THE GEOCHEMISTRY OF SOME KEWEENAWAN METABASITES

FROM MAMAINSE POINT, ONTARIO

by

NICHOLAS WILLIAM DAVID MASSEY, B.Sc.

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AUTHOR: Nicholas William David Massey, B.Sc. (Leeds)

SUPERVISOR: Professor Denis M. Shaw

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ABSTRACT

The Mamainse Point Formation formed on the margin of the Late Proterozoic Keweenawan Rift. It consists of olivine- and feldspar-phyric flood basalts with felsites and conglomeratic sediments, and spans the palaeomagnetic reversal normally regarded as the boundary between Lower and Middle Keweenawan. The basalts are classified as olivine and quartz tholeiites, although the dykes show some alkaline tendencies in trace-element characteristics and are better termed transitional basalts.

Formation of the lava pile was accompanied by low-grade burial metamorphism in the zeolite and prehnite-pumpellyite facies. Secondary minerals developed both within the rock and in veins and vesicles. A crude mineral zonation developed from epidote at the base to stilbite at the top of the exposed section. Heterogeneity, with the development of epidote-, chlorite- and albite-rich metadomains, is restricted to feldspar-phyric melaphyres in lower parts of the section. Calcite-laumontite veins are ubiquitous and even cross-cut the higher grade epidote-bearing rocks, suggesting that metamorphism took place in two stages, the second at a lower temperature. Geochemical evidence also suggests that
fluid compositions changed. The initial hydration event established mineral zonation and resulted in addition of $\text{H}_2\text{O}^+$ and alkalalis (K, Rb, Li, Na, Ba) to the rocks. Cu was leached from some rocks and added to others. Latter fluids were more CO$_2$-rich depositing calcite and laumontite, with the resulting addition of CO$_2$ and mobilization of Ca and Sr.

Al, Fe, Mg, Ti, P, Y, Zr, Nb, Ni, Cr, Co, REE's, Th, Ta, Hf and U appear to be immobile or only moderately affected by the alteration. The stratigraphic variation of these elements allows the subdivision of the sequence into five series. The immobile trace-elements confirm the tholeiitic nature of the lavas and suggest an ocean floor to within-plate character. Incompatible element patterns suggest a similarity to E-type MORB.

Shallow-level fractionation of olivine-chromite-plagioclase can account for most of the geochemical variation in the five series, although in differing proportions. Clinopyroxene and Fe-Ti oxides crystallized after extrusion of the lavas. Variations in REE-patterns and incompatible element ratios cannot be explained by fractionation, however, and appear to have resulted during genesis of the primary magmas.

Modelling of REE patterns requires varying degrees of melting of a garnet-lherzolite mantle. However, two source compositions are indicated by initial REE concentrations, one
with a relatively flat chondritic pattern and the others with a LREE-depleted pattern. Other incompatible element variations appear to be consistent with this, although Th and U abundances may point to further heterogeneities. The need for a different mantle source for virtually every series can be reconciled, however, by appealing to a dynamic partial melting model, in which variable batch and incremental melting take place within ascending mantle diapirs, each labelled with slightly different Th/U.

Petrographic and geochemical evidence suggest that some basalts have been contaminated by felsic crustal material, although this is restricted to series III flows and the dykes.
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"For I tell you the earth
itself is a mystery
which we penetrate constantly"

Pat Lowther (1977)

"Chacabuco, the pit"
CHAPTER 1

INTRODUCTION

"Or speak to the earth and it shall teach thee ..."

Job (12:8)

1.1 SCOPE OF THE PROBLEM

Rifts are probably the commonest major lithospheric fractures, reflecting the weakness of rocks in tension. Active rifts have been identified in nearly the full range of plate-tectonic environments and at all stages of the Wilson cycle (Burke, 1978b, 1979). Continental rifts tend to be associated with the initial opening or final closing stages of oceans, but may also result from major transform movements, e.g. the Basin and Range Province, U S A (Burke, 1978b). The actual causal mechanisms of rifting are not understood, however, particularly those leading to the development of continental rifts into oceanic spreading segments.
Neumann and Ramberg (1978) suggest that the "identification of the necessary conditions for rifting to occur and to develop into spreading ridges can only be answered on the basis of detailed investigations of the characteristics, and reconstruction of the tectonic settings of ancient rifts that are known to have failed, and such that caused continental rupture and separation". The Keweenawan sequences of central North America are believed to have developed in a rift that developed new simatic crust, but which failed after only 80-100 km of separation (Chase and Gilmer, 1973; Green, 1977; see 2:1). The Keweenawan Rift is spatially related to the Grenville Orogenic event, although their relative timing is unclear at the moment. The Keweenawan Rift may thus represent a failed rift formed during the Wilson cycle that culminated in the Grenville Orogeny, or it may represent tensional release during, or late in, the orogeny (see 2.1.6). Extrusive and intrusive magmatic products were developed in the rift and their geochemical characteristics may be important clues in understanding the rifting process. Rift systems closely connected with orogeny tend to be isolated, developing complex horst and graben provinces, poorly defined triple junctions and calc-alkaline volcanism (Neumann and Ramberg, 1978). Proto-oceanic rifts, however, tend to have an obvious main axis with well-defined triple junctions and alkaline to tholeiitic magmatism.
The Mamainse Point Formation allows the study of a well exposed 3-4 km sequence of mafic and felsic magmatic products developed on the margins of, and during the earlier stages of the rift. Like other Keweenawan sequences, they have suffered low-grade metamorphism, accompanied by chemical readjustments and Cu-Ag mineralization, during formation (Chapter 4). However, it was hoped that by studying elements that had not been affected by the alteration, enough primary information may be gleaned to characterize the lavas (Chapter 5) and determine their petrogenetic histories (Chapter 6). The use of rare-earth and other incompatible elements may also allow some inferences about the composition and homogeneity of the Keweenawan mantle, perhaps contributing to the understanding of the evolution of the mantle-crust system through time.

1.2 PREVIOUS WORK

Like the flows of the type-area, the Keweenawan Peninsula, Michigan, the Keweenawan Mamainse Point Formation contains deposits of native copper and cuprite, with accessory silver. They have attracted the attention of man from ancient times. Shallow pits were dug by Indian miners just east of Hibbard Bay, similar to pits found on Isle Royale dated as 3800 ± 500 years old (Drier, 1961). European miners sank shafts in the area during the mid-nineteenth century, but exploitation of the vein
deposits did not start until 1965. All mining activity has now ceased in the area.

Initial mapping of the area was carried out by Sir William Logan for the Geological Survey of Canada (Logan, 1863), with more detailed follow up work by MacFarlane (1866) and Bell (1877). More recent mapping has been carried out by the Ontario Department of Mines -- Moore (1926), Thompson (1953), Nuffield (1955) and Giblin (1969a-d). The latter's maps provided the base maps for the sampling program undertaken in this study. Detailed studies of the petrography, stratigraphy and chemistry were carried out by Annells (1973), and Smith (1974) provided descriptions of the alteration effects seen in some parts of the sequence.

A fairly extensive body of literature exists discussing aspects of Keweenawan geology in other areas, ranging from earlier works by Irving (1883) and Van Hise and Leith (1911) to more recent reviews of Green (1977) and Halls (1978). These are reviewed and synthesised in 2.1 and provide the geological and geophysical framework within which the present geochemical studies function.
CHAPTER 2

THE GEOLOGICAL BACKGROUND

"It is useful to be assured that the heavings of the earth are not the work of angry deities. These phenomena have causes of their own."

Seneca (4 B.C. – A.D. 65)

2.1 REGIONAL GEOLOGY

2.1.1 Introduction

Late Proterozoic rocks outcrop extensively along the borders of Lake Superior, forming part of the Southern Province of the Canadian Shield. They are bounded to the north and south by older Proterozoic rocks of the Southern Province or Archaean rocks of the Superior Province.

The majority of the Late Proterozoic rocks of this area have been assigned to the Keweenawan Supergroup. Some groups such as the Sioux Quartzite, Barron Quartzite and Sibley Group...
are now considered to be Pre-Keweenawan (Craddock, 1972). Keweenawan sequences are most completely preserved in the type areas of western Michigan and northwestern Wisconsin, but also underlie extensive areas to the west in Minnesota, to the north in the Black Bay Peninsula and Nipigon areas, and also the east in Michigan and Ontario (see Fig. 2.1). Geophysical and borehole data also suggest that Keweenawan rocks continue to the southwest into Iowa, Nebraska and Kansas and to the southeast beneath the Michigan Basin. A number of small offset segments continue as far south as Tennessee (Keller et al., 1975).

