however, be explained if it is considered that no fractionation of Ir from Au has occurred in these lavas. In that case the Au and Ir contents of the upper lavas are probably similar to the noble metals concentrations in the lavas' parental magmas. This suggestion can only hold if the upper lavas are related by partial melting rather than fractional crystallization, as fractional would have fractionated Ir from Au. In the alternative, the correlation of Au with Ir in the upper lavas may suggest a common host for the two noble metals in these lavas.

Table 5-5

Correlation Matrix for Noble Metals and Other Element in TMC (Coefficient of Correlation Significant at 95% Confidence Limit)

Rock type		Au	Ir	Pt	Pd	SiO_2	Al_2O_3	FeO^T	MgO	CaO	Na_2O	K_2O	MnO	S	Cr	Ni	Co	Zr
Harzburgite	Au																	
N = 7	Ir										-0.75	-0.87						
	Pt																	
	Pd					0.88	0.73			0.77	-0.71			0.94		-0.89		
Cumulate dunite	Au																	
N = 7	Ir														0.63			
	Pt				0.80			0.73					0.72			-0.69	0.69	0.89
	Pd			0.80			0.66	0.69				0.85	0.71	0.78		-0.80	0.64	0.78
Pyroxenite	Au																	
N = 14	Ir			0.63														
	Pt		0.63		0.95													
	Pd			0.95														
Cumulate gabbro	Au										-0.85							
N = 4	Ir			0.99					0.89						0.99	0.84		
	Pt											0.97						
	Pd		0.99				-0.88		0.82									

Table 5-5 (Continued)

Rock type		Au	Ir	Pt	Pd	SiO_2	Al_2O_3	FeO^T	MgO	CaO	Na_2O	K_2O	MnO	S	Cr	Ni	Co	Zn
Type I lava	Au															0.80		
N = 11	Ir														0.91			
	Pt																	
	Pd							0.69										
Type II lava	Au														0.93			
	Ir				-0.75						-0.84				0.73^7	0.63		
	Pt																	
	Pd		-0.75			-0.64												
Upper lava	Au		0.82					-0.65					-0.64				-0.65	
N = 8	Ir	0.82													0.87^7	0.76^7		
	Pt																	
	Pd						-0.75		0.66	-0.64								

N = Number of samples

n^7 = Number of samples used in calculations

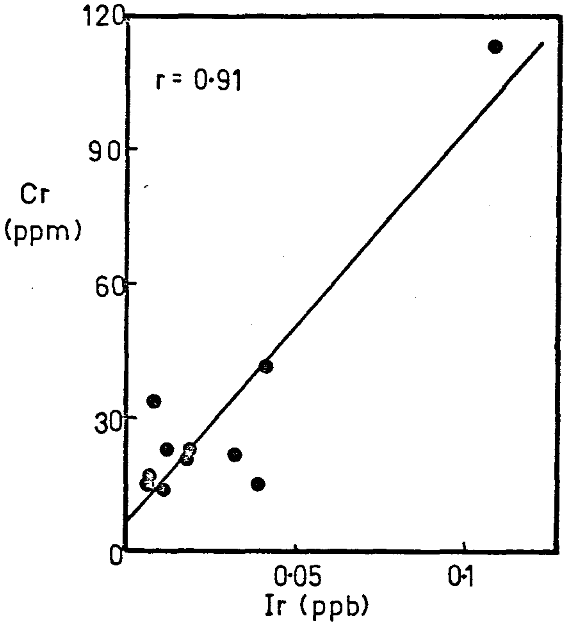
Iridium. Iridium consistently shows a negative or weak positive correlation with the incompatible elements such as Y, Zr, Zn and Cu while in some rocks it shows strong positive correlation with Ni and Cr. In some of the lavas, where there appears to be no Ir-Cr, Ir-Ni correlation, plots of Ir against Ni and Cr (Figure 5-5) indicate that one or two samples may be anomalous due to possible enrichment or loss in Ni and Cr by secondary processes. Omission of these anomalous samples shows that Ir correlates significantly with both Ni and Cr in the lavas. However, in the case of the type I lavas the correlation of Ir with Cr is highly dependent on the sample with high Ir and high Cr. The non-correlation of Ir with the incompatible elements and its correlation with Ni and Cr further affirms the residual nature of Ir. The simultaneous correlation of Ir with Ni and Cr in the lavas may suggest that Ir is hosted by olivine. However, the negative correlation of Ir with MgO in all cases argues against such a suggestion.

Except of the upper lavas (already discussed) Ir does not correlate with Au. There is no systematic pattern of Ir correlation with the other PGE, Pt and Pd. In the pyroxenites Ir correlates positively with Pt. There is also a strong positive Ir-Pd correlation in the cumulate gabbro while in the type II lavas Ir correlates negatively and rather strongly with Pd. In the other rock types Ir either correlates very weakly or shows no correlation with the other PGE (Pt and Pd). The negative Ir-Pd correlation in the type II lavas and the lack of any significant correlation between Ir and the other PGE

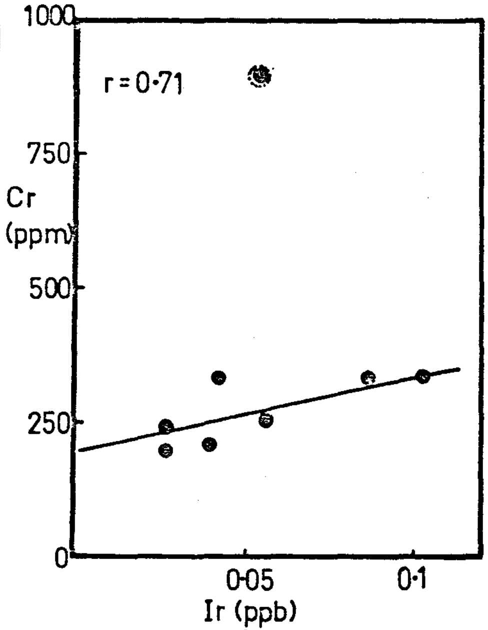
Figure 5-5. Correlation of Cr and Ni with Ir in volcanic rocks of TMC.

(a) Cr vs Ir (type I lava); (b) Cr vs Ir (type II lava;

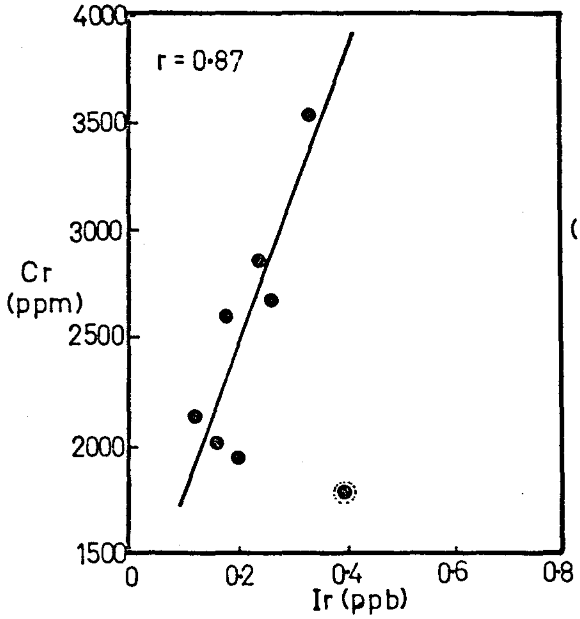
(c) Cr vs Ir (upper lava); (d) Ni vs Ir (upper lava)


r = 0·91
Cr (ppm)
120
90
60
30
0
0·05
0·1
Ir (ppb)

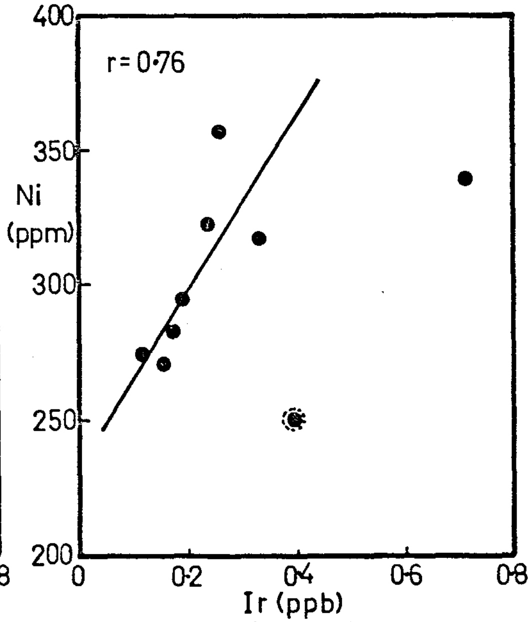
(a)


r = 0·71
Cr (ppm)
1000
750
500
250
0
0·05
0·1
Ir (ppb)

(b)


r = 0·87
Cr (ppm)
4000
3500
3000
2500
2000
1500
0
0·2
0·4
0·6
0·8
Ir (ppb)

(c)


r = 0·76
Ni (ppm)
400
350
300
250
200
0
0·2
0·4
0·6
0·8
Ir (ppb)

(d)

are consistent with the idea that Ir is readily fractionated from the other PGE during magmatic differentiation. The positive Ir-Pt correlation in the pyroxenites and strong positive Ir-Pd correlation in the cumulate gabbro suggest that Ir and Pt, and Ir and Pd are probably hosted by the same phase in the pyroxenites and cumulate gabbro respectively.

Platinum and Palladium. Neither Pt nor Pd show any consistent correlation with other elements. However, with the exception of the cumulate gabbro, Pd correlates strongly and negatively with Ni. This is noteworthy because in sulfide ores and assocated rocks, Pd usually correlates positively with Ni via a Pd-Ni-S association. The negative correlation of Pd and Ni in the Thetford Mines ophiolites strongly suggests that in sulfur poor rocks, Pd and Ni are hosted by different phases and have disimilar geochemical behavior.

It is not clear whether the positive correlation of Pt and Pd with FeO, MnO, Co and Zn in the cumulate dunites indicates some substitution of Pt and Pd for Fe, Mn, Co and Zn since these correlations are not observed in any other rock type. It is, however, possible that the physico-chemical conditions of the crystallizing magma during the formation of the cumulate dunites were more conducive to substitution of these elements by Pt and Pd than during the formation of the other rock types.

Pt correlates strongly and positively with Pd in the ultramafic rocks, particularly in the cumulate dunites and pyroxenites, due to the similarity in the geochemical behavior of Pt and Pd during fractional crystallization.

5.2 Behavior of Noble Metals during Secondary Processes

During post-igneous processes such as metamorphism and weathering, rocks are chemically broken down and then reconstituted. The fate of an element in the altered rock during the initial breakdown depends on many factors including the siting of the element in the rock and its solubility in the medium effecting the rock alteration.

For metals such as Cu and Zn which are soluble or have sufficiently soluble compounds, their transportation and eventual deposition in suitable places may concentrate them as mineral deposits. The genesis of most mineral deposits, particularly those where there is easy access to transporting media either aqueous or gaseous is modelled on the basis of such secondary redistribution of metals. While the redistribution of the base metals by secondary processes is well known, the role of secondary processes in concentrating the noble metals, with the possible exception of Au, is still poorly known.

It is generally believed that the noble metals, at least in the native form, are not significantly affected by secondary processes. This is because of their chemical inertness in the laboratory. Placer deposits of some of the noble metals in almost pure metal form further support the idea that the noble metals are insoluble in aqueous solution.

However, slight supergene enrichment of some noble metals, particularly gold, and lack of residual noble metal deposits are indicative of some chemical transportation of the noble metals during secondary processes. Because of the high oxidation potential of noble metals in general, it is believed that rather than forming simple ions, the noble metals will be transported mostly as suspended small particles (Razin and Razhkov, 1963, 1966) or as chloride and sulfide complexes (e.g. Hummel, 1957; Krauskopf, 1955; Helgeson and Garrels, 1968; Barnes and Czamaraske, 1967; Weissenburg, 1970; Crocket, 1974).

If the noble metals are transported as complexes then their solubility during secondary processes will depend mainly on: 1) the nature of the aqueous medium involved in the secondary process, and 2) the stability of the complex ions in such medium. Bonding in complex ions is mainly covalent and therefore the noble metal with the greatest ability to form covalent bonds will most readily form complex ions. Gold has the highest electronegativity, oxidation potential and largest size and may be expected to form complex ions more readily than the other noble metals.

5.2.1 Serpentinization in the Thetford Mines Complex

The important factor which determines whether elements are lost or not from serpentinized rocks is the mode of the serpentinization process. Serpentinization takes place under both constant volume (Thayer, 1966; Condie and Madison, 1969; Springer, 1974; Ashley, 1975) and constant chemical composition conditions (Coleman and Keith, 1971; Bogolepov, 1969; Page, 1967, Wicks, 1969). An open system in which elements are exchanged between the altered rocks and the serpentinizing fluid can only occur under constant volume condition.

In Thetford Mines, Kacira (1972), Laurent (1975), Laurent and Hebert (1979) have indicated that the dominant mode of serpentinization is by variable composition (constant volume) with a possible loss of MgO or a gain of SiO_2. Fe and Ni are also believed to have been slightly lost. However, the fracturing of some chromites and olivines in the serpentinized rocks also suggests that serpentinization also involves some minor volume changes.

Two episodes of serpentinization are recognized in the Thetford Mines complex (see Section 2.4.1). According to Laurent and Hebert (1979) the first stage occurred in an oceanic environment and involved the hydration of olivine and orthopyroxene in the ultramafic to lizardite, magnetite and awaruite in a reducing environment

$$\text{olivine} + \text{enstatite} + H_2O \rightarrow \text{lizardite} + \text{magnetite} + \text{awaruite} + H_2O$$

The harzburgite rocks were only slightly altered but the cumulate dunites were pervasively altered. During this episode Si, Al, Fe, Ca and Mg were believed to have been removed from the rocks and water added. The second episode occurred on the continent during or after the tectonic emplacement of the ophiolites. This involved initial fracturing of the ultramafic rocks, followed by replacement of the earlier formed lizardite and also olivine by chrysotile in oxidizing environment

$$\text{lizardite} + H_2O + O_2 \rightarrow \text{clinochrysotile} + \text{magnetite} + \text{brucite} +$$

excess SiO_2 (removed).

In the second episode, the cumulate dunites were feebly affected because they were plastic during emplacement on the continent due to earlier serpentinization. The harzburgite, on the other hand, were extensively serpentinized since they were brittle and fractured more easily during their tectonic emplacement. Asbestos fibres were developed in fractures during this second episode.

The presence of talc and carbonate minerals in some of the serpentinized rocks indicate that the rocks have also undergone some talc carbonate alteration after serpentinization by CO_2 metasomatism.

Index of Degree of Serpentinization. The effect of serpentinization on the distribution of an element is best evaluated by comparing the abundance of the element in serpentinized and fresh rocks. This is not possible in the Thetford Mines rocks since fresh rocks are very rare. However, an evaluation can still be made by comparing element abundances with the degree of serpentinization. Serpentinization is a hydrous process which for the dunites may be written as below according to Coleman (1977):

$$2Mg_2SiO_4 + 3H_2O \rightarrow Mg_3Si_2O_5\,(OH)_4 + Mg\,(OH)_2 \qquad (1)$$

constant composition

$$2Mg_2SiO_4 + 2H_2O \rightarrow Mg_3Si_2O_5\,(OH)_4 + MgO \qquad (2)$$

constant volume

$$3Mg_2SiO_4 + 4H_2O + SiO_2 \rightarrow 2Mg_3Si_2O_5\,(OH)_4 \qquad (3)$$

constant volume

and for harzburgite as

$$Mg_2Si_2O_4 + MgSiO_2 + H_2O \rightarrow Mg_3Si_2O_5\ (OH)_4 \qquad (4)$$

The above equations suggest that the water content of a serpentinized rock could be used as an index of serpentinization, as serpentinization depends on the addition of water to rocks. However, petrographic observation of the serpentinized rocks in the Thetford Mines ophiolites indicate that the degree of serpentinization (abundance of serpentine minerals) does not correspond to the amount of water or total volatiles in the rocks. This is probably due to the later talc carbonate alteration of the serpentinized rocks during which water was lost

$$2\ \text{serpentine} + 3CO_2 \rightarrow \text{talc} + 3\ \text{magnesite} + \underset{\text{(removed)}}{3H_2O}$$

In the harzburgite, the degree of serpentinization could be evaluated by estimating the volume percentage of the primary minerals that have been replaced by serpentine minerals from thin section study. In the dunites, all the minerals have totally been replaced by serpentine minerals such that all the samples can be classified as greater than 95% serpentinized. However, following the work of Prichard (1979), different stages in the serpentinization process can be recognized in the olivine of the altered rocks. These stages are used in this study as indicies of serpentinization in the dunites. The stages are as follows:

(1) Unserpentinized olivine (fresh rock) Figure 5-6A

(2) 1st stage of serpentinization: olivine is cut by incipient serpentine veins but olivine outline is preserved. Figure

5-6B, Plate 5-1

(3) 2nd stage: serpentine veins (lizardite) in olivine widen but olivine outline remains preserved. Some olivine cores are also preserved. Figure 5-6C, Plate 5-2

(4) 3rd stage: olivine cores are fractured and partly filled with serpentine. Mineral outline may still be preserved. Figure 5-6D, Plate 5-3

(5) 4th stage: olivine cores are completely replaced by serpentine (lizardite). Figure 5-6E, Plate 5-4

(6) 5th stage: chrysotile veins develop in rocks. Figure 5-6F, Plate 5-5

(7) 6th stage: lizardite is replaced by antigorite starting from the core of the altered mineral. Figure 5-6G, Plate 5-6

(8) Final stage of serpentinization: complete replacement of lizardite by antigorite. Figure 5-6H, Plate 5-7. Segmented chrysotile fibres may be heavily lined with magnetite at this stage.

The last two stages probably occurred in response to increases in temperature during prograde metamorphism and may not be related to the main serpentinization phase. The stages described above only relate to the first serpentinization episode. The second episode involved only dissolution, solution and transportation of materials into rock fractures.

Figure 5-6. Stages of serpentinization of olivine in ultramafic rocks of TMC. (The various stages are described in the text.)

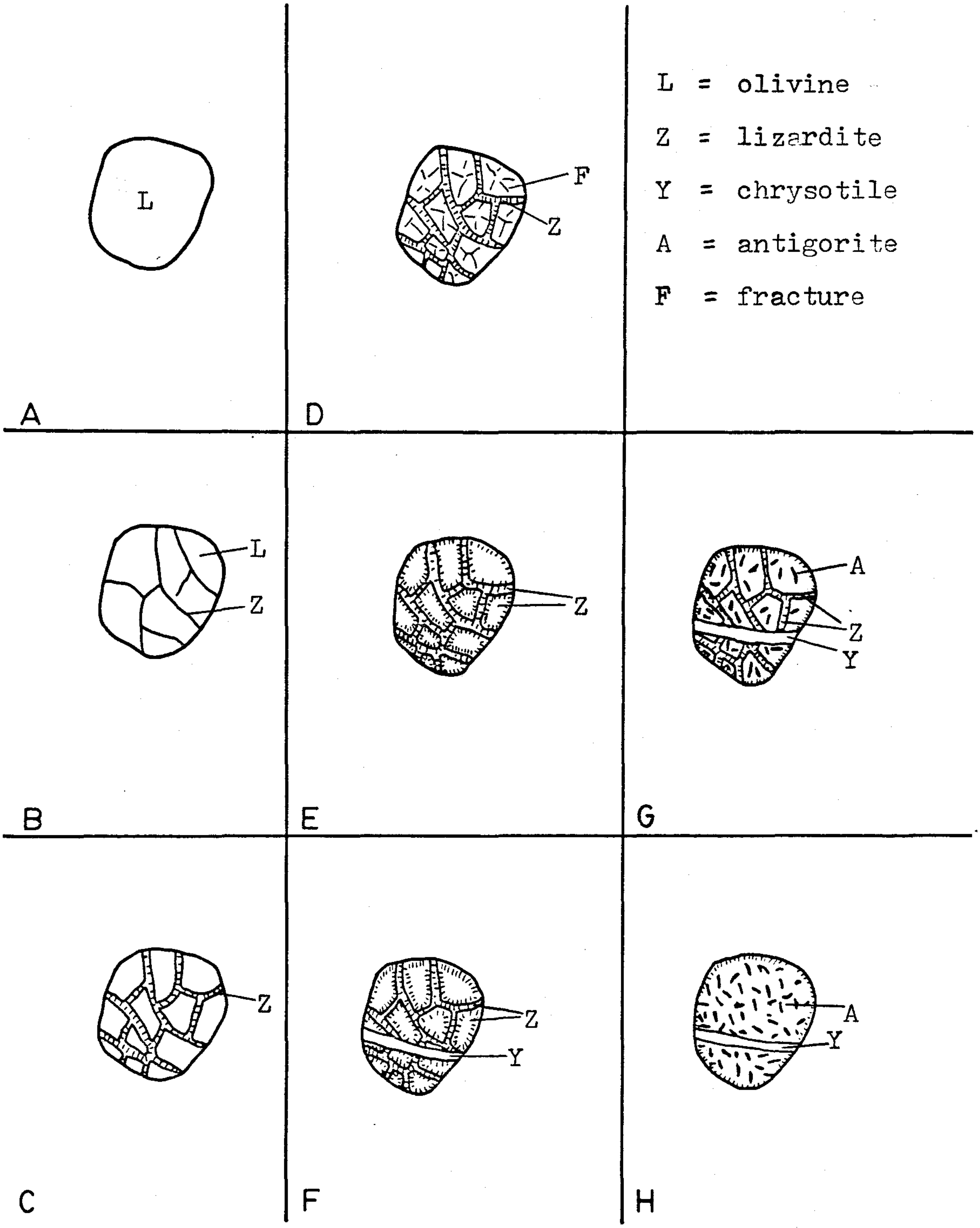

L = olivine
Z = lizardite
Y = chrysotile
A = antigorite
F = fracture
A
L
D
F
Z
B
L
Z
E
Z
G
A
Z
Y
C
Z
F
Z
Y
H
A
Y

Plate 5-1. First stage of serpentinization. Development of serpentine veins.

Crossed nicols x 63

Sample 9PH3A

Plate 5-2. Second stage of serpentinization. Widening of serpentine (lizardite, Z) veins. Olivine (L) preserved in cores of serpentine network.

Crossed nicols x 63

Sample MPH2A

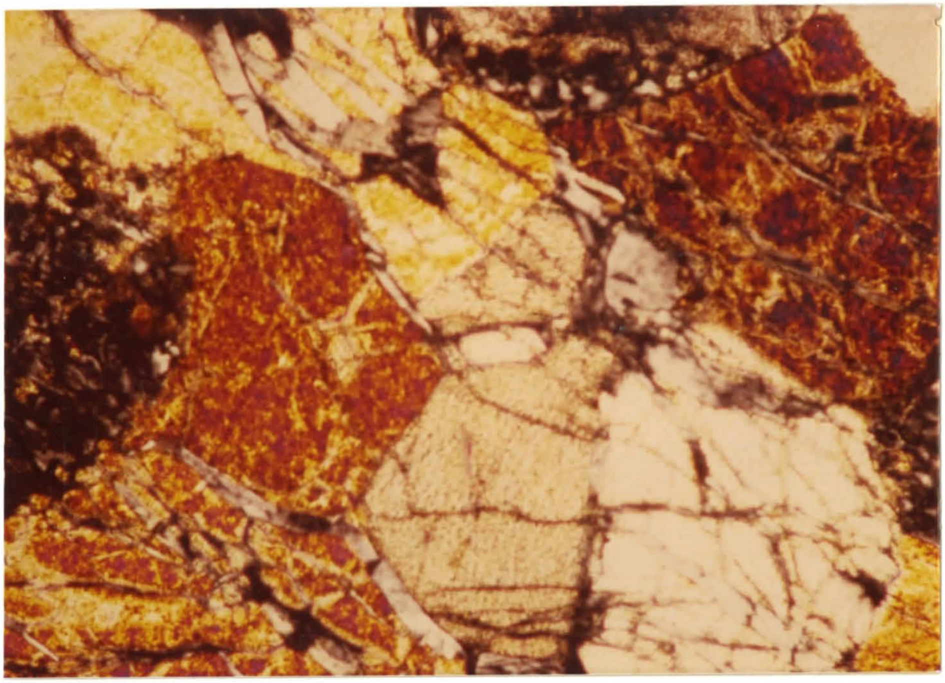


Plate 5-1

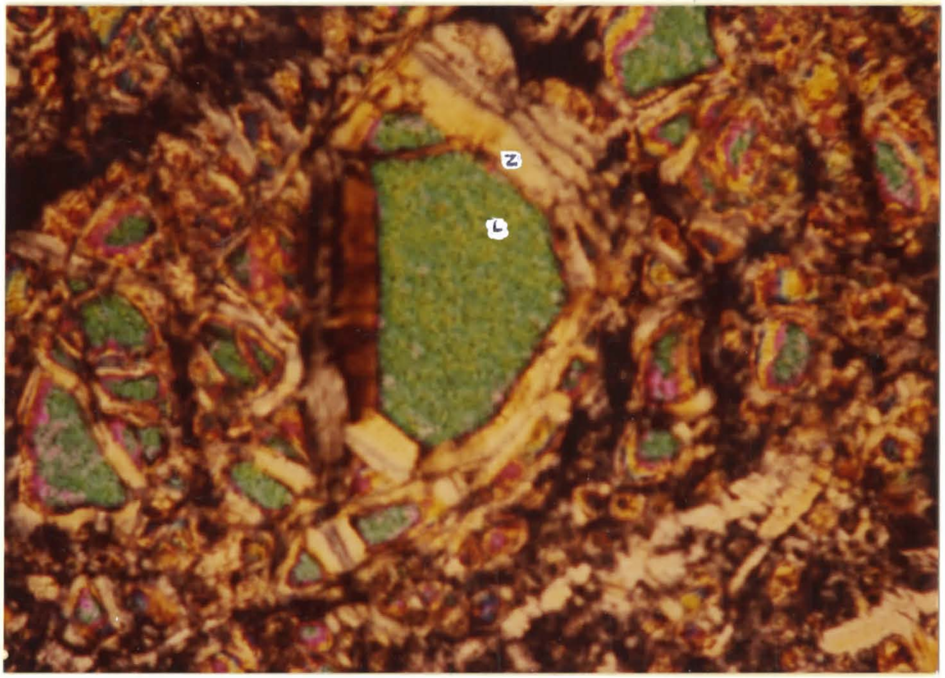


Plate 5-2

Plate 5-3. Third stage of serpentinization. Fracturing of olivine cores.

Crossed nicols x 63

Sample 9DH3F

Plate 5-4. Fourth stage of serpentinization. Complete replacement of olivine by serpentine (lizardite).

Crossed nicols x 63

Sample CCD3C

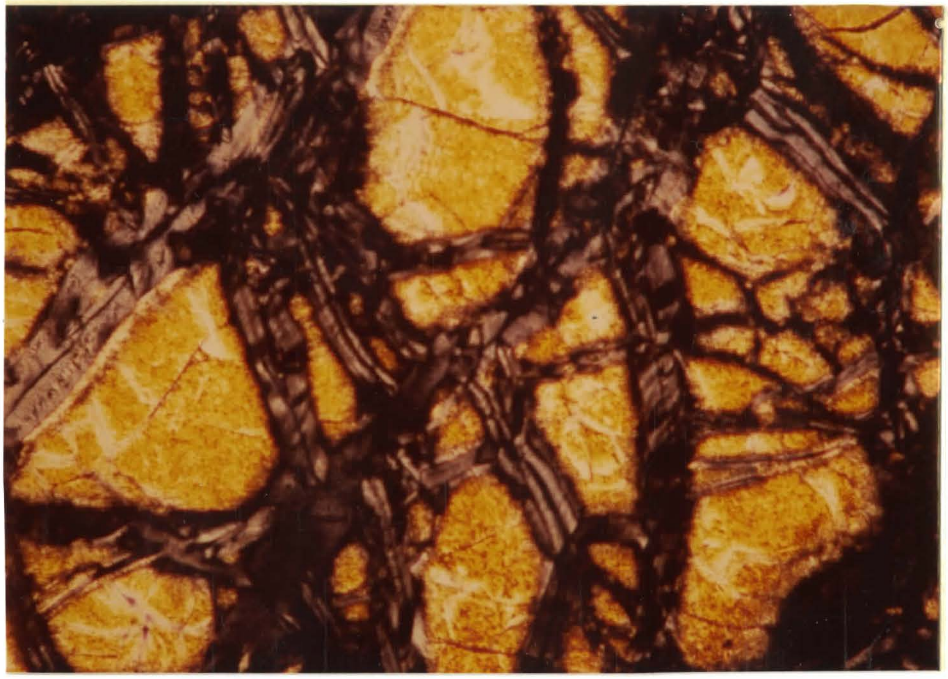


Plate 5-3

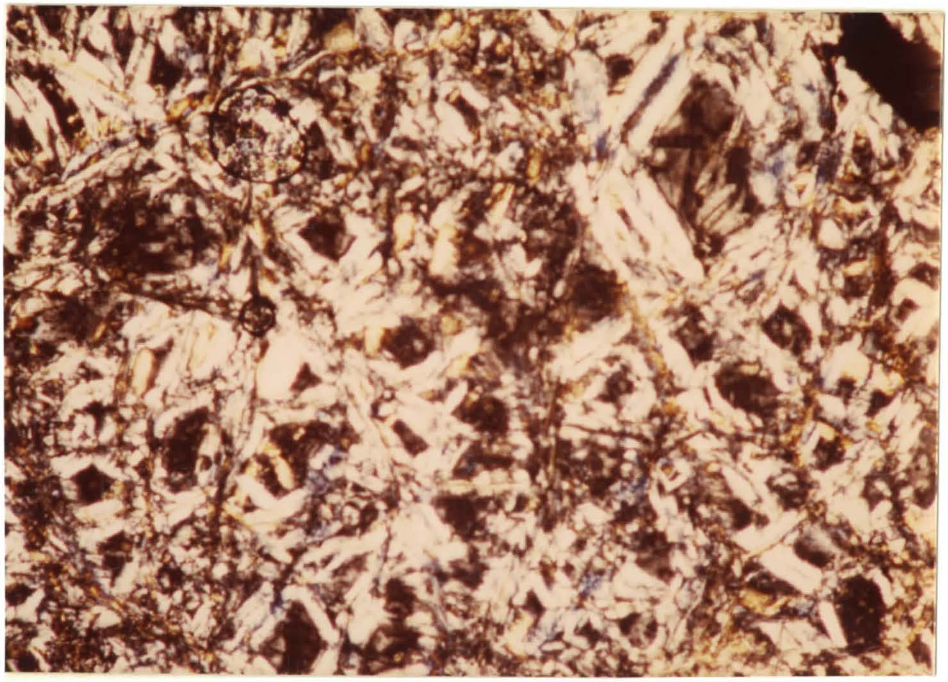


Plate 5-4

Plate 5-5. Fifth stage of serpentinization. Formation of fibrous serpentine mineral (chrysotile, Y).

Crossed nicols x 63

Sample 9CD7B

Plate 5-6. Sixth stage of serpentinization. Replacement of lizardite (Z) at core of altered olivine by antigorite (A).

Crossed nicols x 63

Sample 9CD7A

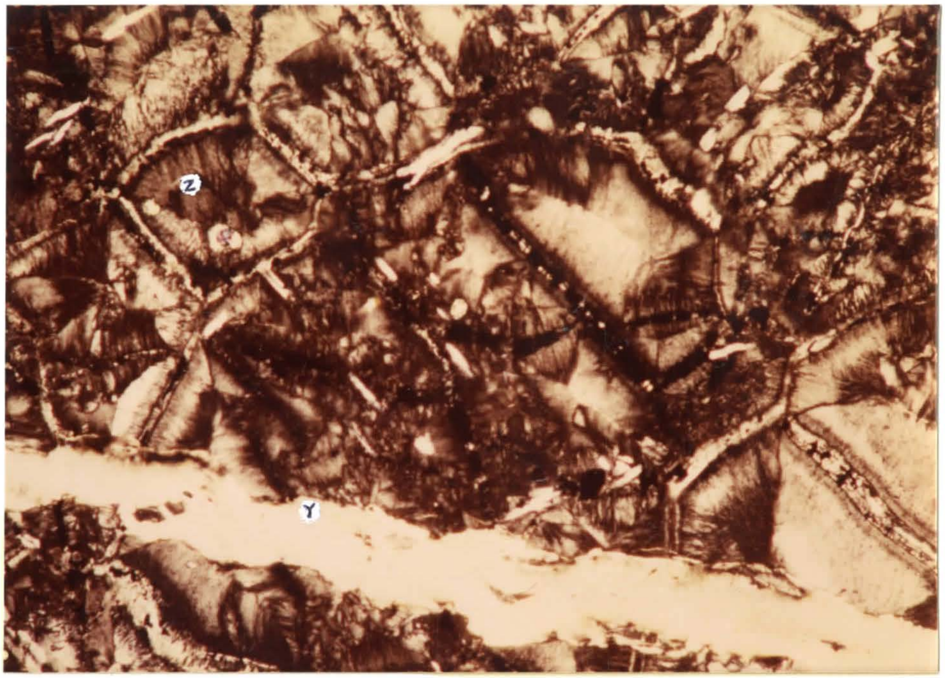


Plate 5-5

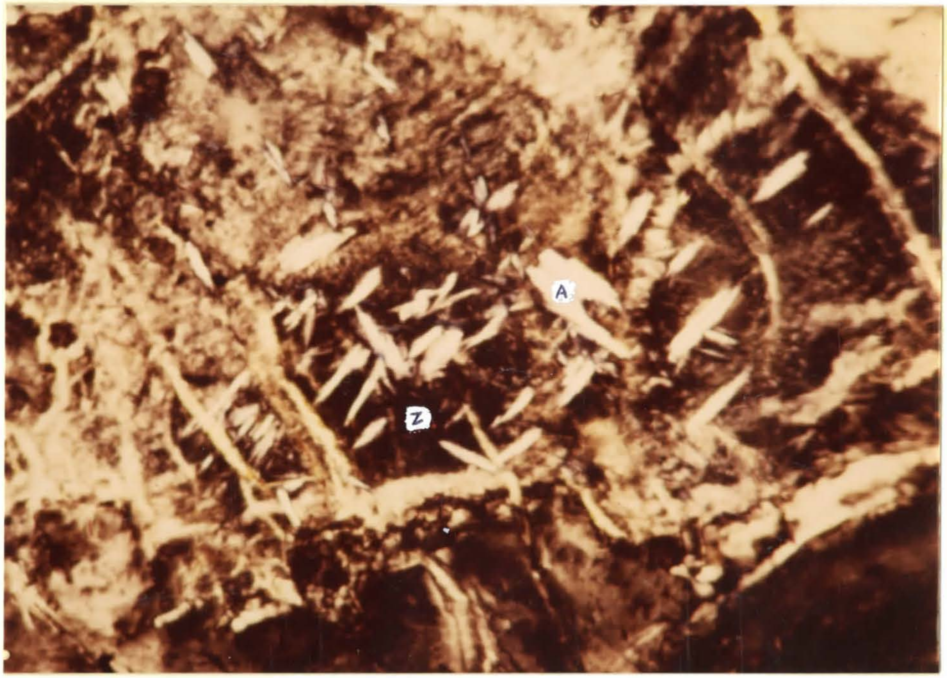


Plate 5-6

Plate 5-7. Final stage of serpentinization. Complete replacement of lizardite by antigorite.

Crossed nicols x 63

Sample 9CD6D

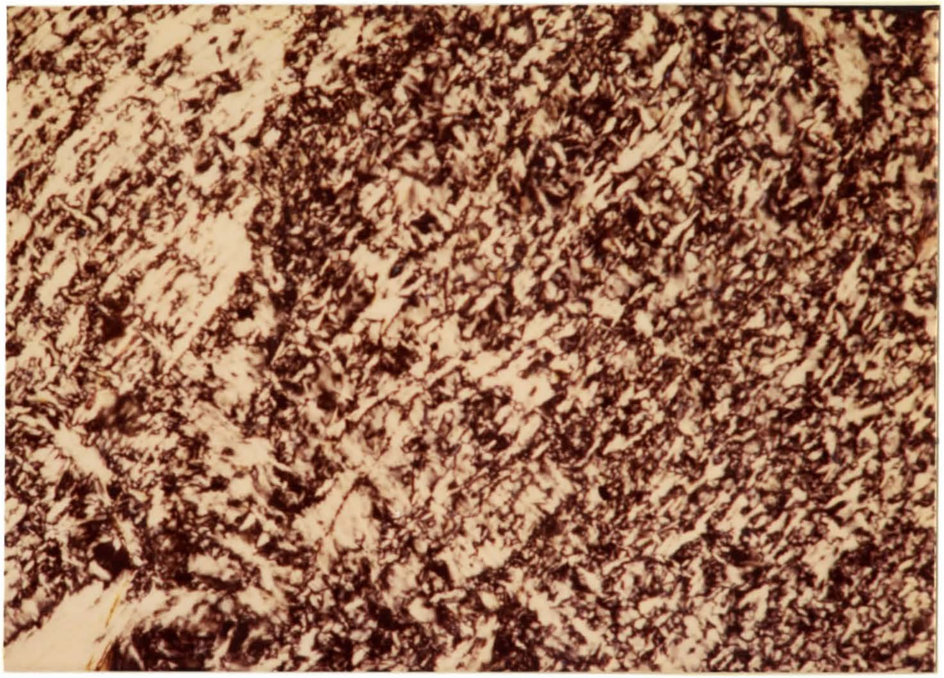


Plate 5-7

5.2.2 Behavior of the Noble Metals during Serpentinization of Thetford Mines Ophiolites

The geochemical behavior of various noble metals during serpentinization has been studied by some workers. Chyi (1968) reported that in the Mt. Albert Pluton, Ir and Os are not sensitive to the leaching effect of serpentinization, but Au and Pd are readily carried in solution. Keays and Davidson (1976) and Ross and Keays (1979) are also of the opinion that Au but not Pd is mobilized during serpentinization and talc carbonization of ultramafic rocks associated with Ni-sulfide ores in Western Australia. Razin et al. (1965) indicated that some Pt metals are lost during the serpentinization of the Inaglinish Massif, USSR. The data of Crocket (1974) (Table 78-E-1) also show that serpentinization may enrich rocks in the platinum metals. For example, the highly serpentinized rocks of Munchberg gneiss, Oberfranken, Germany, has 300 ppb Pd, 85 ppb Pt, as compared to their weakly serpentinized counterpart with only 12 ppb Pd and 26 ppb Pt.

The concentration of the noble metals in the serpentinized rocks of Thetford Mines ophiolites are plotted against 1) degrees of serpentinization, and 2) the CO_2 contents of the rocks. The plot against CO_2 is designed to evaluate the effect of talc carbonate alteration on the noble metals. Regression lines have been drawn through the data points and the coefficients of correlation between the noble metals and degrees of alteration calculated (Figures 5-7,

Figure 5-7. Correlation of noble metals with CO_2 in serpentinized ultramafic rocks of TMC.

r = coefficient of correlation in harzburgite

r_a = coefficient of correlation in cumulate dunite

r_b = coefficient of correlation in cumulate dunite excluding the chromite-rich samples

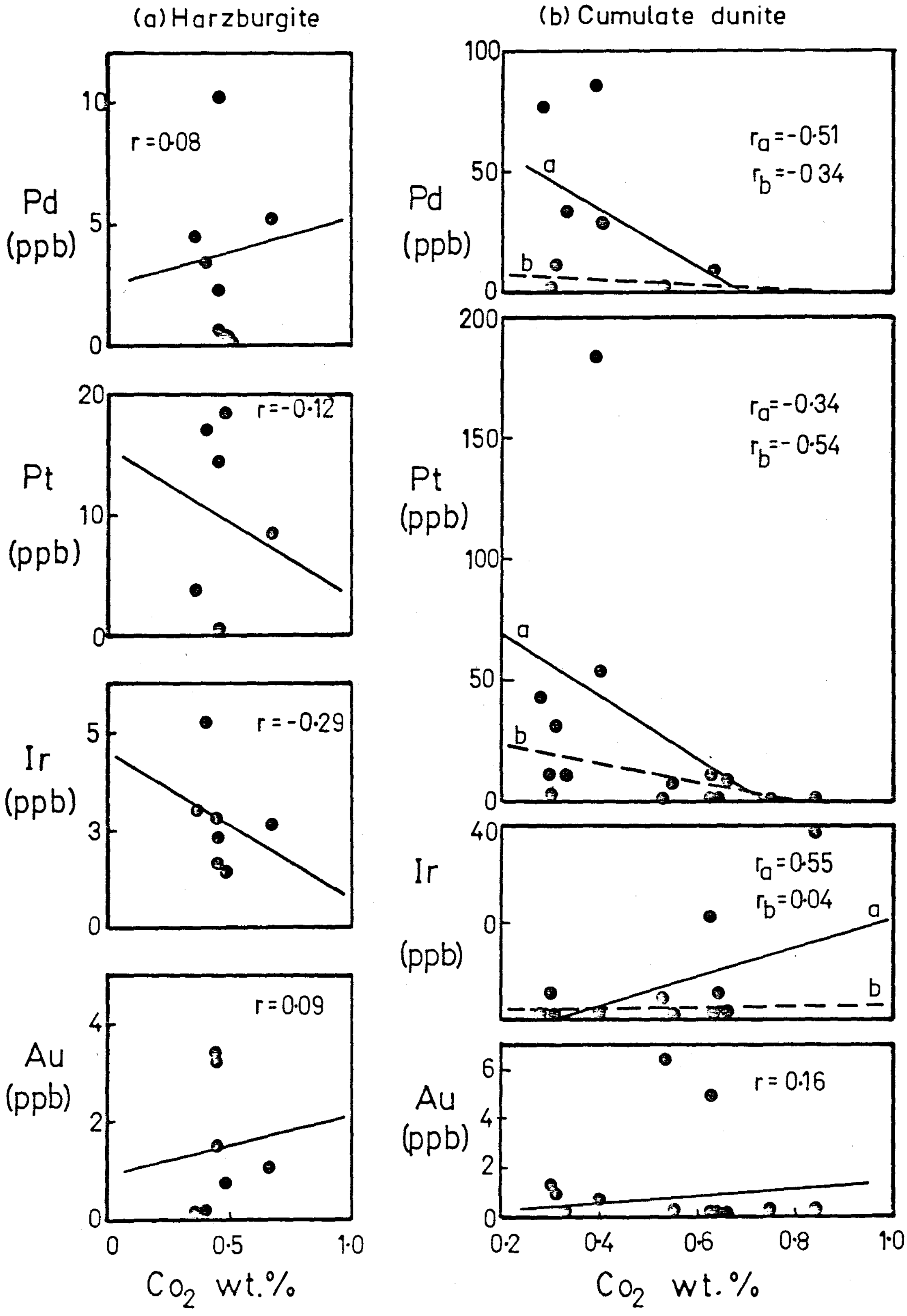
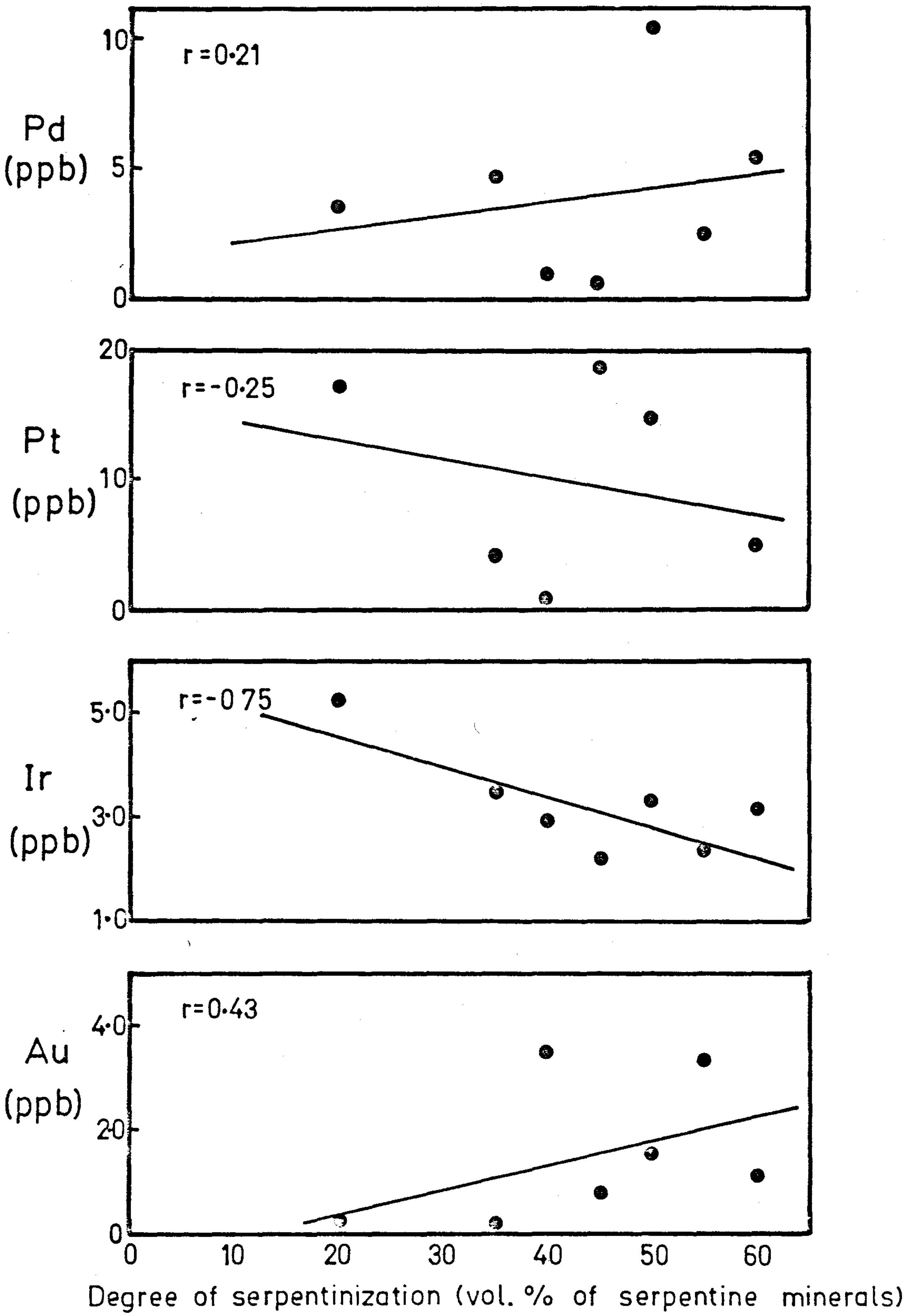

(a) Harzburgite
(b) Cumulate dunite
Pd (ppb)
r = 0·08
0
5
10
Pt (ppb)
r = -0·12
0
10
20
Ir (ppb)
r = -0·29
0
3
5
Au (ppb)
r = 0·09
0
2
4
0
0·5
1·0
CO_2 wt.%
Pd (ppb)
r_a = -0·51
r_b = -0·34
a
b
0
50
100
Pt (ppb)
r_a = -0·34
r_b = -0·54
a
b
0
50
100
150
200
Ir (ppb)
r_a = 0·55
r_b = 0·04
a
b
0
40
Au (ppb)
r = 0·16
0
2
4
6
0·2
0·4
0·6
0·8
1·0
CO_2 wt.%

Figure 5-8. Correlation of noble metals with degree of serpentinization in harzburgite (TMC).


r = 0·21
Pd
(ppb)
0
5
10
r = -0·25
Pt
(ppb)
0
10
20
r = -0 75
Ir
(ppb)
1·0
3·0
5·0
r = 0·43
Au
(ppb)
0
2·0
4·0
0
10
20
30
40
50
60
Degree of serpentinization (vol. % of serpentine minerals)

5-8, and 5-9.

Harzburgite. No noble metal correlates with CO_2. Au correlates weakly and positively with degrees of serpentinization while Ir shows a strong negative correlation. Neither Pt nor Pd correlates significantly with degrees of serpentinization. The lack of any correlation between the noble metals and CO_2 may be due to the rather restricted range of CO_2 contents of the rocks. It appears that there was no mobilization of the noble metals during the carbonation of the harzburgite. This is in contrast to the findings of Fyon (1980) who found significant Au mobilization during intense talc carbonate alteration of the mafic-ultramafic rocks of the Timmins area, Ontario. Groves and Keays (1979) also found that Au was mobilized during the carbonation of some host rocks of sulfide ores in Australia. The lack of mobility of Au and the other noble metals in Thetford Mines ophiolite may be due to their relatively low degree of carbonation.

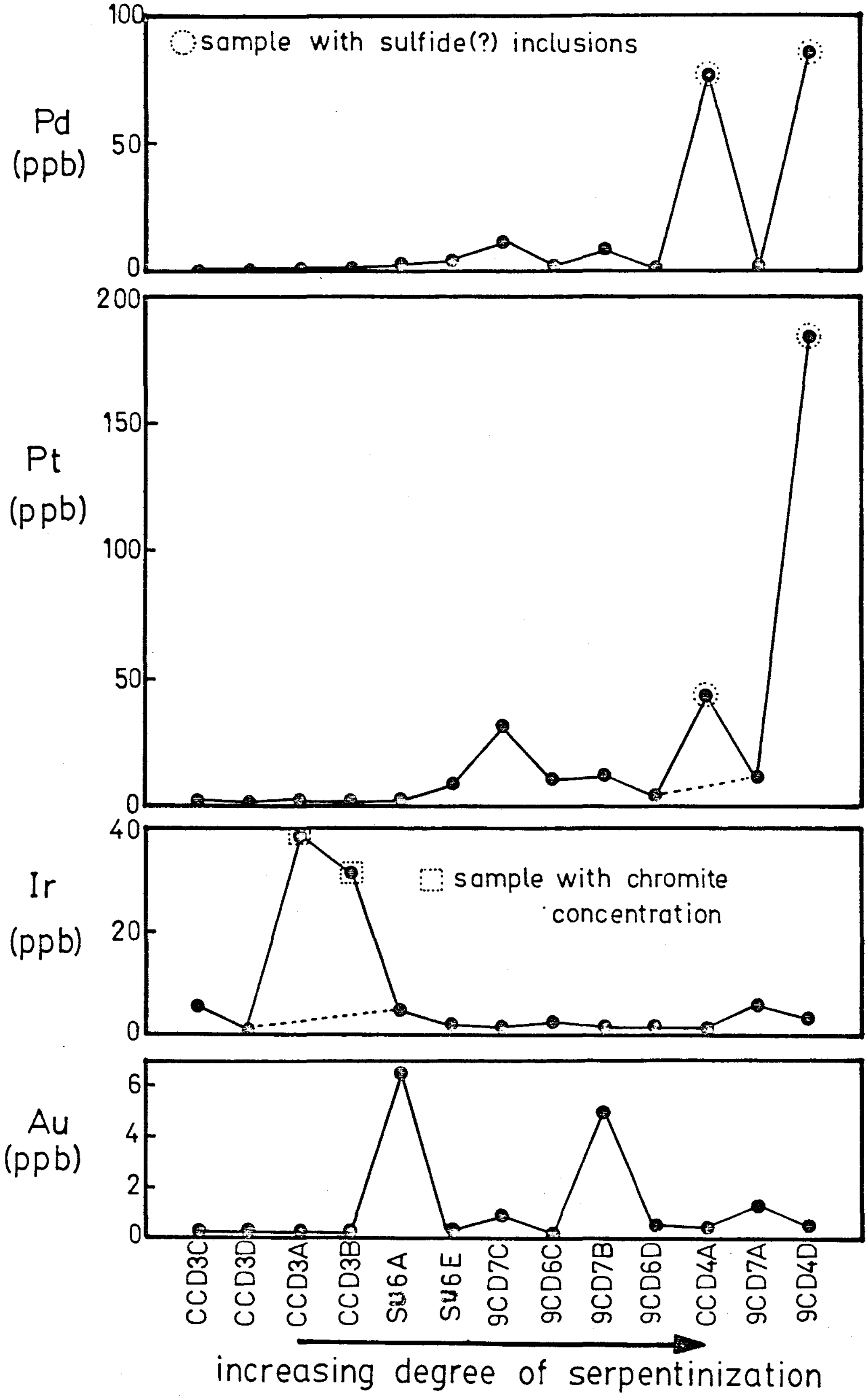
In contrast to their behavior during carbonation, the noble metals were mobilized in the harzburgite to varying degrees during serpentinization. Ir appears to have been systematically, although slightly, removed from the serpentinized rocks. This is surprising and at variance with the general belief that Ir is immobile during secondary processes (e.g., Cousins, 1973). The observed Ir behavior is also in contrast to Chyi's (1968) observation that Ir was not mobilized in the Mt. Albert pluton during serpentinization. An explanation for the mobilization of Ir in the Thetford Mines rocks is suggested in a later discussion.

Although the correlation coefficients for Pt and Pt are not significant, the large scatter in the data points for these metals suggests that the metals were mobilized during serpentinization. Such mobilization was probably local and might have involved redistribution of metals between adjacent rock layers only. The rather systematic increase in Au with an increase in the degree of serpentinization is difficult to explain in terms of local redistribution of Au. Rather, it appears that Au have been added to the serpentinized rocks from the serpentinizing solution. Addition of Au to rocks could be by adsorption of Au particles on the serpentine minerals.

The Dunites. The plot of noble metals against CO_2 in the dunites (Figure 5-7b) indicates a positive correlation of Ir and a negative correlation of Pt and Pd with CO_2. Au does not show any correlation. This could be taken as an increase in Ir contents and a decrease in both Pt and Pd with an increase in carbonation. It was, however, suggested earlier (section 5.1.2) that some dunites samples probably have a phase which concentrates Pt and Pd and that the chromite in the olivine-chromite rocks might concentrate Ir. If these samples with the Pt metal enrichment are disregarded, then it is seen that the noble metals do not show any significant correlation with CO_2.

There is no systematic relationship between Au and CO_2 or degree of serpentinization. Both Pt and Pd, however, appear to increase with an increasing degree of serpentinization which might suggest

Figure 5-9. Variation of noble metal contents with degree of serpentinization in the cumulate dunites of TMC.


◌ sample with sulfide(?) inclusions
Pd (ppb)
100
50
0
200
150
100
50
0
Pt (ppb)
40
20
0
Ir (ppb)
□ sample with chromite concentration
6
4
2
0
Au (ppb)
CCD3C
CCD3D
CCD3A
CCD3B
Su6A
Su6E
9CD7C
9CD6C
9CD7B
9CD6D
CCD4A
9CD7A
9CD4D
increasing degree of serpentinization

enrichment in these metals during serpentinization. However, the interpretation of the data is not that simple. The effect of igneous differentiation has to be taken into account in interpreting the observed trends and certain factors have to be considered: 1) in the dunites, differentiation increases stratigraphically upwards. Differentiation is characterized by an upward increase in Pt and Pd. ii) CO_2 contents decrease stratigraphically upwards as indicated by 0.84 wt % CO_2 in Lac du Caribou, 0.66 - 0.31 wt % CO_2 in Lac Rond and Petit Lac St. Francois and 0.40 - 0.28 wt % CO_2 in Lac de l'Est. iii) The degree of serpentinization increases upwards - in the opposite direction of the CO_2 trend. The decrease in Pt and Pd with the increase in CO_2 and their increase with increasing serpentinization, therefore, merely reflects the opposite trend in Pt and Pd abundances due to differentiation and the trend in CO_2 contents on the one hand, and the similar stratigraphic trend in differentiation and serpentinization on the other hand. In other words, neither carbonate alteration nor serpentinization has had any significant effect on the distribution of the noble metals in the dunites.

5.2.2.1 Discussion.

Two important features emerge from the behavior of noble metals during serpentinization of the ophiolitic ultramafic rocks in Thetford Mines. 1) Mobilization of noble metals is only observed in the harzburgites. Noble metals in the dunites seem to be insensitive to serpentinization. 2) In the harzburgite Ir is slightly but systematically removed from the serpentinized rocks, Au is gained while Pt and Pd show erratic mobilization.

The absence of any effect of serpentinization on the noble metals in the dunite, despite the total replacement of their primary minerals by serpentine minerals in contrast to the less serpentinized harzburgites, is puzzling. One plausible explanation for the different behavior of the noble metals in the harzburgite and in the dunite may be that the mobility of noble metals is controlled by the environment of serpentinization. As discussed earlier, the dunites were pervasively serpentinized in the oceanic environment under a reducing condition. The harzburgites, on the other hand, were more serpentinized on the continent under an oxidizing condition. If the noble metals are transported as complex ions, they must first be oxidized. It is not possible to oxidize the noble metals under the reducing condition in which dunites were serpentinized, hence the noble metals were not mobilized during serpentinization. On the other hand, on the continent, the oxygen of the air could oxidize the noble metals (Krauskopf, 1979), the ions formed may then form complex ions with some anions, chlorides or sulfates from the serpentinizing solutions. This, therefore, means that the mobilization of the noble metals in the harzburgite took place only during the second serpentinization episode. Because Au was added to the serpentinized rocks instead of being redistributed in rocks like Pt or Pd, or being removed as in the case of Ir, it is possible that the serpentinizing fluids carried some Au. This is quite possible if the fluid was meteoritic ground water, as suggested by Laurent (1975), as opposed to sea water. Meteoric waters have been known to carry Au (e.g. Weissenberg, 1970). Reaction of such water with rocks could lead to deposition of Au in the rocks while the fluids are still potent enough to leach the other noble metals.

Another possible explanation for the mobility of the noble metals in the harzburgite may be related to the mineralogical siting of the noble metals in the harzburgite and in the dunite. This explanation is borne from the observation that Ir is systematically removed from the serpentinized rocks. If Ir is as residual and inert as its chemistry predicts and as is generally believed, then the systematic removal of Ir from rocks could only be explained if Ir was mechanically removed rather than chemically transported in solution as complex ions. This is because formation of complex ions depends on many factors which are not systematic in nature. In section 4.1.3 it was shown that the bulk of the Ir and to a lesser extent, Pt and Pd in the harzburgite occur along the chromite-olivine grain boundary while the noble metals are mostly within the minerals in the dunite, probably in solid solution. Obliteration of mineral boundaries during serpentinization would therefore release the noble metals in the harzburgites. The amount of metal relased will depend on the amount of grain boundary destroyed, i.e. degree of serpentinization. Because some of the Pt, Au and Pd still occur in mineral lattices, their removal will not ocrrelate with the degree of serpentinization. And since the noble metals occur in the mineral lattice in the dunites, they are not affected. If this explanation is corret, then mobilization of the noble metals in the harzburgites may also occur in the oceanic environment during their first serpentinization as well as during the second serpentinization on the continent.

5.2.3 Geochemical Behavior of the Noble Metals during Hydrothermal Alteration of the Lavas

Stratabound massive cuperiferous sulfide ores occur within the hydrothermally altered pillow lavas of many ophiolites, such as Troodos ophiolites (Bear, 1963; Garrett and Pantazis, 1971; Johnson, 1972; Searle, 1972), Oman ophiolites (Bailey and Coleman, 1975), Apennine ophiolites (Spooner and Fyfe, 1973; Bonatti *et al*., 1976), Bay of Island ophiolites (Duke and Hutchinson, 1973). Spatially associated with these sulfide deposits are metalliferous Fe-Mn rich sediments which are also invariably rich in Cu, Zn, Ni, Pb, Co, Cr, Sn, and Ag (e.g. Elderfield *et al*., 1972; Bonatti *et al*., 1976; Bonatti, 1975).

Occurrences of deep sea metalliferous sediments have also been reported in modern day active spreading centres such as East Pacific Rise, Indian Ridge, Red Sea Rift, and Mid-Atlantic Ridge. The metalliferous sediments on the oceanic ridges are believed to have been derived along the spreading centers (Bostrom and Peterson, 1966; Corliss, 1971; Piper, 1973; Bonatti, 1975). This view is supported by direct observation of the metal deposits of some shallow water hydrothermal veins in volcanic areas such as Santonian (Greece) and Matupi Harbour (New Britain, Southwest Pacific).

The similarity in the chemical composition of the sediments overlying some ophiolites and the oceanic ridges, and the stratigraphic position of the sediments on ophiolitic basalt, have led to the view that a similar process is responsible for the generation of the metalliferous sediments in both the ophiolites and the oceanic ridges. This process, which is also believed to be responsible for the formation of the cuperiferous sulfide ores within some ophiolites, is linked to hydrothermal alteration of lava by sea water.

The hydrothermal circulation model (e.g. Spooner and Fyfe, 1973) can be summarized as follows: cooling of extruded lavas on the sea floor liberates heat. The liberated thermal energy heats up sea water and causes a sea-floor convection. Rapid cooling also causes lava to fracture, thereby allowing sea water to infiltrate. The infiltrated sea water descends into the volcanic pile. Intrusion of rocks under the volcanic pile generates heat which heats up the descending water and causes the water to finally return to the lava/sea-water interface, without any appreciable recirculation. During the passage of sea water in the lavas, the sea water continuously changes composition - becoming more reduced and acidic - and behaving more like a hydrothermal fluid. Interaction of the hydrothermal fluid with the lava causes some mineralogical changes in the lava similar to wall rock alteration in the geothermal systems. Chemical exchange occurs between the hydrothermal fluid and the lava. Some elements such as Cu, Zn, Ni, Cr are presumably leached into the fluid while the lavas gain H^+ as H_2O. Most of the leached metals are probably carried as complex ions in solution. As the circulated fluid returns to the rock/water interface, some elements which have a high affinity for sulfur, such as Fe, Cu, and Zn may undergo an exchange reaction with sulfide ions (S^{-2}) to form metal sulfides in response to decreasing temperature. When the fluid is finally discharged into the sea water, interaction of the sea water with the fluid causes precipitation of metals as metalliferous sediments on the leached lava.

This hydrothermal hypothesis of the formation of ore and metalliferous sediments in the ophiolites is supported by the observed depletion of some trace elements in the altered lavas of some ophiolites relative to their fresh equivalents (e.g. Garrett and Pantazis, 1971). Altered basalts from oceanic ridges have also been shown to be depleted in some elements such as Fe, Mn, Cr, Ni, Zn, found in the overlying sediments (e.g.Humphris and Thompson, 1977).

At this point, it is important to distinguish between 1) hydrothermal leaching of metals from the lavas, as has just been described, in which there is an exchange of materials between a circulating fluid and the lavas which are being mineralogically modified; and 2) loss of elements from the lavas due to interaction with cold sea water when they are extruded on the sea floor. Materials may also be extracted from the sea water by the lavas. In the following text, the first type will be referred to as hydrothermal alteration while the second will be referred to as sea-water alteration.

The effect of hydrothermal activity on the noble metals in lavas has not been studied experimentally and data on naturally altered basalts are scanty. However, some available data do suggest that some of the noble metals are mobilized during hydrothermal and sea-water alteration of basalts. For example, Keays and Scott (1976) found that interaction of sea water and basalt may result in a loss of Au and Ag held in later stage phases in the interior of basalts. Crocket and Teruta (1977) suggested that Pd and Ir are leached from the sea-floor basalts from MAR Leg 37 during their interaction with sea water. Bavinton and Keays (1978) suggested that sea-floor leaching of Au and to a lesser extent Pd, but not Ir, from submarine flows might be responsible for the noble metal content of the interflow sedimentary rocks in a komatiite suite in Western Australia. Agiorgitis and Becker (1979) also attributed the low Au content of the lower pillow lavas of Troodos ophiolites to hydrothermal mobilization. However, with the exception of Keays and Scott (1976) who actually compared the noble metal content of fresh and altered basalts from the same area, the idea that the noble metals are mobilized during alteration of basalts is circumstansial. Most workers tend to base their arguments on the very low noble metal content of the analyzed rocks. It is also possible that such low values are purely genetic and unrelated to any mobilization. For the purpose of supplementing the available data on the effect of hydrothermal and sea-water alteration on noble metals in basalts, the distribution of noble metals in the Thetford Mines ophiolite lava is considered in some detail.

5.2.3.1 Theoretical Considerations. Leaching of the noble metals from rocks during the passage of hydrothermal fluid involves two main processes: 1) dissolution of noble metals, and 2) transport of the metals by hydrothermal fluids. Au has been shown to be carried as a sulfide complex in an alkaline medium (Weissenberg, 1970; Seward, 1973, 1979) or as a chloride complex (Helgeson, 1964; Weissenberg, 1970) in an acidic medium. The data of White (1968) on the Salton Sea geothermal system and the experimental results of Hajash (1975) on the fluid which reacted with basalt, indicate that hydrothermal solutions become acidic during their reaction with basalt. This is suggestive that Au and possibly other noble metals will be transported as chloride complexes.

The formation of noble metal chloride complexes requires an abundant supply of chloride ions (Cl^-) and the oxidation of the noble metals. Spooner and Fyfe (1973) indicate that the sea-water hydrothermal fluid contains abundant dissolved Cl^- among other ions. However, as shown in Table 5-3 the common ions of the noble metals have such high oxidation potentials that it is doubtful if the noble metals could be oxidized under the conditions of hydrothermal alteration of the lavas. However, Krauskopf (1979) showed that in the simultaneous presence of a powerful oxidizing agent such as MnO_2 or O_2 and a solution of chloride ions, the Au chloride complex $AuCl_4^-$ may be formed because of the lower oxidation potential of the chloride complex. Other noble metals may likewise form chloride complexes under similar conditions. High concentrations of Fe^{+2} and Cu^{+2} may also act as possible oxidizing agents (Krauskopf, 1979). The oxidation and chloride complex formation of the noble metals may be written as:

$$Au + 2\ Cl^- + 1/2\ MnO_2 + 2\ H^+ \rightleftharpoons AuCl_2^- + 1/2\ Mn^{+2} + H_2O \text{ ---------- } (1)$$

$E° = -0.45$ v

$$Au + 4\ Cl^- + 1\ 1/2\ MnO_2 + 6\ H^+ \rightleftharpoons AuCl_4^- + 1\ 1/2\ Mn^{+2} + 3\ H_2O \text{ ---- } (2)$$

$E° = 0.23$ v

$$Pd + 4\ Cl^- + MnO_2 + 4\ H^+ \rightleftharpoons PdCl_4^{-2} + Mn^{+2} + 2\ H_2O \text{ --------------- } (3)$$

$E° = 0.61$ v

$$Pt + 4\ Cl^- + MnO_2 + 4\ H^+ \rightleftharpoons PtCl_4^{-2} + Mn^{+2} + 2\ H_2O \text{ --------------- } (4)$$

$E° = 0.50$

$$Ir + 6\ Cl^- + 2\ MnO_2 + 8\ H^+ \rightleftharpoons IrCl_6^{-2} + 2\ Mn^{+2} + 4\ H_2O \text{ ----------- } (5)$$

$E° = ?$

The electrode potential for the Ir-complex is not known but it is probably between that of Pt and Au. From the relationship $\Delta G = -nFE°$, where ΔG is free energy change, the negative values of ΔG for reactions (2) to (4) show that these reactions will proceed to the right. The solubility of the complexes can be calculated from the relationship $\Delta G = -RT \log K$ where K is the solubility constant, T the absolute temperature, and R the gas constant. The solubility of the complexes for different Cl^- and H^+ concentrations at 350°C taken as the average temperature of the greenschists, are shown in Table 5-6. Details of calculations are presented in the Appendix.

Table 5-6 shows that the solubility of the complexes decreases with the decrease in the acidity of the fluid. For example, a change in the pH of the hydrothermal fluid by one unit may cause a decrease in the solubility of the noble metals complexes by more than three

Table 5-6

Solubility of Noble Metals in the Presence of MnO_2 at 350°

Ion Concentration			Concentration of Noble Metal Complex					
H^+	Cl^-	pH	$AuCl_4^-$ mol/l	Au ppm	$PdCl^{-2}$ mol/l	Pd ppm	$PtCl^{-2}$ mol/l	Pt ppm
10^{-1}	10^{-1}	1	1.67×10^{-3}	330	8.71	9.27×10^{5}	1.12	2.19×10^{5}
10^{-2}	10^{-2}	2	1.67×10^{-7}	3.3×10^{-2}	8.71×10^{-4}	92.67	1.12×10^{-4}	21.89
10^{-3}	10^{-3}	3	1.67×10^{-11}	3.3×10^{-6}	8.71×10^{-8}	9.27×10^{-3}	1.12×10^{-8}	2.19×10^{-3}
10^{-5}	10^{-5}	5	1.67×10^{-19}	3.3×10^{-14}	8.71×10^{-16}	9.27×10^{-11}	1.12×10^{-16}	2.19×10^{-11}
10^{-7}	10^{-7}	7	1.67×10^{-27}	3.3×10^{-22}	8.71×10^{-24}	9.27×10^{-19}	1.12×10^{-24}	2.19×10^{-19}
10^{-9}	10^{-9}	9	1.67×10^{-35}	3.3×10^{-30}	8.71×10^{-32}	9.27×10^{-27}	1.12×10^{-32}	2.19×10^{-27}

order of magnitude. It is, however, possible to increase the solubility of the complexes at high pH if the concentration of the chloride is increased considerably. It, therefore, follows that for any appreciable leaching of the noble metals to ocean during hydrothermal alteration of lavas, the hydrothermal solutions must have a high concentration of chloride ions. It is of interest to note that at any pH, the Au-chloride complex is less soluble than either the Pd or Pt complex.

5.2.4 Mobility of the Noble Metals during Hydrothermal Alteration of the Thetford Mines Ophiolite Lavas

Due to lack of fresh representative samples for comparison with altered samples from the same flows, a quantitative evaluation of noble metal mobility during hydrothermal alteration of the ophiolitic lavas is difficult. It is still possible, however, to assess the effect of alteration on the noble metals by some criteria as follows:

1) Correlation of the noble metal contents with stratigraphic position,

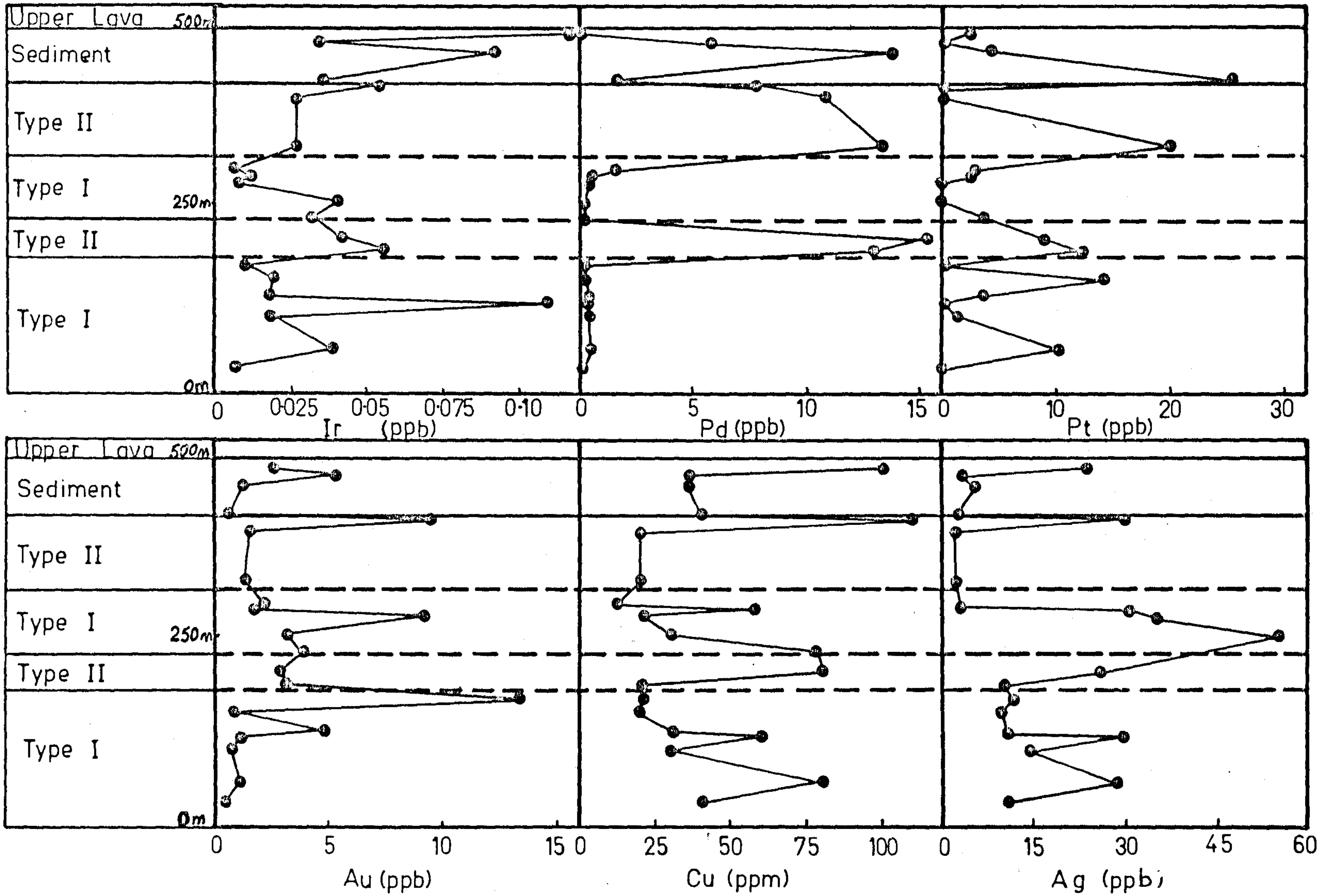
2) Correlation of the noble metal content with the degree of alteration. Because the upper lavas are only slightly altered, they are not considered.

5.2.4.1 Correlation of Noble Metals with Stratigraphic Position.

Henley (1973) has shown that the amount of base metal that may be leached from a rock during hydrothermal alteration depends mainly on the temperature of the hydrothermal fluid. Similarly it is expected that the leachability of the noble metals during hydrothermal alteration of the lavas will depend on the temperature of the circulating sea water. Metamorphic mineral paragenesis indicates that the temperature in the lavas increases with depth. This is consistent with the idea that the source of heat for driving back the circulating sea water to the water/rock interface comes from liberated heat of intruding rocks beneath the lavas. It is, therefore, expected that if leaching of the noble metals occurs during hydrothermal activity in the lavas, samples at the base of the pile should be depleted relative to the other samples. The stratigraphic distribution of the noble metals in the lavas in the Lac de l'Est section of Thetford Mines is shown in Figure 5-10. The distribution of Cu and Ag, two metals which are believed to be easily leached from hydrothermally altered rocks are also shown for comparison with the noble metals.

Iridium. There is no evidence of stratigraphic control on Ir content in the lavas. Rather, Ir content is influenced by the rock type. With the exception of one sample with very high Ir value, type I lavas generally have marginally lower Ir content than the type II lavas. It is difficult to relate the stratigraphic variation of Ir to any leaching of the metal by hydrothermal fluid.

Figure 5-10. Stratigraphic variation in Cu and noble metal contents in the volcanic rocks at Lac de l'Est (TMC).


Upper Lava
500m
Sediment
Type II
Type I
250m
Type II
Type I
0m
0
0·025
0·05
0·075
0·10
Ir (ppb)
0
5
10
15
Pd (ppb)
0
10
20
30
Pt (ppb)
Upper Lava
500m
Sediment
Type II
Type I
250m
Type II
Type I
0m
0
5
10
15
Au (ppb)
0
25
50
75
100
Cu (ppm)
0
15
30
45
60
Ag (ppb)

Platinum. The variability of Pt values is difficult to interpret in terms of hydrothermal leaching, as zones of depletion and enrichment appear to alternate throughout the stratigraphic column. If Pt was mobilized during hydrothermal activity, the metal was probably redistributed within the lava pile. However, it is possible that Pt was originally inhomogeneously distributed in the lavas. It is also highly probable that the variability of Pt results reflects a higher degree of analytical uncertainty than for the other metals.

Palladium and Gold. Pd and Au to a smaller degree are depleted in samples occurring at the stratigraphic base of the lava relative to samples higher up in the sequence. This might suggest some leaching of the metals from the bottom of the lava sequence. However, it is noted in the case of Pd that all the samples showing depletion are type I lavas while all those that show enrichment are the type II lavas. It is unrealistic to expect that only the type I lavas would be stripped of their Pd contents. It could be argued that due to differences in chemistry and texture, the type I lavas are more susceptible to leaching. However, one factor, the uniformity in noble metal contents in the 'depleted' samples, argues against this selective leaching. Au content like Pd are remarkably uniform in the depleted samples despite the fact that some depleted samples occur at the top of the lava flow and in both lava types. The similarity of the Au content of both type I and type II lavas argue against any preferential leaching due to chemistry or texture of the lavas. Also, if leaching depends on temperature, then it is difficult to explain why samples at the base of the lower sequence should have similar noble metals as those near the top. Comparison with reported noble metal contents of other oceanic basalts such as the data of Gottfried and Greenland (1972), and Crocket and Teruta (1977), indicate that the depleted samples have similar Au and Pd contents to those of oceanic basalts. Perhaps then, the samples with low Au and Pd values are not depleted, rather those with high values have been enriched.

Since the low Pd and high Pd values are restricted to type I and type II lavas respectively, it is suggested that leaching of Pd from the lavas did not occur during alteration. Variations in Pd values are mainly genetic. On the other hand some samples have been enriched in Au.