The Keweenawan Sequence was traditionally thought to have accumulated in an elongate basin within a cratonic setting - the Lake Superior Syncline. Studies in the last decade or so on the interpretation of gravity, magnetic and some explosion seismic experiments in the Lake Superior area and on the Mid-Continent Geophysical Anomaly have suggested that the syncline is in fact a rift valley (King and Zietz, 1971), in which normal crustal (i.e. sialic) rocks have been largely replaced by denser material with high seismic velocities (6.6-6.7 km/sec) (Weber and Goodacre, 1966; Smith et al., 1966). The depth to the Moho varies from 20 km just west of the lake, to 55 km or more in the eastern half of the lake. The width of the rift varies from 40 km in Kansas, to more than 85 km in central Lake Superior (Chase and Gilmer, 1973). The Keweenawan Rift
Figure 2.1 Generalized Geological Map of the Keweenawan Rift

Key to Symbols

- e Bayfield-Jacobsville Group
- d Oronto Group and equivalents
- c Intrusive Rocks
- b Lower and Middle Keweenawan Volcanics
- a Pre- and Lower Keweenawan Sediments

Note: Strata shown shaded where exposed, unshaded where buried beneath Palaeozoic cover (boundaries shown with dashed lines)

- Heavy dashed lines: Major Faults
- MP: Mamainse Point
- MBA: Michigan Basin Gravity Anomaly
- MGA: Mid-Continent Geophysical Anomaly
- GF: Grenville Front
conforms with the simplified definition of rifts proposed by Burke (1978a) - "elongate depressions overlying places where the entire thickness of the lithosphere has ruptured in extension". However, it lacks well-defined boundary faults associated with the extension - the major faults in the Keweenawan Rift being associated with a late compressive stage (see section 2.1.5 and Table 2.3).

Within the rift, a number of individual "basins" have been recognised by White (1960, 1972) on the basis of structural and stratigraphic evidence. The basins are arranged en echelon and each basin has developed its own stratigraphy independently of other basins. This has led to a revision of the traditional tripartite division of the Keweenawan Supergroup (Lower sedimentary unit, Middle volcanic unit and Upper sedimentary unit). Presently accepted divisions and correlations are illustrated in Table 2.1. Paleomagnetic studies have contributed to the stratigraphic discussions and in particular a reverse-to-normal polarity change is now used to define the Lower-Middle Keweenawan boundary (Books, 1968).

2.1.2 Pre-Keweenawan Sediments

The Sibley Group of Ontario, the Barron Quartzite of Wisconsin and the Sioux Quartzite of Minnesota are similar in
<table>
<thead>
<tr>
<th>Code</th>
<th>Description</th>
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<tr>
<td>EPB</td>
<td>Ely's Peak Basalts</td>
</tr>
<tr>
<td>GPL</td>
<td>Grand Portage Lavas</td>
</tr>
<tr>
<td>HL</td>
<td>Hovland Lavas</td>
</tr>
<tr>
<td>NS</td>
<td>Nopeming Sandstone</td>
</tr>
<tr>
<td>PF</td>
<td>Puckwunge Formation</td>
</tr>
</tbody>
</table>

Sources include Green (1972a), Hubbard (1975a, 1975b), Halls (1974), Annells (1973, 1974), Morey (1972), Austin (1972), and Craddock (1972).
composition, structure and stratigraphic position. They are red bed sequences comprising basal conglomerate, red well-cemented quartzites and intercalated mudstones and conglomerates (Austin, 1972; Card et al., 1972). Thin stromatolitic cherts and limestones are also reported in the Sibley. They have been assigned a Pre-Keweenawan age by Craddock (1972), although Dott and Mattis (1972) asserted that these three groups were correlative with Lower Keweenawan sediments such as the Puckwunge Formation, Minnesota. They were interpreted as remnants of a widespread southward thickening sand blanket that formed in a shallow, agitated shelf environment on a stable continental margin, later disturbed by plate collision during the Elsonian Orogeny (1200-1400 Ma).

Franklin et al. (1972) disagree with this interpretation and suggest that the Sibley Group formed in an intra-cratic basin, possibly a half graben with an active faultscarp to the west, that formed during initial stages of Keweenawan rifting. As the basin filled, it overflowed northwards onto the craton. The inferred environment was equatorial and semi-arid.

Card et al. (1972) support this interpretation, comparing the Sibley Group to a molasse deposit formed after deformation and uplift of the Penokean fold belt. The sediments accumulated in a graben-like basin. Sedimentary structures indicate subaqueous deposition - the mudstones under quiet, possibly lagoonal
conditions; the sandstones under more turbulent conditions, where wave and current action prevailed. Climatic conditions were hot and semi-arid, with highly saline waters involved in clay diagenesis. Sedimentation finally encroached onto the craton, with subsequent slow accumulation of mudstone and limestone under fluvial or restricted basin conditions, in a piedmont or valley flat environment.

The large distances involved in correlation, plus the difference in interpretation of the Sibley Group, may suggest that the correlation of Sibley, Sioux and Barron is false. The Sibley Group may prove to be younger than the Sioux and represent a change from the stable cratonic conditions of the Sioux to the initial stages of rifting and continental break-up.

The absolute ages of the three Pre-Keweenawan groups have not yet been determined with confidence. Whole rock Rb-Sr isochron ages for Sibley Group red beds indicate an age of $1376 \pm 22$ Ma (Franklin and Kustra, 1970). A Rb-Sr age of $1470 \pm 50$ Ma on a slightly altered rhyolite flow within the Sioux Quartzite in a well at Hull, Iowa, has been interpreted by Lidiak (1971) as a minimum age for the deposition of the Sioux Quartzite. This would support the assertion above that the Sioux Quartzite is older than the Sibley Group. No radiometric ages have been reported for the Barron Quartzite.
2.1.3 Lower Keweenawan Sediments

Thin clastic sedimentary sequences, found in some localities to underlie thick mafic volcanic sequences, were used by Van Hise and Leith (1911) to define the Lower Keweenawan. These sequences are developed just north of the Gogebic Range in Wisconsin and Michigan (the Bessemer Quartzite); near Grand Portage, Minnesota (the Puckwunge Formation); and in the Black Bay Peninsula, Ontario (basal unit of the Osler Group). All three formations show the development of local basal conglomerates passing up into light coloured grey to buff or pink quartzites often showing cross-bedding. The three formations may not, however, be exact time equivalents, as the Bessemer Quartzite underlies normally magnetized lavas of the Siemens Creek Formation and are thus lowermost Keweenawan (Table 2.1). The Osler Group sediments include interbedded mafic flows of reverse polarity and are thus younger than the Bessemer Quartzite. The Puckwunge Formation underlies reversally magnetized flows but its exact age is unknown.

These Lower Keweenawan sediments have been interpreted as forming in a shallow water environment such as a transgressive sea (Mattis, 1972). The presence of subaerial flows in Michigan and Ontario opposes any widespread marine conditions at this time, and points further to the continuing development of the Keweenawan rift.
2.1.4 Keweenawan Igneous Activity

Thick sequences of Keweenawan volcanics and intrusives underlie much of Lake Superior and the surrounding area. Intrusions vary in size from the large Igneous Complex to smaller alkaline intrusions like the Port Caldwell Complex, and mafic dykes and sills of the Logan Intrusives. The volcanic rocks are mainly plateau basalts with associated rhyolites, which appear to have formed by fissure eruptions in several major basins (White, 1966, 1972). Varying proportions of interflow sandstone and conglomerate also occur. Thickness estimates for the different sequences vary from 6000 ft to 40,000 ft. Green (1977) has correlated the Keweenawan volcanic sequences and recognised seven distinct accumulations separated from each other geographically or stratigraphically (Table 2.2, Figure 2.2).

Igneous activity in the region commenced in the Lower Keweenawan with the mafic Logan Intrusions of the Thunder Bay - Nipigon - Grand Portage region. These intrude Pre-Keweenawan sediments as well as Archaean and Animikie rocks. Probable Lower Keweenawan dykes are found elsewhere in Ontario and Michigan.

The earliest extrusive activity is represented by the Siemens Creek Formation (Hubbard, 1975a) in the Ironwood, Michigan, area (Figure 2.2). These flows show normal magnetic
<table>
<thead>
<tr>
<th>STAGE</th>
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<th>THICKNESS (km)</th>
<th>MAGNETIC POLARITY</th>
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<tr>
<td>4</td>
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<td>normal</td>
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<td>Isle Royale</td>
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<td>North Shore</td>
<td>3.7 - 7.1</td>
<td>normal</td>
</tr>
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<td></td>
<td>Mamainse - Michipicoten</td>
<td>4.1 - 5.1</td>
<td>normal</td>
</tr>
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<td></td>
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<td>2.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Michipicoten Island</td>
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<td></td>
<td>Osler</td>
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<tr>
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<td>2.75</td>
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<td></td>
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<td>3.0 - 6.3</td>
<td>reversed</td>
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<tr>
<td>1</td>
<td>Siemens Creek</td>
<td>0.12</td>
<td>normal</td>
</tr>
</tbody>
</table>
Figure 2.2 Development of the Keweenawan Lava Plateaus during opening of the Rift

(Adapted and amended after Green, 1977)

Stages as in Table 2.2

SC  Siemen's Creek Plateau
IGPN Ironwood-Grand Portage-Nopeming Plateau
O   Osler Plateau
MP  Mamainse Point Plateau
NS  North Shore Plateau
KIR Keweenawan-Isle Royale Plateau
MI  Michipicoten Island Central Volcano
PM  Porcupine Mountain Central Volcano
polarity and are conformable with the underlying Bessemer Quartzite. They are of unknown original extent, although probably small. They pass up into the more extensive lavas of the Kallender Creek Formation. The reverse magnetic polarity of these lavas allows correlation with flows developed in the Nopeming and Grand Portage areas of the North Shore Volcanics. Green (1972) has suggested these three formations were erupted in the same basin. Two other basins were also starting to infill with lavas at this time – the Osler Volcanics of the Black Bay – Nipigon area, and the Alona Bay, the lowermost Mamainse Point and the Gargantua Point rocks of eastern Superior. Dyke swarms showing reverse polarity represent contemporaneous intrusive activity and, where they cut Pre-Keweenawan rocks, may indicate that the lava plateaux were originally larger than presently defined with significant erosion having taken place around the margins of basins.