Comparison of the stratigraphic variation of Au, Cu, and Ag shows some superficial similarity in their trends. However, in detail, the distribution of both Cu and Ag are different from that of Au; for example some of the lowest lavas do not show any depletion in Cu and Ag. Secondly,those samples that appear to be enriched in Cu and Ag actually have metal contents similar to the average Cu and Ag contents of basalts in contrast to the high Au values which are significantly higher than the average Au contents for basalts.

The stratigraphic positioning of the samples with low Cu and Ag contents is noteworthy. These samples occur at or near the top of the lava of each type. If the lavas have been extruded on the sea floor in cycles as suggested by the stratigraphy, it appears that interaction of sea water with the top layer of each type as resulted in some loss of Cu and Ag from the lavas. In other words, loss of Cu and Ag from the lavas appears to be related to cold sea water interaction of the lavas rather than the hydrothermal alteration.

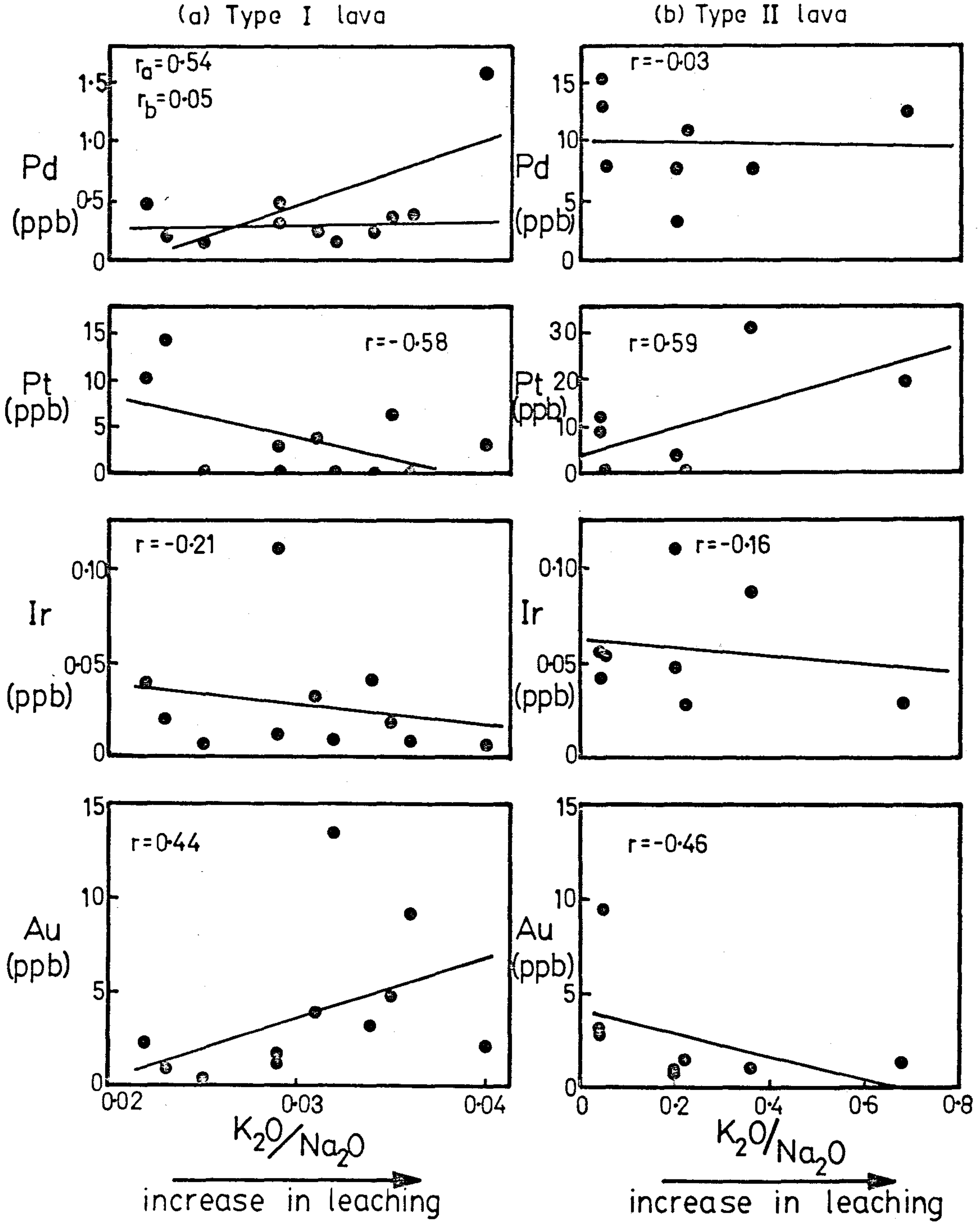
5.2.4.2 Correlation of Noble Metal with the Index of Alteration. It is appropriate to assume that if the noble metals have been leached by hydrothermal fluid, their content in the altered rocks correlates with the degree of leaching suffered by the rocks. Studies of fluid inclusions from hydrothermally altered rocks (e.g. Casaderall and Ohmoto, 1977) show that the K/Na ratio of the fluid inclusion increases with intensity of leaching. If the fluid inclusion is in equilibrium with the altered rocks, then the K/Na ratio of the altered rocks should also increase with leaching. The studies of Meyer et al. (1968) on the hydrothermally altered rocks of Butte, Montana, also indicate that with the increase in alteration Na decreases much more than K in the altered wall rocks. Thus the K/Na or K_2O/Na_2O ratio of the lavas may be used as an index of leaching. Plots of the noble metals as a function of K_2O/Na_2O are shown in Figure 5-11.

Iridium and Palladium. Ir does not show any correlation with K_2O/Na_2O. Pd appears to correlate positively with K_2O/Na_2O in the type I lavas. However, if one sample which appears to be anomalous

Figure 5-11. Correlation of noble metals with K_2O/Na_2O (index of hydrothermal leaching) in TMC lavas.

r = coefficient of correlation for Pd vs K_2O/Na_2O in type I lava

r_b = coefficient of correlation for Pd vs K_2O/Na_2O in type I lava omitting data for sample 9LB4X with anomalous Pd value.

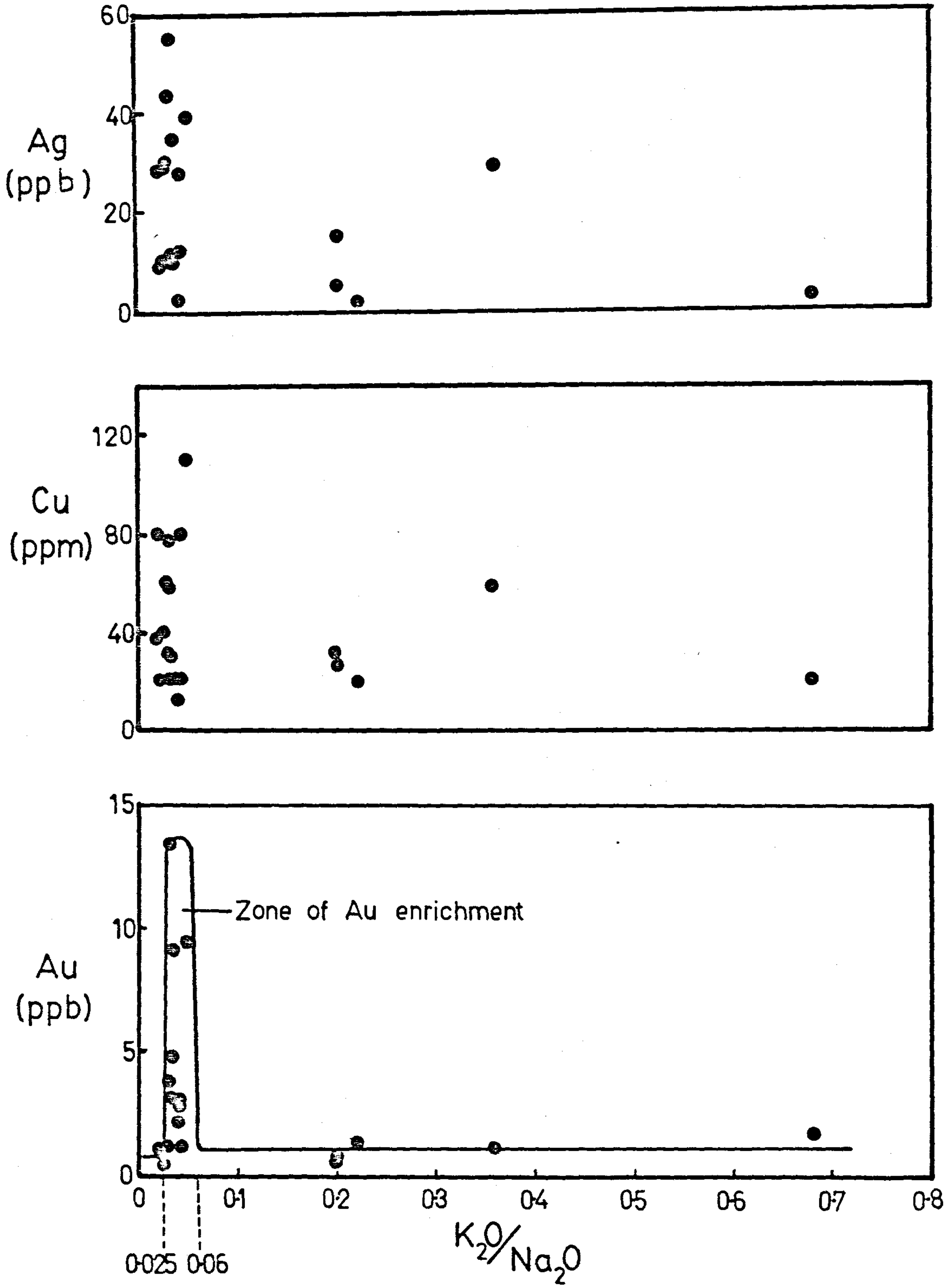

(a) Type I lava
(b) Type II lava
r_a=0·54
r_b=0·05
Pd (ppb)
1·5
1·0
0·5
0
r=-0·03
15
10
5
0
Pt (ppb)
15
10
5
0
r=-0·58
30
20
10
0
r=0·59
Ir (ppb)
0·10
0·05
0
r=-0·21
r=-0·16
Au (ppb)
15
10
5
0
r=0·44
r=-0·46
0·02
0·03
0·04
0
0·2
0·4
0·6
0·8
K_2O/Na_2O
increase in leaching

with respect to the remaining ten is rejected, there is no correlation between Pd and the degree of leaching. The lack of correlation between Ir, Pd and K_2O/Na_2O suggests that both Ir and Pd are unaffected by hydrothermal alteration of the lavas. Alternatively, it may mean that lavas have been stripped of Ir and Pd to a similar level irrespective of the degree of leaching.

Gold. Au correlates rather weakly with the K_2O/Na_2O but the trends in the two lava types are different and opposite. In the type I lava, Au contents increase while in the type II lava, Au contents decrease with increases in K_2O/Na_2O. This suggests that Au was being removed in type II lavas and added to the type I lavas during hydrothermal alteration. Why Au behaves differently in the two lava types is not known. Chemical and mineralogical differences may be responsible. For example, Skinner (1979) indicated that the type of rock that reacts with the hydrothermal fluid can strongly influence the type of trace element released in solution. Does it then mean that the more mafic type II lava is more susceptible to Au-leaching than the less mafic type I lava?

In plotting the Au values of all the lavas together (Figure 5-12), it is observed that those samples with high Au values are restricted to those with low K_2O/Na_2O ratios between 0.025-0.06, irrespective of lava type. The low K_2O/Na_2O ratios of these samples indicate that they are probably the least hydrothermally leached samples. It may then be assumed that they have the least modified Au

Figure 5-12 Variation of Cu, Ag and Au with K_2O/Na_2O in TMC lavas.


60
40
20
0
Ag
(ppb)
120
80
40
0
Cu
(ppm)
15
10
5
0
Au
(ppb)
Zone of Au enrichment
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·025
0·06
K2O/Na2O

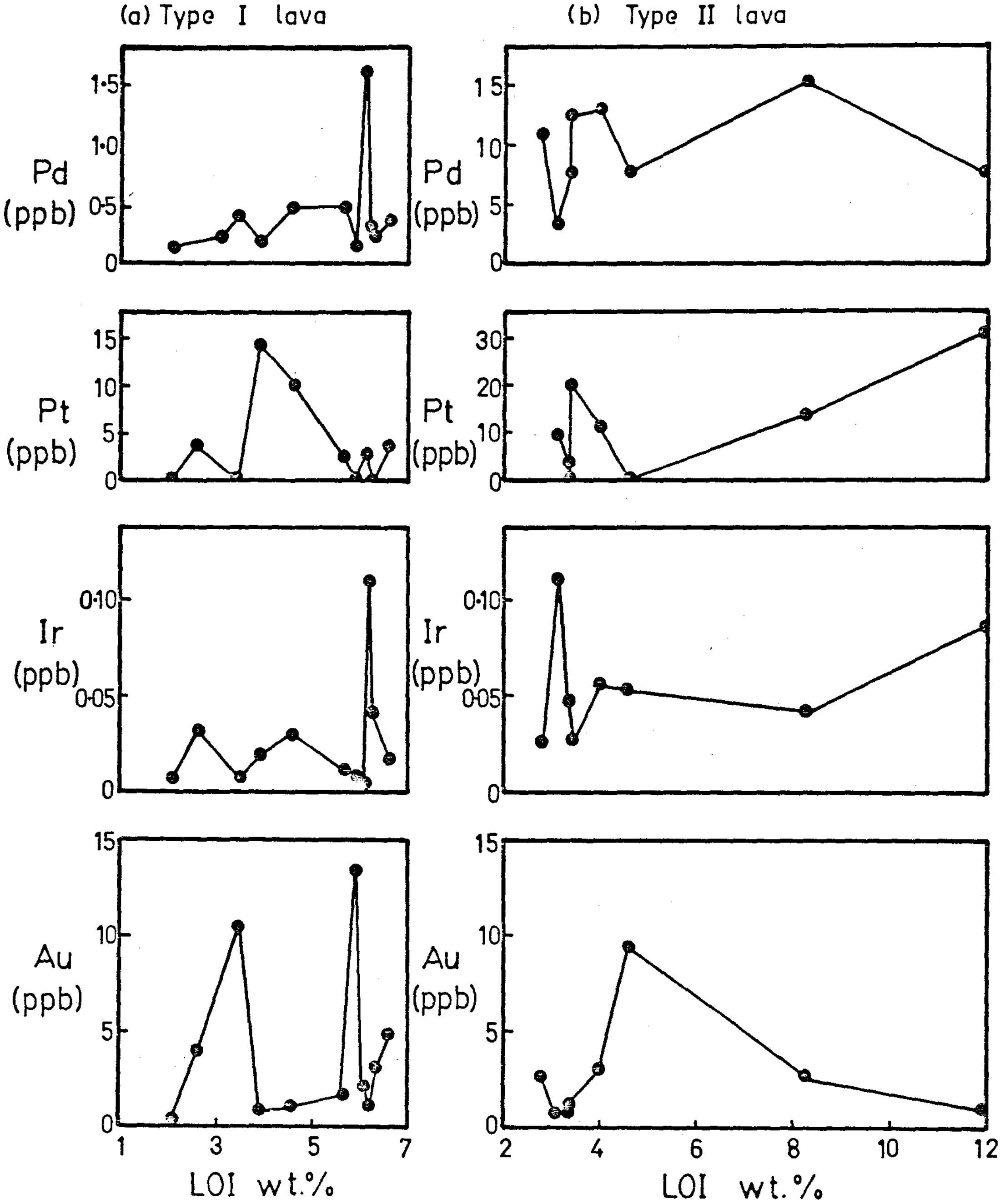
contents. However, within these restricted K_2O/Na_2O values, Au contents range from 2.14 ppb to 13.40 ppb with an average of 5.77 ppb. Such a wide range of Au contents could not possibly represent the original range of Au contents in these lavas. In addition the average Au value for this group of samples is considerably higher than the average Au content of basalt - either continental or oceanic.

The more altered lavas, i.e., those with higher K_2O/Na_2O ratios on the other hand, have a very restricted range of Au contents (0.42-1.71 ppb with an average of 1.09 ppb). The uniformity in their Au contents is suggestive that these samples have not lost their Au or it may also suggest that they have lost Au to the same level irrespective of their degree of alteration. At present, it is difficult to choose between the two alternatives.

Platinum. Pt shows a negative correlation with K_2O/Na_2O in type I but a positive correlation in type II lavas. However, these correlations depend highly on very few samples and there is no systematic variation of Pt with K_2O/Na_2O. It is therefore difficult to interpret the Pt data, but the distribution of the majority of the samples does not indicate any relationship with the degree of leaching.

The total volatile content of the lavas (loss on ignition) may be taken to represent the amount of fluid, sea water and dissolved gasses, that reacted with the lavas during the alteration. The plots of the noble metals as a function of loss on ignition show no systematic variation of the noble metals (Figure 5-13). The non-systematic

Figure 5-13 Variation of noble metals with loss on ignition in TMC lavas.


(a) Type I lava
(b) Type II lava
Pd (ppb)
Pt (ppb)
Ir (ppb)
Au (ppb)
1·5
1·0
0·5
0
15
10
5
0·10
0·05
30
20
1
3
5
7
2
4
6
8
10
12
LOI wt.%

variation of the noble metals with loss of ignition suggests that even if the noble metals have been leached the intensity of lava alteration is not the controlling factor in their mobility.

Discussion. From the consideration of the correlation of the noble metals with the stratigraphic position and indicies of alteration, it appears that Ir and Pd were not mobilized during alteration of the lavas. The behavior of Pt is more difficult to interpret because of analytical uncertainty but it seems that it has also remained immobile. Au, however, show evidence of mobilization although Au values do not show correlation with the degree of alteration. The reason for suggesting mobilization for Au is the high degree of variability in Au contents which unlike Ir, Pt, or Pd, cannot be related to rock type or analytical uncertainty. It is not known yet whether the lavas have gained or lost Au during alteration.

Three models are proposed for the observed variability in Au contents in the lavas:

1) Loss of anomalous gold. In this model two types of Au are distinguished: a) threshold gold, and b) anomalous gold. The threshold Au represents the Au that is in the solid solution in the mineral lattices of the lavas and is not available for leaching during the alteration of the lavas. The threshold Au is probably represented by the Au content of the most leached lavas, i.e., those with 0.42 ppb - 1.71 ppb Au. The anomalous Au occurs outside the mineral lattice, probably on mineral surfaces, along grain boundaries or in inter pillow

spaces as alloys or discrete minerals. This gold is leachable and since its distribution is not controlled by solid solution, its abundance is highly variable. The lavas which still possess their anomalous gold are represented by those samples with 2.14 ppb - 13.40 ppb Au and they are the least leached lavas.

In this model, it is suggested that during the water interaction with the lavas and during hydrothermal alteration of the lavas, the lossely held anomalous gold is easily flushed out of the lavas, leaving the threshold gold. Only a moderate degree of alteration is probably needed to remove all the anomalous gold. Further leaching will have no effect on the Au in the mineral lattices, hence the uniform Au content of the more leached samples irrespective of their varying degrees of alteration as indicated by their K_2O/Na_2O ratios. The least altered lavas would still keep most of their anomalous gold, hence the high Au contents.

This model is similar to the one given by Keays and Scott (1976) to explain the difference between the Au contents of the rim and core fo some ocean-ridge basalt. The model may also be applicable to the variation in the Cu and Ag contents of the lavas.

2) Addition of the Au to lavas from extraneous sources. In this model it is proposed that gold was not leached from the lavas. Rather, the samples with high Au contents have been enriched in Au. The source of the Au that was added was probably magmatic. According to the model of hydrothermal alteration of lavas, the sea water which percolates through the lava is heated up by the heat of some magma

which intruded at the base of the lava pile. It is possible that the residual fraction of the intruding magma contaminated the circulating sea water. If this residual magma fraction contained Au, it would be carried by the sea water toward the water/rock interface through the lavas. Local changes in temperature and/or chemical properties of the circulating fluids may cause deposition of Au in some of the lavas.

It is difficult to test this model since there is no means of recognizing the magmatic Au. However, since the residual magma would be expected to contain other metals such as Cu, Ag, and Zn, those samples which are enriched in Au should also be enriched in Cu, Ag, and Zn. It is also expected that Cu/Au, Ag/Au and Zn/Au should be fairly uniform in these samples. The metal ratios in the samples are highly variable and correlation between the Au and other metals is poor indicating that this model may not be significant.

3) Redistribution of the Au within the lava. This model is similar to the hydrothermal model of formation of ore and metalliferous sediments. That is, Au is leached from some part of the volcanic unit and deposited in other parts. Temperature differences within the volcanic unit may be the controlling factor. The argument against this model for Au is the erratic distribution of low and high Au in the stratigraphy of the lava. Metamorphic mineral assemblages show a gradual decrease of temperature upwards. Also, in known occurrences of sulfide ores, the ores usually occur at the top of the lava sequence where temperature is minimal.

Redistribution of Au as observed can only occur if the Au has not been mobilized by hydrothermal fluid but has been released during sea-water lava interaction. In that case, the released Au did not move very far and might just diffuse from one flow to the adjacent lava flow.

In conclusion, any or a combination of the three models outlined above could be responsible for the variation in Au content of the lavas. However, uniform Au content of the more altered rocks, and lack of stratigraphic correlation of Au is best explained by the first model, i.e., removal of anomalous Au from the lavas. The apparent immobility of Ir, Pd, and possibly Pt may be due to their being in solid solution in mineral lattice where they are not available for leaching, in contrast to Au which may occur on the surface of minerals.

5.3 Summary

The salient geochemical characteristics of the noble metals in the ophiolites are summarized as follows:

1) Au is insensitive to magmatic differentiation and rocks formed by fractional crystallization tend to have uniform Au content for the most part of the magma cooling history. Late formed rocks may be enriched in Au if they contain appreciable amounts of post-cumulus material as Au tends to concentrate in residual magma fractions -- being rejected by most silicate minerals.

2) Iridium tends to concentrate rather efficiently in early

formed minerals, particularly chromite, leaving the middle and last formed rocks in a differentiating magma severely depleted.

3) Platinum and Palladium contents increase in rocks during fractional crystallization but Pt is more fractionated into early formed rocks than Pd. Saturation of a crystallizing magma with sulfur at any stage of the cooling history of the magma may cause a reversal of the Pt-Pd trend such that Pd partitions more than the Pt in the early formed rocks, if these rocks contain sulfides. This is probably due to higher affinity of Pd for sulfur than Pt.

4) The fractionation trends of noble metals may be used as indices of magmatic differentiation. Metal ratios like Pt/Pd, Pt/Pt + Pd decrease while ratios like Pd/Ir, Pd/Pd + Ir increase with increasing differentiation. However, use of these metal ratios may be limited severely when the crystallizing magma becomes saturated in sulfur at any stage of the magma's cooling history.

5) The noble metals correlate with a number of elements which may suggest some ionic substitution of these elements by the noble metals, e.g., Pd and Pt for Fe; or Ir for Cr. Correlation may also indicate the similar tendency, or otherwise, of noble metals and correlated elements to partition into early or late phases during crystallization. For example, positive correlation of Au with Zr, both being concentrated in residual magma fractions, or the negative correlation of Ir with Cu, Ir being concentrated in early formed minerals while Cu is being concentrated in the residual magma fraction. Positive correlation of Au with Cr may also reflect their common host.

6) Noble metals in dunites do not seem to be mobilized during serpentinization but in the harzburgite, Ir is lost, Au is gained, while Pd and Pt are being redistributed in the rocks. The different behavior of noble metals in dunites and harzburgites is attributed to: 1) the reducing environment in which the dunites were serpentinized. The reducing condition prevented the oxidation of noble metals so that they could not form complex ions - the form in which they are soluble in the serpentinizing solution. 2) The noble metals are in solid solution in the mineral lattice of the dunites and are not available for leaching by the serpentinizing solution.

The Au that was gained by the harzburgite is believed to have come from the meteoric serpentinizing solution.

7) During the alteration of ophiolite lavas, Ir, Pd and possibly Pt were not mobilized in contrast to Au, which shows some degree of mobilization. Three models were proposed for the mobility of the Au but the model which best explains the distribution of Au in the lavas is the model in which anomalous Au which occur loosely on mineral surfaces or grain boundaries are removed during alteration. The immobility of Ir, Pt and Pd in the lavas therefore imply that they were mostly in solid solution in the lavas.

In conclusion, the reported noble metal contents, particularly for the Ir, Pt and Pd for the ophiolite rocks probably reflect their original abundances. Au contents might have been modified in some samples in the harzburgites and in lavas due to serpentinization and hydrothermal alteration but this has not significantly altered the igneous geochemical behavior of Au.

Mobility of the noble metal by secondary processes appears to be predominantly controlled by the environment and mineralogical siting of the noble metals.

CHAPTER SIX

PETROGENESIS OF THETFORD MINES OPHIOLITES

6.1 The Ophiolite Problem

Most students of ophiolites contend that ophiolites represent part of ancient oceanic crust and mantle now stranded on land. This interpretation is based largely on the similarity between ophiolite stratigraphy and that of oceanic crust inferred from geophysical observations, similarity in the chemistry of some ophiolitic rocks and oceanic crustal rocks, and the association of deep sea metalliferous sediemnts with both ophiolites and oceanic crust. However, certain aspects of ophiolite studies remain controversial. Two questions - the mode of genesis and the tectonic environment of formation of the ophiolites have created the most controversy and they remain problematic.

Many models have been suggested for the mode of formation of ophiolites. They may be grouped into two: 1) one magma models, and 2) multi-magma models. In the one magma model (e.g. Gass, 1968; Greenbaum, 1972) ophiolites are regarded as formed by fusion of the upper mantle, followed by gravitational fractionation of the melt produced at depth to form the cumulates. Part of the melt is injected and extruded as dikes and pillow lavas. On the other hand, the multi-magma model (e.g. Reindhart, 1969; Coleman, 1977; Evart, 1977; Hopson and Frano, 1977) suggests that ophiolites are formed by two or more separate events, and that the magmas formed in any of these events may give rise to any of the ophiolitic rocks. This model further suggests that the magmas formed at one stage may not bear any petrogenetic reationship to other magmas involved in the formation of the same ophiolitic suite.

Regarding tectonic environment of formation, it now appears that ophiolites may be generated at many oceanic environments, and every ophiolite occurrence must be treated on its own. However, the same set of petrological and geochemical characteristics are often interpreted differently by different investigators. The Troodos complex is a typical case. The Troodos ophiolites have been interpreted as formed in an island arc (Miyashiro, 1973; Ewart and Bryan, 1972), at a mid-oceanic spreading center (Moores and Vines, 1971), and in a back-arc marginal basin (Smewing *et al.*, 1975; Pearce, 1975).

6.2 Genesis of Thetford Mines Ophiolites

Any plausible petrogenetic model for the Thetford Mines ophiolites must take into account the relationship between the various rock types of the suite. Field relationships indicate that some rock types may be genetically related to one another. However, the process by which the rocks are related is still poorly understood, and certain questions remain. For example, are the ophiolitic rocks formed from one or more magmas? What is the relationship between the cumulates and the non-cumulates? Is the metamorphic dunite related to the harzburgite or the cumulate rocks? What is the relationship between the lava types? Field observations alone cannot answer all these questions, and some additional insight may be gained by considering the geochemical behavior of certain elements in the rocks.

6.2.1 Lava Petrogenesis

Two geological processes - fractional crystallization and partial melting - are usually invoked to explain the relationship between members of igneous rock suites. In some cases, however, other processes such as magma mixing or magma contamination must be considered. These igneous processes can be identified from the abundances and behavior of some major and trace elements that are sufficiently sensitive to these different processes. In recent years, various workers (e.g. Gast, 1968; Shaw, 1970; Ringwood, 1975; Allegre *et al.*, 1977; Minster *et al.*, 1977; Pearce and Flower, 1977; Pearce and Norry, 1979) have modelled major and trace element behavior during fractional crystallization of magma and partial melting of magma sources. However, because of the mobilization of elements during metamorphism of the lavas, only a few elements may be expected to give reliable information. In this respect, the noble metals, particularly Ir and Pd which are relatively immobile during alteration, are important.

In this study, a semi-qualitative use of elemental geochemistry in identifying the dominant genetic process is adopted. The basic premise is that the behavior of an element during fractional crystallization and partial melting is controlled by its bulk (whole rock) solid-liquid partition coefficient (D), and that elements are fractionated from one another due to the difference in their D values. The effects on element fractionation are not the same for fractional crystallization and partial melting, and by noting the extent of fractionation between pairs of elements it is possible to evaluate the dominant process involved. The mineral phases which are fractionated or melted can be deduced by comparing the observed element fractionation trend with theoretically modelled mineral vectors similar to those of Pearce and Norry (1979).

On the basis of solid-liquid partition coefficients, three groups of elements are recognized:

a) Elements with high solid-liquid partition coefficient ($D > 1$); e.g. Ir, Ni, and Cr. These elements tend to be severely depleted in residual magma fractions during fractional crystallization. During partial melting, the initial melt may be low in these elements if the degree of melting is low, otherwise they are not significantly affected by the degree of melting of the magma source (see e.g. Treuil, 1973; Allegre and Minster, 1978).

b) Elements with low solid-liquid partition coefficient ($D \leq 0.1$); e.g. Ta. These elements are strongly partitioned into residual liquids during magma fractionation. During partial melting, their abundances in successive melts vary inversely as the degree of melting (e.g. Sigvaldson et al., 1974; Pearce and Flower, 1977). No such element is considered in this study but Zr may approximate this type of behavior, depending on the type of mineral phases involved.

c) Elements with intermediate solid-liquid partition coefficient, e.g. Y, Ti, Zr, Au and Pd. These elements behave like those with low solid-liquid partition coefficients, but to a lesser extent.

Diagrams illustrating the correlation of various elements or element ratios in the volcanic rocks are presented in Figures 6-1 to 6-5. The elements compared are grouped according to their D values, that is, comparisons are made for elements of high D values, elements of intermediate D values and for elements of high D values against elements of intermediate D values. Further, the elements used are those believed to have suffered the least degree of mobilization during alteration of the lavas. In the case of Au, only those samples with no anomalous Au, that is, samples with no enriched or intergranular Au (see Section 5.2.4) are used.

a) Elements with high solid-liquid partition coefficients against elements with intermediate solid-liquid partition coefficients.

Since the elements with high D values are less sensitive to partial melting than fractional crystallization, the two groups of elements are less fractionated from one another by partial melting than fractional crystallization. In lavas related by fractional crystallization, the extent of fractionation between the elements will also depend on the crystallizing mineral phases.

(i) Ir-Au, Ir-Pd diagrams (Figure 6-1a and Figure 6-1b)

Because of the insensitivity of Au to fractional crystallization the

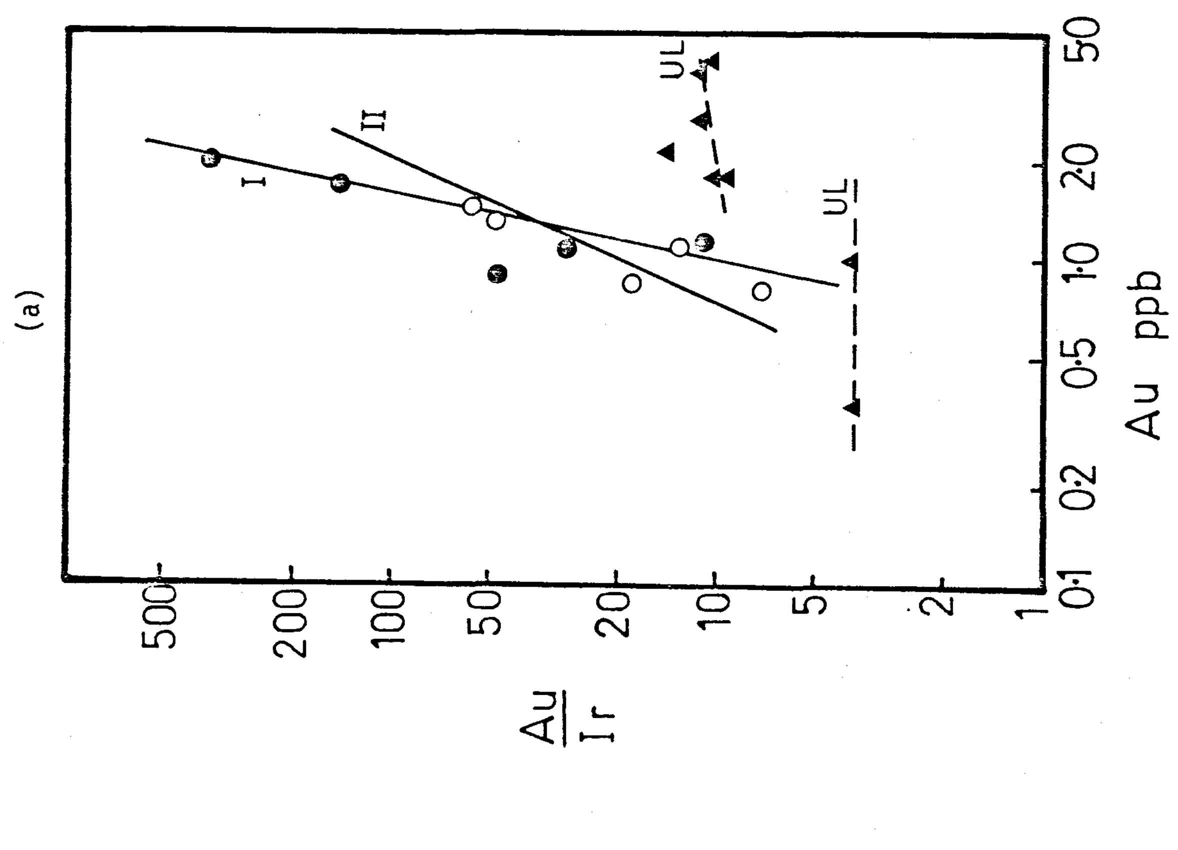
Figure 6-1a. Variation in Au/Ir against Au concentrations in TMC lavas.

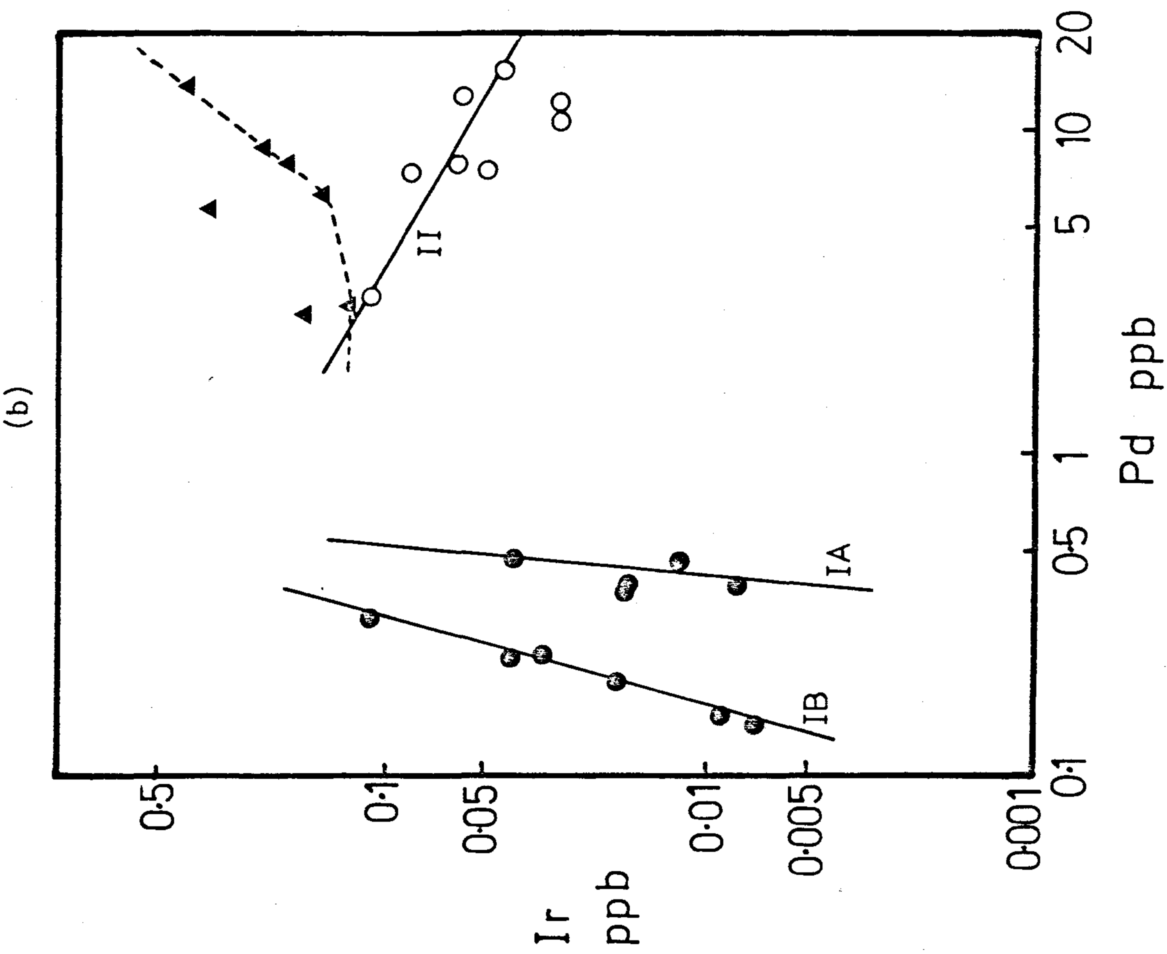
I = type I

II = type II

UL = upper lava

Figure 6-1b. Variation of Ir with Pd in TMC lavas. Symbols are the same as in Figure 6-1a.


(a)
Au/Ir
500
200
100
50
20
10
5
2
1
0·1
0·2
0·5
1·0
20
50
Au ppb
I
II
UL
UL


(b)
Ir ppb
0·5
0·1
0·05
0·01
0·005
0·001
0·1
0·5
1
5
10
20
Pd ppb
IA
IB
II

bulk solid-liquid partition coefficient of Au is believed to be close to unity. If this is true, then Au will also be insensitive to partial melting. Therefore, Ir will not be significantly fractionated from Au by different degrees of partial melting as long as the same phases are melted. In Figure 6-1a, both type I and type II lavas show large variations in their Au/Ir ratio but have restricted Au values. This can only be interpreted as due to fractional crystallization during which Ir, but not Au, was partitioned into the early mineral phases. The upper lavas on the other hand display Au/Ir ratios which appear to define at least two sub-parallel trends. Each of these trends has relatively constant Au/Ir ratios but variable Au values. The uniform Au/Ir ratios in these upper lavas is best explained as due to partial melting. The two different Au/Ir ratios suggest either selective loss of Au from the lavas with the lower Au/Ir ratio or formation of the low Au/Ir lavas from a different source with lower Au content.