Extrusive activity continued into the Middle Keweenawan, although often with a stratigraphic break accompanying the magnetic reversal. The bulk of the exposed North Shore Volcanics and the eastern Superior sequences developed during this period. Normally magnetized flows were recognised by Halls (1974) at the top of the Osler Group, and show continuation of activity in this basin also. The North Shore Volcanics were accompanied by the emplacement of the Duluth
Complex and associated intrusions.

The Portage Lake Lavas of the Michigan-Wisconsin area probably represent the youngest of the lava groups. They developed in a basin that extended from the Keweenaw Peninsula into Wisconsin and across the Isle Royale. The waning stages of extrusive activity gave rise to localised central-volcanic complexes with intermediate compositions such as at Porcupine Mountains (Hubbard, 1975b) and Michipicoten Island (Annells, 1974).

Throughout the extrusive history of the Lake Superior area conditions were terrestrial and subaerial. The only subaqueous flows recognised or suggested to date (Green, 1972a; Giblin, 1974) are localised, and probably represent fluvial or lacustrine conditions. Inter-flow sediments suggest a hot, semi-arid climate and alluvial-fan environments.

Few reliable radiometric ages are available for the Keweenawan extrusive rocks due to alteration and also to the difficulty in distinguishing sills from flows. Chaudhuri and Faure (1967, 1968) have published Rb-Sr dates for felsite flows, pebbles and a syenodiorite intrusion in Keweenaw Peninsula, which suggest that volcanism commenced prior to 1180 Ma. Van Schmus (1971) obtained Rb-Sr dates on mafic and felsic rocks from Mamainse Point and assigned them an overall age of 1070 ± 50 Ma, with some as old as 1100 ± 30 Ma. Leeman
(1977a) obtained a Rb/Sr age of 1120 Ma for felsic and mafic rocks of the North Shore Volcanics, although the mafic rocks treated separately yield an apparent age of 1450 Ma. Silver and Green (1972) on the basis of U-Pb dating of zircons, suggested that the bulk of the Keweenawan igneous event occurred in a 20 Ma period from 1140 to 1120 Ma, with the magnetic reversal at 1130-1140 Ma. Hanson (1975) used the $^{40}\text{Ar} / ^{39}\text{Ar}$ method to obtain ages of 1150 to 1170 Ma for reversely polarized Logan Sills, suggesting the period of active rifting may have been longer than Silver and Green assert.

2.1.5 Upper Keweenawan Sediments

Sedimentary sequences overlying the lava flows are found under Lake Superior and in the area to the south. They are usually assigned to the Upper Keweenawan and have been divided into two groups - a lower Oronto Group and an upper Bayfield-Jacobsville Group. A period of tectonism and deformation appears to separate the two groups.

In the type area of northwest Wisconsin - western Michigan, the Oronto Group is subdivided into the Copper Harbour Conglomerate, the Nonesuch Formation, and the Freda Formation, in ascending order. The Copper Harbour Conglomerate shows a gradational contact with the Portage Lake Lavas and
is marked by lava flows (the 'Lake Shore Traps') interbedded with red to brown conglomerates and sandstones. Sedimentation shows a tendency to fine upwards into the Nonesuch Formation, which consists of grey siltstone, shale and sandstone. The lower part of the formation has yielded organic compounds, microfossils and crude oil, as well as being the locus for extensive copper mineralization at the White Pine mine. The Freda Formation consists of red arkosic sandstones, siltstones and micaceous shale representing continued subsidence in the Keweenawan Rift. This subsidence was rapid and pulsating (Hamblin, 1961), influenced perhaps by faulting. A terrestrial environment is considered most likely, probably flood plains with standing bodies of water. Morey (1974) also considered the Oronto Group to have accumulated in a number of fault bounded basins along the axis of the rift.

In Minnesota, the Oronto Group is represented by the subsurface Solor Church Formation (Morey, 1972). This is characterized by a monotonous succession of immature, poorly-sorted sandstones, siltstones and mudstones with local limestone, and is believed to conformably overlie the volcanic rocks. Cyclic repetition of lithologic types has been recognized. Fining-upward cycles are interpreted as indicating alluvial deposition. Larger cycles ('Major cycles' of Morey, 1974) are also found, which also show fining-upward
tendencies, with repetitive sandstone beds gradually being replaced with mudstone or shale horizons. The smaller fining-upward cycles also become less well-defined. Each cycle probably started with extensive braided channel activity, which slowly gave way to more incised meanders and shoals as deposition outpaced subsidence. Final deposition was probably on mudflats and in shallow oxbow lakes. Each major cycle reflects episodic movements along faults in the rift. Gradual infilling of the rift resulted also in a change of provenance from local basaltic terranes to more distant granitic sources.

Following deposition of the Oronto Group and Solor Church Formation, a period of lithification and deformation ensued. This caused folding and reverse faulting in Wisconsin and Michigan, and near vertical dips in the southwestern limb of the Lake Superior syncline. This suggests that a compressive phase of deformation took place. During or after this phase axial horsts, such as the St. Croix Horst, rose in the western section of the rift. Flanking basins became the loci of sedimentation for the Fond du Lac Formation with subsidence taking place during sedimentation.

In both surface and subsurface occurrences the Fond du Lac Formation is characterized by beds of red lenticular sandstone and interbedded mudstone. They are texturally and mineralogically fairly immature, with sources both in the
granitic terrane and in the St. Croix Horst, which stood up as a small positive feature. Sedimentological features such as fining-upward cycles, cut-and-fill structures, cross-bedding, mudcracks and rain-prints, point to alluvial deposition in a shallow deltaic environment with more than one stream operative.

Overlying the Fond du Lac Formation are sandstones of the Hinckley Formation. These are medium to coarse-grained, well-sorted, mature sandstones with variable silica cement. Reworking of older sandstones is suggested plus new material from metamorphic terranes. Tryham and Ojakangas (1972) suggested a near-shore, high-energy environment with a shore-line slowly transgressing the fluvial-deltaic complex. There is no palaeontological evidence, however, that the Hinckley Formation formed under marine conditions and a large, stable, shallow-water lacustrine environment was proposed. Movement on faults followed Hinckley deposition and minor rejuvenation continued into the Palaeozoic (Morey, 1972).

In Wisconsin, Michigan and Ontario, post-Oronto deposition is represented by the Bayfield and Jacobsville Groups. These well-sorted sandstones range in composition from arkoses to quartzarenites, but characteristically are quartzose with simple heavy mineral suites. Hamblin (1961) suggested that this group represents a second-cycle sand deposited under
fluvial conditions, probably fans merging into alluvial plains near the margins of the rift, and lacustrine conditions in the deepest parts.

In Lower Michigan, Upper Keweenawan sediments were retrieved from a deep borehole. These red beds consist of recurring units of sandstone grading upward into mudstones. The sandstones-mudstone cycles are believed by Fowler and Kuenzi (1978) to resemble Bouma sequences, recording pulses of turbidity current and fluidized sediment flow, which interrupted normal deposition of finer sediments by low velocity currents and pelagic fallout. Deposition was envisioned taking place in a large elongate proto-oceanic basin, which foundered isostatically following arrestment of Keweenawan rifting. Initial infilling of the basin was by smoothly draped piedmont arkoses and interfingering transgressive marine quartzarenites. Continued foundering produced a deepened marine basin in which turbidites accumulated. Eventually the basin shoaled and turbidite activity gave way to fluvial-deltaic sedimentation which filled the basin. Although Fowler and Kuenzi favour a marine basin for the turbidite deposition, there is no evidence for specifically marine conditions and a large lake may be more likely in this intra-cratic rift.

The actual ages of the Oronto and Bayfield-Jacobsville
Groups and their equivalents are poorly known. Chaudhuri and Faure (1967) reported a Rb-Sr age of 1075 ± 50 Ma for the Nonesuch Formation. Chaudhuri (1976) also obtained a date of 1007 ± 25 Ma for the Bear Lake rhyolite which intrudes the Freda Formation. Controversy surrounds the age of the Bayfield-Jacobsville Group, however. It is generally reported that they are unconformable on the Oronto Group, and in turn are overlain unconformably by Upper Cambrian beds, but within this range the exact age is unknown. Babcock (1976) has proposed that, at least in part, the Jacobsville may be correlative with the lower part of the Portage Lake Lavas. Comparison of Jacobsville palaeomagnetic pole positions with other published data suggest they are consistent with a Hadrynian age - 550-750 Ma (DuBois, 1962; French and van der Voo, 1975), although Roy and Robertson (1978) conclude that the Jacobsville is probably 1100 Ma in age. They distinguish between the sediments of the Sault Ste Marie region, which appear to be contemporaneous with the Nonesuch and Freda Formations, and those of the Keweenaw Peninsula, which are younger.
2.1.6 The Keweenawan Rift

The geophysical and geological evidence points to the development of the Keweenawan Supergroup in a rift. The crust beneath Lake Superior and the Mid-Continent Geophysical Anomaly is mafic in composition. Chase and Gilmer (1973) suggested that this was new crustal material infilling the gap between the parted edges of continental plates in a process analogous to that believed to be happening along modern oceanic ridge systems. They further postulated that the en echelon segments of the MGA were offset by transform faults, the orientations of which, along with the widths of rifting at varying points, define a single pole of rotation at 36°N 107°W. Recent seismicity data in Kansas and Nebraska support this idea of transform faults (Dobiecki and LaFountain, 1975). The amount of rotation between the northern Minnesota Plate and the southern Wisconsin Plate is estimated to be 2.6° ± 0.7°.