In the Ir-Pd diagram (Figure 6-1b) type I lavas display two sub-parallel trends which suggest that these lavas were probably formed in two series. Since Ir decreases while Pd increases during magmatic differentiation (Section 5.1.2) the trends observed in the type I lavas, where Ir decreases with decreases in Pd suggest that these lavas might not be related by fractional crystallization. On the other hand, the large variation in Ir content is best explained by fractional crystallization. Furthermore, the type I lavas at the base of the volcanic unit tend to have higher Ir contents than their counterparts higher up in the volcanic stratigraphy (see Figure 5-10), consistent with the idea that Ir concentrates in the early formed rocks during fractional crystallization. The decrease in Ir with a decrease in Pd in type I lavas probably reflects the hosting of Ir and Pd by the same phase.

The trend in type II lavas in which Ir decreases with increases in Pd is consistent with derivation of these lavas by some fractional crystallization process. By contrast, the trend in the upper lavas cannot be related to fractional crystallization, and like the Ir-Au variation, variation between Ir and Pd in the upper lava is probably a feature due to partial melting.

Because the mineral-magma partition coefficient of Ir, Pd and Au are not known, it is difficult to distinguish the mineral phases which may have been involved in fractional crystallization in type I and type II lavas.

(ii) Cr-Ti, Al_2O_3-TiO_2 diagrams (Figure 6-2a and Figure 6-2b) On both diagrams, the type I and type II lavas show significant variation in element ratios. The trend of decrease in both Cr/Ti and Al_2O_3/TiO_2 ratios with an increase in Ti is similar to what is expected of lavas derived by fractional crystallization. Partial melting would have resulted in less fractionation of Al_2O_3 and Cr from TiO_2. Comparison of trends in these lavas with the theoretical model of Pearce and Norry (1977) suggests from the Cr-Ti diagram that crystallization of the parental magma of the type I and type II lavas must have involved olivine and spinel subtraction while the Al_2O_3-TiO_2

Figure 6-2a. Variation in Cr/Ti against Ti concentrations in TMC lava. Fractionation vectors of Pearce and Norry (1979) based on mineral-liquid partition coefficient are shown for comparison with the trends in TMC.

I = type I lava
II = type II lava
UL = upper lava

Figure 6-2b. Variation in Al_2O_3/TiO_2 against TiO_2 concentrations in TMC lavas. All symbols are the same as Figure 6-2a.

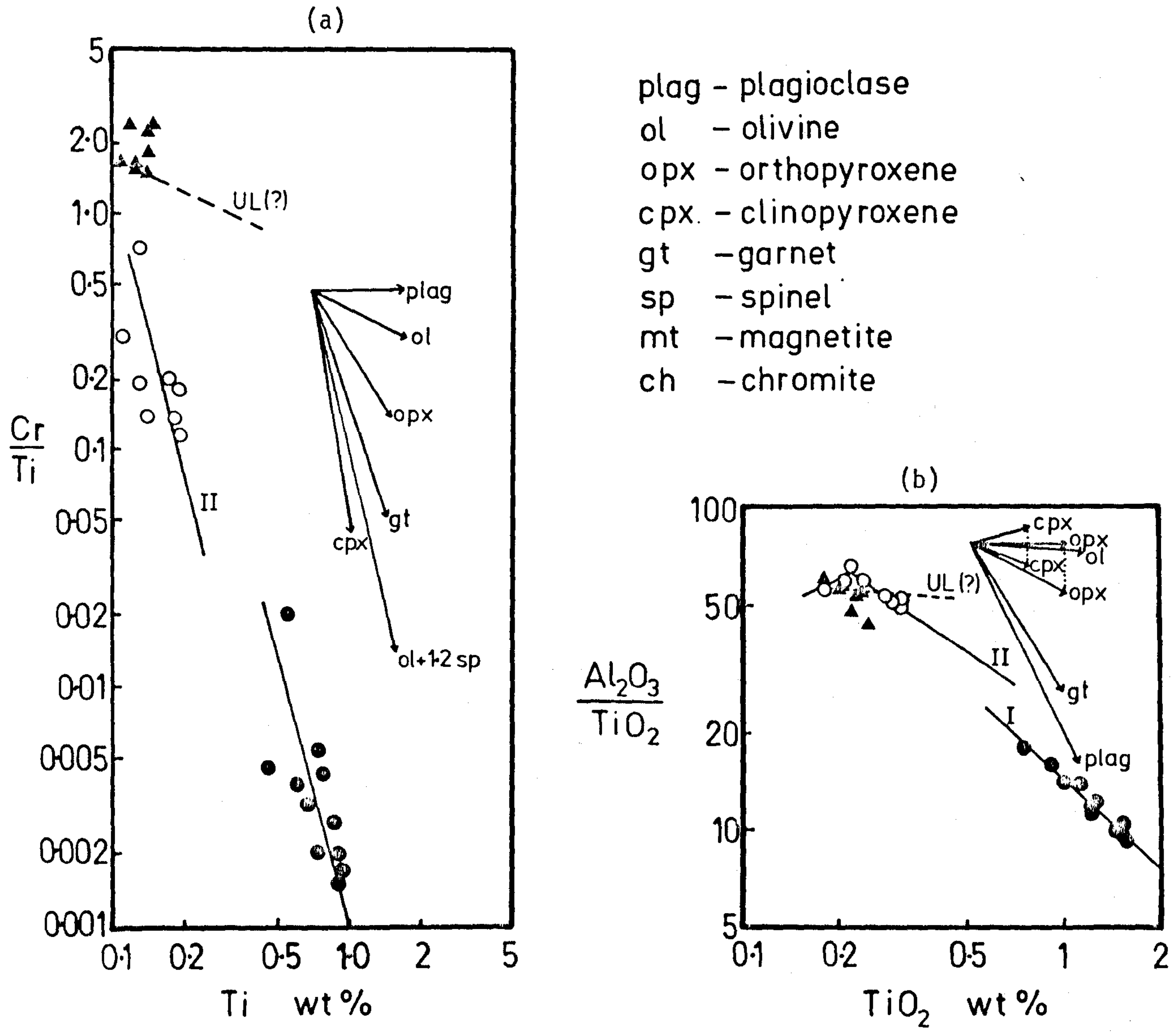

(a)
Cr/Ti
Ti wt %
5
2·0
1·0
0·5
0·2
0·1
0·05
0·02
0·01
0·005
0·002
0·001
0·1
0·2
0·5
1·0
2
5
UL(?)
II
plag
ol
opx
gt
cpx
ol+1·2 sp
plag - plagioclase
ol - olivine
opx - orthopyroxene
cpx. - clinopyroxene
gt - garnet
sp - spinel
mt - magnetite
ch - chromite
(b)
Al$_2$O$_3$/TiO$_2$
TiO$_2$ wt %
100
50
20
10
5
0·1
0·2
0·5
1
2
cpx
opx
ol
cpx
opx
UL(?)
II
gt
I
plag

diagram suggests that crystallization was controlled by plagioclase and clinopyroxene fractional crystallization in type I lavas and predominantly clinopyroxene crystallization in the type II lavas.

The upper lavas are more difficult to interpret. Their restricted Cr/Ti and Al_2O_3/TiO_2 ratios and limited variation in TiO_2 suggest that they were probably not formed by fractional crystallization but by partial melting. However, some of these lavas could be related to a trend that is similar to the olivine fractionation trend on the theoretical model. It is worthy to note that these samples with an olivine fractionation trend occur at the stratigraphic base of the lavas which suggests that they are probably cumulates. It is difficult to determine the correct explanation for these diagrams and other element plots have to be considered.

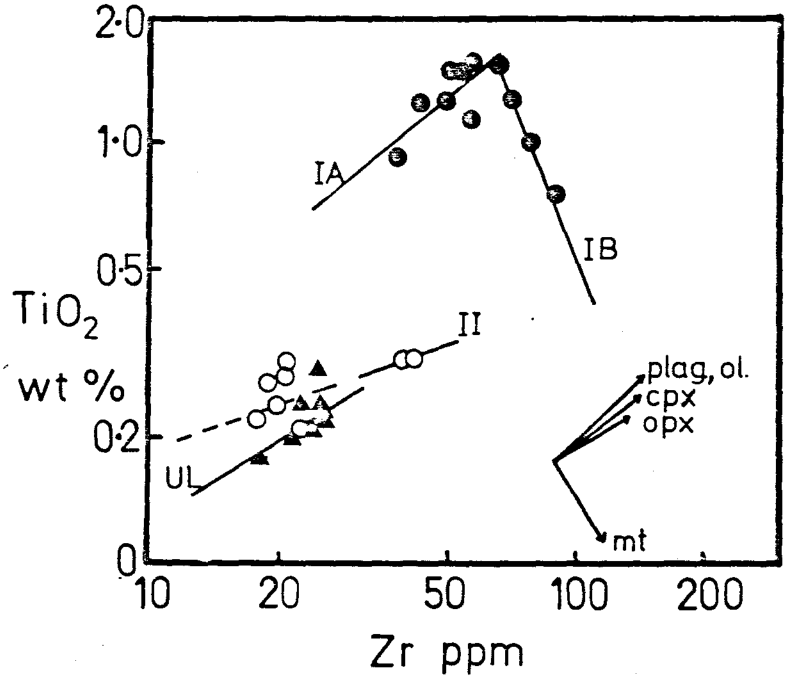
b) Variation between two elements with intermediate solid-liquid partition coefficient. These elements tend to be enriched in residual liquid fractions produced by fractional crystallization, but such enrichment usually does not significantly fractionate the elements from one another. On the other hand, depending on the mineral phases melted, elements with low or intermediate D values may be significantly fractionated from one another by varying degrees of partial melting. This fractionation is most effective for fractional melting.

(i) Y-Zr, Zr/Y-Zr diagrams (Figures 6-3a and 6-3b)

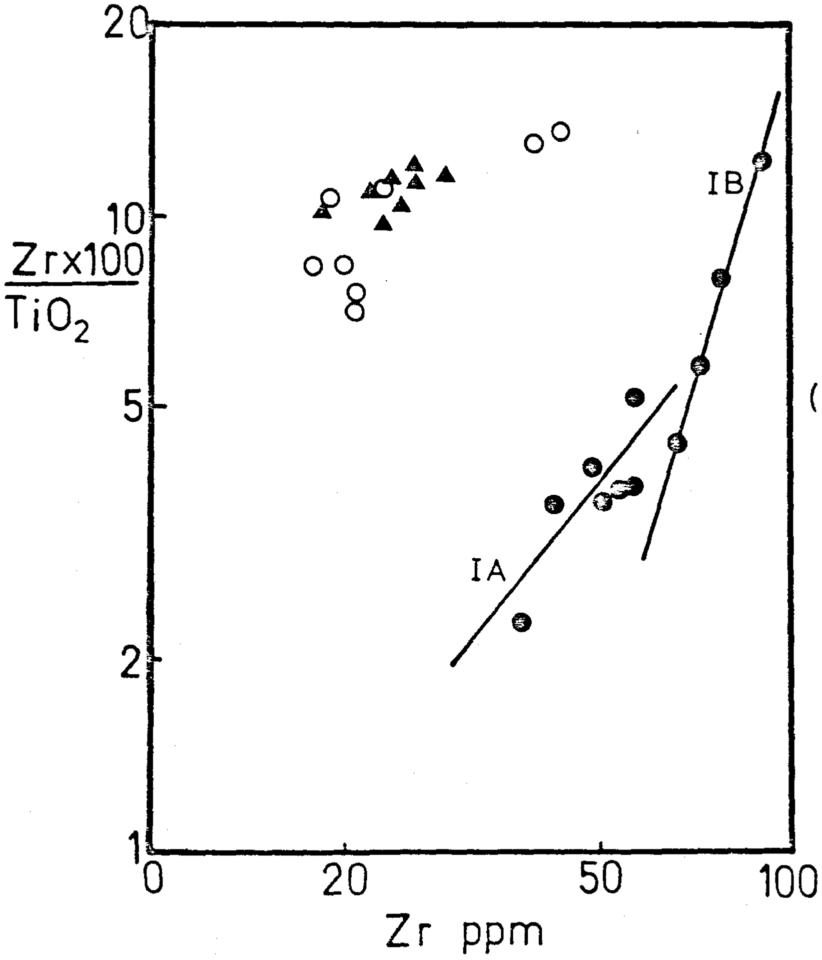
Unlike other pairs with intermediate D values, Y and Zr may be significantly fractionated from one another during fractional crystal-

Figure 6-3a. Variation of TiO_2 with Zr in TMC lavas. Symbols as Figure 6-2a.

Figure 6-3b. Variation of Zr/TiO_2 with Zr in TMC lavas. Symbols as Figure 6-2a.


2·0
1·0
0·5
0·2
0
TiO$_2$
wt %
IA
IB
II
UL
plag, ol.
cpx
opx
mt
10
20
50
100
200
Zr ppm

(a)


20
10
5
2
1
Zrx100
TiO$_2$
IB
IA
0
20
50
100
Zr ppm

(b)

lization. The fractionation of Y from Zr in rocks depends critically on the crystallization of clinopyroxene or garnet as Y is concentrated by a factor of about 6 in clinopyroxene and 7 in garnet relative to Zr.

In the Y-Zr diagram (Figure 6-3a) all the lava types show an increase in Y with an increase in Zr. Whereas both types I and II lavas show slight variations in Zr/Y ratios, the upper lavas display a rather wide Zr/Y variation for their Zr contents. The trend in the type I lavas could be interpreted in terms of fractional crystallization in which neither clinopyroxene nor garnet was an important phase. Comparison of the type I lava trends with the mineral vector model for both Y-Zr and Zr/Y-Zr diagrams indicates that trends in type I lavas may be explained by fractional crystallization involving plagioclase, magnetite and clinopyroxene as the crystallizing phases.

The type II lavas are more difficult to interpret because of the wide data scatter. Two samples have higher Zr contents than the others. It is not known if these samples are contaminated or not. On the Y-Zr plot, the least square fit through the data points gives a trend which is compatible with fractional crystallization of a combination of plagioclase, clinopyroxene and magnetite or orthopyroxene. On the Zr/Y-Zr diagram, the observed trend could be explained by crystallization of garnet and clinopyroxene, but this explanation seems improbable since garnet is not observed in these lavas.

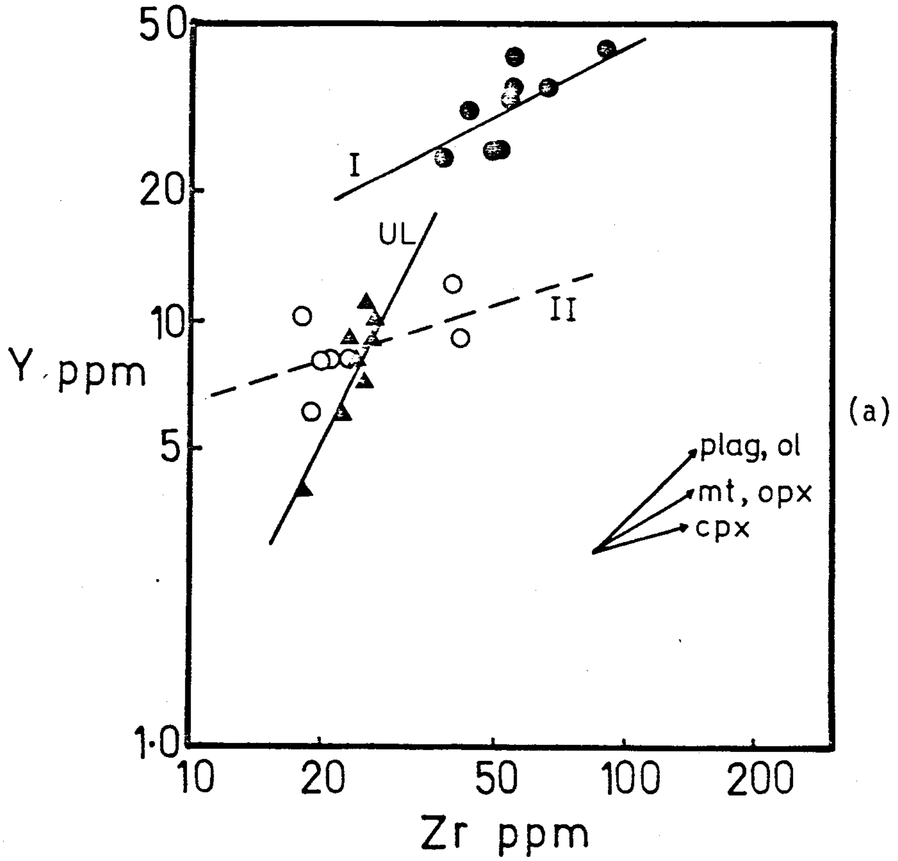
Both the Y-Zr and Zr/Y-Zr diagrams indicate that there is a greater increase in Y relative to Zr in the upper lavas. As $D_{Zr}^{solid\text{-}liquid}$ is less than $D_{Y}^{solid\text{-}liquid}$, the trend observed in the upper lavas cannot be explained by fractional crystallization as there would have been a greater increase in Zr than Y. The best explanation for the Y-Zr trends in the upper lavas is probably the formation of the lavas by partial melting. However, the large variation in Zr/Y ratios of the lavas cannot be explained by single stage melting. This feature is best explained by fractional melting of a source rich in clinopyroxene or garnet but depleted in Zr. Such a source could be a mantle material which has undergone a previous melting during which Zr was partitioned into the melt while Y was retained in the residual solid probably in clinopyroxene and/or garnet. Fractional melting of this residual solid would produce melts in which each successive batch is richer in Y relative to Zr.

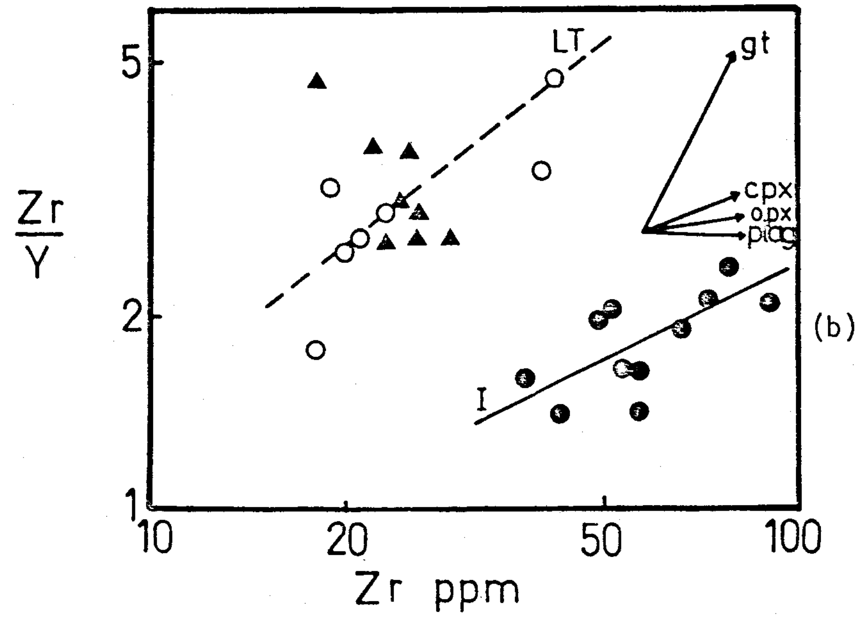
(iii) TiO_2-Zr, Zr/TiO_2-Zr diagrams (Figures 6-4a and 6-4b)

Type I lavas display two trends on the TiO_2-Zr diagram. These trends probably represent two sequences in the evolution of the lavas. In the first sequence (trend 1A) TiO_2 increases as Zr increases, suggesting the effect of plagioclase or clinopyroxene crystallization. In the second sequence (trend 1B) however, TiO_2 decreases as Zr increases indicating the effect of crystallization of a mineral phase which has high $D_{Ti}^{min-liq}$ such as magnetite or hornblende. Comparison of the trend with the mineral vector diagram suggests that this mineral is magnetite, and inference supported by the occurrence of magnetite in some of the lavas. The two sequences are also recognized on the Zr/TiO_2-Zr diagram (Figure 6-4b). The trend with the steeper slope (1B) represents the second sequence. It appears, therefore, that the magnetite

Figure 6-4a. Variation of Y with Zr in TMC lavas. Symbols as Figure 6-2a.

Figure 6-4b. Variation of Zr/Y with Zr in TMC lavas. Symbols as Figure 6-2a.


50
20
10
5
1·0
Y ppm
10
20
50
100
200
Zr ppm
I
UL
II
plag, ol
mt, opx
cpx
(a)


5
2
1
Zr/Y
10
20
50
100
Zr ppm
LT
gt
cpx
opx
plag
I
(b)

in these lavas is primary and not metamorphic as previously thought (e.g. see Figure 2-2).

The scatter of data points on the Zr-TiO_2 diagram suggests that some of the type II lavas may be contaminated in Zr. If the samples with high Zr contents are omitted from consideration, then both the type II and the upper lavas have restricted Ti and Zr contents which can only be explained by very limited fractionation or formation from a residual source in which Zr and Ti have been removed by a previous melting episode.

c) Variation of two elements with high D values.

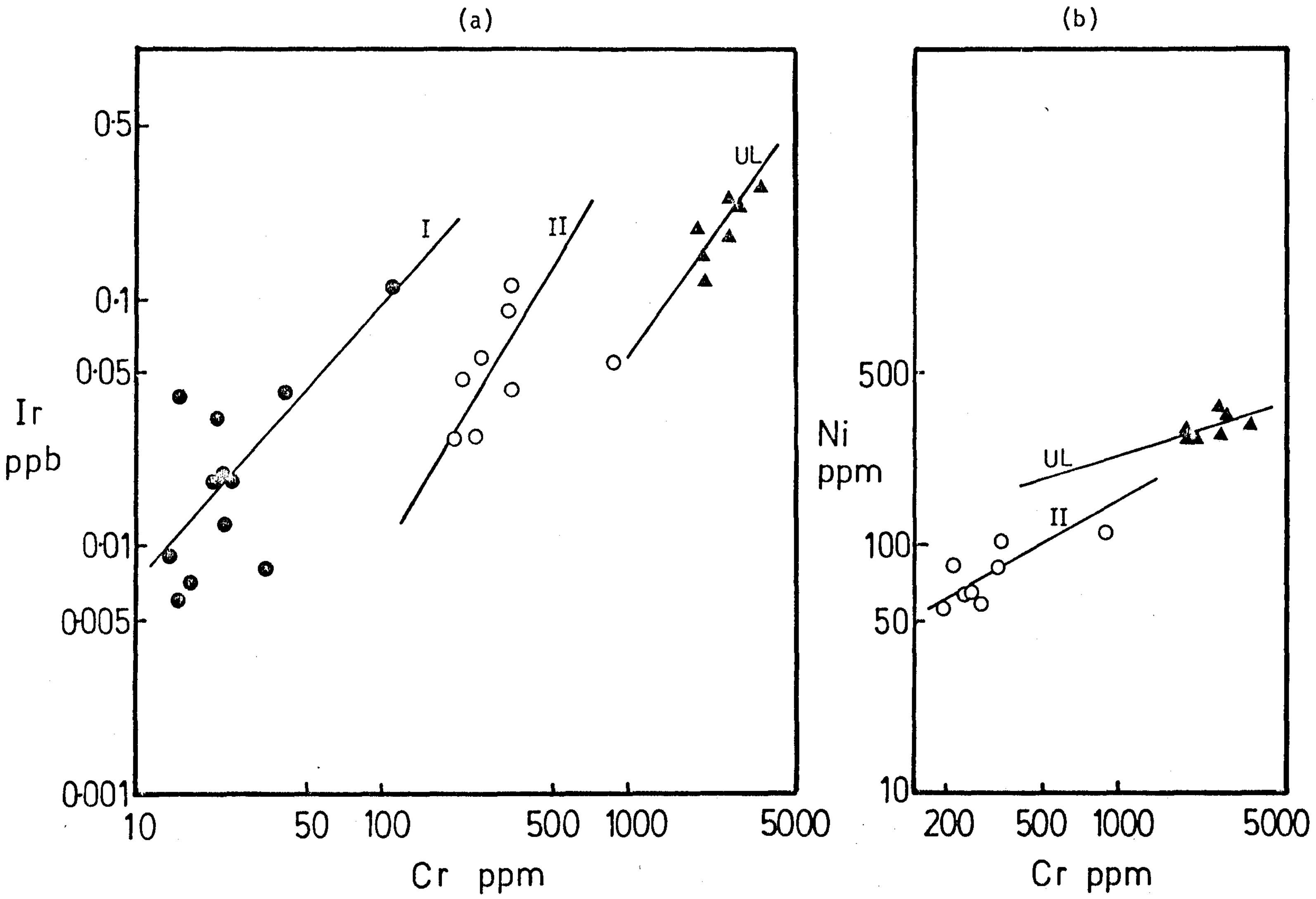
Ir-Cr, Ni-Cr diagrams (Figures 6-5a and 6-5b)

In all lavas, Ir correlates positively with Cr. This is probably a reflection of substitution of Ir for Cr. However, such substitution can only be significant if formation of the lavas involved spinel crystallization. The Ni-Cr diagram is of great significance, at least with respect to the upper lava. If the upper lavas were formed by olivine fractionation as suggested by the Cr-Ti and Al_2O_3 diagrams, Ni should decrease very rapidly with only slight decrease in Cr since Ni partitions into olivine more readily than Cr. The observed trend, however, shows that Ni is relatively uniform in the upper lavas, suggesting that they were not formed by olivine fractionation. The type II lavas on the other hand display a Ni-Cr trend compatible with pyroxene fractionation.

The genetic processes involved in the generation of Thetford

Figure 6-5a. Variations of Ir with Cr in TMC lavas. Symbols as Figure 6-1a.

Figure 6-5b. Variation of Ni with Cr in TMC lavas. Symbols as Figure 6-1a.


(a)
Ir
ppb
0·5
0·1
0·05
0·01
0·005
0·001
10
50
100
500
1000
5000
Cr ppm
I
II
UL
(b)
Ni
ppm
500
100
50
10
200
500
1000
5000
Cr ppm
UL
II

Mines lavas as deduced from various trace element correlations are summarized below in Table 6-1.

Table 6-1

Genetic Processes in Thetford Mines Lavas

Lava Type	Ir-Au, Ir-Pd	Cr-Ti, Al_2O_3-TiO_2	Y-Zr, Zr/Y-Zr	TiO_2-Zr Zr/TiO_2-Zr	Ir-Cr, Ir-Ni
I	Fractional cryst. in 2 sequences	Fractional cryst. of ol, sp, plg and cpx.	Fractional cryst. of plg, cpx and mag.	Fractional cryst. of plg, cpx and mag.	
II	Fractional crystallization	Fractional cryst. of ol, sp and cpx.	Fractional cryst. of cpx, plg and garnet (?)	Formation from a residual source	Fractional cryst. of pyroxene
Upper Lavas	Formation from primary melt.	Formation from primary melt and ol fract.	Fractional melting of a residual source depleted in Zr	Formation from a residual source depleted in Ti	Formation from primary melt

From Table 6-1, it is concluded that type I lavas were derived by fractional crystallization of plagioclase, clinopyroxene and magnetite while type II lavas were formed by fractional crystallization of olivine, spinel, clinopyroxene and plagioclase. The upper lavas, on the other hand, probably represent unfractionated partial metls from a depleted mantle source rock.

The crystallization of magnetite and plagioclase in type I lavas suggests that the type I lavas are tholeiites as plagioclase, magnetite and amphibole crystallization are believed to be responsible for terminating iron enrichment trends in tholeiites during the middle stages of crystallization (Evarts, 1977). This is rather important in view of the uncertainty in classifying the lavas from such diagrams as the AFM, FeO^T/MgO vs TiO_2, SiO_2 vs FeO^T/MgO diagrams as discussed in Chapter Three.

6.2.2 Nature of the Volcanic Parental Magmas

One hypothesis for the origin of ophiolitic volcanic rocks is that they represent the residual liquid fraction of the parental magma of the ophiolites after the formation of the cumulates. If this is true, the fractionated nature of the lavas should be reflected in their chemistry.

Seguin and Laurent (1975) argued that the ophiolitic lavas in Thetford Mines have not undergone any large scale shallow fractionation because they have restricted values of Kuno's index of fractionation (51-61). Seguin and Laurent (1975) further argued that the lavas must have been formed at an early stage of magma evolution. However, the very low Ni and Cr contents of the type I lavas at Lac de l'Est do not support their derivation from an unfractionated magma.

The nature of the parental magma for the Thetford Mines lavas may be assessed from their noble metal abundances. The low Pd/Ir ratio (average of 16) of the type I lavas, in comparison to the type II lavas (average Pd/Ir 174) suggests that the type I lavas are much more primitive than the type II lavas (e.g. Pd/Ir = 1 for chondrite). However, the type I lavas have a much lower Ir and Pd content than type II lavas. As indicated in Section 5 (Figure 5-2b and Figure 5-3) low Pd contents may be found in either early differentiates of a magma such as dunites or in late differentiates due to removal of the Pd mostly as sulfides, in the middle stages of magma crystallization. The late differentiates, however, may be distinguished from the early magma differentiates by their low Ir contents. Since type I lavas are also characterized by very low Ir contents, they are interpreted as late magmatic differentiates or the products of a very fractionated magma. Their low Pd/Ir is, therefore, not regarded as a reflection of their primitive nature but as due to low Ir contents which reflect a fractionated nature.

The low Ni, Cr and Ir contents of the type II lavas also indicate that they were not derived from a primary melt. Their high Pd contents, however, suggest that their parental magma has undergone limited fractionation. It is most probable that the parental magma has undergone some chromite and olivine segregation during which Ni, Cr and Ir but not Pd were removed.

The upper lavas are characterized by Ir contents comparable to those of some rocks regarded as primary melts, such as the chilled marginal gabbro of Bushveld and Stillwater complexes. This further supports an earlier suggestion that the upper lavas probably represent undifferentiated primary melts.

One feature common to both type II and upper lavas is that they are characterized by high Al_2O_3/TiO_2 ratios (average = 40) and low contents of incompatible elements such as Ti, Zr and Y. One way of producing low contents of the incompatible elements is by extensive partial melting of the source material for the lavas. This may be compared to the generation of komatiites by extensive partial melting of an undepleted mantle source (40% for basaltic komatiite, 60% for for peridotite komatiite) (e.g. Green, 1975). As discussed in Section 3.3.3.2, the upper lavas have many characteristics similar to those of komatiites. For example, they have TiO_2/Zr ratios (106) and Zr/Y ratios (average = 3) that are similar to ratios found in chondrite (TiO_2/Zr = 100), Zr/Y = 2.5).

One main objection to the model of extensive partial melting is that if harzburgite is the residual solid left after an extensive partial melting of the mantle source, the melt produced would have been richer in MgO than that observed in the lavas. For example, Mysen and Kushiro (1977) have shown that melts produced by extensive partial melting of lherzolite contain 19.6 wt % MgO. High pressure melting experiments on the peridotite komatiites (Bickle et al., 1977) also suggest that at 10 kb pressure, liquids in equilibrium with olivine and orthopyroxene (the minerals in harzburgite) contain 18-19 wt % MgO.

The low contents of incompatible elements in the lavas could be explained by two stage melting of a mantle source. Sun and Nesbitt (1978), Coish and Church (1979) and Duncan and Green (1980) have suggested that the low incompatible elements and high Al_2O_3/TiO_2 ratios in some ophiolitic lavas are due to the remelting of a source already depleted in incompatible elements by a previous episode of magma extraction from the source. Regarding the high Al_2O_3/TiO_2 ratios, Sun and Nesbitt (1978) argued that since TiO_2 is an incompatible element, it is partitioned more strongly than Al_2O_3 into early melts. Removal of such melts and remelting of the solid residue would produce liquids with Al_2O_3/TiO_2 greater than chondritic.

Since the MgO contents of the lavas are too low to be accounted for by extensive partial melting, the author agrees with the two-stage melting model of Sun and Nesbitt (1978), Coish and Church (1979), and Dundas and Green (1980); that is, the lavas with low incompatible elements (type II and upper lavas) are derived from melts produced by second stage melting of a mantle source.

6.2.3 Genetic Relationship between the Lavas

As mentioned earlier, one of the keys to the correct modelling of the genesis of the ophiolites is a better knowledge of the genetic relationship between the various lava types.

The close field association of the lavas might suggest some genetic relationship between them. However, the chemistry of the rocks indicates that although the type I lavas interfinger with the type II lavas, they cannot be related by any genetic process. For example, in almost all of the trace element diagrams (Figure 6-1 to Figure 6-4), the type I lavas lie on separate fractionation trends from the type II lavas. Although similar minerals must have been involved in both cases as indicated by the parallelism in some of the fractionation trends of type I and type II lavas, the initial magmas of the lavas are different. Furthermore, there appear to be no lavas with intermediate trace element contents between those of type I and type II. For example, the TiO_2 contents of the lavas form two distinct groups. It is impossible to quantiatively increase the TiO_2 contents of type II to those of type I lavas without about 80% crystallization of the type II magma. Such an extensive crystallization would have substantially increased the silica content and decreased the MgO contents of the residual magma fraction more than observed in the type I lavas.

Another line of evidence that type I lavas were not derived from the type II lavas is seen in their K_2O contents. Type II lavas have much higher K_2O than the type I lavas and since K_2O increases with differentiation, it is impossible to derive type I lavas with lower K_2O contents from the type II lavas by any mode of fractional crystallization. The different Pd contents of the lavas also do not argue in favour of any relationship between the two lava types.

Similarity in the incompatible element contents and ratio in type II lavas and the upper lavas tends to suggest a genetic relationship between these two lava types. It is quite possible that type II lava were formed from the upper lava magma via fractional crystallization. This is supported by both the Cr/Ti-Ti (Figure 6-2a) and Ni-Cr (Figure 6-5b) diagrams which show that the type II lavas can be related to a source magma of similar composition to that of some of the upper lavas. Calculations based on Raleigh's fractionation law, expressed as

$$C^1/C_o = F^{K-1}$$

where C^1 = concentration of element in melt; C_o = original concentration of element in magma; F = fraction of magma remaining after crystallization; and K = partition coefficient of element between magma and crystallizing phase, indicate that using $K^{\text{olivine-magma}} = 13$, the average Ni content in the type II lavas could be obtained from the average Ni content of the upper lavas by 10% olivine fractionation. The Cr content in type II lavas may similarly be explained by crystallization of spinel. Such olivine and spinel removal from the original melt would have no significant effect on the incompatible elements of the residual liquid, and hence the similarity in the average incompatible element contents and ratios in the type II and upper lavas. Fractional crystallization of olivine and spinel from a magma similar in composition to the average composition of the upper lavas is also compatible with the lower Ir and higher Pd contents in the type II lavas as compared with the upper lavas.

The main objection to derivation of the type II lavas from the upper lavas is that they are separated by sediments considered by Laurent (1977) as deep sea and mid-oceanic ridge type. A time interval between the extrusion of the lavas is, therefore, implied. This objection is further reinforced if the upper lavas were formed in a different environment from that of the type II lavas as suggested by Seguin and Laurent (1975) and Laurent (1977).

It is, however, possible that the type II lavas were not derived directly from the upper lavas but from a magma which is related to the parental magma of the upper lavas by virtue of the magmas being successive melts from the same depleted mantle source. In this case, the sediments mark the hiatus in volcanism during the formation of the lavas.

In conclusion, it is suggested that there were at least three magma types involved in the generation of the ophiolitic lavas the Thetford Mines. These magmas are presumed to have erupted in three stages. The first involved the formation of type I lavas from a well fractionated magma. Type I lavas were followed by the eruption of a less fractionated magma derived from a depleted mantle source to form the type II lavas. Further melting of the mantle residue produced melts which were erupted without fractionation, as the upper lavas. Details of these processes are discussed later.

6.2.4 Relationship between the Lavas, the Cumulates and the Hypabyssal Rocks

Since the upper lavas are believed to have been derived from primary melts, it is doubtful if they are related to the cumulates. The type II lavas may also be unrelated to the cumulates since they were formed from a magma that has undergone limited fractional crystallization.

The type I lavas which are derived from a well fractionated magma may, however, represent the residual liquid of a more primitive magma from which ferromagnesian minerals and plagioclase have separated to form the cumulate rocks. This suggestion is consistent with the hypothesis that ophiolitic lavas and cumulates are cogenetic (Coleman, 1977; Elthon, 1979). Evidence for the cogenetic relationship of the type I lavas and the cumulates is seen in the distribution of their noble metals (e.g. see Figure 4-3). Ir systematically decreases from the first formed cumulates (dunites) through the pyroxenites and the cumulate gabbro to the type I lavas. The very low Pd contents of the type I lavas are also best explained by the hypothesis that most of the metal has been removed by the cumulate dunites and pyroxenites.

If the cumulates and the type I lavas were derived from the same magma, the primary magma must have been very basic, perhaps komatiitic as suggested by Laurent (1979), although there is no direct evidence for the komatiitic nature of the parental magma. No 'chilled margin' rocks representative of the parental magma are known, and it is difficult to quantitatively estimate the composition of the parental magma from the chemistry of the exposed rocks since the volume of each of the rock types is not adeuqately known. Furthermore, there is evidence that the cumulates were formed by an open system fractional crystallization which implies that the magma probably did not reach a steady state during the formation of the cumulates.

The origin or relationship of the hypabyssal rocks which include dikes and metagabbros to the other rock types is uncertain. Some of the metagabbros have low TiO_2, Zr, Y and P_2O_5 contents similar to the type II and the upper lavas but their low Ni, Cr and noble metals suggest that they are as fractionated as the type I lavas. Some diabase dikes and metagabbros, e.g. samples 9MG4 A, are similar to the type II lavas in both major and trace elements but have high noble metal contents. It appears then that the hypabyssal rocks were derived from different magmas which may be related to the parental magma of the different lava types.

6.2.5 Origin of the Metamorphic Dunite

There is a consensus that the harzburgite of the metamorphic peridotite in ophiolites represents the residual solid of the mantle after the extraction of melts which are now represented by the associated plutonic and volcanic rocks. On the other hand, other hypotheses have been proposed to explain the origin of the dunites and the pyroxenites within the metamorphic peridotite. These hypotheses include:

1) gravitational settling of olivine and pyroxene from a basaltic magma,

2) metamorphic or tectonic differentiation of peridotite,

3) igneous intrusion,

4) partial melting of host peridotite with dunites as residue,

and

5) metasomatism of host peridotite by aqueous vapor phases through desilification and Ca removal.