Halls (1978), however, pointed out the difficulty of such rotation to explain the eastern half of the Keweenawan Rift. He suggested an alternative spreading direction along lines of present longitude. This would explain the symmetry of the rift about a N-S line, and the N-S orientation of the narrowest segments of the rift. Closure would also remove the offsets in pre-Keweenawan geology. However, this spreading
direction will not satisfy the spatial variation in spreading width required by rigid plate theory, nor account for the en echelon offsets along N-W lines seen in the western Rift.

The Keweenawan Rift is considered to be similar to the northern Red Sea, representing an evolutionary stage between the East African-type rifts and the Mid-Oceanic systems. The Keweenawan differs from its modern analogues, however, by lacking a marine incursion following the development of new crust (Wilson, 1973; Dickinson, 1974). Except possibly for the Jacobsville Group in Lower Michigan (Fowler and Kuenzi, 1978), marine conditions appear to be entirely absent from the area. A summary of the development of the rift is presented in Table 2.3.

The cause for rifting is unknown and several hypotheses have been proposed:

A. Plume Generated Rifting (Burke and Dewey, 1973; McIlwaine et al., 1974; Sawkins, 1976a,b; Figure 2.3a)

Rise of a mantle-plume causes uplifting and doming in the overlying lithosphere. Crestal rifts develop, typically in a triple-junction pattern, and commonly two of these rifts diverge and spread, whereas the third will 'fall'. The curved nature of the Lake Superior segment of the rift has
Figure 2.3 Models of the Origin of Keweenawan Rift

2.3a Plume-Generated Rifting

Stippled  Lower and Middle Keweenawan
Filled-in Circles  Alkaline Complexes
Stars  Suggested location for the triple junction

a) McIlwaine et al., 1974
b) Burke and Dewey (1973), Sawkins (1976a, 1976b)

NP  Nipigon Plate
MGA  Mid-Continent Geophysical Anomaly
KH  Kapuskasing High
MBA  Michigan Basin Gravity Anomaly

2.3b Rifting Due to Grenville Shearing

From McWilliams and Dunlop (1978)
Pole of Opening after Chase and Gilmer (1973)

2.3c Opening of Grenville Proto-Atlantic Ocean

From Baragar (1977)
<table>
<thead>
<tr>
<th>STAGE</th>
<th>TIME</th>
<th>ACTIVITY</th>
<th>STRATIGRAPHIC UNITS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initiation I</td>
<td>Pre-Keweenawan</td>
<td>Stable continental crust, ?marine shelf</td>
<td>Sioux and Barron Quartzites</td>
</tr>
<tr>
<td>Ia</td>
<td></td>
<td>Initial rifting. Pluvial and restricted basin deposits.</td>
<td>Sibley Group</td>
</tr>
<tr>
<td>Expansion II</td>
<td>Lower Keweenawan</td>
<td>Crustal fissuring and dyke injection. Small sedimentary basins develop and initial volcanic activity.</td>
<td>Nonesuchor Formation Puckwungo Formation</td>
</tr>
<tr>
<td>Crustal Separation III</td>
<td>Lower - Middle Keweenawan</td>
<td>New silicic crust created with extensive mafic volcanic activity. Partial fusion of silicic blocks yields felsic volcanics.</td>
<td>NorthShore Volcanics Color Formation Hamains Point Fm. Duluth Gabbro</td>
</tr>
<tr>
<td>IV</td>
<td>Middle Keweenawan</td>
<td>Volcanism diminishes and shifts to Wisconsin-Michigan basin. Localized central-volcanic complexes in waning stages.</td>
<td>Portage Lake Fm Michipicoten Island Fm</td>
</tr>
<tr>
<td>Foundering V</td>
<td>Upper Keweenawan</td>
<td>Sedimentary basins develop in areas of major fissuring. Become wider with broad isostatic subsidence of the rift.</td>
<td>Oronto Group Bayfield-Jacobsville Groups</td>
</tr>
<tr>
<td>Compression VI</td>
<td>Upper Keweenawan</td>
<td>Crustal compression (?Granvillean) locally steepens limbs of rift, and causes major strike-faulting and uplift of central horst block in western arm.</td>
<td>Fond du Lac Fm Hinckley Formation</td>
</tr>
<tr>
<td>VII</td>
<td>Late Keweenawan to Palaeozoic</td>
<td>Erosion produced pre-Michigan Basin surface. Local reactivation of Keweenawan boundary faults. Subsidence in Michigan Basin.</td>
<td></td>
</tr>
</tbody>
</table>
given rise to the idea that the MGA and the Michigan Basin Gravity Anomaly represent the spreading arms, and the Kapuskasing High the failed arm of the triple-junction system in the Keweenawan. The Kapuskasing High is an older feature that was reactivated and intruded by alkaline complexes during Keweenawan times. The Nipigon Plate may be an alternative candidate for the third failed arm (Card et al., 1972; McIlwaine et al., 1974). The hot spot activity may be related to events in the Grenville province (Burke and Dewey, 1973; see section B below), or to more global phenomena, like the break-up of proto-Pangea (Sawkins, 1976b).

B. Opening of Grenvillian Proto-Atlantic Ocean
(Burke and Dewey, 1973; Windley, 1977; Baer, 1976; Baragar, 1977; Figure 2.3c)

Several models for the evolution of the Grenville Province have involved the opening and closing of a proto-Atlantic Ocean. The Keweenawan Rift and the Seal Lake Graben of Labrador are considered to be related to this ocean, either as active extensions or as aulacogens. The former model allows for hot spot activity under Lake Superior (as suggested in model A above), whereas the latter would displace the hot spot to the southeast of the present Grenville Front.
C. Rifting Due to Grenville Shearing (Baer, 1977; McWilliams and Dunlop, 1978; Donaldson and Irving, 1977; Figure 2.3b)

Causal relationships between the contemporaneous Grenville events and the Keweenawan have been proposed by many authors. Palaeomagnetic studies have demonstrated that large-scale relative motions of all or part of the Grenville Province have taken place relative to the rest of North America. This has led the above authors to suggest that during the late stages of the Grenville deformation, dextral slip occurs along the Grenville Front. An irregular bulge in the Grenville Front south of the Great Lakes causes locking of the Grenville Block to Interior Laurasia and a resultant slowing of the motion. Tensional stresses generated during this slow-down give rise to the Keweenawan Rift, and perhaps the earlier Mackenzie and Abitibi dyke swarms.

D. Rifting Related to the Grenville Collision Event (Sawkins, 1976b).

Sawkins mentions the possibility of the Keweenawan Rift being an impactogen (Burke, 1978a), a product of the Grenville collision event, comparable to the Rhine Graben and Lake Baikal Rift. Although volcanism is present in the
modern analogues, extensive simatic crust, as in the Keweenawan is not developed, perhaps arguing against such comparisons.

It is difficult to choose adequately between these models. A connection between the Keweenawan and the Grenville appears necessary due to their temporal and spacial relationships. Model B, and variants of A, would place development of the Keweenawan before the Grenville deformation. Models C and D would place it during or after the Grenville deformation. Rb-Sr dates from granite and tonalite-granodiorite plutons in southeast Ontario, which are pre-Grenville Orogeny, agree with Lower and Middle Keweenawan igneous ages (Davidson, et al., 1979), supporting a model like A or B. However, the final compressive phase of the Keweenawan Rift may be related to Grenville tectonism, especially as the boundary faults appear to be most strongly developed where they parallel the Grenville Front. The uncertainties in dating of the Keweenawan and Grenville events preclude any definite solution to the problem, which must await further study.
2.2 THE GEOLOGY OF THE MAMAINSE POINT AREA

2.2.1 Introduction

The Keweenawan sequence of Mamainse Point and Alona Bay lies at the eastern end of the exposed Keweenawan Rift, resting unconformably on Archaean granite-greenstone terrane of the Superior Province (Figure 2.4). The sequence is dominated by the Mamainse Point Formation, which strikes north to northwest and dips towards Lake Superior at 15°-45°, with an outcrop width of about 10 km across strike. Lower ground near the lake is covered by thick glaciolacustrine deposits restricting outcrops to the lake shore and road cuts, although, inland, flow cuestas rise to 900 ft above the lake.