Baldwin (1976) suggested that the metamorphic dunites in Thetford Mines ophiolites may be the residue of harzburgite after partial melting while Laurent (1977) was of the opinion that the metamorphic dunite and orthopyroxenite may be intrusive into the harzburgite. Kacira (1972), on the other hand, suggested that the dunites are part of the overlying cumulate dunites.

The dunitic bodies observed in the study area are not parallel to the tectonic foliation of the host harzburgite. This argues against their derivation by metamorphic or tectonic differentiation. Although contacts between the dunites and harzburgite are sometimes sharp, there is no evidence of chilled margin or recrystallization of marginal minerals which might suggest magmatic intrusion. The sharp boundary also argues against any form of metasomatism. Fractional crystallization produces diverse lithologies and variability in rock composition while partial fusion tends to leave a solid residue with nearly uniform mineralogy and composition (Dick, 1977). If the dunites and the pyroxenite bodies in the harzburgite are co-genetic, their occurrence is best explained by fractional crystallization. Variability in the Cr contents and $\mathrm{Fe\overset{T}{O}/MgO}$ ratios in the metamorphic dunite also argue against a partial melting model.

Distribution of the noble metals in the metamorphic dunites is also best explained by fractional crystallization. For example, in

Figure 6-6, the harzburgite displays a nearly unfractionated chondritic normalized abundance pattern. Since the noble metals are mainly concentrated in spinel (see Section 4.1) partial fusion of the harzburgite which melts mainly the pyroxene leaving a residue of olivine and spinel as dunite, could not produce a residue with substantial change in the original chondritic pattern. The marked difference in the chondritic normallized noble metal abundance patterns of the harzburgite and dunite is, therefore, incompatible with an origin of the dunite by partial melting of harzburgite. The low Pd, Pt and Au but high Ir contents of the metamorphic dunites are consistent with early accumulations of spinel and olivine from a melt, similar to the cumulate dunites at Lac du Caribou. The similarity between the metamorphic dunites and the cumulate dunites at Lac du Caribou is further shown by their Ir normallized noble metal abundance pattern (Figure 6-7).

Similarity in trace elements between the cumulate and metamorphic dunites suggests that the two are genetically related. The metamorphic dunite might represent part of the cumulate dunites that were injected into the harzburgite (Kacira, 1972). This is, however, highly unlikely if the harzburgite represents the residue of the mantle after two or more stages of melting while the cumulate dunites were formed before the second stage melting of the mantle source.

The similarity in the abundance pattern of the cumulate and metamorphic dunites may be a result of origin by similar genetic process but not processes that were co-magmatic. It is, therefore,

Figure 6-6. Chondrite normalized noble metal abundances for harzburgite, metamorphic dunite and cumulate dunite (Lac du Caribou) of TMC. Data for the chondrites are those of Crocket (1974, 1979) - 518 ppb (Ir); 1050 ppb (Pt); 575 ppb (Pd) and 140 ppb (Au). The noble metals are arranged in order of increasing volatility.

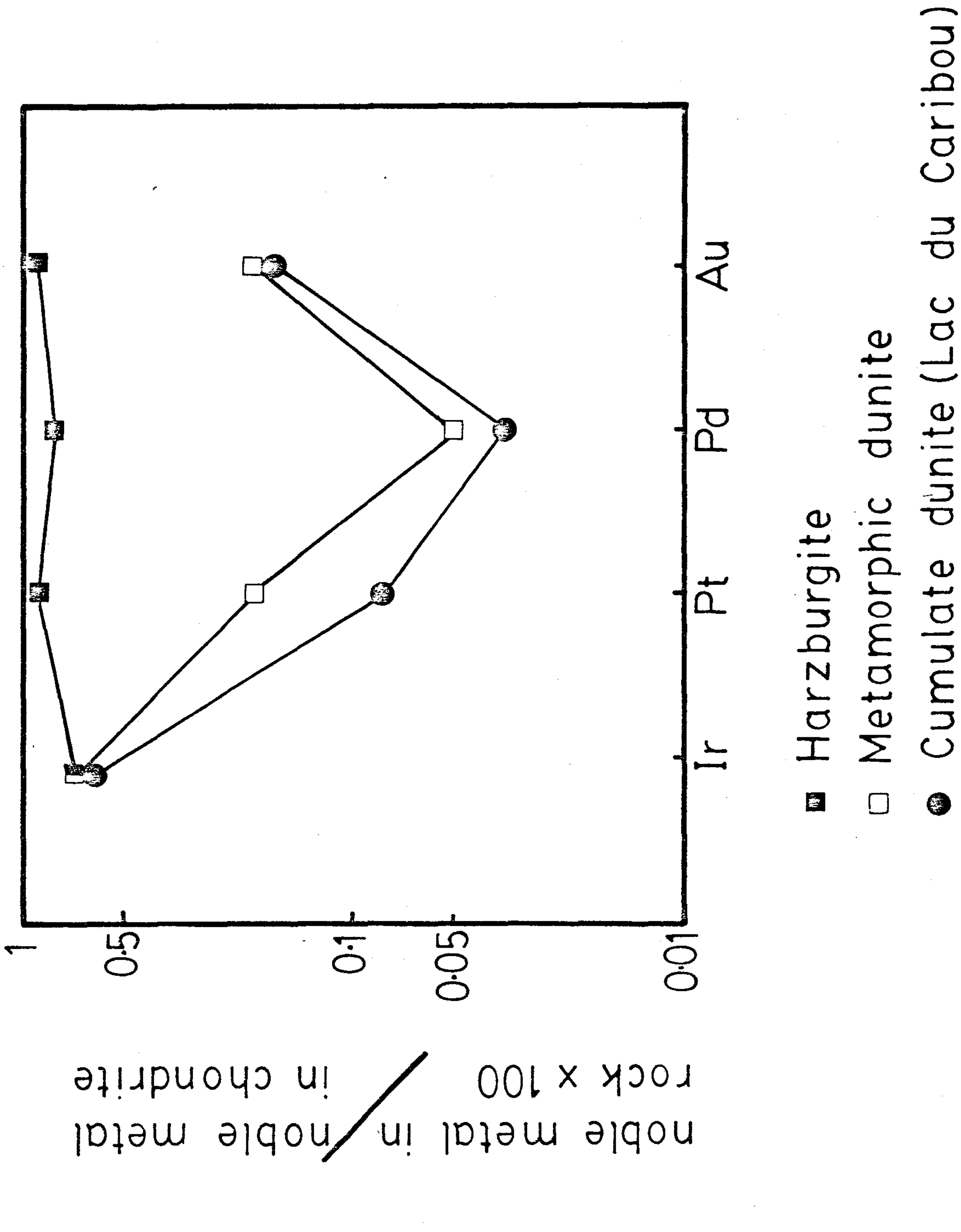
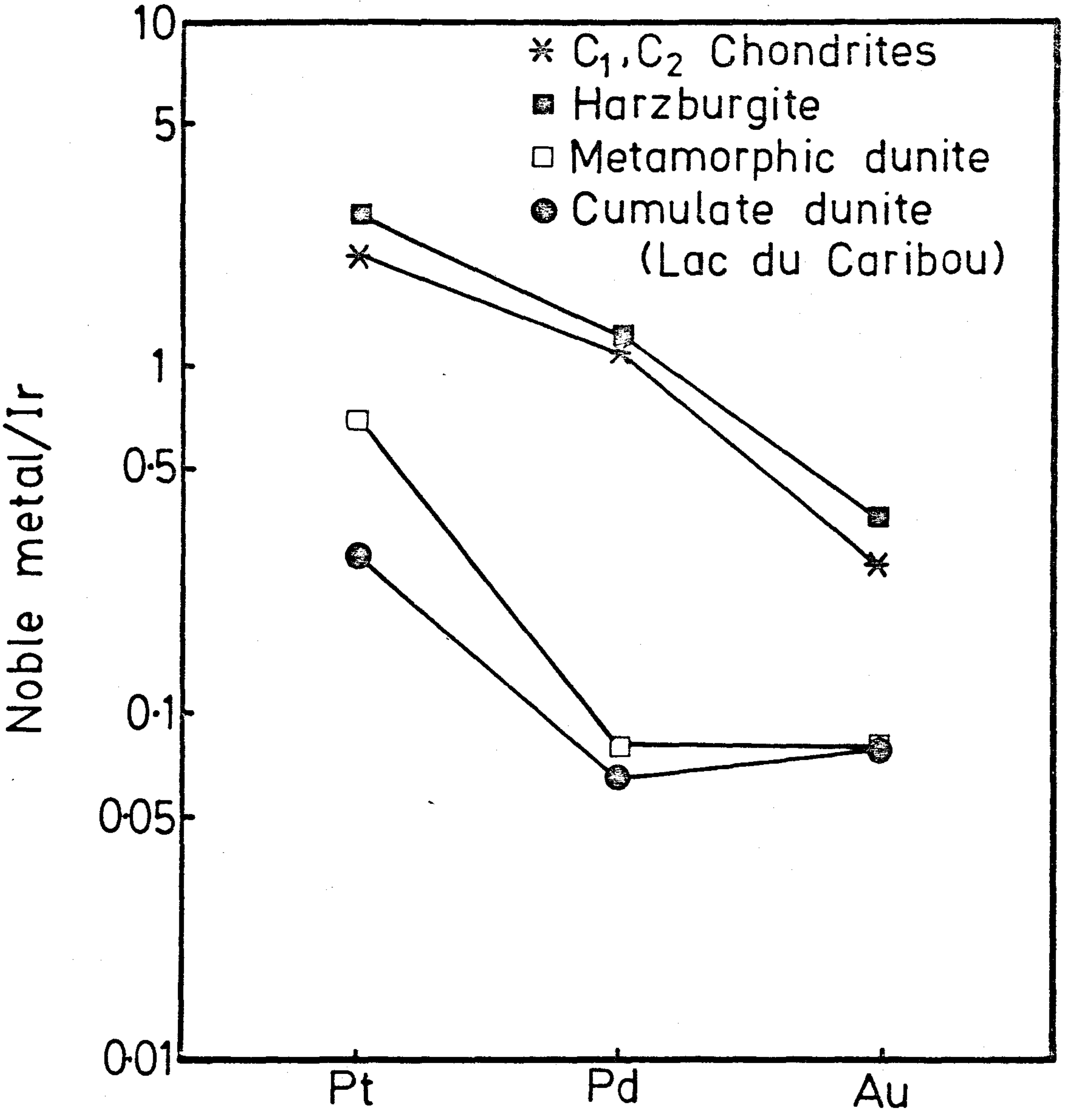

noble metal in rock x 100 / noble metal in chondrite
1
0.5
0.1
0.05
0.01
Ir
Pt
Pd
Au
■ Harzburgite
□ Metamorphic dunite
● Cumulate dunite (Lac du Caribou)

Figure 6-7. Ir normalized noble metal abundances for harzburgite, metamorphic dunites and cumulate (Lac due Caribou) dunites of TMC. Data for chrondrites as Figure 6-6.


10
5
1
0·5
0·1
0·05
0·01
Noble metal/Ir
Pt
Pd
Au
* C_1, C_2 Chondrites
■ Harzburgite
□ Metamorphic dunite
● Cumulate dunite (Lac du Caribou)

suggested that the metamorphic dunites were formed by gravitational settling of olivine and spinel from a melt. The type II lavas have previsouly been shown to represent the residual liquid fraction of a melt after separation of olivine and spinel. It is, therefore, possible that the metamorphic dunites represent the separated olivine and spinel from the parental magma to the type II lavas.

6.2.6 A Petrogenetic Model for the Thetford Mines Ophiolites

A model for the genesis of the Thetford Mines ophiolites which may also be applicable to other ophiolitic complexes in southern Quebec is hereby proposed. The model is based on the conclusions arrived at in the preceeding section.

The proposed model is summarized in Figure 6-8 and Table 6-2. The ophiolites are believed to have been formed by three main igneous events. The final stages of the first event probably overlapped with the early stages of the second event but there was a hiatus, marked by sedimentation, between the second and third events.

Stage I Formation of Ocean Crust

Substage IA. A rising mantle diapir underwent extensive partial melting (30-40%). The melt produced was segregated into a magma chamber where it underwent fractional crystallization by gravity settling of olivine, chromite, pyroxene and plagioclase to form the cumulate rocks.

Substage IB. Towards the end of fractional crystallization, the differentiated magma was tapped to form part of the hypabyssal rocks at the roof of the magma chamber. Solidification of the hypabyssal rocks probably proceeded downwards while formation of the cumulates continued upwards. There is an indication that the magma chamber was being replenished by new batches of magma at some stages during crystallization.

Substage IC. At the end of fractional crystallization, the residual liquid was extruded along some zones of weakness on to the sea floor as the type I lavas.

Stage II

Substage IIA. The residual mantle diapir left after the extraction of the melt in stage I rose, probably in response to movement of the system to a new tectonic environment or the spreading of the newly formed oceanic crust, and underwent further partial melting (probably less than 10% melting) to produce a melt depleted in the incompatible elements such as Ti, Zr, Y and P due to earlier melting. The melt was extracted into a magma chamber, leaving a solid residue of harzburgite(?). Perhaps, prior to separation of melt from the solid residue (harzburgite) olivine, spinel and pyroxene were segregated in situ from the melt to form the dunite and pyroxenite bodies now retained in the harzburgite. Alternatively, the dunite and pyroxenite may precipitate out as lag masses in the harzburgite during the passage of the melt through the residual harzburgite.

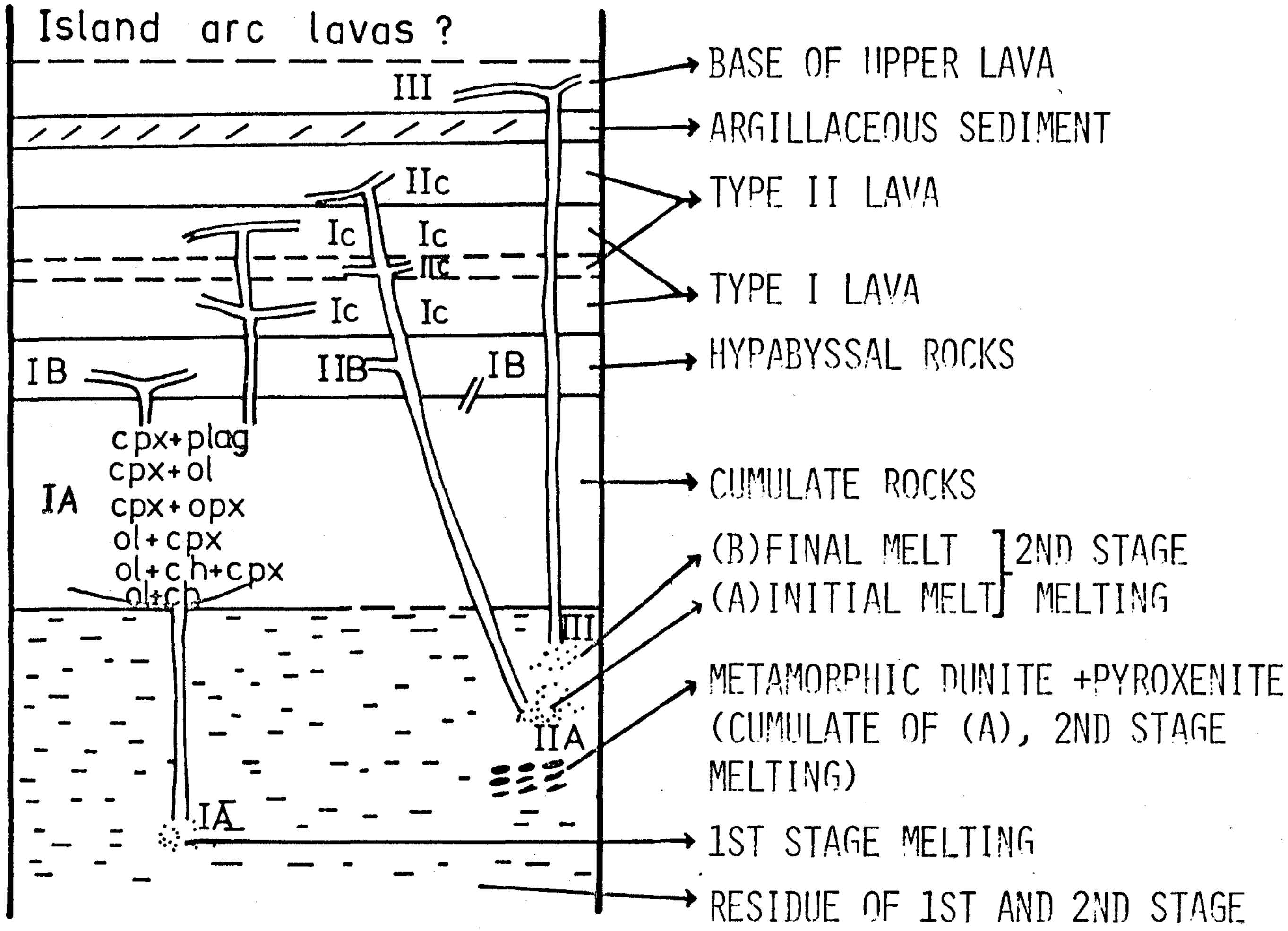
Substages IIB and IIC. The residual liquid after the separation of olivine, spinel and pyroxene was tapped through zones of weakness in the overlying crust to be extruded as the type II lavas on the sea floor above the type I lavas. Some of the melt probably failed to reach the surface and formed part of the hypabyssal rocks. The feeders for these lavas are now represented by some of the dikes cutting the cumulate and hypabyssal rocks. It is possible that the early stages of the lava extrusion in stage IIC was coincident with the late stages of lava estrusion in stage IC - hence the interdigitation of type I and type II lavas in the stratigraphic middle of the volcanic unit. In this case, the magma chambers containing type I and type II magmas were probably adjacent to one another. The interfingering of the top layer of type II lavas with argillaceous sediments also indicates that active sedimentation started before the end of volcanism in stage II. There was cessation of volcanism during which the lavas were subjected to hydrothermal alteration.

Stage III

This stage was marked by the renewal of volcanism during which lavas which form the base of the upper volcanic unit were extruded. The magmas involved probably represents the successive melt to the melt produced in stage II. That is, the magma was produced by fusion of a depleted mantle source, but unlike in stage II, the magma did not undergo any fractional crystallization prior to extrusion.

It is difficult to determine the relationships of the base of the upper lava unit studied here to the remaining part of the upper volcanic unit as the top part was not sampled. However, other studies (e.g. Laurent, 1975; Seguin and Laurent, 1975) indicate that the

Figure 6-8. Diagram showing sequence of genetic events in Thetford Mines ophiolites.


Island arc lavas ?
III
IIc
Ic
Ic
IIc
Ic
Ic
IB
IIB
IB
cpx+plag
cpx+ol
IA
cpx+opx
ol+cpx
ol+ch+cpx
ol+ch
III
IIA
IA
BASE OF UPPER LAVA
ARGILLACEOUS SEDIMENT
TYPE II LAVA
TYPE I LAVA
HYPABYSSAL ROCKS
CUMULATE ROCKS
(B) FINAL MELT
(A) INITIAL MELT
2ND STAGE MELTING
METAMORPHIC DUNITE +PYROXENITE (CUMULATE OF (A), 2ND STAGE MELTING)
1ST STAGE MELTING
RESIDUE OF 1ST AND 2ND STAGE MELTING (HARZBURGITE)

(not to scale)

Table 6-2

Correlation of Genetic Events in Thetford Mines Ophiolites

	Island arc volcanism (?)		
Renewal of volcanism			upper lava (ol + cpx + plg)
Hiatus	Sedimentation		
Substage C: Formation of lavas	Type I lava (plg + cpx)	Type II lava ol(?) + cpx + plg	
Substage B: Formation of hypabyssal rocks	metagabbro dike (cpx + plg)	metagabbro dike ol(?) + cpx + plg	
Substage A: Formation of cumulates	Gabbro (cpx + plg + hor(?)) Pyroxenite (ol + cpx + opx + plg) Dunite - wehrlite (ol + ch + cpx)	Pyroxenite (opx + cpx) Dunite (ol + ch)	
Stage (partial melting of mantle)	I	II	III

unsampled lavas may be island arc lavas.

6.3 Tectonic Environment of Formation

Various tectonic settings have been suggested for the environment in which the Thetford Mines ophiolites formed. Bird et al. (1977) suggested that the Ordovician Appalachian ophiolites, which include Thetford Mines ophiolites, were formed during the establishment of marginal basins. Seguin and Laurent (1975) and Laurent (1977) argued that the lower volcanic rocks (type I and type II lavas) are similar in magnetic and chemical properties to mid-oceanic ridge basalts and that the associated sediments are pelagic and similar to deep sea sediments. Laurent (1977) and Laurent and Hebert (1977) further indicated that the upper lavas were formed in an island arc environment. In a later paper, however, Laurent (1979) suggested that the ophiolites in southern Quebec may have formed in a marginal basin.

Ti-Zr-Y discriminant diagrams of Pearce and Cann (1973) do not suggest very likely environment of formation for the type II and upper lavas, but the type I lavas fall within the mid-ocean ridge basalt and island arc fields (see Figure 3-14 and Figure 3-15). Ophiolites with both oceanic ridge and island arc geochemical properties have been characterized as transitional and are believed to form at marginal basins (e.g. Saunders et al., 1979). In view of the mobilization of elements during the alteration of the lvas, it is difficult to know whether the 'transitional' character of the lavas is real or due to mobilization of elements. Hence, it would be premature to regard Thetford Mines ophiolites of marginal basin type on the basis of the 'transitional' character of some of the lavas.

Low TiO_2 basalts similar to type II and the upper lavas are believed by some workers (e.g. Sun and Nesbitt, 1978) to be generated in an interarc basin or beneath an island arc. But, as pointed out by Coish and Church (1979) and Duncan and Green (1980), the dominant factor which controls the low TiO_2 contents of basalts is their mode of genesis, that is their derivation from depleted ultramafic or mantle sources. It follows that given the necessary physico-chemical conditions for melting, a depleted mantle source could yield melts with low TiO_2 contents in any tectonic environment (Smewing and Potts, 1976). The author agrees with Coish and Church (1979) that the mode of genesis of the low TiO_2 basalts is the most significant factor which determines their TiO_2 contents, but it is also true that certain oceanic environments are more suitable for remelting of a depleted mantle residue than others. As pointed out by Sun and Nesbitt (1978) an island arc environment in which water is liberated during subduction is more suitable for providing the water necessary to lower the melting point of the refractory residual mantle. Nevertheless, an island arc environment cannot be assigned to the Thetford Mines ophiolites on the basis of their low TiO_2 lavas alone, and other factors have to be considered.

Comparison of the noble metal contents in Thetford Mines lavas and basalts from various oceanic environments (Table 6-3) shows that

Table 6-3

Comparison of Noble Metal Contents of TMC Lavas and Other Oceanic Basaltic Rocks

	Rock Type and Locality	No. of Samples	Noble Metal Contents in ppb				Reference
			Au	Ir	Pt	Pd	
Ocean Ridge and Rise	East Pacific Rise basalt	3	0.18	0.043			Laul *et al.*, 1972
	East Pacific Rise basalt		0.40	0.2			Ehman *et al.*, 1970
	Mid-Atlantic Ridge basalt		0.34	0.039			Laul *et al.*, 1972
	Mid-Atlantic Ridge basalt	3, 2	0.27	0.2			Ehman *et al.*, 1970
	Mid-Atlantic Ridge basalt	6	0.74	<0.035			Scott and Keays, 1976
	Mid-Atlantic Ridge Leg 37 DSDP basalt	13, 12,	2.9	<0.025		<0.69	Crocket and Teruta, 1977
	Ocean Ridge and Rise Tholeiites	9	0.6	<0.05			Gottfried and Greenland, 1972
	Ocean Ridge and Rise Alakali basalt		0.8	<0.05			Gottfried and Greenland, 1972
Oceanic Island	Tholeiites, Hawaii	3	4.2	1.77			Ehman *et al.*, 1970
	Ocean Island basalt, Hawaii, Mauna Loa, Kilauea	10	2.35	0.22			Gottfried and Greenland, 1972
	Intraplate and off ridge ocean island basalt	27, 14		0.36		1.6	Crocket, 1979
T M C	Type I lava	10, 10, 6, 10	2.35	0.019	6.18	<0.31	This study
	Type II lava	7, 8, 6, 8	1.65	0.056	9.15	7.92	This study
	Upper lava	8, 8, 5, 7	2.21	0.234	16.04	6.81	This study

type I lavas are similar in their Au, Ir and Pd contents to the MAR Leg 37 basalts and oceanic ridge tholeiites. Type II lavas are also similar in Au and Ir to oceanic ridge tholeiites but have much higher Pd contents. The noble metal contents of the upper lavas are comparable only to the oceanic island and intraplate basalts. Gottfried and Greeland (1972) in their studies of variation of Ir and Au in oceanic and continental basalts suggested that variation of Au/Ir ratios of basalts is a reflection of regional variation in their Au and Ir contents. The different Au/Ir ratios in the ophiolitic lavas would therefore suggest that the lavas were derived from different tectonic sites. However, the geochemical behavior of both Au and Ir observed in this study suggests that the Au/Ir ratio of a rock also depends on its evolutionary history. A low Au/Ir ratio such as that of the upper lavas indicates that the lavas were derived from an unfractionated melt while the high Au/Ir ratios of type I lavas are a reflection of very low Ir contents in the rocks due to fractionation of Ir from their parental magma. It seems, rather regretably, that noble metal distribution in the ophiolites is not very useful in distinguishing the tectonic regime of formation of the ophiolites. A more effective use of noble metals might be possible if there were more noble metal data on basalts from environments such as island arcs and marginal basins so that the Thetford Mines lavas could be adequately compared with lavas from the different oceanic environments.

Two aspects of the Thetford Mines ophiolites which might provide insight into their tectonic environment of formation are 1) the internal structure of the ophiolites, and 2) their associated sediments. The cross cutting and lateral pinching of layers in the cumulate section of the ophiolites suggests that the cumulates were emplaced in an active tectonic regime - most probably in an environment similar to an actively rifting ridge such as a spreading center. However, the absence of a well developed dike complex implies a relatively stable non-tensional regime different from that obtained under normal spreading centers. Such an environment may exist in a marginal basin spreading center where spreading is more diffusely distributed (Evarts, 1977).

Comparison of the sediments overlying the lower volcanic unit of the Thetford Mines ophiolites with sediments associated with ocean ridges and other ophiolites such as Troodos indicate that Thetford Mines sediments are non-metalliferous and have low Fe for a given Mn content and vice-versa (Table 6-4). If the metalliferous and high Fe-Mn rich sediments of oceanic ridges and some ophiolites have been formed by hydrothermal activity at oceanic ridges (Bonatti et al., 1975; Spooner and Fyfe, 1973; Fryer and Hutchinson, 1977) then the sediments associated with the Thetford Mines ophiolites were probably not formed in the same manner or an environment similar to an oceanic ridge.

The Al contents of the sediments (Table 6-4) may also provide a clue to the question of the source of the sediments. The Al contents of Thetford Mines ophiolitic sediments average 8.2 wt %. This is too high for oceanic ridge or pelagic sediments which average less than 4 wt %. The high Al contents of these sediments must be due to a source rich in Al such as rocks from a continental or an arc environment. This

Table 6-4

Comparison of Chemical Composition of TMC Sediments and Sediments Associated with Ocean Ridges and Ophiolites

Rock Type and Locality	No. of Samples	wt %				p p m			Reference
		Si	Al	Fe	Mn	Ni	Cu	Zn	
Mudstone, Troodos	2	7.94	1.14	37.80	5.52	210	6200	375	Elderfield *et al*., 1971
Black chert, Troodos	2	30.55	0.76	14.21	3.10	470	120	110	Elderfield *et al*., 1971
Ochres, Troodos	2		2.05	55.80	1.54				Constaninou and Govett, 1972
Umbers, Troodos	2		3.35	43.2	17.3				Constaninou and Govett, 1972
Metalliferous sed., Apennines		16.95	0.22	0.13	43.34	120	420	67	Bonatti *et al*., 1976
East Pacific Rise sed., 12-16°S	15	14.3	0.32	28.3	10.7				Böstrom, 1973
East Pacific Rise sed.		6.1	0.5	18.0	6.0	430	730	380	Bonatti, 1975
Mid-Atlantic Ridge				0.01	39.2	100	12		Bonatti, 1975
TMC Argillaceous Chert	4	27.78	8.2	7.68	0.1	106	53	60	This study

implies that the environment of formation of the ophiolites was close to a continent or an arc. Such an environment could be an island arc, and interarc basin or a marginal basin.

Three points are of importance from the above considerations. 1) The ophiolites were probably formed in a non-tensional spreading center. 2) Presence of low TiO_2 lavas suggest formation of some of the ophiolitic lavas by remelting of a depleted mantle probably in an environment such as island arc or an environment close to a source of water, e.g. a subduction zone. 3) The sediments associated with Thetford Mines ophiolites are most probably derived from a source rich in Al such as rocks from the continents or from arc environments.

The first point does not argue in favor of formation of Thetford Mines ophiolites from an island arc. Similarly, the second and third points do not favor formation of the ophiolites from a mid-oceanic ridge environment. All the three points are consistent with the formation of the ophiolites from an inter-arc basin or a marginal basin.

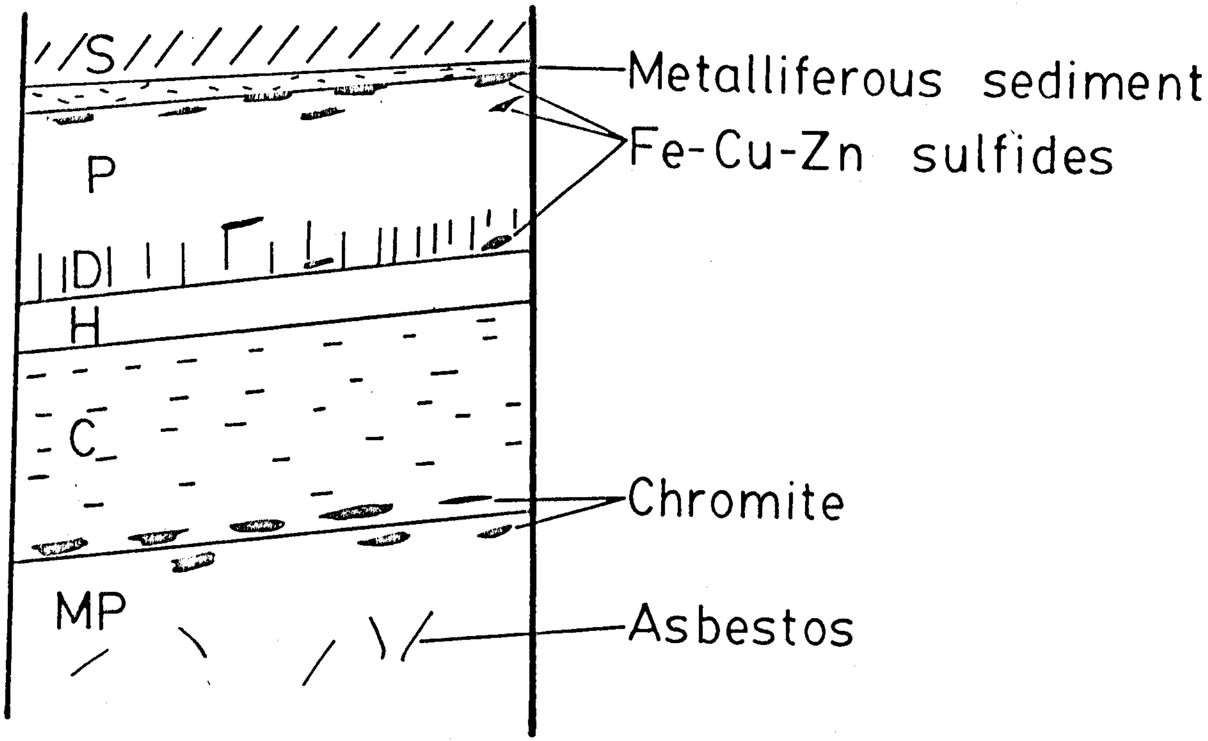
CHAPTER SEVEN

ECONOMIC EVALUATION OF THETFORD MINES OPHIOLITES

Ore bodies of both igneous and metamorphic origin have been reported in many ophiolites. Although Au and Ag may occur as minor or trace constituents in some of these deposits (Thayer, 1976; Coleman, 1977; Griffitts et al., 1972; Hutchinson, 1973) no noble metal deposits or major occurrences of noble metals have been reported in any ophiolite. This may result from the lack of attention to noble metals in ophiolites in general. One of the objectives of this study is to evaluate the economic potential of Thetford Mines ophiolites, particularly with respect to the noble metals.

The most important of the ore deposits in ophiolites are the metal sulfide deposits (Figure 7-1). These normally occur as stratabound lenses of massive pyrite-chalcopyrite ore within the volcanic units, usually along altered zones. In some ophiolites such as Troodos, York Harbor of Bay of Island, Apennines and Oman, the altered zone lies at the stratigraphic top of the volcanic unit while in others such as Betts Cove parts of the Apennines and Bay of Island, the altered zone occurs near the base of the volcanic unit. These sulfide bodies are usually overlain by metalliferous sediments, the base of which may be cuperiferous. At Troodos, York Harbor and Oman,

Figure 7-1. Generalized diagram showing the distribution of mineral deposits in ophiolites.



MP, Metamorphic peridotite; C, Cumulates;
H, Hypabyssal rock; D, Dike swarm;
P, Pillow basalt; S, Sediments

these sediments are overlain by another volcanic unit which is invariably unmineralized.

Some ore deposits in ophiolites are exploited for Cu and Zn. Of the noble metals, only Au and Ag have been reported as minor constituents in the ore bodies (e.g. Griffitts et al., 1972; Hutchinson, 1973; Thayer, 1976; Sawkins, 1976; Coleman, 1977). The tenor of the noble metals is high enough to be economic. For example, Bear (1963) reported Au concentrations of up to 2 troy oz/ton (62 ppm) and Ag concentrations of about 6 troy oz/ton (186 ppm) in some Troodos sulfide deposits. Bailey et al. (1967) also reported Au concentrations of 2.2 troy oz/ton (68 ppm) and Ag concentrations of 11 troy oz/ton (322 ppm) in some ophiolitic sulfide deposits.

Since metal sulfide deposits and metalliferous sediments are common in ophiolites, it might be expected that Thetford Mines ophiolites would also contain some ore deposits. Harron (1973) indicated that some sulfide deposits, mainly massive pyrrhotite-pyrite-chalcopyrite bodies, with minor amounts of lead, silver and gold occur concordantly within the volcanic rocks of the ophiolites in the Eastern Townships of Quebec. However, the map of Sauve et al. (1972) shows that these deposits are located further south of the Thetford Mines complex (Orford complex). The most important of these deposits are the Quebec Copper Ltd. deposits around the Towship of Eastman. These deposits produced about 2 million tons of low grade copper (0.9 % Cu) between 1953 and 1958. No metal sulfide deposits have been reported in Thetford Mines ophiolites, and with the exception of some insignificant disseminated pyrite in the schistose and massive lavas at the base of the volcanic unit at Lac de l'Est, Thetford Mines lavas show no indication, from this study, of any sulfide mineralization. If these pyritic schistose lavas actually represent a weakly mineralized zone of the volcanic unit, this would further demonstrate the similarity between Thetford Mines and Betts Cove ophiolites where the mineralized zone also occurs at the base of the volcanic unit. The geochemical similarity between Thetford Mines and Betts Cove ophiolites has been previously noted (Church, 1976, this study Chapter 3). In addition to the lack of mineralization in the volcanic unit, these sediments capping Thetford Mines ophiolites are also unmineralized.

A lack of significant metal sulfide mineralization is also observed in Circum-Pacific ophiolites (Coleman, 1977). The reason for this lack of mineralization in these ophiolites is not known. Factors which are fundamental to the formation of ore deposits in ophiolites and oceanic crust are briefly reviewed and discussed in relation to the Thetford Mines ophiolites.

1) Sea water circulation and leaching of metals. Formation of the ore deposits in ophiolites or oceanic ridges depends largely on whether or not metals are leached from the lavas lying below these deposits. Leaching of metals from the lavas depends on many factors including lava/sea water ratio, textures of lavas, Eh-pH and temperature of the circulating sea water. Of these factors, temperature is the most significant (Hajash, 1975). Comparison of metamorphic

mineral assemblages in altered lavas from Thetford Mines and other ophiolites like Troodos and Oman where mineralization is observed indicates that the temperature attained during hydrothermal metamorphism in Thetford Mines was comparable to other ophiolites. It has also been shown that various elements were mobilized during alteration of Thetford Mines lavas. The lack of mineralization in Thetford Mines, therefore, is probably not due to the lack of leaching and mobilization of metals from the lavas, at least for Au, Ag and the base metals.

2) Tectonic environment. It was suggested earlier that Thetford Mines ophiolites were most probably formed in a marginal basin. It might be argued that formation of the Thetford Mines ophiolites in an environment other than a mid-ocean ridge environment might be responsible for the lack of mineralization. However, other ophiolites such as those of Oman which are believed to have formed in a marginal basin (Pearce, 1979) are mineralized. It seems, however, that the most important factor is not the tectonic environment but the physico-chemical characteristics of the environment. Deposition of leached metals from lavas depends essentially on the oxidation potential of the environment. For example, the metalliferous sediments are precipitated by the mixing of a metalliferous hydrothermal fluid with the more alkaline and oxidizing sea water (Cronan, 1976) while deposition of the sulfides requires low redox conditions. It is possible that the redox potential at Thetford Mines was not suitable for the deposition of the leached metals.

The occurrence of Cu-Fe mineralization (Bonatti et al., 1976) and manganese deposits (Scott et al., 1974) in some oceanic fracture zones, suggest that perhaps metallogenesis in oceanic crust occurs in tectonic settings where crustal fractures, either at spreading centers or fracture zones, provide adequate channels for sea water hydrothermal circulation and also for upward injection of upper mantle metalliferous volatiles. Some fractures may also locally serve as small pockets where sea water circulation is restricted. Such pockets should be reducing and ideal for sulfide precipitation. It is possible that Thetford Mines ophiolites were formed in part of the marginal basin where there are no rift or any tectonic features which might provide adequate channels for circulation of hydrothermal sea water. Paucity of fractures within the Thetford Mines lavas also reduce the chances of local precipitation of sulfides.

3) Low sulfur content in lavas. Formation of metal sulfide deposits requires an adequate supply of sulfur. The lack of mineralization in Thetford Mines may be due to low available sulfur. Sulfur isotope studies in the Troodos complex indicate that the sulfide of the ore deposits is partly from sea water by reduction of sea water sulfate, and partly from sulfur leached from the lavas. Low available sulfur in the Thetford Mines ophiolites may arise from 1) non-reduction of sea water sulfate due to excessively high redox potential in the hydrothermal system, and 2) low sulfur content of fresh lavas.