The Mamainse Point Formation is dominated by mafic flows, with felsic intrusions and interlayered clastic sediments. It is overlain in the north by the Upper Keweenawan Mica Bay Formation (Giblin, 1974). To the south, sandstones of the Jacobsville Group are in presumed fault contact with the Mamainse Point Formation.

2.2.2 The Mamainse Point Formation

2.2.2a Introduction

The Mamainse Point Formation was defined by Annells
Figure 2.4  Geology of the Mamainse Point and Alona Bay Areas

(after Giblin, 1969a-d, and Nuffield, 1955)
(1973), with his type section forming the shore from Mica Bay to Pancake Point (Figure 2.4). The Alona Bay flows were considered to be equivalent to the basal part of the sequence. The formation consists of flood basalts with conglomerate and sandstone intercalations and shallow-level felsic intrusions. The total thickness of the formation, including the Quebec Mine Member on Michipicoten Island, is estimated to be 21,000 ft (6800 m) (Annells, 1974). Within the study area, however, the succession is estimated to be 14,300 ft (4290 m) thick along the shore and 19,960 ft (5988 m) in the thickest section. These estimates, however, do not take account of possible repetitions due to faulting, nor of dilation of the basalt pile by the felsic intrusions.

Stratigraphic subdivision of the section is difficult due to the lack of suitably distinctive marker horizons. Annells (1973) informally divided the sequence into two divisions using the thick 'Great Conglomerate' to mark the base of the Upper Division. Smith (1974) also looked at the sequence and attempted a lithological partition (Figure 2.5).

The contact of the basal Mamainse Point flows with the underlying Archaean is poorly exposed within the area of study. Where seen, it appears to be undulating, indicating an irregular land surface. The best exposure of the contact
Figure 2.5 Stratigraphy of the Mamainse Point Area

A) After Annells (1973)

B) After Smith (1974)
STRATIGRAPHY
of the
MAMAINSE POINT AREA

(A) ALONA BAY

(B) MAMAINSE POINT

Archean

Lower Division

Upper Division

Quartzite

Tuff

26.4% sandstone

19.2% siltstone

11.8% shale

11.6% coal

10.8% sandstone

5% siltstone

3.8% shale

2% coal

1.0% sandstone

0.6% siltstone

0.4% shale

0.1% coal

0.0% sandstone

0.0% siltstone

0.0% shale

0.0% coal

0.0% sandstone

0.0% siltstone

0.0% shale

0.0% coal

0.0% sandstone

0.0% siltstone

0.0% shale

0.0% coal

0.0% sandstone

0.0% siltstone

0.0% shale

0.0% coal

0.0% sandstone

0.0% siltstone

0.0% shale

0.0% coal
occurs at Chippewa Falls, about 25 km south of the study area. Here the unconformity is very irregular and basalt is seen injecting fractures in the Archaean trondhjemite. Although generally clean and free of weathered material, the trondhjemite surface does show the occasional development of a pre-flow regolith. Possible pillowed lavas on a basal flow overlying the regolith may suggest stream activity on this surface.

2.2.2b Mafic Volcanics

Basaltic flows make up approximately 70% of the Mamainse Point Formation. Over 300 flows have been counted (Annells, 1973) showing a great variation in thickness. Most flows are 5-30 ft (1.5-9.0 m) thick, but range up to 100 ft (30 m). The thicker flows are often made up of several thin flow units, each with vesicular tops and bottoms. These represent separate, though closely successive, pulses of the same eruption (Nicholls, 1936). Pahoehoe toes are also recognised.

Tops of flows frequently show ropey pahoehoe features or are gently billowing. Some, however, are scoriaceous with infilling red silty material. Wave-cut exposures along the shore line sometimes show rounded vesicular humps on flow tops, which may be small tumuli or pressure ridges.
(schollendomes). All flows show the development of amygdular tops which are quite often oxidized. Vesicles are generally rounded and up to 1 in (2.5 cm) diameter. They may be flattened in the uppermost part of the flow, and some large irregular-shaped vesicles can be seen in more central zones of flows along with segregation cylinders. Basal vesicular zones are less common than tops and usually thinner. Pipe vesicles are common in these basal zones and they usually are inclined in the flow direction. All vesicles are filled with secondary minerals, most commonly chlorite, calcite, quartz, agate and laumontite (see Section 2.2.5).

Inclusions and xenoliths were not observed in the flows, although Annells (1973) reported occasional gabbroic inclusions in flows intercalated with the Great Conglomerate. Very fine-grained brown flinty inclusions are found in some flows representing silty sediment ripped up by the flow and baked. Coarser clastic sediment is also found in clasolyte (clastic crevice) infillings in upper parts of flows and in wider clastic dykes.

Two main textural types are seen in the flows (Figure 2.6). Ophites show a mottled appearance on surfaces due to large spheroidal augite grains poikilitically enclosing small plagioclase laths. The mottles range up to 2 cm across and are commonly 0.5-1.0 cm. Ophites vary in colour
Figure 2.6 Lithologic and Mineralogic Variation in the Mamainse Point Formation
from dark grey to red, and show either spheroidal or crumbly weathering. Melaphyres are fine-grained flows in which few minerals are discernible to the naked eye. They vary in colour from grey to greenish-grey to red. They may show chloritic streaks parallel to the flow direction, representing altered glassy mesostasis. These flows generally are fractured and splintery in appearance and weather to angular blocks. One melaphyre showed the development of red whorls in a liesegang ring pattern. A less common lithology is diabasic, where augite and plagioclase form a medium to coarse intergranular texture. Some thicker flows, usually ophitic, also show the development of coarse-grained pegmatitic feldspar-rich bands similar to those described in the Greenstone Flow of Michigan (Cornwall, 1951), and believed to represent in situ fractionation of the flow.

The only really distinctive lithology is the glomeroporphyritic 'Daisy Stone' flow. This thick flow shows a spectacular concentration of radial clumps of plagioclase laths with interstitial augite in a fine-grained matrix. Daisies average about 2.5 cm in diameter. The Daisy Stone Flow has been correlated with a similar glomeroporphyritic flow at Cape Gargantua, about 60 km along strike (Annells, 1971). This compares with the 90 km along strike for the Greenstone Flow in Michigan and demonstrates how extensive
Keweenawan flood basalts were.

Phenocrysts of olivine and plagioclase are developed in many flows, although usually small in size. Figure 2.6 shows the distribution of lithologies and phenocryst type in the Mamainse Point section. At the base, melaphyres are dominant and these are often olivine-phric, sometimes strongly so, which may suggest the incorporation of some cumulate olivines in these flows. Higher in the sequence melaphyres and ophites alternate. Plagioclase phenocrysts appear first with olivine and later alone. This association of basal olivine-phric flows passing up into feldspar-phric flows is similar to that in Western Greenland (Clarke, 1970, 1977), a sequence also believed to have developed during rifting of sialic crust.

Mafic dykes are rare in the Mamainse Point and Alona Bay sections. They are usually grey, medium-grained diabasic rocks. They are about a metre wide and show good chilled edges, perpendicular prismatic jointing and occasional small vesicles. They usually cross-cut the flows at a steep angle. Although no direct physical connections are found, the dykes are probably feeders to the flows above. The scarcity of dykes in the section reflects its location on the edge of the rift, overlapping onto the sialic basement. Ropery tops and pipe vesicles indicate that most flows had sources from
further southwest in more axial regions of the rift, and under present Lake Superior.

Mafic dykes are seen cutting the Archaean rocks. These are greenish-black, medium- to coarse-grained diabases which are up to 10 m or more thick. They are very fractured with chlorite common on fracture surfaces. Veining of calcite and epidote are also found. These dykes differ from those seen intruding the Mamainse Point Formation, and are probably earlier Lower Keweenawan dykes formed during dilation of the crust in the initial stages of rifting.

2.2.2c Felsic Volcanics

A variety of acidic rocks occur within the Mamainse Point Formation, making up about 15% of the total thickness. The thickest bodies are stratiform and occur in the central parts of the area and around Pancake Point. Smaller bodies are found in other areas. The felsites are commonly pink to grey in colour, with small quartz and/or feldspar phenocrysts set in an aphanitic matrix. Coarser quartz porphyries are also seen in some places. Chemical analyses show these rocks to be predominantly rhyolites and altered rhyolites with minor dacites (Annells, 1973; Jackson, 1977).

Smaller bodies usually show intrusive, cross-cutting
relationships with the enclosing mafic flows. They may be plugs, dykes or sheets, commonly with auto-brecciated margins. Flow laminations, which may be contorted, are also common. Stratiform bodies have also been interpreted as shallow-level intrusions (Giblin, 1974, p.59), although contacts are often poorly exposed. Contemporaneity of felsic and mafic volcanism is shown by the occurrence of a composite dyke near the middle of the sequence. Small rounded inclusions of the marginal basalt are included in the central rhyolite near the mafic-felsic interface. These inclusions were interpreted by Annells (1973) to be loose-mush clusters, indicating incomplete consolidation of the basalt before intrusion of the rhyolite. Contemporaneous bimodal volcanism has always presented a problem to petrologists, as it is difficult to explain in terms of normal fractionation processes. The close proximity of Archaean granites and gneisses may suggest that the felsites were derived by fusion of pre-existing sialic crust under high heat flow conditions, generated by rifting and mafic volcanism.