It is apparent that no definite reason can be given to explain the lack of mineralization in the volcanic unit of Thetford Mines ophiolites. Perhaps all the three factors discussed are relevant, but formation of the ophiolites in a non-fractured environment and low sulfur content of the lavas seem the most probable causes for the absence of metal sulfides.

Apart from mineralization assocated with the lavas, ophiolitic ultramafic rocks are also potential sources of metal deposits which may include the noble metals. In layered complexes such as Bushveld and Stillwater, the cumulates are assocated with base metal sulfides and chromite layers which also carry economic concentrations of noble metals, particularly Pt and Pd. Although no base metal sulfide of economic significance has been reported in the cumulate section of Thetford Mines or any other ophiolites, the metamorphic peridotite and cumulate sections of many ophiolites do carry segregations of chromite. In many cases these chromite segregations form deposits which are mined for chrome. These chromite deposits are potential sources of economic noble metals. For example, in the Acoje chromite mine in the Phillippines, 5500 oz of Pt and Pd were recovered in 1972 (Thayer, 1976).

In Thetford Mines, mining of chromite deposits dated back to 1894 (Denis, 1932) and continued, although rather intermittently, till after the Second World War. Before mining ceased in 1950, a total of 91,000 tons of chrome ore had been mined (Kacira, 1972). Noble metals were not recovered during the mining of chrome and there is no record that the chromite deposits were ever prospected for noble metals.

The distribution of the noble metals in the ultramafic rocks of Thetford Mines ophiolites as observed in this study, indicates that the rocks are of no economic significance with respect to the noble metals. The highest concentrations of the noble metals are found in the youngest dunites and pyroxenites of the cumulate section. These concentrations (highest values 196 ppb Pt, 133 ppb Pd) are too low to be of any economic importance. The chromites in layers at the base of the cumulate section are also characterized by very low Au, Pt and Pd contents. Even their relatively high Ir content (158 ppb) is equivalent to only 0.005 oz/ton. If the chromite deposits could be mined to the postwar level of 300 tons/year (Kacira, 1972) the amount of recoverable Ir would not exceed 1.5 ounces. At a price of US $300 per oz of Ir (Ontario Mineral policy Paper 7) this will fetch only $450.

The chromite in the harzburgite has higher concentrations of Au and the platinum metals than the chromite in the cumulate section. However, the proportion of chromite in this rock is too small and the chromite too randomly distributed to be of any economic significance. Extreme concentration of the chromite either by weathering or some other secondary processes would be needed to make the noble metals in the harzburgite economic.

As discussed earlier, it seems that the main reason the ultramafic rocks of Thetford Mines ophiolites are poor in the noble metals is their low sulfide content which might act as noble metal carriers. It is also possible that the parental magmas for the ophiolites were low in the noble metals.

Of more importance than the metal sulfides are the asbestos deposits in some ophiolites. The asbestos are fibrous chrysotile developed during the serpentinization of the harzburgite. Not all serpentinized ophiolites have asbestos deposits but Thetford Mines ophiolites are the world's leading producers of asbestos. Formation of asbestos in Thetford Mines is due to fracturing of the harzburgite during tectonic emplacement and migration of solution into fractures.

It was first thought that circulation of serpentinizing solutions could mobilize noble metals in the serpentinized rocks and concentrate them to economic level. However, observations from this study (Section 5-2) indicate that only Au appears to be slightly added to the serpentinized rocks while the other noble metals are redistributed and such mobilization is not effective enough to cause any economic concentration of the noble metals.

In summary, Thetford Mines ophiolites do not seem to have any economic potential for either base or noble metals.

CHAPTER EIGHT

CONCLUSIONS

Thetford Mines ophiolites were formed from three different magmas injected in at least three stages (Figure 6-4, Table 6-2). First stage: The first stage probably occurred during the initial development of a marginal basin behind a subduction zone. A rising mantle diapir underwent partial melting (about 30 - 40 %) to produce a very basic magma. This magma was segregated into a chamber in which gravitational settling of olivine, chromite, pyroxene and plagioclase formed a layered cumulate sequence of dunite, pyroxenite and gabbro, and left residual liquid depleted in Mg, Ni, Cr and Ir. The residual magma was later emplaced to form part of the hypabyssal rocks and the type I lavas. The cumulates, hypabyssal rocks and the type I lavas formed the first crust of the marginal basin.

Second stage: As the marginal basin matured and spreading of the new crust progressed, the depleted mantle underwent a second melting episode (less than 10 %) which produced a melt depleted in the incompatible elements such as Ti, Zr, Y and P. This melt underwent crystallization and gravitational fractionation of olivine, chromite and pyroxene to produce dunites and pyroxenites which are retained as lenses and pods in the residual mantle (harzburgite). The residual liquid was later erupted forming part of the hypabyssal rocks and the type II lavas. Because olivine, and pyroxene fractionation was not extensive during second stage melting. the residual liquid was not as depleted in Mg, Ni, Cr and Ir as was the residual liquid from the first melt.

These events were followed by a hiatus in volcanism during which the lavas were subjected to hydrothermal alteration. The lavas were metamorphosed to greenschist facies and the hypabyssal rocks to greenschist and amphibolite facies. Sediments derived from the adjacent arc environment were also deposited on the lavas.

Third stage: Further melting of the depleted mantle diapir produced a final batch of melt which was extruded over the sediments. This melt was low in Ti and other incompatible elements but high in Mg, Cr, Ni and Ir and has the characteristics of basaltic komatiites. Perhaps, at this time the new crust had migrated very close to the adjacent island arc such that the lavas produced by the island arc volcanism came to lie on the low Ti lavas (Stage 3) above the sediments.

At some stage during the evolution of the new crust, sea water penetrated the volcanic pile reaching the ultramafic rocks and caused serpentinization of the residual mantle (harzburgite) and the ultramafic cumulates. However, the harzburgite was not as heavily altered as the cumulate dunites.

During the closing of the marginal basin, a portion of the crust and the mantle residual were not destroyed or subducted, but emplaced on the continental margin either by obduction (Coleman, 1977) or by some other mechanism to form the present day ophiolites.

During the emplacement of the ophiolites the harzburgite was fractured and subsequent migration of meteoric fluid through these fractures induced another serpentinization in the rocks. This second serpentinization was responsible for the formation of asbestos fibres in the harzburgites.

During the fractional crystallization of the first magmas to form the cumulates, Ir was concentrated in the early chromite-rich dunites while Pt and Pd were partitioned in the residual liquid. There was no preferential partitioning of Au between solids and the residual liquid. As crystallization progressed, Ir became depleted while Pt and Pd were accumulated in the residual magma together with S and incompatible elements such as B, As and Te. During the formation of the youngest dunites and the oldest pyroxenites at the middle stages of magma crystallization, Pt and Pd were precipitated with sulfides or as native metals, probably due to a reduction of f_{O2} or increase in f_{S2} of the magma. This leads to a high concentration of Pt and Pd in the youngest dunites and the oldest pyroxenites.

The high concentration of Pt and Pd in the dunites and pyroxenites must have depleted the magma in these elements and hence low abundance of these metals are found in the residual magma represented by the type I lavas.

Because the melt produced during the second stage melting did not suffer much fractional crystallization, the residual magma, represented by the type II lavas was not depleted in Pt and Pd. However, fractionation of chromite from the parental magam slightly depleted type II magmas in Ir.

The low Ti lavas lying above the sediments (upper lava) were derived from a relatively unfractionated melt. Consequently they are not depleted in the noble metals, and their noble metal abundances are comparable to those of other oceanic unfractionated or primitive lavas such as oceanic island basalts.

Observations of the geochemical behavior of the noble metals during fractional crystallization indicate that for sulfur poor magmas such as the parental magma for Thetford Mines cumulates, Pt/Pt + Pd ratios decrease while Pd/Pd + Ir ratios increase with increasing magmatic differentiation. This is in contrast to komatiites and sulfur rich magmas in which Pt/Pt + Pd ratios increase with increasing magmatic differentiation.

Geochemical behavior of Pd and Ir suggests that the ratio Pd/Ir commonly used as an index of primitiveness by many workers should be treated with caution as both early and late differentiates of a crystallizing magma may have low Pd/Ir ratios which would indicate primitiveness. However, early magmatic differentiates may be distinguished from late differentiates by their higher Ir contents.

Correlation of Ir with Cr and of Pt and Pd with Fe suggests possible substitution of Ir^{+4} for Cr^{+3} and Pt^{+2}, Pd^{+2} for Fe^{+2} in minerals. But, on other geochemical grounds (ionization potential, electronegativity crystal field stabilization energy) only limited ionic solid solution between the noble metals and these other elements is possible, and most substitutions probably occur via lattice vacancies or some other structural defects in minerals.

Except for Ir which is hosted by chromite, there is no mineralogical control on the distribution of the noble metals in either the plutonic or volcanic rocks. However, in the metamorphic peridotite (harzburgite) the noble metals appear to be hosted by chromite, mostly along grain boundaries.

Most of the major and trace elements were mobilized during the hydrothermal alteration of the lavas. Although theoretically the noble metals should be mobilized like the other elements, only Au appears to be affected by hydrothermal alteration. It is suggested that the noble metals were inert probably because the physico-chemical conditions of the hydrothermal system were not oxidizing enough to cause any dissolution of noble metals. Mobilization of Au in the altered lavas is believed to have involved only anomalous Au that was loosely held in grain boundaries or on grain surfaces.

The noble metals were also immobile during serpentinization of the ophiolites in the oceanic environment, probably because reducing conditions prevailed during serpentinization which prevented any dissolution of the noble metals. However, during the second serpentinization episode, the PGE were redistributed in the serpentinized rock and Au was added to the rock from the serpentinizing fluid.

Unlike some ophiolites which carry economic mineral deposits, Thetford Mines ophiolites appear to lack both base and noble metal mineralization. The following reasons are suggested for the lack of mineralization of Thetford Mines ophiolites.

1) Hydrothermal activity was probably not intense enough in Thetford Mines lavas to cause appreciable leaching of metals from the lavas. This may be due to the lack of adequate fractures to provide channels for sea water circulation.

2) The redox potential in the hydrothermal system within the ophiolites was probably too oxidizing to allow any reduction of sea water sulfate to sulfide or the formation of metal sulfide and precipitation of metalliferous sediments during hydrothermal alteration of the ophiolitic lavas.

3) The sulfur content of the ophiolitic rocks was too low for sufficient sulfides to be formed from leached lavas.

4) The parental magmas of the ophiolites were probably low in noble and base metals.

5) Due to the low sulfur contents of the parental magmas, insufficient immiscible sulfide formed to concentrate the noble metals to economic level during fractional crystallization.

6) Due to the reducing conditions of the oceanic environment during major serpentinization of the ultramafic rocks, the noble metals could not be mobilized to economic concentrations by serpentinization.

APPENDIX I

SAMPLING

I.1 Field Sampling

The main objective in sampling Thetford Mines ophiolites was to obtain rocks that would represent the most complete sequence of the ophiolite suite. Consequently most samples were collected from the Lac de l'Est area where the most complete section of the ophiolite suite is preserved. Sampling was made easier in the case of the harzburgite and dunite as these rocks were extensively blasted in many localities for asbestos and chromite workings. The lavas are mostly flat lying and difficult to sample. In most cases they were sampled by taking chips from many parts of an outcrop with a chisel and a hammer.

Outcrops were located using maps prepared by Y. Hebert of the Universite de Laval, Quebec and a Field Guide prepared by B. Baldwin of Middlebury College. Each sample was assigned a number for identification. Samples were collected during 1978 and 1979 summer and samples whose identification numbers start with 9 were collected in 1979. Brief explanations of the identification numbers are as follows.

MPH denotes metamorphic peridotite - harzburgite

MPD denotes metamorphic peridotite - dunite

CD denotes cumulate dunite

CPY or CY denotes cumulate pyroxenite
SU denotes serpentinized ultramafic
CG denotes cumulate gabbro
MG denotes metagabbro (part of hypabyssal rocks)
LB denotes lavas of the lower volcanic unit
UB denotes lavas of the upper volcanic unit

The last figure of an identification number represents the locality number of the sample while the last letter represents the nth sample collected at the locality: e.g. A is the first while D is the fourth sample collected. Locality numbers are as follows:

1. Black Lake
2. Vimy Ridge
3. Lac du Caribou
4. Lac de l'Est
5. Mt. Adstock
6. Lac Rond
7. Petit Lac St. François/Bisby Lake
9. Coleraine

I.2 Sample Preparation for Analysis

Weathered surfaces were removed from the chunks of sample with a hand hammer. Cleaned chunks were then broken up into chips less than 1.5 cm in diameter with a sledge hammer. The pieces were then quartered. The fraction selected for analysis was washed in hot and distilled water. After drying, the pieces were fed into a ceramic lined pulverizer to be broken into finer pieces. The pulverized sample was then fed into a ceramic shatterbox and crushed until everything passed through a 200 mesh bolting cloth. The crushed powder was stored in a glass bottle.

APPENDIX II

NEUTRON ACTIVATION ANALYSIS (NAA)

Au, Ir Pt, Pd and Ag were analyzed in whole rock and mineral separates by radio-chemical neutron activation procedures. The principle of neutron activation is well discussed in a number of textbooks (e.g. Overman and Clark, 1960 and De Soete et al., 1972). The neutron activation method was chosen because of its proven sensitivity for noble metals.

II.1 Theoretical Background

Briefly, NAA involves the exposure of the element whose concentration is to be measured to neutrons, to produce daughter isotopes of the element. Some of the daughter isotopes are radioactive and decay spontaneously by emitting some radiations usually γ radiation. The induced activity in radioisotope is a measure of the number of radioisotopoe atoms produced during the exposure of the parent element to neutrons (irradiation). The induced activity depends on many factors including the concentration of the target (parent) element. It is this factor that forms the basis of NAA (De Soette, 1972).

NAA is a comparator method. The activity produced by the radioisotope of the element whose concentration is sought in a sample is compared with that of a standard source containing a known amount of the same element. Both the sample and the standard are irradiated and their activities measured under the same conditions. Because activity of the sample is not measured at the same time as that of the standard, it is necessary to normalize all activities to a common time.

The induced activity in a radiated sample (A) is given by the equation

$$A = R.E.I\ (1 - e^{-\lambda t_i})\ e^{-\lambda t_d} \tag{II-1}$$

where R = rate of production of daughter radioisotopes for a target element; E = the efficiency of the device used for measuring the activity; I = the intensity of radiation; t_i = time of irradiation; and t_d = decay time. R is also defined as

$$R = N\ a\sigma F \qquad \text{(Faure, 1972)} \tag{II-2}$$

where N = the number of target atoms; a = the isotopic abundance of the target isotope; σ = the neutron capture cross section of the target isotope; and F = the neutron flux of the neutron source.

Substituting for R in equation II-1

$$A = N\alpha\sigma FEI\ (1 - e^{-\lambda t_i})\ e^{-\lambda t_d} \tag{II-3}$$

Equation II-3 indicates that the measured activity is directly proportional to the number of atoms of the target element.

$$A \propto N \text{ or } A \propto CW$$

where C is the concentration of the irradiated element and W the weight of the sample containing the element

Or $$A = kCW \tag{II-4}$$

For a sample and a standard irradiated together

$$k = A_o{}^S/C^SW^S = A_o{}^T/C^TW^T \qquad \text{II-5}$$

where C^S, C^T are the concentration of the element in the sample and standard, and W^S, W^T are the weight of the sample and standard respectively.

Rearranging equation II-5

$$A_o{}^S/A_o{}^T = C^SW^S/C^TW^T \qquad \text{II-6}$$

Knowing $A_o{}^S$, $A_o{}^T$, W^S, W^T and C^T, the concentration of the element in the sample (C^S) can be calculated.

II.2 Nuclear Reactions

The pertinent equations for the (n, γ) nuclear reactions for the analysis of the noble metals are as follows:

$^{197}Au\ (n, \gamma)\ ^{198}Au$ ($T_{1/2}$ = 2.696 d, γ - 411.8 kev)

$^{191}Ir\ (n, \gamma)\ ^{192}Ir$ ($T_{1/2}$ = 74.2 d, γ - 296, 308, 317 and 464 kev)

$^{198}Pt\ (n, \gamma)\ ^{199}Pt \xrightarrow[B^-]{30\ min} {}^{199}Au$ ($T_{1/2}$ = 3.14 d γ - 58.4 kev)

$^{108}Pd\ (n, \gamma)\ ^{109}Pd$ ($T_{1/2}$ = 13.46 h B^- - 1030 kev)

$^{109}Ag\ (n, \gamma)\ ^{110}Ag$ ($T_{1/2}$ = 252 d γ - 658 kev)

II.3 Analytical Procedure

The analytical procedures used in this study are modified from the standard multi-component radio-cehmical neutron activation analysis procedure described by Crocket *et al*. (1968) and Keays *et al*. (1974). The procedures involved irradiation of samples and standard solutions containing a known concentration of the noble metals, chemical isolation of the noble metals from the irradiated samples and the standards and measuring the activities produced by the decay of theradioactive daughter element nuclei of the noble metals. The concentration of the noble metals were determined according to the equation II-6.

II.3.1 Sample Preparation

About 200 mg of each sample powder (less than 80 mg for mineral separates) was weighed into a pre-cleaned (cleaned with aqua regia and distilled water) fused silica ampoule (inner diameter approx. 2mm, length approx. 30 mm), which has been heat sealed at one end. The open end was then sealed with aluminum foil. The outside of the ampoule was then cleaned with acetone to remove surface contamination, labelled and then stored in a desiccator. For Ir and Ag analyses which required long irradiation, the open end of the ampoule was sealed with an H_2/O_2 flame.

II.3.2 Preparation of Standard and Carrier Solutions

Solutions of each metal were prepared from Johnson Mathey specpure gold sponge, sodium chloroiridate, platinum sponge, palladium foil and silver pellets. About 1 gm of each of the metals was digested in aqua regia and converted to chlorides by concentrated HCl. The chloride was taken up in 100 ml of 2M HCl (2M HNO_3 for Ag). From these stock solutions, working standard solutions were prepared by appropriate dilution. The final working standard solutions were:

a) Au-Ir-Pd standard containing approximately 20 ng/g Au, approx 10 ng/g Ir and approx. 50 ng/g Pd in 2M HCl.
b) Pt standard solution containing approx. 2 μg/g Pt in 2M HCl.
c) Ag standard solution containing approx. 100 ng/g Ag in 2M HNO_3.

The solutions were stored in plastic bottles and labelled.

Carrier solutions were made in the same manner as the standard solutions using commercial grades of the metals of their salts. Separate carrier solutions were made for each metal. The concentrations in the carrier solutions were:

a) Au carrier: 10 mg Au/ml in 2M HCl.
b) Pd carrier: 5 mg Pd/ml in 2M HCl.
c) Ag carrier: 10 mg Ag/ml in 2M HNO_3.
d) Ir carrier: 1.5 mg Ir/ml in 2M HCl.

No Pt carrier was needed as Pt was determined as Au, consequently Au carrier was used.

About 60 mg of each of the standard solution was introduced by a capillary tube into a pre-cleaned fused silica ampoule. Enough silica powder to soak all the standard solution was added and the moistened silica powder was dried at 60°C for 72 hours.

The ampoule was heat sealed with a H_2-O_2 flame, cleaned with acetone and stored in a desiccator.

II.3.3 Irradiation

Irradiations were carried out in the McMaster University Reactor at total neutron flux of 2.10^{13} $n/cm^2/sec$. Each irradiation package consists of either 5 rocks powder samples, one USGS rock standard powder samples, 3 standard samples of Pt, and 3 standard samples of Au-Ir-Pd. For the determination of Ir and Ag, each irradiation package consists of 9 rock samples, one USGS rock standard samples and 3 standard samples of Ir or Ag. Table II-1 is the summary of the irradiation and cooling schedule.

Table II-1

Irradiation and Cooling Schedule

Metal Analyzed	Rock Type	Irradiation Time	Cooling Time
Au-Ir-Pt-Pd	Ultramafic	1st Irrad: 48 hr 2nd Irrad: 12 hr	72 hr 24 hr
Au-Pd-Pt	Mafic rocks & sediments	6 hr	24 hr
Ir	Mafic rocks & sediments	7 days	6 weeks
Ag	Mafic rocks & sediments	7 days	6 weeks

Double irradiations were carried out for the ultramafic rocks. The first irradiation was to induce Au, Ir and Pt activity while the second irradiation was to induce 13.5 hr ^{109}Pd activity after a 72 hr cooling period. Because of the high contents of Na and K in the mafic and sedimentary rocks, both of which generate high activity from the reaction

^{23}Na (n, γ)^{24}Na $\qquad T_{1/2}$ = 15.02 h

and ^{41}K (n, γ)^{42}K $\qquad T_{1/2}$ = 12.36 h

it was necessary to reduce the irradiation time to 6 hours. A 6 hr irradiation is not adeuqate to generate sufficient Ir or Ag activity in the rocks, hence a separate irradiation for Ir and Ag.

II.3.4 Radiochemical Separation

Figure II-1 is the flow chart for the chemical separation of Au, Ir, Pd and Ag from the irradiated samples and standards. Radiochemical separation consists of four steps: 1) fusion of samples, 2) ion exchange separation, 3) solvent extraction, and 4) purification of the separated element. No specific radiochemical separation of Pt was required because Pt is determined by counting ^{199}Au.

II.3.4.1 Sample Procedure. a) Fusion: i) Prior to fusion, pipette 2 ml of Au, 5 ml of Ir, 1 ml of Pd and 2 ml of Ag carrier solutions into a Zr crucible. Add 2 pellets of NaOH and put on a hot plate set at low to dry.

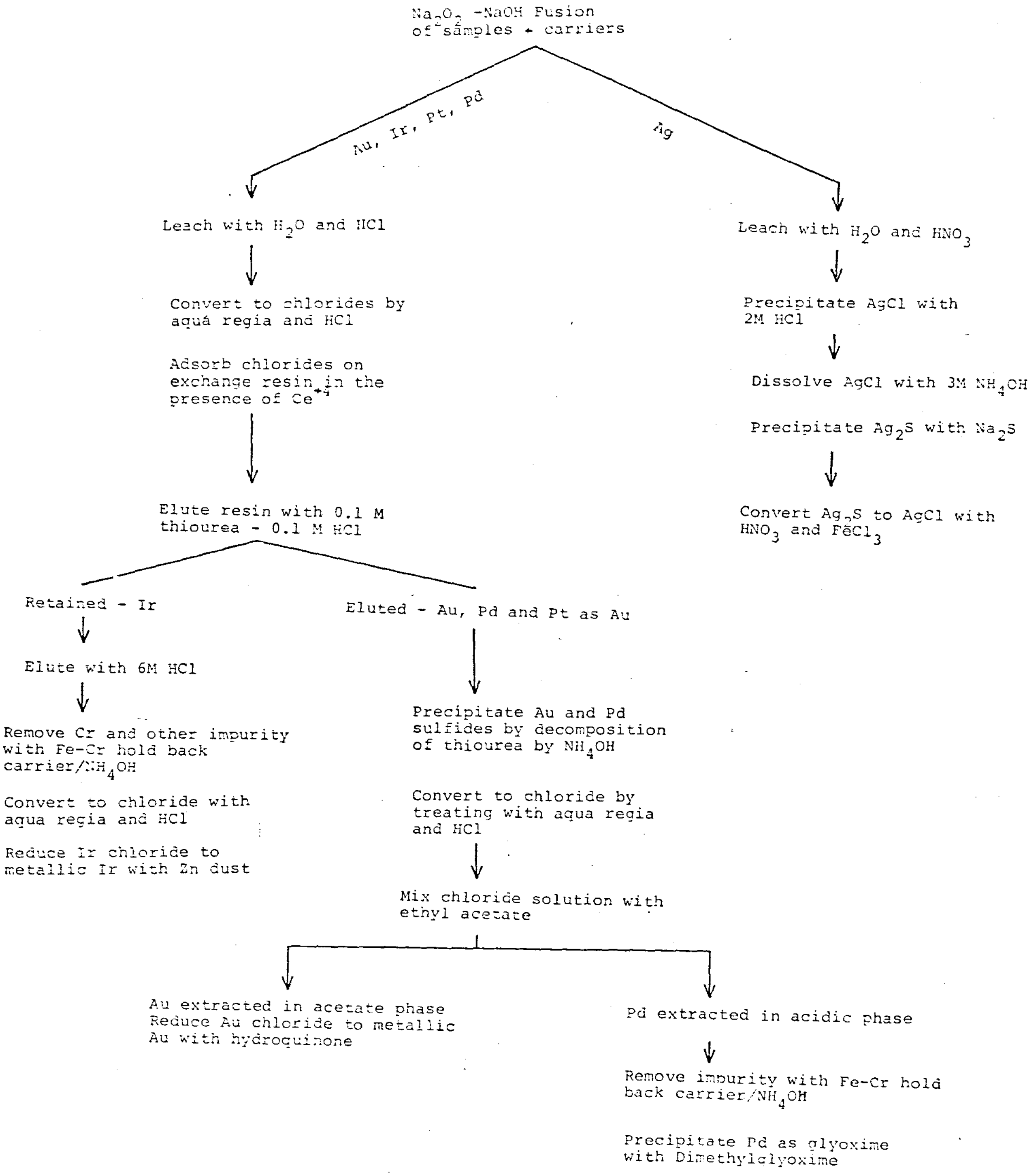


Figure II-1. Flow chart for the chemical separation of Au, Ir, Pt, Pd and Ag in irradiated samples.

ii) Transfer the irradiated sample into the Zr crucible containing the dry carriers, add about 1 g of Na_2O_2 and 6 pellets of NaOH. Mix the peroxide and sample and add about 1/4 g Na_2O_2 to cover the sample/peroxide mixture. Cover crucible with lid and heat over a Meeker burner, first with low flame and then with full blast until the sample is completely fused (sample becomes molten and dull red when completely fused).

b) Dissolution of sample: i) Remove crucible from flame and cool. ii) When the crucible is still warm, transfer into a 400 ml beaker and leach the fused cake with about 10 ml water and 15 ml 2M HCl. Leach any residue left with 15 ml conc. HCl. Add 2 ml conc. HNO_2. For Ag, leach only with water and dissolve any remaining residue with conc. HNO_3.

c) Conversion of sample to chloride (Au-Ir-Pt-Pd): i) Transfer the beaker containing the dissolved sample onto a hot plate and evaporate to about 10 ml. ii) Treat evaporated solution with 10 ml aqua regia and twice with 5 ml conc. HCl to convert to chlorides, taking the final acid digestion to complete dryness. iii) Dissolve the salts in 40 ml of freshly prepared 0.5 M HCl containing approximately 0.27 mg Ce^{+4}/ml (prepared by dissolving 3.3 g of cerric ammonium nitrate in 10 ml 0.5 M HCl). If Ir is not analyzed, dissolve the salts in 40 ml of 0.5 M HCl. The use of $(NH_4)_2\ Ce(NO_3)_6$ prevents the reduction of Ir^{+4} to Ir^{+3} which is weakly adsorbed on the anion exchange resin.

For Ag only: i) Transfer the dissolved fused sample onto a hot plate and warm till the solution is clear. If the solution remains cloudy (due to silica) add conc. HNO_3 until the solution is clear. ii) Evaporate the solution to about 30 ml. Add 10 ml 2M HCl to precipitate AgCl and transfer into a centrifuge tube. iii) Allow the precipitate to stand for about 1 hr, centrifuge and discard the supernatant liquid.

d) Ion-exchange separation (Au-Ir-Pt-Pd): i) Pass 60 ml of cerric ammonium nitrate (or 0.5M HCl if Ir is not analyzed) through a 1.75 by 1 cm diameter bed of Dowes AG1-X8 analytical grade anion-exchange resin, 100-200 mesh, chloride form. ii) Centrifuge the sample solution (in fume hood) and filter through Whatman No. 541 filter paper. Put solution through the column at a rate of 1 ml per min and wash with 120 ml of 0.5M HCl. iii) Elute Au and Pd with 120 ml of 0.1M thiourea/ 0.1M HCl solution. (Pt to be determined by ^{199}Au - see Section II.2.) iv) Wash resin with 10 ml 0.5M HCl to remove thiourea and elute Ir with 120 ml of 6M HCl.

e) Solvent extraction (Au and Pd): i) Transfer beaker containing Au and Pd in thiourea onto a hot plate, heat solution to near boiling and add 30 ml conc. NH_4OH to decompose thiourea and precipitate Au and Pd as sulfides. ii) Evaporate to 80-90 ml, centrifuge the sulfides and wash with <u>hot</u> water. iii) Dissolve sulfide in 2 ml aqua regia, evaporate to incipient dryness and treat twice with 0.5 ml conc. HCl to convert to Au and Pd chlorides. iv) Take Au and Pd chlorides up in 15 ml 6M HCl, transfer to a separatory funnel and extract in ethyl acetate; the Au transfers to the acetate fraction and the Pd to the acid fraction.

v) Transfer Au and Pd fraction into separate beaker.

f) Purification (Au, Ir, Pd, and Ag)

Gold: i) Add an equal volume of 2M HCl to Au acetate solution, place on a hot plate at low heat and allow Au to transfer to HCl phase and acetate to evaporate. ii) Boil Au-HCl solution for about 1 minute, transfer to a centrifuge tube and add hydroquinone to precipitate Au metal. iii) Centrifuge, wash twice with hot water and then with H_2O/ethanol and finally ethanol.Transfer to a pre-weighed 1/2 dram vial and dry under a heat lamp.

Palladium: i) Evaporate the Pd-HCl fraction to about 10 ml. Add 1 ml of Fe-Cr holdback solution containing 0.9 mg Fe and 0.1 mg Cr per ml. Transfer solution into a centrifuge tube and add a few drops of NH_4OH to precipitate $Fe(OH)_3$ along with other contaminants. Centrifuge and discard the precipitate. ii) Transfer supernatant solution to a small beaker and adjust the pH to about 6 with few drops of conc. HCl (solution turns faint yellow). iii) Put acidified solution on hot plate and warm until solution becomes deep yellow. iv) Transfer solution into a centrifuge tube and add 10 ml 1.5% dimethylglyoxime to precipitate Pd glyoxime. Centrifuge, wash the Pd glyoxime precipitate with hot water.
v) Dissolve the precipitate in aqua regia, convert to chloride and repeat the $Fe(OH)_3$ scavenging and dimethylglyoxime precipitation (important for removal of Cr for analysis of ultramafic rocks).
vi) Centrifuge, wash twice with hot water, then with 1:1 H_2O/ethanol

and finally with ethanol, transfer to a pre-weighed aluminum planchet and dry under a heat lamp.

Iridium: i) Add 1 ml of the Fe-Cr hold back carrier to the Ir solution from step 'd'. Evaporate the solution to about 5 ml, add approximately 5 ml H_2O, transfer to centrifuge tube and add a few drops of conc. NH_4OH to precipitate $Fe(OH)_3$, Cr and other contaminants. Centrifuge and discard the precipitate. ii) Transfer supernatant solution to a beaker and evaporate to incipient dryness. Digest with aqua regia and conc. HCl and take up in 50 ml 2M HCl. iii) Heat solution to near boiling and add Zn metal dust slowly (beware of strong effervescence!) to reduce Ir to the metal. iv) Heat solution for about one hour and dissolve excess Zn with conc. HCl. Cool and centrifuge. v) Boil the Ir in 10 ml 6M HCl for about 1 min, wash with water twice, then with 1:1 H_2O/ethanol and finally in ethanol, transfer into a 1/2 dram vial and dry under a heat lamp.

Silver: i) Dissolve AgCl precipitate from step 'b' in a minimal quantity of 3M NH_2OH, centrifuge and dicard the residue which is mainly silica. ii) Add Na_2S solution to supernate to precipitate black Ag_2S. Centrifuge, discard the supernate and dissolve Ag_2S by heating in about 2 ml conc. HNO_3. Add 5-10 ml $FeCl_3$ solution containing 1 mg Fe^3/ml in 1M HCl and warm to precipitate AgCl. iii) Repeat the dissolution of AgCl in 3M NH_4OH. precipitation and dissolution of Ag_2S and precipitation of AgCl. iv) Wash the final AgCl in water and alcohol or acetone. Filter, transfer into a pre-weighed 1 dram vial and dry under a heat lamp.

II.3.4.2 Standard Procedure. Au-Ir-Pd: i) Scratch ampoule containing the irradiated standard Au, Ir and Pd with a steel file and break ampoule into a 50 ml beaker containing Au, Ir and Pd carriers (2 ml of Au, 5 ml of Ir and 1 ml of Pd carrier solutions). ii) Add 10 ml aqua regia, warm solution and use a capillary pipette to flush standard from broken ampoules with carrier solution. Remove broken pieces of ampoule from solution. iii) Evaporate solution to incipient dryness, treat with aqua regia and conc. HCl and take up in 15 ml o.5M HCl containing 0.27 Ce^{+4}/ml or 0.5M HCl if Ir is not analyzed. iv) Treat standard as described for sample in step 'c' to step 'f'.

Platinum: i) Break the Pt standard ampoule into a 50 ml beaker containing 2 ml Au carrier solution. ii) Add 10 ml aqua regia, warm the solution and use a capillary pipette to flush standard from ampoule and remove pieces of broken ampoule. iii) Evaporate the solution to incipient dryness, treat with aqua regia and conc. HCl and take up in 15 ml 6M HCl. iv) Filter solution into a separatory funnel, removing the undissolved silica powder. Add ethyl acetate to extract ^{199}Au produced by Pt, transfer Au acetate to a beaker and add equal amounts of 2M HCl. v) Treat as Au sample described in step 'f'.

Silver: i) Break the Ag standard ampoule into a 50 ml beaker containing 2 ml Ag carrier. ii) Add 10 ml H_2O, warm the solution, use a capillary pipette to flush standard from ampoule with carrier solution and remove pieces of broken ampoule. iii) Filter solution to a centrifuge tube to remove silica powder and add 10 ml 2M HCl to the supernate to precipitate AgCl. iv) Wash AgCl in water and alcohol or acetone. Transfer AgCl into a pre-weighed 1 dram vial and dry under a heat lamp.

II.3.5 Chemical Yield Determination

After drying, weigh the vial or planchet to determine the weight. The chemical yield is the percentage of the recovered metal to the weight of the carrier used. Apply a gravimetric factor of 0.3165 for Pd-glyoxime.

II.3.6 Radioactivity Measurement

II.3.6.1 Equipment and Procedure. (Au, Ir, Pt and Ag): The induced radioactivity in Au, Ir, Pt and Ag was measured with an Ortec Li-drifted Ge detector having an active volume of 30 cm^3 and a photopeak/compton ratio of 15. The detector is connected to a 4096 channel analyzer linked to a Telex teleprinter and a data processor (Nuclear Data ND 812). The energy resolution of the system is 2.0 kev at 662 kev of ^{137}Cs at FWHM (Full Width at Half Maximum). Only 1024 channels were used in this study.

Although the energy photopeaks of the radiation emitted by the metals are listed in the literature, these peaks were usually checked with the standard prior to counting. This was necessary to correct for any drift in the counting system.

The standards were counted for one hour each, but the counting time of the samples depended on the activity in each sample. Samples with high activity were counted for one to two hours while those with low activity (usually samples with low Ir contents) were counted for up to 10 hours so that the activity for metal photopeak was greater than 1000 counts above background for the duration of counting. The photopeaks of the metals are:

Au: 412 kev for 2.696 day ^{198}Au and 158 kev for 3.15 day ^{199}Au
Ir: 296, 308 and 317 kev for 74.2 day ^{192} Ir
Pt: 158 kev for 3.15 day ^{199}Au and 412 kev for 2.696 day ^{198}Au
Ag: 658 kev for 252 day ^{110}Ag

Palladium: Pd activity was determined by beta counting using a gas counting system consisting of a gas flow Geiger-Muller proportional counting tube with coincidence shielding, a scaler time, automatic sample changer and a paper printer (Nuclear-Chicago system). The average backgound count for the system was 2 counts per minute. Drift in the system was monitored with a uranyl acetate standard.

II.3.6.2 Data Processing. (Au, Ir and Ag): In order to determine the induced activity produced by a nuclide, the net peak area of one of the major gamma ray energy peaks was calculated. Net peak area is calculated by subtracting the background area from the total peak area. For the standards and most samples with high counts, this exercise was done by the data processor using a peak fitting and peak stripping program (ND 4410 Basic Physics Analyzer Program 41-1060 and

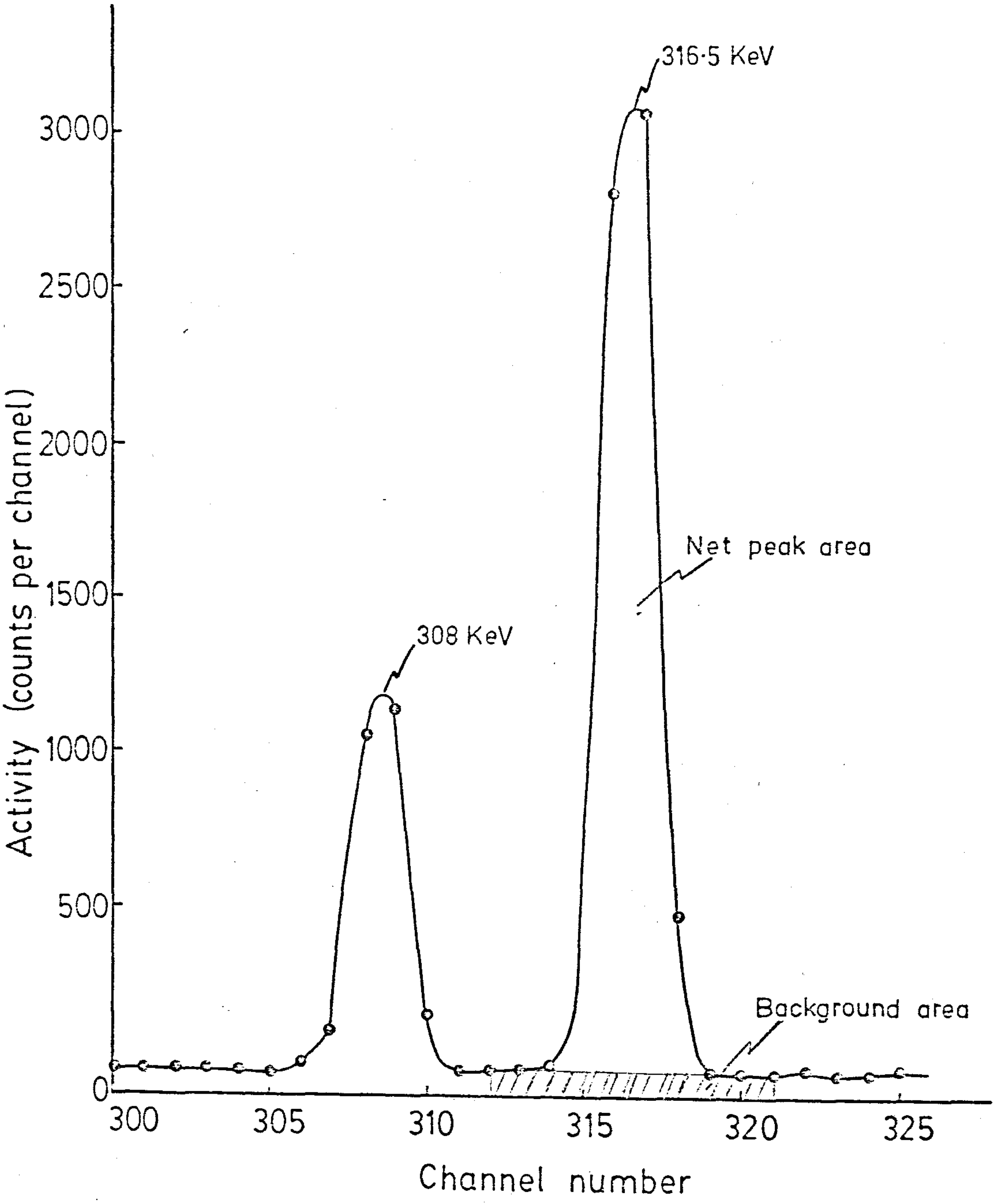


Figure II-2. Typical ^{192}Ir gamma spectrum for PCC-1. The net peak and background (in stripes) areas for channels 312-321 are also shown.