Quartz-feldspar porphyries and Cu-Mo mineralized breccia pipes are found in the Archaean terrane to the east of Mamainse Point. These appear to be of Keweenawan age based on radiometric and geological relationships (Giblin, 1974), and may be genetically related to the felsites of
the Mamainse Point Formation.

2.2.2d Intra-flow Sediments

Coarse sandstones and conglomerates make up about 15% of the Mamainse Point Formation. They range in thickness from a foot or so (30 cm) up to the 1800 ft (540 m) for the Great Conglomerate, with many being over 100 ft (30 m). The majority occur within the upper part of the sequence.

The conglomerates are polymictic with clasts of Archaean granites, gneisses, greenstone and quartzite, together with Keweenawan basalt and rhyolite. Clasts are well-rounded and vary up to 4 ft (1.2 m) in diameter. They are set in a reddish-brown, dominantly basaltic sandy matrix. Sandy lenses often show cross-bedding indicating that streams flowed towards the trough centre.

One distinctive conglomerate unit occurs in the lower part of the sequence and is here informally called the 'Lower Conglomerate'. Clasts in this are almost entirely of Keweenawan basalts, though various lithologies are present - amygdaloidal, ophite, feldspar melaphyres, etc. The clasts are rounded to sub-rounded, varying in size up to 50 cm. Red-brown silty lenses show cross-bedding and ripple marks. The distinctive clast assemblage, plus the presence of amoeboid-shaped fragments, led Annells (1973) to interpret
this unit as a basalt breccia. Observations by the present
author and Giblin (1974, 1976 pers. comm.) seem more in line
with a sedimentary origin similar to the other conglomerates.

The conglomerates represent fanglomerates and small
deltas deposited by short-lived streams flowing into the
rift from the surrounding Archaean highlands (Annells, 1973).
Rare, fine-grained siltstones and mudstones probably represent
the development of small temporary lakes. The abundance of
sediment in the upper part of the sequence suggests there
was frequent subsidence of the pile during this time, maybe
as a result of movement along faults.

2.2.3 Upper Keweenawan Sediments

2.2.3a The Mica Bay Formation

Clastic sedimentary rocks of this formation uncon-
formably overlie Keweenawan basalt and Archaean granites in
Mica Bay and Alona Bay (Giblin, 1969a; Nuffield, 1955). The
sediments are about 200 ft (60 m) thick and predominantly
grey-brown in colour. A thin basal conglomerate passes up
into siltstones with lesser arkoses and pebble conglomerates.
Sedimentary structures include ripple-marks, graded-bedding,
cross-bedding, flame structures, ball-and-pillow structures,
channel washouts, flute casts and clastic dykes. The
structures are indicative of shallow water deposition, perhaps in a large lake.

The age and correlation of this formation is uncertain. The unconformable relationship with the Mamainse Point Formation shows it to be post-Middle Keweenawan. It would appear to underlie the Jacobsville Group sandstones that form nearby islands in Lake Superior. This suggests that the Mica Bay Formation is Upper Keweenawan in age and correlative with part of the Oronto Group, possibly the Freda Formation (Giblin, 1974).

2.2.3b The Jacobsville Group

Sandstones assigned to the Jacobsville Group (Giblin, 1969d,e, 1974) outcrop around Batchawana Bay and south of Pancake Bay. They are coarse- to medium-grained, red and white mottled and streaked sandstones and gritstones. Cross-bedding is common. Scattered granules and pebbles of quartz occur in the sandstones as well as large disc-shaped argillite clasts. Contacts with the Mamainse Point Formation are not seen and are inferred to be faulted (Giblin, 1969d,e).
2.2.4 Structure

The outcrop area of the Mamainse Point Formation forms an arc convex to Lake Superior. (see Figure 2.4), strikes of flows swinging from N 30° W in the north to N 55° W in the south. Dips are to the south and gradually decrease upsection from 55-60° in basal flows to 15-20° near Coppermine Point. This change in dip is probably due to periodic subsidence of the basin taking place during the volcanic episode (Hotchkiss, 1923). Local disturbance of dips occurs near some felsite bodies.

Rocks of the Mica Bay Formation strike eastwards, and are gently folded, dipping to the north or south at 15-30°. Jacobsville Group sandstones strike N 25° W to N 40° W and dip west at 15-25°.

Small normal faults are fairly numerous, particularly in the upper parts of the sequence. Most of these faults trend northeast or northwest, oblique to the strike of the flows. Vertical displacements on these faults appear small, but are difficult to estimate due to lack of distinctive marker horizons. Two major orthogonal faults were postulated by Giblin (1969c), one running northwestwards, subparallel to the strike of the flows (the Hibbard Bay Fault), and one trending northeastwards, transverse to the flows (the Pancake Bay - Mamainse Lake Fault). Another strike-fault was
postulated by Palmer (1970) to explain the triple reversal in palaeomagnetic stratigraphy, although this has been refuted because of lack of geological evidence and lack of repetition in the geochemical trends (Massey, 1979).

Joints, clastic dykes and other fractures are common throughout the sequence. Some jointing can be related to cooling of the flows, and Annells (1972) has interpreted the clastic dykes as indicating minor earth movements contemporaneous with the accumulation of the pile.

2.2.5 Metamorphism

Like other Keweenawan volcanic sequences, the Mamainse Point and Alona Bay sequences have suffered low-grade metamorphism (Jolly and Smith, 1972; Stoiber and Davidson, 1959; Morey, 1978). This has led to changes in the primary mineralogy of the flows and the development of secondary minerals in veins and vesicles.

Figure 2.6 shows the distribution of secondary minerals throughout the pile. A crude zonation is apparent with a subdivision into three zones:

1. Stilbite-laumontite
2. Laumontite
3. Epidote-laumontite
Laumontite is found throughout the pile, along with calcite, in veins and vesicles. Epidote is restricted to the lower part of the sequence, although it can also be seen in gangue material associated with copper mineralization higher in the pile. Stilbite makes its appearance just above the Green Conglomerate and is found sporadically as joint-plane coatings and in veins. Secondary silica is usually quartz, but agate predominates in two horizons. Chlorite and hematite occur in vesicles, on joint-planes and within the rocks throughout the pile. Pumpellyite and prehnite were not positively identified in the field, although they have been reported along with copper mineralization in central sections of the pile (Sabina, 1963; Annells, 1973). They were, however, observed in thin sections (see section 3.2.2).

In the basal feldspar-phryic melaphyres, below the Lower Conglomerate, metamorphism has resulted in the development of heterogeneity, with differentiation of secondary minerals into different metadomains, similar to features described in Michigan (Jolly and Smith, 1972). Flow-tops and bottoms show yellow–green epidotized patches in a darker green chloritized matrix. Centres of thicker flows are homogeneous, grey, albitized melaphyre with vesicles infilled with calcite, laumontite, chlorite and epidote. Metadomains have diffuse boundaries and are variable in shape. Veins may
show the development of epidote in them and the surrounding rock, resulting in elongate metadomains which might extend into the homogeneous melaphyre.

In summary, metamorphism in the Mamainse Point - Alona Bay Keweenawan flows appears to have taken place under zeolite and sub-greenschist facies conditions. The crude metamorphic zonation produced is similar to that observed in Michigan (Jolly and Smith, 1972), except for the paucity of prehnite and pumpellyite. Greenschist assemblages, as found in Minnesota (Green, 1972a), and the South Range (Hubbard, 1975a,b), are not observed. Metamorphic effects are most apparent in flow tops and bottoms, and along joint-plane surfaces, suggesting control by fluid passage-ways. Burial metamorphism, penecontemporaneous with lava eruption, is the most likely explanation, similar to that observed in Iceland (Walker, 1960; Wood et al., 1976). Complex cross-cutting relationships between clasolyte fracture infillings and veins, plus the presence of broken metamorphosed basaltic fragments in the conglomerates, support this view.

2.2.6 Conclusions

The Mamainse Point Formation is typical of Keweenawan volcanic sequences with the development of a bimodal mafic-
felsic volcanic pile and coarse clastic intra-flow sediments. Volcanic activity appears to have been entirely subaerial flows with little or no volcaniclastic activity. Flow direction indicators suggest sources to the south and west, within the central part of the Keweenawan Rift. Paucity of dykes in the pile, coupled with adjacent Archaean rocks, suggests that the pile accumulated on the edge of the rift, overlapping onto the sialic basement. Fanning of dips points to continuous subsidence of the rift basin during eruption of the lavas. Low-grade burial metamorphism, penecontemporaneous with eruption, caused the infilling of vesicles and veins, and some heterogeneity in the flows.
CHAPTER 3

PETROGRAPHY

"You blocks, you stones, you worse than senseless things!"

Julius Caesar (Act I, Sc. 1)

3.1 PRIMARY FEATURES

3.1.1 The Lavas

3.1.1a Introduction.

About eighty-five thin-sections of Mamainse Point and Alona Bay lavas were examined. The majority of these were from central parts of flows, but some amygdaloidal zones were also sampled. Extensive secondary alteration has affected these rocks (section 3.2), but primary mineralogy and textures can still be discerned or interpreted from relict cores, pseudomorphed crystals, etc.
3.1.1b Primary Mineralogy

The flows consisted essentially of plagioclase, clino-
pyroxene and opaques, with varying proportions of olivine and
glass. Modal analysis of the thin-sections is severely limited
by the secondary alteration and was not carried out.