41-1061). Net peak area was given as net count over the selected channels which represent the background and peak area (e.g. Figure II-2). In cases where low count might introduce large statistical errors the net peak area was calculated manually by graphical means.

The peaks were 412 kev for Au and 658 kev for Ag. Three peaks were used for Ir: 296, 309 and 317 kev. Background area usually covered 3 to 5 channels on either side of the photopeak.

Platinum: In this study, Pt was determined in the Au spectrum. The energy of the gamma radiation produced by Pt (e.g. ^{197}Pt, γ - 77 kev) is too low to permit efficient gamma activity counting with the Ge(Li) counting system. On the other hand, the reaction

$$^{198}\text{Pt}\ (n,\ \gamma)\ ^{199}\text{Pt} \xrightarrow[B^-]{30\ \text{min}} {}^{199}\text{Au}\ (T_{1/2} = 3.15\ \text{d} \quad \gamma\text{- } 158\ \text{kev})$$

permits the use of the higher energy of ^{199}Au to determine Pt. However, ^{199}Au is also produced by a double neutron capture of ^{197}Au

$$^{197}\text{Au}\ 2(n,\ \gamma)\ ^{199}\text{Au}$$

It is therefore necessary to subtract the activity of ^{199}Au produced by ^{197}Au double neutron capture from that produced by the Pt reaction. The activity contributed by ^{199}Au via double neutron capture can be established from the activity of Au in the 412 kev.

Consider the Au spectrum from 100 to 500 kev gamma energy peaks (Figure II-3)

Let A_I = total activity at 158 kev

A_{II}= total activity at 412 kev

$$A_I = A_I + A_2^1 \qquad (1)$$

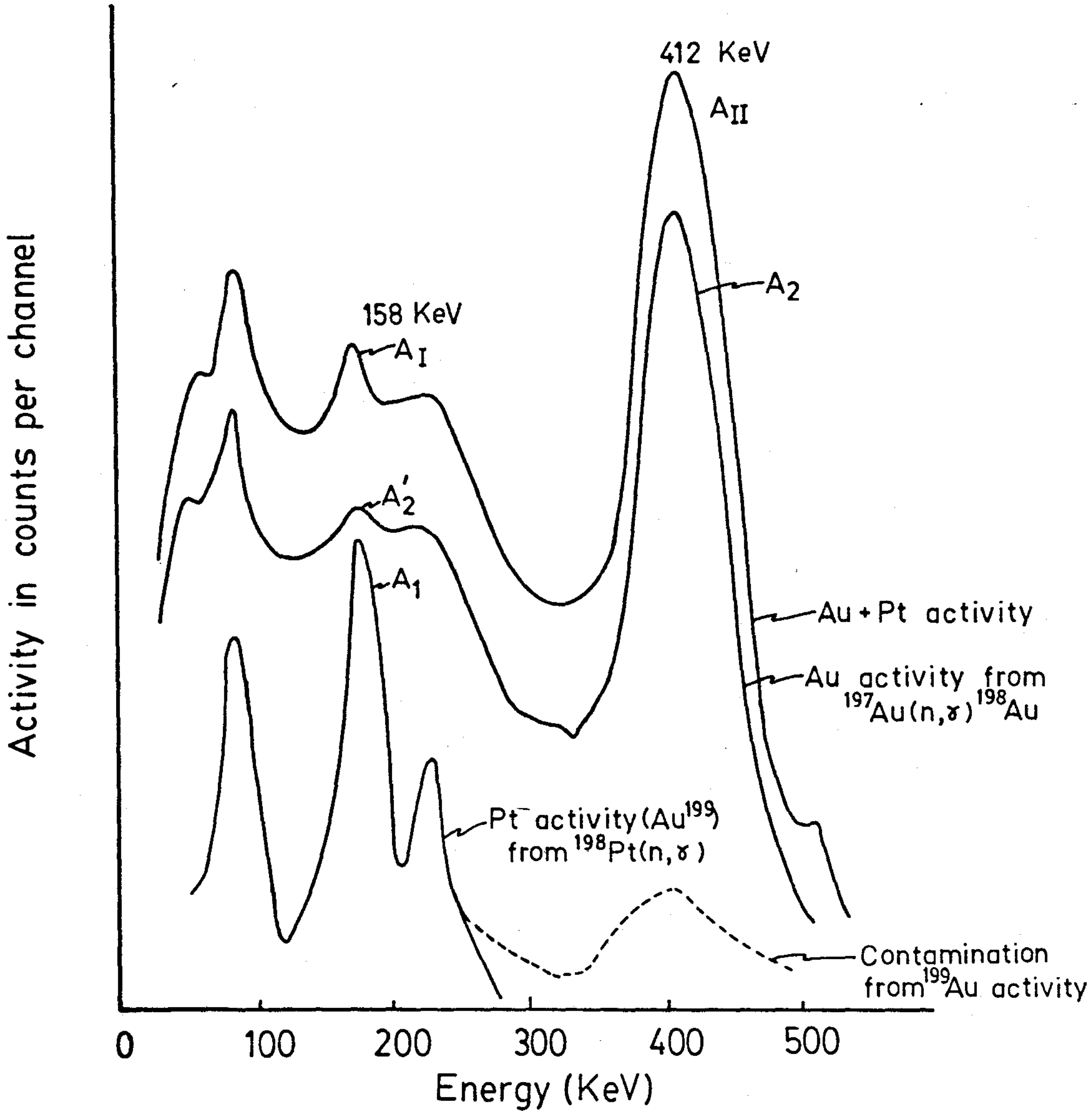


Figure II-3. Typical gamma spectra between 100 and 500 KeV in a sample containing Au and Pt.

where A_1 = activity due to ^{199}Au from ^{198}Pt reaction at 158 kev

A_2^1 = activity due to ^{199}Au from ^{197}Au double neutron capture at 158 kev

Similarly,

$$A_{II} = A_1^2 + A_2 \tag{2}$$

where A_1^2 = activity due to ^{199}Au at 412 kev

A_2 = activity due to ^{197}Au reaction at 412 kev

The relationship between the activity produced by ^{198}Pt reaction at 158 kev (A_1) and ^{199}Au at 412 kev (A_1^2) may be expressed as

$$K_1 = A_1^2/A_1 \tag{3}$$

Similarly, the relationship between the activity produced by ^{197}Au reaction at 412 kev (A_2) and at 158 kev (A_2^1) may be expressed as

$$K_2 = A_2^1/A_2 \tag{4}$$

Substituting for A_2^1 and A_1^2 in equations (1) and (2)

$$A_I = A_1 + K_2A_2 \tag{5}$$

$$A_{II} = A_2 + K_1A_1 \tag{6}$$

In practice $A_2 >> K_1A_1$ such that

$$A_{II} = A_2$$

The observed activity at 158 kev (A_I) is, therefore, the sum of the activity due to ^{198}Pt (A_1) and the activity due to ^{197}Au reaction (A_2) multiplied by a factor, K_2. K_2 can be determined by observing the activity due to standard Au at 158 kev (A_{2T}^1) and at 412 kev (A_{2T}) using equation (4):

that is

$$K_2 \text{ (standard)} = \frac{\text{activity of Au standard at 158 kev}}{\text{activity of Au standard at 412 kev}}$$

It is assumed that for all samples and standards irradiated under the same conditions and at the same time,

$$K_2 \text{ (standard)} = K_2 \text{ (sample)}$$

Knowing K_2 for the standard, the activity due to platinum can be calculated from equation (5).

Palladium: Unlike gamma counting individual energy peaks cannot be isolated in beta counting. The registered activity includes activity from Pd isotopes and other contaminants. In order to isolate the induced activity due to ^{109}Pd ($T_{1/2}$ = 13.5 hr) it was necessary to construct a decay curve (Figure II-4). The first part of the curve is mainly due to ^{109}Pd and the latter part due to contaminants and possibly the 21 hr ^{112}Pd produced by ^{235}U fission. This part was subtracted from the total curve leaving only the curve due to ^{109}Pd.

II.3.7 Calculations

The concentrations of the metals in the sample were calculated according to equation II-6, that is,

$$A_o^S / A_o^T = C^S W^S / C^T W^T$$

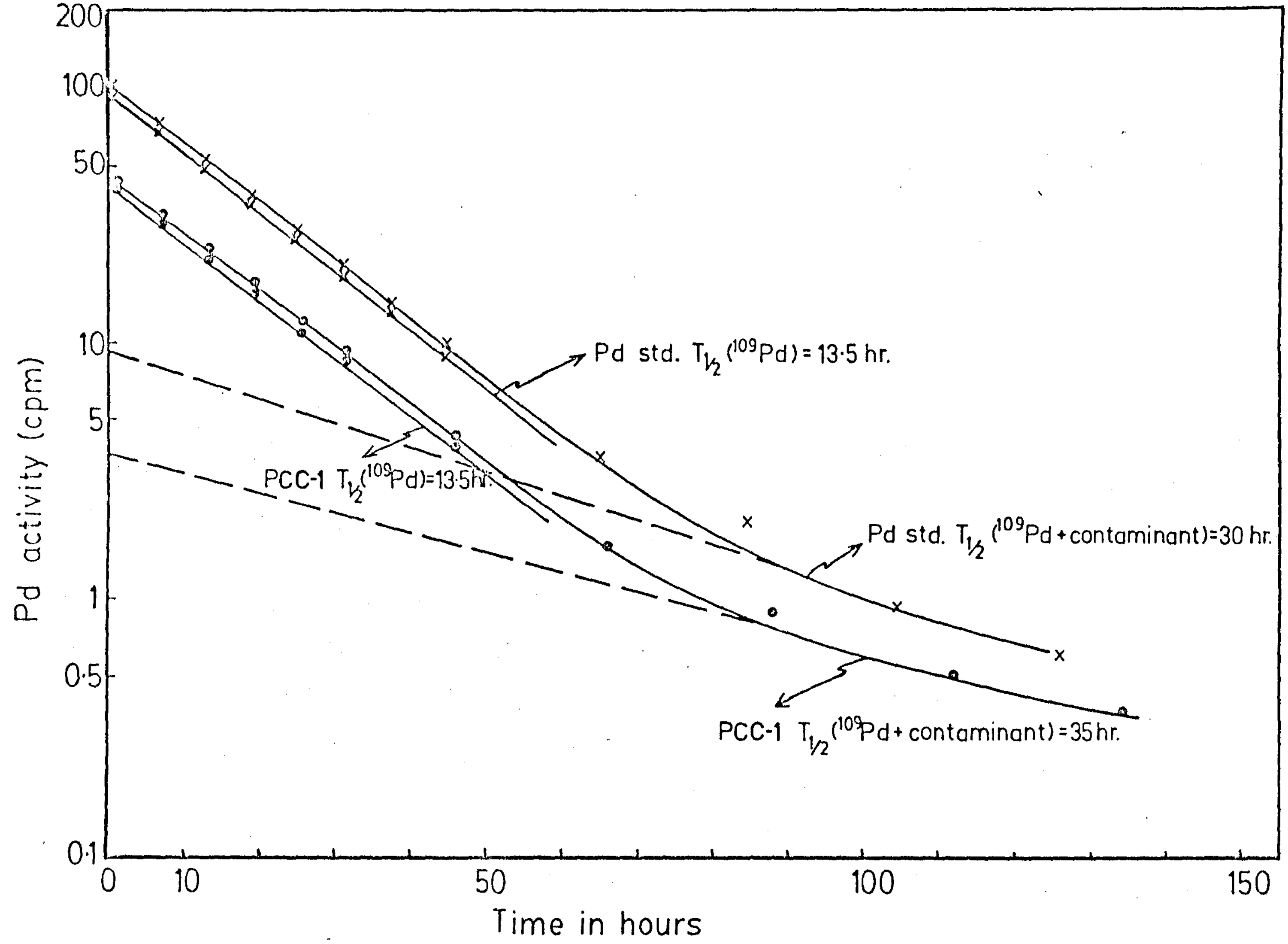


Figure II-4. Typical beta decay curve for Pd in PCC-1 and Pd standard.

For Au, Ir, Pt and Ag A_o is determined from the equation

$$A_o = \frac{Ae^{\lambda(t_c - t_o)}}{Y}$$

where A is the observed net count for the gamma photopeak of the metal

λ is the decay constant

t_c is the time of counting

t_o is an arbitrary time usually taken as the time of counting of the first metal standard

Y is the chemical yield

Therefore, for a given weight of a sample W^S, weight of metal standard, W^T with a metal concentration of C^T, the concentration of the metal in the sample, C^S, is given as

$$C^S = \frac{A^S\ e^{\lambda(t_c - t_o)}\ Y^T}{A^T\ e^{\lambda(t_c - t_o)}\ Y^S} \cdot \frac{C^T W^T}{W^S}$$

(superscript s notes sample, superscript T denotes standard). For Pd, the resolved curve of ^{109}Pd (Figure II-4) was projected to the y axis and the count at t = 0 was taken as the initial induced activity A_o. C^S was then calculated according to euqation II-6.

II.4 Evaluation of Data

The results of the analyses have been presented in Table 4-3. Analytical data are usually evaluated by the reproducibility of data (precision), how data compare with results on the same material obtained by an independent analytical method (accuracy) and the sensitivity of the analytical method. These specifications are usually checked from replicate analyses of samples. In this study, samples were not routinely analyzed in replicate unless a sample gave a suspicious result. However, in each batch of samples analyzed, one rock standard sample was included. The primary objective of including a rock standard with the samples was to check for any gross contamination during analysis or other analytical error. Marked deviation of analytical results for the rock standard from the recommended values would suggest some error in analysis. The rock standards used were USGS PCC-1 and USGS W-1 for Au, Ir, Pt and Pd and USGS AGV-1 and BCR-1 for Ag. With the exception of BCR-1 the rock standards were analyzed at least four times each. The analytical methods may therefore be evaluated from the replicate analyses of the rock standards. The results for the rock standards are shown in Table II-2.

<u>i) Precision</u>. The reproducibility of analytical data (precision) is usually measured in terms of the standard deviation (S) where

$$S^2 = \frac{1}{N - 1} \sum_{i = 1}^{N} (X_i - \overline{X})^2$$

and N = number of replicate analyses

X_i = value of i^{th} replicate

$\overline{X}$ = mean value

In order to compare standard deviations at different levels of elemental abundance, the coefficient of variation (V) is often used, where

Table II-2

Noble Metal Contents in USGS Rock Standards in ppb

	PCC-1				W-1				
	Au	Ir	Pt	Pd	Au	Ir	Pt	Pd	Ag(ppb)
	0.50	2.85	3.73	5.37					BCR-1
	0.54	3.33	2.24	3.56					
	0.90	3.32	6.16	3.85					27.9
	0.50	6.69	9.91	3.05					
	0.59	6.73	3.35	4.22					AVG-1
	0.59	3.07	7.91	3.72					
	0.60	6.79	6.59	4.00	4.68	0.39	16.15	12.13	85.8
	0.89	2.76	2.77	3.38	5.05	0.34	13.51	11.00	78.8
	0.83	3.96	5.25	3.61	5.21	0.34	10.23	12.38	77.5
	0.64	7.36	8.07	3.86	4.85	0.37	18.80	9.70	80.5
	0.85	7.38	7.94	3.52		0.28			
	0.83	6.77	9.96	4.32		0.29			
	1.14	5.21	3.28	4.94					
	0.85	3.60	10.41	4.71					
			7.12	3.68					
Mean ($\overline{X}$)	0.73	5.00	6.31	4.00	4.95	0.34	14.69	11.30	80.7
Standard Deviation (S)	0.19	1.87	2.76	0.63	0.23	0.04	3.63	1.23	3.7
Standard Error (σ)	0.05	0.50	0.71	0.16	0.12	0.02	1.82	0.62	1.8
Coefficient of Var. (V)%	26.18	37.50	43.79	15.72	4.67	12.91	24.73	10.84	4.6
$\sigma_{.05}$	0.11	1.08	1.53	0.39	0.37	0.04	5.77	1.96	5.8
$V_{.05}$ (%)	56.55	81	93.71	33.79	14.85	33.17	78.64	34.47	14.5
No. of analyses (N)	14	14	15	15	4	6	4	4	4

$$V = \frac{S}{\overline{X}}$$

or $$V\% = \frac{100S}{\overline{X}}$$

$$V\% \; \frac{100S}{\overline{X}} \cdot t_{(1 - \delta/2)\gamma} \text{ at } (1 - \delta) \text{ probability}$$

where t = the abscissa of the student t function

δ = the level of significance

γ = the degree of freedom $N = 1$

The coefficient of variation of the noble metals for the rock standards are shown in Table II-2.

<u>Gold</u>. Of the noble metals analyzed, gold is expected to give the highest precision. This is because the extracted Au from the irradiated sample is usually very pure such that the ^{198}Au 412 kev photopeak is usually free of any interference. Furthermore, Au has a large neutron cross-section so that high activity is generated during irradiation and this minimizes statistical counting error. The precision for Au in PCC-1 is, therefore, poorer than expected. However, precision is quite good for W-1 and it is suggested that the poor precision in PCC-1 is due to heterogeneous distribution of Au in the rock.

<u>The platinum metals</u>. Precision for the platinum metals follow the order Pd > Ir > Pt. The poorest precision in Pt may be attributed, in part, to the increase in statistical counting error in Pt activity due to the subtraction of the activity contributed by Au. This error may be very

large for samples with high Au activity.

By comparison, higher precisions are obtained in W-1 than PCC-1. This might suggest greater sample homogeneity in W-1. On a closer study, the result for PCC-1, particularly Ir and Pt values suggest that the data may be grouped into two populations. For Ir, one group has an average of 3.27 ppb Ir with coefficient of variation of 13% and the second group has an average of 6.70 ppb Ir with a coefficient of variation of 10.8%. Similarly, Pt values may be grouped into one population of average value of 3.07 ppb Pt with coefficient of variation of 18.8% and another group of average 7.93 ppb Pt with a coefficient of variation of 21.8%. The precision in each of these groups is comparable to that of W-1 for the respective metal.

Statistical test (Table II-3) shows that the grouping of the Ir and Pt values in PCC-1 is valid. It appears then that there may be some phase which controls the content of Ir and Pt and possibly other noble metals in PCC-1. It was indicated earlier that in Thetford Mines harzburgite, a similar rock both petrologically and chemically to PCC-1, the noble metals are largely hosted by chromite. If this is true for PCC-1, then the proportion of chromite in the analyzed PCC-1 fraction determined the noble metal results obtained.

It seems, therefore, in retrospect that PCC-1 is a poor choice for estimating the precision of analytical methods with respect to the noble metals. It is difficult to evaluate the effect of sample heterogeneity in the determination of the precision of the analytical

Table II-3

Statistical Test of Significance for Differences in Population of Ir and Pt Values for PCC-1

	Sample Mean	Sample Std. Dev.	Sample Size	Popul. Mean	Popul. Std. Dev.	Degree of Freedom	$t_{0.995}$
Population A	$\overline{X}_1$	S_1	N_1	u_1	σ_1	12	3.06
Ir	3.27 ppb	0.425	7				
Pt	3.07 ppb	0.577	7				
Population B	$\overline{X}_2$	S_2	N_2	u_2	σ_1	13	3.01
Ir	6.70 ppb	0.724	5				
Pt	7.93 ppb	1.73	10				

$t_{0.995}$ = percentile for students t distribution

To test the hypothesis H_o that the samples (noble metal values) come from the same population.

H_o: $u_1 = u_2$, $\sigma_1 = \sigma_2$

H_1: $u_1 \neq u_2$, $\sigma_1 \neq \sigma_2$

t score is given by

$$t = \frac{X_1 - X_2}{\sigma \sqrt{1/N_1 + 1/N_2}} \qquad (1)$$

Table II-3 (Continued)

where

$$\sigma = \sqrt{\frac{N_1 S_1^2 + N_2 S_2^2}{N_1 + N_2 - 2}} \qquad (2)$$

(Spiegel, 1972, p. 189)

At level of significance of 0.005

1) Accept the hypothesis if t lies between -3.06 and 3.06 in the case of Ir or if t lies between -3.01 and 3.01 in the case of Pt.

2) Reject the hypothesis otherwise.

Substituting $\overline{X}_1$, $\overline{X}_2$, S_1, S_2, N_1, N_2 in equations (1) and (2)

t = -10.03 for Ir

t = -5.72 for Pt

Since the calculated t values lie outside the acceptance regions, H_o is rejected at 0.005 level of significance. Therefore the samples (Ir and Pt values) belong to two different populations.

method hence it is doubtful if the reported coefficient of variation for the rock standard PCC-1 and W-1 are the true estimates of the precision of the analytical method used in this study. The true precision is probably much better than that reported here.

ii) Accuracy. The accuracy of the method is evaluated by comparing the results for the rock standards with results obtained by other workers (Table II-4). This exercise is, however, limited due to the scarcity of data on some of the noble metals in these standards.

Gold. The reported Au values for PCC-1 in the literature range from 0.76 ppb to 3.2 ppb. Since most of these values have been obtained by the same NAA, it is difficult to assess the true Au contents in PCC-1 from this range of values. The value of 0.73 ± 0.05 ppb obtained in this study is closer to the lower end of the spectrum of the values in the literature. It is most likely that the Au values for PCC-1 obtained by Green et al. (1970) and Laul et al. (1970) are too high. If this is so, then the results of this study are comparable to other results.

Unlike PCC-1, Au values reported for W-1 in the literature are relatively uniform. The result of 5.00 ± 0.12 ppb Au obtained for W-1 in this study lies well within the range of the published values.

Iridium. Values reported for PCC-1 (Flanagan, 1976) vary from 3.0 ppb Ir to 6.6 ppb Ir. This range in values probably reflect the variability in the proportion of chromite or any Ir bearing phase in the analyzed PCC-1 samples as discussed earlier. The average Ir values obtained in this study is 5.00 ± 0.50 ppb Ir which is probably superior to most of the values in the literature because of the large number of analyses involved. Most of the reported averages in the literature have been computed from less than four replicate analyses. The large number of replicate anaylses in this study tend to reduce the effect of non homogeneous distribution of the Ir bearing phase in the rock standard.

The Ir content of W-1 determined in this study is similar to the results of Ehman et al. (1970) and Baedecker et al. (1971) but higher than the result of Crocket et al. (1968) and that of Greenland et al. (1971). The analytical method used in this study is similar to that of Crocket et al. (1968) although precision and sensitivity have been improved. It is difficult to give an explanation for the different in the results obtained in this study and that of Crocket et al. (1968) other than to speculate that the difference is probably real and may be due to different Ir contents of the different batches of W-1 sample analyzed.

Platinum. Platinum has proved to be the most difficult platinum metal to analyze. Most of the reported platinum data in the literature have been obtained by analytical methods whose sensitivites are as poor as 20 ppb. It is, therefore, difficult to assess the accuracy of the Pt data in this study based on most of the Pt values in the literature. Pt data compiled by Flanagan (1970) show that PCC-1 values range from 3.5 ppb to 11.0 ppb. It is the opinion of this writer that, as in the case of Ir, these values reflect in part, the influence of a Pt bearing phase in the PCC-1 samples analyzed. The average Pt value obtained in this study (6.31 ± 0.71 ppb) lies within the reported values by Flanagan (1976) whose average is 7.8 ppb Pt.

The average Pt content in W-1 obtained in this study is higher than the average value obtained by Rowe and Simon (1971) and De Sarma et al. (1965) but is comparable to the data of Dorrazapf and Brown (1970). Although analytical error is greater for Pt than other noble metals in this study, it is doubtful if the difference in results is solely due to analytical error. Sample heterogeneity and possibly a difference in sensitivity of the methods used here and by the other workers may also have contributed to the difference in results.

Palladium. The results for Pd obtained in this study are comparable to those reported for W-1 but the average Pd for PCC-1 is about 24% lower than the average of the data compiled by Flanagan (1976). In view of the large number of replicate analyses and small standard deviation in this study, the results here are probably more accurate than most of those reported in Flanagan's compilation.

Silver. One analysis of Ag gives a value of 27.9 ppb Ag for BCR-1. This value is similar to the result of Ganapathy et al. (1970), Anders et al. (1971), Brunfelt et al. (1971) and Brunfelt and Steinnes (1971). However, the accuracy of the method cannot be based on one analysis alone.

Results for AGV-1 are lower than those reported by Brunfelt and Steinnes (1969) (94 ppb Ag) and Greenland and Fones (1971) (110 ppb Ag). Judging from the Ag values obtained for BCR-1 by these authors, for

Table II-4

Comparison of Noble Metal Data on PCC-1 and W-1 (in ppb)

PCC-1

Au	Ir	Pt	Pd	Method	Source
		5.7	4.4	FA-AS	Page *et al.*, 1980
0.89(4)				NAA	Anoshin and Perezhogin, 1969*
0.76				NAA	Bartel, 1969*
0.80(3)	6.6			NAA	Ehman *et al.*, 1970
2.28(2)				NAA	Green *et al.*, 1970
3.2(2)				NAA	Laul *et al.*, 1970
1.02(2)	5.5	3.5	6.0(2)	NAA	Millard and Bartel, 1971
		5.8(4)	4.7(3)	FA-NAA	Rowe and Simon, 1971
		10.5	5.5	FA-OS	Dorrzaph and Brown, 1970
		11(4)	5.5(4)	FA-OS	Heady, 1969*
	5.7			NAA	Baedecker *et al.*, 1971*
	3.0(4)			FA-NAA	Greenland *et al.*, 1971
0.77	5.1	8	5.4		Average from Flanagan, 1976 calculated by Chou, 1978
0.73(14)	5.0(14)	6.3(15)	4.0(15)	NAA	This study

W-1

Au	Ir	Pt	Pd	Method	Source
		10.2	10.1	FA-AS	Page *et al.*, 1980
5.0					Shcherbakov and Perezhogiun, 1964
5.8(12)	0.26(8)		11.5(17)	NAA	Crocket *et al.*, 1968
	0.32			NAA	Ehman *et al.*, 1970
	0.32			NAA	Baedecker *et al.*, 1971*
	0.24			FA-NAA	Greenland *et al.*, 1971
4.6					Fritze and Robertson, 1969
4.2				NAA	Laul *et al.*, 1970
4.3				NAA	Anoshin and Perezhogin, 1971*
		9.8	12.2	FA-NAA	Rowe and Simon, 1971
		14.9			Dorrzapf and Brown, 1970
		9.2	15.4	FA-OS	Das Sarma *et al.*, 1965
5.0(4)	0.34(6)	14.7(4)	11.3(4)	NAA	This study

Key to Table II-4

* In Flanagan, 1976

FA - fire assay; AS - atomic absorption spectrographic; OS - optical spectrographic; NAA - neutron activation analysis

(3) - number of determinations

example, Brunfelt and Steinnes (1969) (36 ppb Ag), Greenland and Fones (1971) (36 ppb Ag), it appears that there is a systematic difference between the results of this study and those of these workers.

iii) Sensitivity (Dectection Limit). The sensitivity of determination of an analytical method for a given element may be expressed as the minimum amount of that element that must be present in a sample to be quantitatively detectable. Crocket and Teruta (1977) who used this method in determining Au, Ir, Pd and Pt in ocean floor basalts estimated sensitivity to be 0.05 ppb for Au, 0.01 ppb for Ir, 0.1-0.2 for Pd, and 20 ppb for Pt.

Sensitivity depends on many factors and it appears that sensitivity has been improved in this study over that reported by Crocket and Teruta (1977) probably due to longer irradiation and cooling periods in some cases and higher neutron flux of the Reactor used in irradiating the samples. For example, by irradiating the samples for 7 days at 2 MWH (compared to 1 MWH by Crocket and Teruta) and cooling for 6 weeks to decrease the interference in Ir activity by other radioisotopes of shorter half life than ^{192}Ir, it has been possible to determine Ir content of 0.005 ppb in some of the mafic rocks. Pt sensitivity has also improved, but sensitivity appears to depend on rock types. For example, while Pt content of 0.5 ppb was determined in some of the ultramafic rocks, no Pt was detected in mafic rocks with less than 1.5 ppb Pt.

The estimated sensitivity of the procedure in this study is 0.05

ppb for Au, 0.005 ppb for Ir, 0.1 ppb for Pd and 0.5-1.5 ppb for Pt.

In conclusion, the analytical method used in determining Au, Ir, Pd, Pt and Ag in this study is accurate and sensitive enough to correctly determine the contents of these metals in the rocks studied. Due to the heterogeneity of the rock standards on which precision is evaluated, it is not possible to determine the real precision of the method. However, it is suggested that analytical error associated with the determination of the noble metals in this study is not greater than the coefficient of variation of these metals as observed in the rock standard W-1 and AGV-1; that is < 5% for Au, < 25% for Pt, < 11% for Pd and < 5% for Ag. Although Pt has the highest analytical uncertainty, it is believed that this uncertainty is not serious emough to affect the observations and conclusions reached in this study.

APPENDIX III

MAJOR AND TRACE ELEMENT ANALYSIS

Major and trace elements were determined by X-ray flourescence spectrography, using a Phillips PW1450 automatic sequential machine.

For major elements, analyses were performed on fused beads of 0.5000 g rock sample powder and 3.0000 g mixture of 1:1 lithium tetraborate and lithium metaborate. The procedures used are similar to those described by Norrish and Chappel (1967) and Westerman (1977).

Trace elements were determined on pressed powder pellets according to the method of Marchand (1973). The detection limits of the XRF methods are listed in Table III-1.

Cu contents in the lavas were determined by atomic absorption spectrography using a perkin-Elmer 603 spectrometer. The rock standards USGS JB-1 and BCR-1 were analyzed together with the samples. These rock standards gave an average of 53 ppm (JB-1) and 21 (BCR-1). These are comparable to the recommended values of 56 ppm and 19 ppm for JB-1 and BCR-1 respectively.

The results of the analyses are reported in Table III-2. CIPW normative minerals were calculated from the results according to the method of C. Kelse using a modified computer program compiled by N. Massey of McMaster University. FeO was calculated from the total iron oxide (FeO^T) using the equations of Le Maitre (1976).

For plutonic rocks

$$FeO/FeO^T = 0.88 - 0.0016\ SiO_2 - 0.027\ (Na_2O + K_2O)$$

For volcanic rocks

$$FeO/FeO^T = 0.93 - 0.0042\ SiO_2 - 0.022\ (Na_2O + K_2O)$$

Table III-1

Detection Limit for Trace Elements Analyzed by XRF Method

Ni	6 ppm	Zr	3 ppm
Cr	3 ppm	Y	4 ppm
Zn	2 ppm	Pb	3 ppm

Table III-2A Major Element Oxide Concentrations (wt %) in Metamorphic Peridotes (TMC)

Sample	SiO_2	Al_2O_3	FeO^T	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	CO_2	H_2O
<u>Harzburgite</u>												
MPH 1A	39.08	0.79	8.44	40.92	0.85	0.40	0.06	0.02	0.16	-	0.45	8.83
MPH 1C	39.50	0.68	8.74	40.41	0.84	0.37	0.07	0.01	0.16	-	0.48	8.72
MPH 2A	39.75	1.29	8.69	38.20	1.60	0.08	0.05	0.02	0.16	-	0.67	9.48
MPH 2B	40.91	1.43	8.58	39.86	1.61	0.06	0.06	0.02	0.17	-	0.45	6.85
9PH 3A	39.52	0.67	8.47	42.56	0.96	-	0.04	0.01	0.14	-	0.40	7.23
9PH 3B	39.37	0.67	8.20	41.07	1.22	0.26	0.06	0.02	0.17	-	0.36	8.61
9PH 9A	38.99	0.26	8.47	43.73	0.37	0.32	0.06	0.05	0.13	-	0.45	3.05
<u>Dunite</u>												
MPD 2A	36.30	0.15	5.77	44.09	0.22	nd	0.06	0.01	0.14	nd	0.62	12.64
MPD 2B	34.97	0.12	4.88	43.89	0.21	0.16	0.05	0.01	0.13	nd	0.60	14.98
9DH 2C	35.85	0.21	5.81	43.49	0.25	0.09	0.06	0.01	0.14	nd	0.70	13.39
9DH 3F	35.78	0.21	6.92	43.40	0.25	nd	0.06	0.01	0.15	nd	0.60	12.62

Table III-2B Major Element Oxide Concentrations (wt %) in Cumulate Dunites (TMC)

Sample	Type	SiO_2	Al_2O_3	FeO^T	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	CO_2	H_2O
CCD 3A	Dunite with chromite band	25.40	6.19	12.45	33.96	0.28	nd	0.08	0.12	0.26	nd	0.84	8.53
CCD 3B		31.73	2.30	8.65	38.93	0.29	0.33	0.08	0.05	0.21	nd	0.63	11.67
CCD 3C	Dunites with abundant disseminated chromite	34.80	0.58	7.13	42.04	0.26	nd	0.06	0.02	0.17	nd	0.64	14.31
CCD 3D		35.19	0.30	7.34	41.43	0.20	nd	0.06	0.02	0.15	nd	0.75	14.56
9CD 6C		39.43	0.34	8.59	38.32	0.39	nd	0.06	0.02	0.14	nd	0.66	12.04
9CD 6D		42.89	0.15	6.70	38.06	0.20	0.03	0.06	0.02	0.16	nd	0.30	11.44
SU 6A		37.03	0.53	10.89	37.47	0.25	nd	0.06	0.02	0.17	nd	0.53	13.06
SU 6E		39.08	0.38	9.04	37.63	0.37	0.20	0.06	0.02	0.13	nd	0.55	12.55
9CD 7A		41.82	0.93	6.90	37.51	0.20	nd	0.06	0.02	0.17	nd	0.30	12.10
9CD 7B		34.87	0.33	9.91	40.36	0.23	nd	0.06	0.02	0.16	nd	0.63	13.43
9CD 7C		38.07	0.57	12.10	36.43	0.22	0.27	0.06	0.03	0.16	nd	0.31	11.80
CCD 4A		41.02	0.44	10.77	35.34	0.23	0.14	0.07	0.02	0.17	nd	0.28	11.53
CCD 4B		40.55	0.47	11.15	36.28	0.31	nd	0.07	0.02	0.17	nd	0.33	10.63
9CD 4C		39.89	0.28	12.46	35.21	0.28	nd	0.06	0.02	0.17	nd	0.40	11.24
9CD 4D		38.16	0.41	13.71	36.06	0.26	0.15	0.07	0.02	0.20	nd	0.39	10.58

Table III-2C Major Element Oxide Concentrations (wt %) in Pyroxenites (TMC)

Sample	Type	SiO_2	Al_2O_3	FeO^T	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	CO_2	H_2O
9CW 4E	Wehrlite	49.11	2.00	7.20	27.77	8.10	0.20	0.08	0.04	0.17	-	0.40	4.92
CCPY4B	Websterite	50.68	1.75	3.81	20.92	18.85	0.24	0.09	0.05	0.11	-	1.41	2.09
CCPY4C	Websterite	51.28	1.63	8.18	28.20	5.59	0.03	0.09	0.04	0.17	-	0.25	4.52
CCPY4D	Wehrlite	39.77	0.56	10.87	32.71	4.33	0.18	0.07	0.02	0.16	-	1.32	10.02
CCPY4E	Clinopyroxenite	55.72	1.46	3.97	21.48	15.63	0.49	0.08	0.04	0.14	-	0.24	1.06
9CY4F	Clinopyroxenite	54.10	2.14	4.71	18.76	19.26	0.19	0.12	0.05	0.11	-	0.29	0.28
9CY4G	Clinopyroxenite	50.49	1.45	4.62	24.02	15.19	0.10	0.08	0.05	0.12	-	0.73	3.16
9CY4H	Clinopyroxenite	51.03	1.95	3.77	19.68	18.02	0.20	0.09	0.05	0.10	-	0.28	4.83
CCPY5H	Plagioclose-Pyroxenite	49.46	11.61	10.67	15.64	5.62	1.51	0.10	0.23	0.17	-	0.37	4.61
CCPY5J	Pyroxenite	52.48	6.18	6.67	17.30	14.08	0.65	0.09	0.09	0.14	-	0.34	1.98
9YD6B	Olivine Pyroxenite	49.07	0.87	9.46	30.80	1.19	0.17	0.07	0.04	0.19	-	0.35	7.79
CCPY6F	Olivine Pyroxenite	46.29	0.96	6.31	31.42	6.23	0.14	0.07	0.05	0.17	-	0.29	8.07
9EY7A	Clinopyroxenite	52.22	2.05	6.47	20.11	16.52	0.11	0.09	0.06	0.13	-	0.33	1.91
9CY7B	Pyroxenite	48.92	1.61	8.87	27.44	6.02	0.05	0.07	0.05	0.18	-	0.27	6.53
9CY7C	Pyroxenite	50.92	2.68	8.52	23.68	9.80	0.18	0.08	0.06	0.16	-	0.23	3.60

Table III-2D. Major Element Oxide Concentrations (wt %) in Gabbros (TMC)