Olivine

Varying proportions of olivine (2-20%) occur within
flows from Alona Bay and the basal section of Mamanse Point.
The olivine forms small (up to 1.5 mm) euhedral to subhedral
phenocrysts, pseudomorphed by chlorite, iddingsite, calcite
and hematite (Plate 3.1). The oxide forms in fractures and
rims of the olivine, with chlorite + iddingsite or calcite
in core areas. Texturally the olivine seems to be mainly
pre-feldspar, though some may be contemporaneous. No signs
of groundmass olivine were found.

Plagioclase

Plagioclase forms laths from 0.3 - 4.0 mm, averaging
0.5 - 0.7 mm. They are usually replaced by one or more of
calcite, chlorite, albite, prehnite, pumpellyite and epidote.
Twinning follows the albite, carlsbad and pericline laws,
and may be preserved during alteration, although usually with
indistinct boundaries. Relict cores of microphenocrysts are
mainly labradorite (An_{55-60}) in composition, although one
Plate 3.1  Olivine Microphenocryst (Rl6)

Transmitted light  Scale Bar = .25 mm

Olivine is pseudomorphed by chlorite O and Fe-oxides.
flow (R63) carried broken xenocrysts of calcic bytownite (An$_{85}$) which may have been derived from the original magma chamber. Where alteration allows determinations to be made groundmass plagioclase microlites are of labradorite composition also. The microlites are also lath-shaped and may show some skeletal tuning-fork or fan-shapes when quenched in vesicular zones.

Three samples (R51, R52 and R54, plus M36 and M37, which were collected from the same outcrops the previous year) possess two distinct plagioclase populations. Apart from phenocryst and groundmass plagioclase similar to other flows (Plate 3.2) they also contain rounded to euhedral xenocrysts with abundant dark inclusions (Plate 3.3). The inclusions are regularly aligned parallel to the long axis of the grains. A clear zone often borders the crystal. The plagioclase is difficult to identify due to the abundant inclusions, but shows higher relief than balsam and may be twinned. Sector zoning of optical properties may be seen. These xenocrysts would appear to be out of equilibrium with the melt and to have reacted with it. None of these features are observed in the bytownite xenocrysts in R63. Also found within these rocks are small irregular rounded patches of matrix of quenched or cryptocrystalline aspect, which differ markedly from the surrounding, coarser, normal matrix (Plate
Plate 3.2 Normal Plagioclase Phenocrysts (M37)

Transmitted light  Scale Bar = 1 mm

Plagioclase phenocrysts partially replaced by chlorite and epidote.

Plate 3.3 Plagioclase Xenocryst (M37)

Transmitted light  Scale Bar = 1 mm
3.4). These two features are distinctive of these three flows and occur in no other thin sections studied. They pose evidence of contamination of the lavas, perhaps by a partially crystalline material (to explain both xenocrysts and quenched patches in the matrix) which has been incompletely mixed in. The geochemical significance of this will be discussed in a later chapter (6.3).

**Clinopyroxene**

Clinopyroxene is usually the only primary mineral relatively unaffected by alteration. It ranges in size from small (<1 mm) granular crystals in the groundmass to large (10 mm) rounded crystals poikilitically enclosing plagioclase laths. Phenocrysts are extremely rare. All the pyroxenes are augitic in composition. Larger grains may show twinning, but zoning is absent.

**Oxides**

Opaque oxides appear to have been magnetite originally, although now partially oxidized to hematite. They occur either as subhedral, interstitial crystals or as skeletal dendrites, scaffolds or needles within devitrified glass.

**Glass**

Nearly all samples examined contained devitrified
Plate 3.4  Irregular Glassy Patch in Matrix (M37)

Transmitted light  Scale Bar = .25 mm

Glass replaced by ?chlorophaeite with oxide dendrites and crystallites.

Plate 3.5  Poikilophitic Texture (R89)

Crossed nicols  Scale Bar = 5 mm

Large spheroidal augites intergrown with plagioclase and surrounded by intersertal areas of plagioclase and opaques in altered mesostasis.
glass, intersertal to plagioclase and augite. It is now replaced by either chlorite or a fine-grained, brown, translucent material (? chlorophaeite).

3.1.1c Primary Textures

The lavas usually display poikilophitic, subophitic or intersertal textures, with occasional diabasic, gabbroic or glomeroporphyritic types.

Poikilophitic

Microphenocrysts of plagioclase are poikilitically enclosed by large, spheroidal, optically-continuous augites (Plate 3.5). Surrounding the augites, the plagioclase microphenocrysts are set in a dark mesostasis of opaques and devitrified glass.

Subophitic

Augite enclosing the plagioclase is not optically continuous. The proportions of glass varies and there is a tendency towards diabasic or intergranular textures in more holocrystalline rocks.

Intersertal

Plagioclase ± olivine microphenocrysts are set in a
groundmass of plagioclase microlites ± granular, augite + glass + opaques (Plate 3.6).

**Gabbroic**

Coarse-grained, holocrystalline rocks with plagioclase laths + subhedral pyroxene + magnetite.

**Glomeroporphyritic**

Large radiating clusters of plagioclase phenocrysts, with interstitial augite, are set in a groundmass of plagioclase + augite + magnetite + glass (Plate 3.7).

3.1.1.8 Conclusions

Although the effects of alteration obscure some detail, it seems that there is little systematic mineralogical difference between the Mamainse Point flows, apart from the presence of olivine in the lower section and its general absence elsewhere. The mineral assemblage of minor olivine + labradorite + augite + magnetite ± glass suggests that these are tholeiites and olivine tholeiites (Turner and Verhoogen, 1960), although only one clinopyroxene is observed. The flows are similar to other Keweenawan flows in Ontario (Annells, 1974; Wallace, 1972), Michigan (Jolly and Smith, 1972), and Minnesota (Green, 1972a). The
Plate 3.6  Intersertal Texture (R81)

'Transmitted light' Scale Bar = 1 mm

Oxides and plagioclase laths in latered mesostasis.

Plate 3.7  Glomeroporphyritic Texture (R18)

Crossed nicols Scale Bar = 5 mm

Clusters of plagioclase phenocrysts with interstitial opaques, augite and altered glass (chlorite, epidote and calcite).
crystallization sequence of olivine + plagioclase + augite + magnetite suggests derivation from a shallow-level magma chamber, $P < 7-8$ kbar (Green and Ringwood, 1967; Bender et al., 1978). Similar crystallization sequences are observed in mid-ocean ridge tholeiites (Johnson, 1979; Batiza et al., 1977; Frey et al., 1974; Shiido et al., 1974).

3.1.2 The Dykes

3.1.2a. Introduction

Dykes are scarce in the Mamainse Point Formation. Only a dozen or so were observed in the field, of which eight have been thin-sectioned and analysed - six from Mamainse Point and two from Alona Bay.

3.1.2b Primary Mineralogy

Olivine

Olivine is absent from the dykes, although R99 contains subhedral to euhedral phenocrysts, pseudomorphed by calcite and minor opaques and chlorite, which could originally have been olivine.

Plagioclase

Labradorite ($An_{55-60}$) phenocrysts are common to scarce. They range in size up to 3 mm. Alteration is
variable from chlorite along fractures to more severe
replacement by calcite + chlorite + albite + prehnite +
epidote. Twinning becomes obscure with progressive altera-
tion.

Groundmass plagioclase microlites are generally
<0.5 mm. Their composition is not readily determinable due
to alteration effects. The microlites often show long
acicular forms with some suggestions of fanning, tuning-
fork structure, etc., indicating quenching.

Clinopyroxene

Groundmass pyroxene is only found in three of the
dykes. It usually occurs as small rounded grains along
with the plagioclase microlites. It has a greenish tinge
with high relief and moderate birefringence. Interference
figures could not be obtained, but the pyroxenes are
probably augitic in composition. Some alteration to chlorite
and hematite is seen.

Opales

Small, sub- to euhedral magnetite is common in the
groundmass. Skeletal opaques are also very common in the
glassy phases, forming dendrites and scaffold-like forms.
The magnetite is oxidized to hematite.
Glass

Glass is present in nearly all the dykes. It is now replaced by chlorophaeite. Skeletal opaques are abundant and quenched plagioclase microlites may also be found.

3.1.2c Primary Textures

R114 was the only holocrystalline sample examined. It displays a well-developed, medium-grained, diabasic texture. All other specimens are porphyritic to interstitial with varying proportions of plagioclase phenocrysts (usually <5%) set in an interstitial matrix of plagioclase + clinopyroxene + magnetite + glass. Vesicles are common, perhaps suggestive of a shallow level of intrusion for most of the dykes.

Glass shows several modes of occurrence in the dykes:

(a) Interstitial mesostasis between plagioclase grains.

(b) Larger irregular segregations within the groundmass, usually 0.5–1.0 mm diameter. These grade into normal groundmass at their edges and may include plagioclase microlites in them.