Sample	Type	SiO_2	Al_2O_3	FeO^T	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	CO_2	H_2O
CCG 4F	Cumulate gabbro	47.68	15.19	5.91	13.73	11.96	1.42	0.59	0.06	0.12	0.01	0.27	3.06
CCG 4G	Cumulate gabbro	47.37	17.08	7.83	9.49	14.22	0.52	0.18	0.10	0.14	0.01	0.38	2.67
CCG 4H	Cumulate gabbro	50.66	15.14	16.92	6.63	3.22	2.24	0.25	0.65	0.30	0.03	0.25	3.71
9CG 4E	Cumulate gabbro	47.12	11.40	6.52	17.89	8.92	2.27	0.21	0.06	0.14	0.01	1.60	3.86
9CG 4J	Pyroxene-rich gabbro	52.25	2.46	6.63	18.24	17.41	0.07	0.12	0.07	0.15	0.01	1.90	0.68
9CG 4K	Hornblende gabbro	47.07	17.36	5.44	10.17	16.43	0.09	0.11	0.06	0.11	0.01	0.57	2.58
9CG 4L	Uralitised gabbro	49.31	1.64	7.48	25.25	11.05	0.10	0.10	0.06	0.16	0.01	0.41	4.43
9MG 4A	Metagabbro	51.07	10.24	9.24	12.83	12.80	1.13	0.52	0.25	0.16	0.01	0.23	1.51
9MG 4B	Metagabbro	52.04	16.09	9.97	6.67	5.12	5.22	0.60	0.06	0.15	0.02	1.05	2.45
9MG 4C	Metagabbro	45.46	19.32	11.81	6.80	8.72	2.60	0.63	0.31	0.17	0.01	0.47	3.68
9MG 4D	Metagabbro	45.41	17.92	9.35	9.08	12.62	1.16	0.48	0.14	0.14	0.01	0.43	3.27
9DB 4M	Diabase	52.52	15.00	8.80	9.73	4.22	5.76	0.15	0.31	0.17	0.02	0.55	2.78

Table III-2E Major Element Oxide Concentrations (wt%) in the lavas (TMC)

	Volcanics (East Lake)	SIO_2	Al_2O_3	FeO^T	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	CO_2	H_2O
	Lower Unit												
9LB 4A	Massive	49.17	15.25	11.47	5.78	4.95	5.21	0.18	1.12	0.19	0.07	3.11	3.50
9LB 4B	Massive	49.33	14.09	13.33	4.14	6.27	6.27	0.14	1.55	0.22	0.06	2.91	1.68
9LB 4C	Pillowed & Brecciated	64.82	13.32	9.47	4.02	0.63	3.90	0.12	0.75	0.26	0.12	0.13	2.47
9LB 4D	Pillowed & Brecciated	57.04	15.48	11.01	4.76	1.49	4.98	0.18	1.26	0.22	0.11	0.69	2.78
9LB 4E	Massive	49.99	14.56	13.32	7.10	3.21	3.84	0.13	1.24	0.26	0.05	1.68	4.62
9LB 4G	Massive	58.29	14.02	10.32	4.72	1.62	5.72	0.13	1.00	0.19	0.07	0.84	3.08
9LB 4H	Massive	53.72	13.53	9.74	5.15	5.61	4.76	0.14	0.91	0.19	0.03	3.64	2.58
9LB 4J	Pillowed	49.51	14.31	13.46	7.20	3.49	4.51	0.13	1.46	0.20	0.05	1.56	4.11
9LB 4K	Massive	51.52	14.51	15.12	4.31	4.96	5.57	0.14	1.48	0.26	0.05	0.28	1.80
9LB 4L	Massive	47.54	15.83	15.26	5.71	3.08	4.63	0.15	1.53	0.29	0.07	2.15	3.76
9LB 4X	Pillowed	50.76	14.04	14.18	6.82	2.89	3.49	0.14	1.24	0.27	0.04	1.68	4.44
9LB 4F	Massive	73.60	12.41	4.75	1.31	0.75	5.30	0.11	0.20	0.11	0.01	0.35	1.09
9LB 4M	Pillowed	48.12	15.04	9.77	7.92	5.91	4.30	0.19	0.23	0.25	0.01	4.14	4.12
9LB 4N	Pillowed	52.49	14.59	11.28	9.97	2.40	4.61	0.19	0.22	0.25	0.01	0.04	3.95
9LB 4P	Pillowed	52.17	15.16	9.94	9.04	4.21	3.36	2.29	0.30	0.16	0.01	0.17	3.19
9LB 4Q	Pillowed	53.67	14.09	8.80	8.85	5.33	5.01	1.08	0.24	0.17	0.01	0.28	2.48
9LB 4R	Pillowed	54.93	16.03	7.33	7.80	4.75	4.49	0.88	0.31	0.11	0.02	-	3.35
9LB 4U	Pillowed	56.18	15.10	7.68	8.57	4.35	3.82	0.75	0.31	0.11	0.02	-	3.10
9LB 4V	Pillowed	49.15	9.88	4.82	6.11	14.89	2.12	0.77	0.18	0.10	0.01	9.28	2.69
9LB 4W	Pillowed	53.22	11.91	7.86	10.46	7.57	3.79	0.19	0.21	0.19	0.01	1.56	3.02
	Upper Unit												
9UB 4A	Vesicular	52.79	12.98	8.50	10.64	5.14	3.66	0.62	0.24	0.21	0.01	1.52	3.70
9UB 4B	Vesicular	51.13	13.36	9.47	13.07	4.44	4.00	0.22	0.24	0.18	0.01	0.13	3.74
9UB 4C	Vesicular	52.92	11.81	8.80	12.75	5.80	3.05	0.23	0.21	0.17	0.01	0.09	4.16
9UB 4D	Vesicular	49.12	10.93	9.49	12.56	9.82	1.98	0.33	0.20	0.18	0.01	1.51	3.87
9UB 4E	Vesicular	51.77	10.77	9.08	13.68	5.81	2.49	0.21	0.25	0.17	0.01	1.39	4.37
9UB 4F	Vesicular	55.21	11.05	6.75	10.05	5.78	3.65	0.56	0.18	0.15	0.01	2.71	2.90
9LB 4S	Vesicular	48.28	10.48	10.29	15.74	8.38	1.26	0.45	0.22	0.20	0.01	0.69	3.99
9LB 4T	Vesicular	52.18	12.16	9.08	12.65	6.43	3.56	0.17	0.23	0.21	0.01	0.24	3.09

Table III-3A Trace element concentrations (ppm) in metamorphic peridotites (TMC)

Sample	S	Cr	Ni	Co	Zn	Cu	Pb	Zr	Y
Harbugite									
MPH1A	31	3503	2522	137	36	nd	9	2	nd
MPH1C	34	5320	2573	129	35	nd	10	2	nd
MPH2A	48	4718	2449	135	34	5	10	4	2
MPH2B	58	4591	2395	121	41	11	12	5	3
9PH3A	34	4707	2535	132	35	2	12	4	2
9PH3B	47	5662	2517	130	33	3	10	nd	nd
9PH9A	39	5453	2573	136	29	nd	6	3	nd
Dunite									
MPD2A	-	2678	3171	123	18	nd	nd	1	nd
MPD2B	-	1353	3588	106	14	nd	nd	2	nd
9DH2C	-	4644	3052	130	19	1	nd	nd	nd
9DH3F	-	5133	2702	126	23	1	nd	2	nd

Table III-3B Trace element concentrations (ppm) in cumulate dunites (TMC)

Sample	S	Cr	Ni	Co	Zn	Cu	Pb	Zr	Y
CCD3A	nd	Cr_2O_3% 10	1390	65	142	3	6	4	1
CCD3B	nd	Cr_2O_3% 4.07	2125	75	65	3	11	2	nd
CCD3C	nd	9868	2642	129	20	6	2	4	nd
CCD3D	nd	5529	2952	133	13	5	1	2	1
CCD6C	nd	4471	2634	126	28	nd	6	nd	nd
9CD6D	21	5884	2079	114	28	2	1	2	nd
SU6A	nd	2985	3036	148	39	nd	11	5	1
SU6E	18	5669	2723	131	26	1	6	1	nd
9CD7A	nd	5356	2770	112	24	3	2	3	nd
9CD7B	nd	5874	2587	150	22	9	7	5	1
9CD7C	nd	4377	1881	176	37	3	16	3	1
CCD4A	106	3409	1419	155	35	13	11	2	1
CCD4B	63	3062	1643	160	35	3	12	4	nd
9CD4C	101	843	1126	192	35	3	11	2	2
9CD4D	49	5792	1099	191	60	4	11	nd	nd

Table III-3C Trace element concentrations (ppm) in pyroxenites (TMC)

Sample	S	Cr	Ni	Co	Zn	Cu	Pb	Zr	Y
9CW4E	22	5545	319	51	29	23	13	2	nd
CCPY4B	354	4832	257	17	20	5	11	8	2
CCPY4C	nd	5857	390	72	36	8	14	7	3
CCPY4D	48	3509	1203	139	32	5	12	4	1
CCPY4E	nd	4819	181	16	20	14	13	7	7
9CY4F	nd	2979	152	18	20	34	10	9	6
9CY4G	70	5840	421	38	21	6	11	4	3
9CY44	126	5655	768	14	21	10	10	5	2
CCPY5H	nd	3670	427	66	64	10	12	21	7
CCPY5J	nd	4710	208	35	39	13	12	9	5
9YD6B	nd	5071	566	95	49	2	13	3	nd
CCPY6F	nd	5891	527	64	42	3	12	5	4
9CY7A	nd	3586	255	33	30	271	13	6	4
9CY7B	nd	3309	398	69	47	5	12	3	nd
9CY7C	7	4885	350	61	45	12	10	5	4

nd - not detected

Table III-3D Trace element concentrations (ppm) in gabbros (TMC)

Sample	S	Cr	Ni	Co	Zn	Cu	Pb	Zr	Y
Cumulate gabbra									
9CG4E	nd	1023	240	39	26	2	13	7	2
CCG4F	nd	211	174	25	26	17	16	4	3
CCG4G	nd	47	45	34	46	51	13	9	5
CCG4H	nd	27	nd	75	145	123	10	18	9
9CG4J	nd	4104	151	29	37	15	12	5	5
9CG4K	316	303	157	22	30	581	14	5	
9CG4L	336	2962	470	47	29	15	12	7	4
Metagabbro									
9MG4A	nd	795	76	40	53	128	9	14	6
9MG4B	nd	91	29	45	24	2	12	40	22
9MG4C	nd	15	4	54	76	13	12	10	4
9MG4D	nd	33	29	54	34	105	12	6	1
9DB4M	nd	1068	150	47	29	15	12	41	4

nd - not detected

Table III-3E Trace element concentrations (ppm) in lavas (TMC)

Sample	S	Cr	Ni	Co	Zn	Cu	Pb	Zr	Y
Type I lavas									
9LG4A	48	21	3	43	81	31	12	57	41
9LB4B	208	15	nd	46	103	80	10	57	35
9LB4C	91	22	nd	25	362	78	15	90	43
9LB4D	423	34	nd	47	182	21	13	72	34
9LB4E	nd	41	14	70	147	30	11	43	31
9LB4G	nd	23	nd	37	96	20	15	78	32
9LB4H	353	113	15	47	71	60	16	38	24
9LB4J	58	23	nd	65	134	58	12	51	25
9LB4K	57	17	nd	57	72	40	10	54	33
9LB4L	nd	14	nd	66	137	21	13	66	35
9LB4X	nd	15	nd	48	155	12	10	49	25
9LB4F	540	25	2	6	72	30	4	46	19
Type II lavas									
9LB4M	nd	335	58	51	126	80	12	21	8
9LB4N	196	253	63	7	64	21	10	18	10
9LB4P	nd	243	63	43	33	20	12	21	8
9LB4Q	nd	199	55	28	59	20	12	20	8
9LB4R	nd	213	84	29	58	26	15	42	9
9LB4U	nd	339	102	27	61	31	15	40	12
9LB4V	nd	335	80	17	36	59	17	19	6
9LB4W	nd	897	109	30	60	110	16	23	8
upper lavas									
9UB4A	nd	2598	283	43	64	50	14	23	9
9UB4B	nd	2132	274	63	89	11	13	25	7
9UB4C	nd	2014	271	45	73	89	12	24	8
9UB4D	nd	2853	322	51	67	80	12	22	6
9UB4E	nd	3541	317	49	57	21	15	29	11
9UB4F	nd	1786	250	40	61	39	15	18	4
9LB4S	nd	2663	357	59	99	44	10		
9LB4T	nd	1949	294	43	102	85	13	26	10

nd - not detected

Table III-4A CIPW Normative Minerals Metamorphic Perdotites (TMC)

Sample	or	ab	an	q	ol	hy	di	ap	il	c	mt	nc	cc
Herzburgite													
MPH 1A	0.39	3.71	0.20	-	79.70	11.18	1.03	-	0.04	-	2.62	-	1.12
MPH 1C	0.45	3.41	-	-	76.75	14.34	1.25	-	0.02	-	2.69	-	1.07
MPH 2A	0.33	0.75	3.33		66.40	24.27	0.60	-	0.04	-	2.61	-	1.68
9PH 3A	0.25	-	1.84	-	78.92	15.10	0.44	-	0.02	-	2.44	-	0.98
9PH 3B	0.39	2.41	0.53	-	78.41	12.01	2.84	-	0.04	-	2.49	-	0.90
9PH 9A	0.38	0.87	-	-	83.74	11.19	-	-	0.10	0.04	2.56	0.41	0.71
Dunites													
MPD 2A	0.41	-	-	-	81.37	19.61	-	-	0.02	1.28	1.73	1.23	0.45
MPD 2B	0.35	-	-	-	87.41	12.58	-	-	0.02	0.95	1.52	1.23	0.44
9DH 2C	0.41	-	-	-	81.11	19.50	-	-	0.02	1.34	1.76	1.40	0.66
9DH 3F	0.41	-	-	-	83.32	16.84	-	-	0.02	1.24	2.06	1.11	0.51

Table III-4B CIPW Normative Minerals in Cumulate Dunites (TMC)

Sample	or	ab	an	q	ol	hy	di	ap	il	c	mt	hem	nc	cc
CCD 3C	0.41	-	-	-	81.87	18.05	-	-	0.04	1.78	2.13	-	1.23	0.54
CCD 3D	0.42	-	-	-	75.17	26.45	-	-	0.04	1.88	2.22	-	1.67	0.42
CCD 4A	0.47	-	-	-	49.54	46.57	-	-	0.04	0.67	3.32	-	0.27	0.46
CCD 4B	0.46	-	-	-	55.12	40.64	-	-	0.04	0.67	3.38	-	0.28	0.78
CCD 4C	0.40	-	-	-	53.26	43.19	-	-	0.04	0.71	3.77	-	0.49	0.56
CCD 4D	0.46	-	-	-	63.78	32.24	-	-	0.04	0.86	4.08	-	0.62	0.68
CCD 6A	0.41	-	-	-	65.42	32.56	-	-	0.04	1.42	3.29	-	0.92	0.51
CCD 6B	0.41	-	-	-	60.88	35.30	-	-	0.04	0.67	2.83	-	0.71	0.76
CCD 6C	0.40	-	-	-	56.33	42.40	-	-	0.04	1.25	2.62	-	0.97	0.79
9CD 6D	0.40	-	-	-	46.55	51.59	-	-	0.04	0.47	2.08	-	0.39	0.40
9CD 7A	0.40	-	-	-	48.02	49.17	-	-	0.04	1.36	2.14	-	0.39	0.41
9CD 7B	0.41	-	-	-	79.24	20.31	-	-	0.04	1.51	2.95	-	1.25	0.47
9CD 7C	0.40	0.73	-	-	68.15	25.64	-	-	0.06	0.43	3.75	-	0.37	0.45

Table III-4C CIPW Normative Minerals in Pyroxenites (TMC)

Sample	or	ab	an	q	ol	hy	di	ap	il	c	mt	hem	cc
9CW 4A	0.50	1.78	4.55	-	18.37	43.84	27.67	-	0.08	-	2.26	-	0.96
CCPY4B	0.54	2.07	3.51	-	9.62	14.87	65.27	-	0.10	-	0.74	-	3.28
CCPY4C	0.55	0.26	4.22	-	6.43	66.38	18.20	-	0.08	-	3.29	-	0.59
CCPY4D	0.46	1.69	0.57	-	54.71	24.74	11.11	-	0.04	-	3.34	-	3.34
CCPY4E	0.48	4.19	1.56	1.18	-	31.49	59.17	-	0.08	-	1.30	-	0.55
9CY 4F	0.71	1.61	4.64	0.57	-	19.79	70.45	-	0.10	-	1.47	-	0.66
9CY 4G	0.49	0.87	3.38	-	12.37	24.85	54.80	-	0.10	-	1.42	-	1.71
9CY 4H	0.56	1.78	4.37	-	4.76	17.58	68.98	-	0.10	-	1.20	-	0.67
CCPY5H	0.62	13.40	25.80	0.42	-	53.71	0.79	-	0.46	-	3.94	-	0.88
CCPY5J	0.54	5.61	13.96	1.20	-	31.82	43.71	-	0.17	-	2.20	-	0.79
9YD 6B	0.45	1.56	1.52	-	13.01	77.51	1.96	-	0.08	-	3.05	-	0.86
ccPY 6F	0.45	1.29	1.94	-	31.94	38.19	23.36	-	0.10	-	2.00	-	0.72
9CY 7A	0.54	0.95	4.93	-	2.18	27.99	60.53	-	0.12	-	2.00	-	0.77
9CY 7B	0.44	0.45	4.24	-	12.74	58.11	20.49	-	0.10	-	2.78	-	0.66

Table III-4D CIPW Normative Minerals in Gabbros (TMC)

Sample	Or	ab	an	q	ol	hy	di	ap	il	c	mt	hem	cc
Cumulate													
CCG 4F	3.60	12.40	34.38	-	15.73	11.07	19.84	0.02	0.12	-	2.21	-	0.63
CCG 4G	1.09	4.52	44.95	0.83	-	24.84	20.16	0.02	0.20	-	2.50	-	0.89
CCG 4H	1.53	19.68	14.75	12.72	-	36.33	-	0.07	1.28	6.21	6.84	-	0.59
9CG 4E	1.29	19.98	21.11	-	22.40	17.37	11.34	0.02	0.12	-	2.58	-	3.78
9CG 4J	0.71	0.60	6.09	2.92	-	28.67	54.49	0.02	0.13	-	2.01	-	4.35
9CG 4K	0.67	0.78	47.88	0.83	-	21.18	25.58	0.02	0.12	-	1.62	-	1.33
9CG 4L	0.62	0.89	3.90	-	15.02	36.08	40.06	0.02	0.12	-	2.32	0	0.98
Metagabbro													
9MG 4A	3.12	9.71	21.66	0.49	-	27.54	33.09	0.02	0.48	-	3.36	-	0.53
9MG 4B	3.64	45.29	19.11	-	6.11	16.83	-	0.05	1.17	0.03	5.34	-	2.45
9MG 4C	3.87	22.85	40.69	-	14.52	10.47	0.88	0.02	0.61	-	4.98		1.11
9MG 4D	2.93	10.15	43.71	-	10.72	13.07	14.85	0.02	0.27	-	3.33	-	0.94
9DB 4M	0.91	50.13	15.05	-	16.60	8.38	2.22	0.05	0.61	-	4.77	-	1.29

Table III-4E CIPW Normative Minerals in Lavas (TMC)

Sample	or	ab	an	q	ol	hy	di	ap	il	c	mt	hem	cc
Lower Unit													
9LB 4A	1.10	45.69	4.61	4.38	-	22.69	-	0.17	2.20	5.03	6.81	-	7.33
9LB 4B	0.84	53.97	10.06	-	5.69	9.34	2.03	0.14	2.99	-	8.21	-	6.73
9LB 4C	0.73	33.83	1.57	-	-	20.77	-	0.29	1.46	6.37	3.57	-	0.30
9LB 4D	1.09	43.34	2.39	16.96	-	18.51	-	0.26	2.46	6.42	6.95	-	1.61
9LB 4E	0.81	34.07	5.22	10.41	-	28.89	-	0.12	2.47	6.58	7.43	-	4.01
9LB 4F	0.66	45.35	1.46	39.16	-	5.61	-	0.02	0.38	3.08	3.47	-	0.80
9LB 4G	0.79	49.94	2.35	14.46	-	17.76	-	0.17	1.96	3.75	6.85	-	1.97
9LB 4H	0.85	41.35	4.75	13.31	-	19.60	-	0.07	1.77	3.95	5.85	-	8.50
9LB 4J	0.80	39.80	7.44	5.04	-	28.16	-	0.12	2.89	4.32	7.73	-	3.70
9LB 4K	0.84	47.95	14.42	0.18	-	17.12	6.45	0.12	2.86	-	9.19	-	0.88
9LB 4L	0.92	40.71	1.28	6.31	-	26.00	-	0.17	3.02	7.90	8.62	-	5.08
9LB 4M	1.17	37.95	3.22	5.66	-	29.32	-	0.02	0.46	6.92	5.47	-	9.82
9LB 4N	1.17	40.61	12.07	1.06	-	35.13	-	0.02	0.44	2.66	6.75		0.09
9LB 4P	13.98	29.16	-	-	3.50	25.63	0.19	0.02	0.59	-	6.16	-	0.40
9LB 4Q	6.54	43.47	13.09	-	9.33	11.12	9.69	0.02	0.47	-	5.62	-	0.65
9LB 4R	5.38	39.31	21.72	2.03	-	24.29	2.02	0.05	0.61	-	4.61	-	-
9LB 4U	4.57	33.36	22.14	6.76	-	27.69	-	00.5	0.61	0.15	4.67	-	-
9LB 4V	1.12	6.83	15.88	27.36	-	21.13	-	0.02	0.36	3.01	2.17	-	22.13
9LB 4W	1.16	33.07	15.39	2.81	-	28.55	10.43	0.02	0.41	-	4.49	-	3.66
9LB 4X	0.87	30.91	3.62	13.98	-	29.06	-	0.10	2.46	7.20	7.81	-	4.00
Upper Unit													
9UB 4A	3.84	23.62	16.61	9.57	-	35.01	-	0.02	0.48	2.24	4.99	-	3.63
9UB 4B	1.35	35.17	18.55	-	11.52	24.50	2.72	0.02	0.47	-	5.39	-	0.31
9UB 4C	1.42	26.93	18.63	1.99	-	36.98	8.54	0.02	0.42	-	4.86	-	0.21
9UB 4D	2.03	17.43	20.77	0.74	-	34.44	15.92	0.02	0.40	-	4.68	-	3.57
9UB 4E	1.30	22.03	18.39	4.45	-	43.25	1.98	0.02	0.50	-	4.78	-	3.31
9UB 4F	3.41	31.81	12.48	8.53	-	29.55	3.54	0.02	0.35	-	3.97	-	6.35
9LB 4S	2.77	11.09	22.48	-	4.30	39.18	13.09	0.02	0.43	-	5.10	-	1.54
9LB 4T	1.04	31.09	17.23	-	4.32	29.06	11.19	0.02	0.45	-	5.04	-	0.56

Table III-5 Major, Minor and Trace Element Concentrations in the Sediments (TMC)

	Sediments (Argillite) Major Elements (wt %)	SiO_2	Al_2O_3	FeO^T	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	CO_2	H_2O
9LS 4C	lower	51.71	18.10	14.02	3.24	1.11	4.92	3.41	0.40	0.15	0.02	0.69	2.23
9LS 4D	sediment	56.33	17.27	12.39	2.15	0.76	3.36	4.81	0.32	0.18	0.01	0.28	2.14
SDLA4P	ophiolitic	61.83	16.22	9.67	1.46	0.50	3.83	4.31	0.27	0.05	0.01	0.37	1.47
SDLA4R		68.25	10.39	7.84	1.92	7.93	0.52	0.64	0.39	0.25	0.05	0.37	1.44

				ppb						ppm					
	Trace Elements	Au	Ir	Pt	Pd	Ag	Cr	Ni	Co	Zn	Cu	Pb	Zr	Y	S
9LS 4C	lower	1.19	0.092	4.24	13.69	5.36	2481	170	73	67		13	34	17	-
9LS 4D	sediment	0.54	0.035	25.28	1.60	2.27	491	94	89	83		10	25	1	-
SDLA4P	ophiolitic	5.33	0.034	-	5.86	3.26	491	75	25	44		13	30	1	-
SDLA4R		2.56	0.116	2.35	0.07	23.62	80	85	31	46		56	86	27	-
	average	2.41±0.92	0.069±0.018	10.62±6.00	5.31±2.64	8.63±4.36									
SDUA4K	upper sediment	1.57	0.102	23.86	0.43	13.60	42	30	10	24		9	26	12	-
SDUA4M	non-ophiolitic	2.22	0.133	-	6.78	8.13	657	150	45	75		19	47	14	-
	average	1.90±0.23	0.118±0.001		3.61±2.25	10.87±1.93									

APPENDIX IV

MINERAL SEPARATION AND ANALYSIS

Chromite, olivine, orthopyroxene and clinopyroxene were analyzed for noble metals. The method of analysis was similar to that used for whole rock but less than 80 mg of each mineral separate was used.

The minerals were separated from a harzburgite (chromite, olivine, and orthopyroxene), a cumulate dunite (chromite) and a websterite (clinopyroxene and orthopyroxene). Figure IV-1 is a flow chart for the separation procedure.

The separation exercise was time consuming and frustrating. The main difficulty arose from the nearly similar densities of the mafic minerals which made separation by heavy liquid (at least those that can be safely used) impossible. The use of the Frantz isodynamic magnetic separator was severely limited because of the similarity of magnetic susceptibility of orthopyroxene and clinopyroxene, on the one hand, and chromite and olivine on the other hand as adherence of magnetite on olivine grains has increased the magnetic susceptibility of olivine. Furthermore, most of the chromite and olivine grains were composite. Attempts to eliminate composite grains by crushing to -300 mesh proved unsuccessful as the grains were too fine to be separated by the magnetic separator and too fine to hand pick.

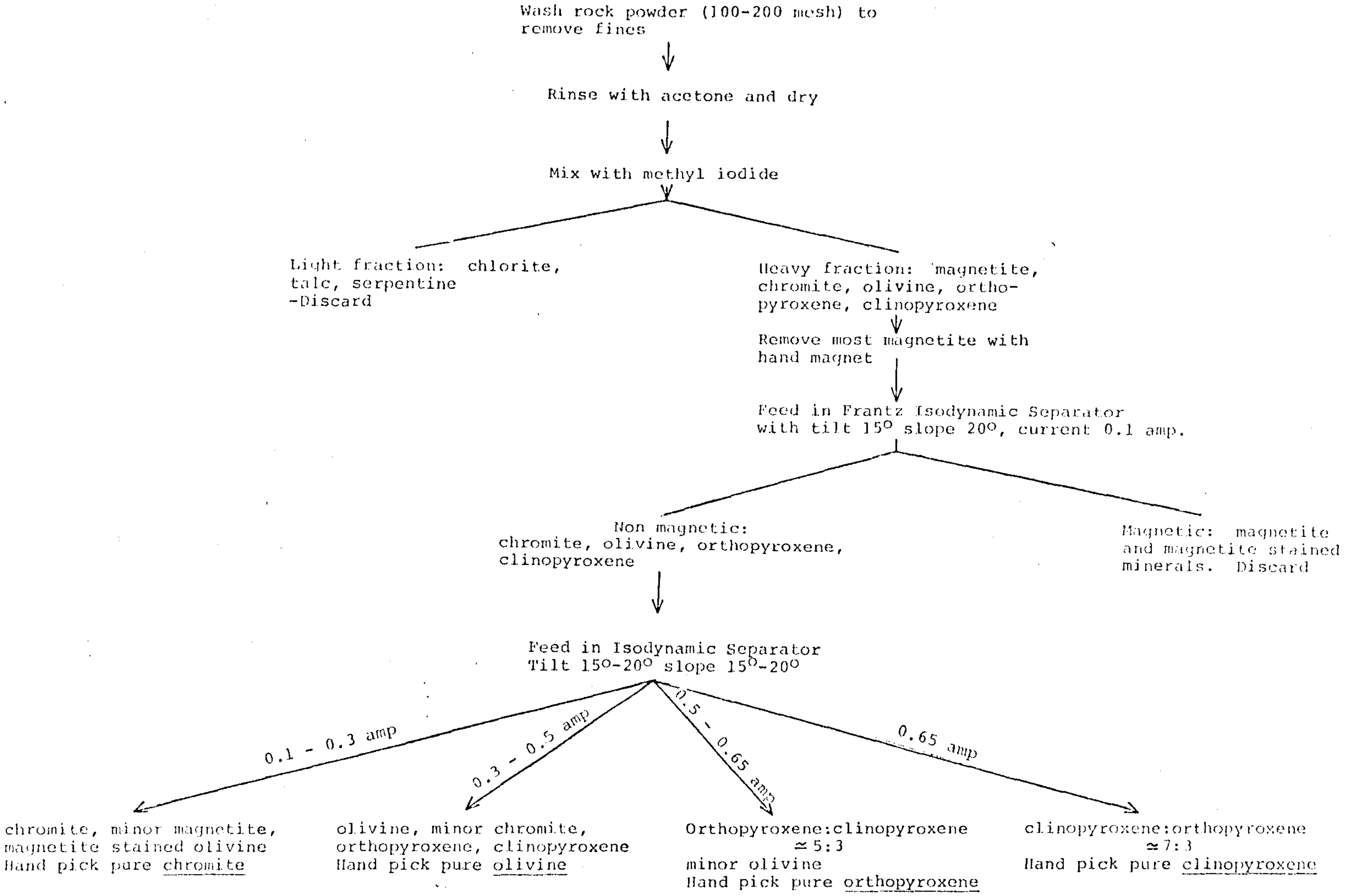


Figure IV-1. Flow chart for mineral separation in TMC ultramafic rocks.

Separates of acceptable purity were eventually obtained by 1) passing the samples through the magnetic separator many times under varying current, slope and tilt conditions, and 2) hand picking the best single grains under a binocular microscope.

The estimated purity of the mineral separates based on optical observations are given in Table IV-1.

Table IV-1

Table Showing the Purity of Mineral Separates

Ident. No.	Rock Sample Host	Mineral	Perc. Purity	Impurity
M-1	9PH3A	chromite	90	inclusion of olivine
M-2	9PH3A	chromite (cleaned with HF & H_2SO_4)	100	-
M-3	9PH3A	olivine	98	dust of magnetite
M-4	9PH3A	orthopyroxene	90	clinopyroxene (exsolution lamellae)
M-5	CCD3A	chromite	90	inclusion of olivine
M-6	CCD3A	chromite (cleaned with HF & H_2SO_4	100	-
M-7	CCPY4C	orthopyroxene	90	clinopyroxene and olivine
M-8	CCPY4C	clinopyroxene	95	orthopyroxene

APPENDIX V

CALCULATION OF THE SOLUBILITY OF NOBLE METALS IN HYDROTHERMAL SOLUTIONS

The solubility of the noble metals in hydrothermal solution with MnO_2 as the oxidizing agent may be calculated from the oxidation reactions.

i) $Au + 4Cl^- + 1\frac{1}{2} MnO_2 + 6H^+ \rightleftharpoons AuCl_4^- + 1\frac{1}{2} Mn^{+2} + 3H_2O$

$E^o = 0.23$ v

ii) $Pd + 4Cl^- + MnO_2 + 4H^+ \rightleftharpoons PdCl_4^{-2} + Mn^{+2} + 2H_2O$

$E^o = 0.61$ v

iii) $Pt + 4Cl^- + MnO_2 + 4H^+ \rightleftharpoons PtCl_4^{-2} + Mn^{+2} = 2H_2O$

$E^o = 0.50$ v

Let K = equilibrium constant for the metal oxidation reaction:

then

$$K_{Au} = \frac{\left[Mn^{+2}\right]^{3/2} \left[AuCl_4^-\right]}{\left[H^+\right]^6 \left[Cl^-\right]^4}$$

$$K_{Pd} = \frac{\left[Mn^{+2}\right] \left[PdCl_4^{-2}\right]}{\left[H^+\right]^4 \left[Cl^-\right]^4}$$

$$K_{Pt} = \frac{\left[Mn^{+2}\right]\left[PtCl_4^{-2}\right]}{\left[H^+\right]^4\left[Cl^-\right]^4}$$

It is assumed that $Mn^{+2} = 0$ at the start of oxidation and that only the Mn^{+2} produced during oxidation exist. Therefore, at equilibrium there will be 3/2 moles of Mn^{+2} for 1 mole of $AuCl_4^-$ or $[Mn^{+2}] = [2/3\ AuCl_4^-]$
1 mole of Mn^2 for 1 mole of $PdCl_4^-$ or $[Mn^{+2}] = [PdCl_4^{-2}]$
1 mole of Mn^2 for 1 mole of $PtCl_4^-$ or $[Mn^{+2}] = [PtCl_4^{-2}]$
that is

$$K_{Au} = \frac{\left[2/3\ AuCl_4^-\right]^{3/2}\left[AuCl^-\right]}{\left[H^+\right]^6\left[Cl^-\right]^4}$$

$$\frac{\left(\frac{8}{27}\right)^{1/2}\left[AuCl^-\right]^{5/2}}{\left[H^+\right]^6\left[Cl^-\right]^4}$$

$$K_{Pd} = \frac{\left[PdCl_4^{-2}\right]^2}{\left[H^+\right]^4\left[Cl^-\right]^4}$$

$$K_{Pt} = \frac{\left[PtCl_4^{-2}\right]^2}{\left[H^+\right]^4\left[Cl^-\right]^4}$$

K is calculated from the equation

$$\log K = \frac{nFE^{o}}{2.303RT}$$

where E^{o} = standard oxidation potential of the reaction in i) to iii)

n = number of electrons transferred during oxidation

F = Faraday's constant 2.31 kcal/volt

R = gas constant 1.99 cal/mole

T = absolute temperature of oxidation

Knowing K, the amount of metal complex as $AuCl_4^-$, $PdCl_4^{-2}$ and $PtCl_4^{-2}$ can be calculated from which the amount of Au, Pd and Pt dissolved can also be calculated for different values of $[H^+]$ and $[Cl^-]$.

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LEGEND

Middle Ordovician

7 Magog Formation

Lower Ordovician

6 St. Daniel Formation

Thetford Mines Ophiolite Complex

Upper Volcanic Sedimentary Formation

5c Red and Green Argillite and Chert

5b Volcanic Breccia

5a Pillow Metabasalts, Metaandesites and Pyroclastics

Lower Volcanic Unit

4 Pillow Metabasalts and Red Argillites

Hypabyssal Rocks

3 Metagabbro Diabase Dykes and Sills

Cumulates

$2c_1$ Gabbro and Trondjhemite ($2c_2$)

2b Pyroxenite

2a Dunite, Olivine-Chromite, Chomitite and Wehrlite

Metamorphic Peridotite

1e Amphibolite

1d Diorite and Monzonite

1c Pyroxenite

1b Dunite

1a Harzburgite

Cambrian

ϵ_1 Graywacke and Shale

ϵ_2 Basaltic Lava

Mines { Chromite ···· C
 Asbestos ···· A

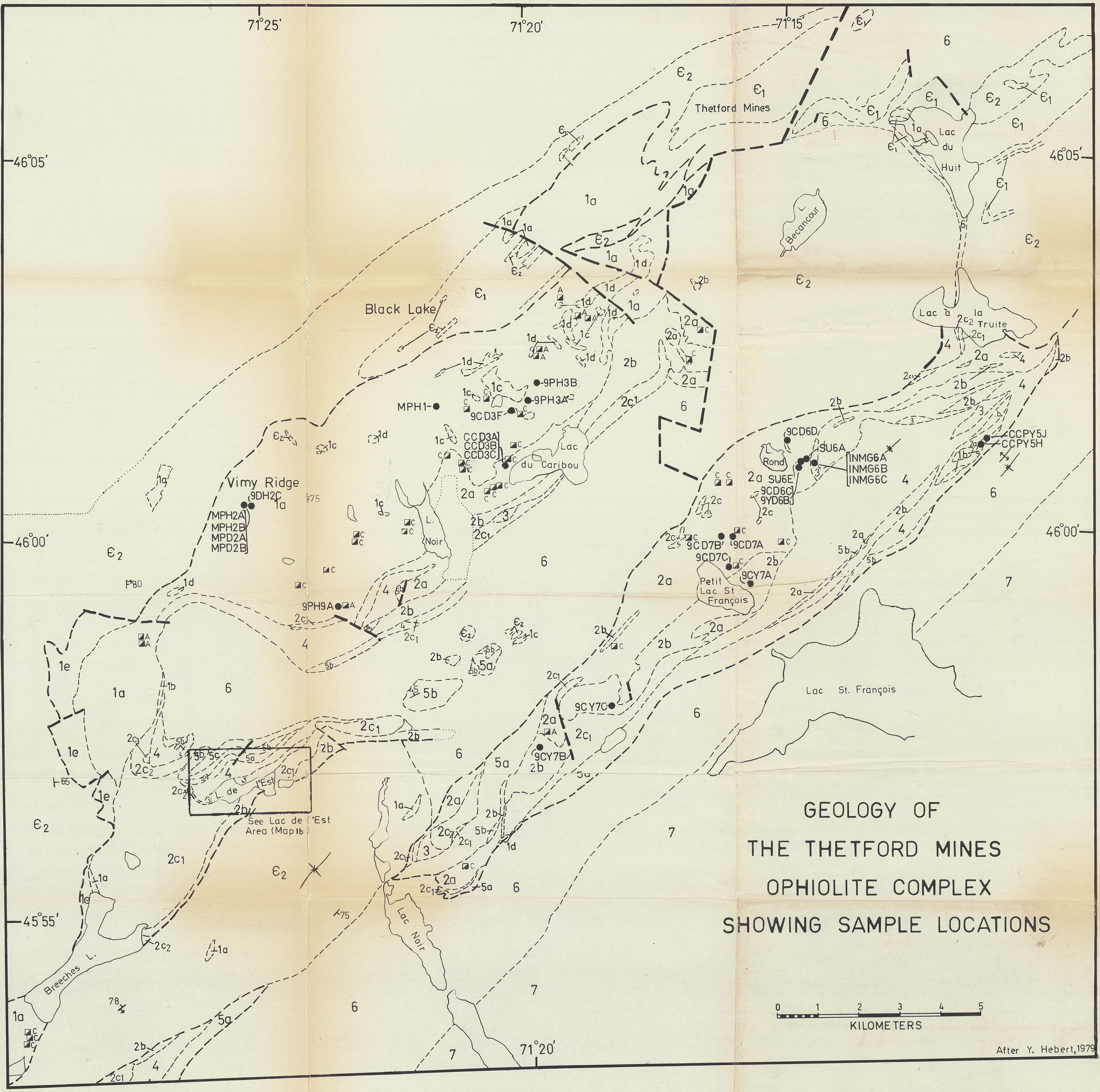
- - - Geologic boundary

— — Fault

Strike and dip

Fold axis; anticlinal, synclinal

●9CY7A Sample location



GEOLOGY OF THE THETFORD MINES OPHIOLITE COMPLEX SHOWING SAMPLE LOCATIONS