(c) As quenches around irregular vesicles. These are larger – up to 5 mm diameter – and very irregularly shaped, like the vesicles they border. Again they grade into normal groundmass glass at their edges.
(d) As spherical globules or bleblets (Plate 3.8). These vary in size from 0.3-1.8 mm diameter, averaging 0.6-0.8 mm. They are rounded in shape with a distinct and clear contact with the surrounding rock. Some globules contain a vesicular "bubble" within them, which is usually centrally located but may be in contact with the globule wall. The "bubbles" have rounded contacts with the glass indicating a gas-liquid meniscus relationship. They may account for up to 80% of the volume of the globule, although usually much less, if present at all.

Within one thin-section, glass is present in one or more of these modes - commonly (a) plus one of the others. There appears to be little optical difference between the glass in either mode within one thin-section, nor between different thin sections.

1.1.2. The Glass Globules

The glass globules are so singular as to warrant further discussion. Vesicles in the same thin-sections are similar in size and shape, although defined by an opaque integumenation rather than any glassy selvedge. It may be that the globules are themselves vesicles which have become infilled with late-stage melt - the "segregation vesicles"
Plate 3.8 Glass Globules and Vesicles (R108)

Transmitted light  Scale Bar = 1 mm

Plate 3.9 Glass Globule with Two Irregular Bubbles (R99)

Transmitted light  Scale Bar = 1 mm
of Smith (1967). Similar features have been observed in ocean-floor basalts (Baragar et al., 1976; Sato, 1978). This process depends upon producing a pressure difference between rock and vesicle, sufficient to overcome viscosity and surface tension effects in the matrix melt-crystal system (Smith, 1967). This seems improbable in the shallow-level intrusive environment envisaged for the dykes. Also any pressure difference would be expected to be homogeneous and all vesicles to be infilled to the same degree. This is not the case, as shown by the variability of former gaseous bubbles in the globules. This mechanism has also been disputed for ocean-floor basalts (Sato, 1978), although the essential interpretation has been accepted.

An alternative explanation is that the globules represent an immiscible silicate melt phase. The normal vesicles, plus the bubbles in the globules, represent a vapour phase immiscible in both silicate phases. The silicate immiscibility may result from separation of two liquid phases during fractionation of the original single melt (Philpotts, 1976, 1977, 1978; Arndt, 1975), or from the incorporation of droplets of felsic melt caught up in the dyke at its contacts with mobilized country rock (Holdgate, 1978). The apparent optical similarity between glass in the globules and in the mesostasis may argue
against immiscibility. Whole-rock analyses of the dykes fall outside the low-temperature two-liquid field on a Greig Diagram (Roedder, 1978) (Figure 3.1), lying on the alkali-rich side. Wide-beam electron microprobe analysis, particularly for the immobile elements Fe, Mg, Ti, P and Al, should allow direct comparison of globules and mesostasis. Without chemical data such as this, the case for liquid immiscibility must remain unproven, resting solely on the textural evidence.

3.1.2e Classification

Petrographic classification of the dykes is difficult, not only because of the effects of alteration, but also because of the hypocrystalline nature of the dykes. The similarity of mineral phases to those in the lavas may suggest that these also are tholeiites. The absence of olivine and the crystallization of magnetite before pyroxene, point to differences however. Chemical classification may help resolve this problem (section 5.2.).

3.2 SECONDARY ALTERATION EFFECTS

3.2.1 Introduction

As described in section 2.2.5 (q.v.), the Mamainse
Figure 3.1 Greig Diagram, Mamainse Point Formation Dykes

Immiscibility fields after Roedder (1978)

'Volcanics' field occupied by most volcanic suites
(from Roedder, 1978, after Brooks and Caffeen 1975)
Point Formation has suffered low-grade burial metamorphism. This has resulted in degradation of the original mineralogy and the development of new mineral assemblages in amygdules. The alteration and recrystallization is not, however, accompanied by any penetrative deformation and primary textures are preserved.

3.1.2 Secondary Mineralogy

The main secondary minerals observed in thin-sections are chlorite, albite, epidote, calcite, laumontite, stilbite, pumpellyite, prehnite, quartz, chloraduny, sphene and hematite. They are found either replacing primary minerals or mesostasis, or infilling vesicles or veins.

Chlorite

Several varieties of chlorite are observed, often two or more in one sample. They differ in optical properties and occurrence:

Chlorite C found replacing olivine. It is pale green, pleochroic, and shows bluish-grey to yellow colours under cross-nicols. It often has a well-developed cleavage and parallel extinction. Hematite and iddingsite are common associates.
Chlorite I found as coatings around vesicles and occasionally replacing glass in the mesostasis. It shows dark olive-green to brownish-green colours in transmitted light and may be pleochroic. It shows anomalous green or yellowish colours under cross-nicols. It is usually microcrystalline or fibrous.

Chlorite II found infilling vesicles, replacing glassy mesostasis, plagioclase and pyroxene. It is pale green to almost colourless with low bluish-grey to black colours under cross-nicols.

Chlorite III similar to chlorite II except that it shows anomalous brown colours under cross-nicols, and may be stained yellowish-brown in transmitted light. It usually only occurs in vesicles and veins, where it post-dates chlorite II.

The textural evidence suggests that chlorites I and II may be deuteric, forming immediately after extrusion and cooling of the lava flow. Chlorites II and III formed during later burial metamorphism.
Albite

Albite occurs replacing plagioclase. Good optical data are difficult to obtain due to the fine-grained nature of the alteration. The albite is recognised mainly by its relief, low birefringence and occurrence. Occasional triclinic figures were obtained. Replacement of the original plagioclase is often patchy, resulting in a checker-board pattern or mosaic. Orange-coloured hematite-staining may accompany this alteration.

Epidote

Epidote occurs in vesicles, veins and replacing plagioclase. Complete replacement of the rock occurs in areas of vesication, although original fabric may be preserved as a faint texture visible in transmitted light. All the epidote is paramagnetic showing typical yellow-green colours and pleochroism. When fine-grained, it often appears brownish. Retardation is high, yielding second- or third-order colours.

Pumpeolite

Pumpeolite replaces plagioclase and occasionally infills vesicles. It is optically similar to epidote, with which it may occur, except for its dark green to brown pleochroism, anomalous blue interference colours and slightly
lower relief.

Prehnite

Prehnite occurs in amygdules and as small flecks replacing plagioclase. It is colourless, with medium relief and moderate birefringence. When microcrystalline, prehnite is difficult to distinguish positively from white mica. Coarser grains, however, show the classical sheaf- and fan-shapes and have the fast ray parallel to the cleavage.

Other minerals

Other minerals observed in amygdules were calcite, laumontite, stilbite, quartz and chalcedony. Calcite could also be seen replacing plagioclase, olivine and groundmass. Quartz and sphene also occurred in the intersertal matrix. Hematite was ubiquitous in the rock and occasionally was found in veins and vesicles.

3.2.3 Textures and Parageneses

Varying degrees of alteration were observed in the samples from minor (mainly amygdule formation) to extreme (in the monomineralic metadomains). The extent of alteration depended not on position in the pile so much as proximity to fluid channel ways (vesicular zones, fractures, etc.). The type of alteration does vary with stratigraphic
position; however, as outlined in section 2.2.5. Epidote was not observed much higher than the Lower Conglomerate, and its best development is below that. Zeolites were observed only rarely in thin-section, which reflects the sampling from central parts of flows rather than amygdalar zones. Field observations on the zeolites are reported in section 2.2.5.

Replacement of primary mineralogy preserves the original grain boundaries. As a consequence, complex multi-mineralic mosaics may form within a grain, particularly a plagioclase (Plate 3.10). Alteration starts along fractures within the plagioclase, usually chlorite filled, but then spread in patches of albite and calcite into the grain. Epidote, pumpellyite and prehnite form small crystals within the grain. A dusting of fine orange hematite is also common.

Intersertal glass is commonly replaced by chlorite and opaques. Occasionally calcite, quartz and epidote also replace glass. The textures suggest the possibility of dissolution of the glass and concentric infilling of the small void. Larger, irregular patches of chlorite, quartz and calcite often have boundaries that, in places, cross-cut original fabrics (Plate 3.12). This also suggests active dissolution of the rock during alteration.
Plate 3.10  Plagioclase Replaced by Pumpellyite, Albite and Epidote (R35)

Transmitted light  Scale Bar = .25 mm

Plate 3.11  Plagioclase Replaced by Pumpellyite, Albite and Epidote (R35)

Crossed nicols  Scale Bar = .25 mm
Plate 3.12 Calcite Patch Cross-Cutting and Replacing Intersertal Matrix (R60)

Transmitted light Scale Bar = 1 mm

Cross-cutting nature of the boundary suggests active dissolution of the rock. Void infilled with calcite.
The commonest amygdale infillings show an initial rim of chlorite I giving way to chlorite II + quartz + calcite. The calcite is commonly younger than the chlorite II + quartz, but may be intergrown with them indicating an overlap in formation. Where epidote and pumpellyite are developed, they occur before the chlorite II + quartz stage, whereas prehnite often occurs afterwards accompanied by calcite. The zeolites laumontite and stilbite occur with calcite and quartz after chlorite II. In detail there may be deviations from these generalised parageneses, in particular calcite and hematite show complex relationships with other minerals and may form at several stages. Native copper was observed in only one thin-section associated with prehnite and calcite.

3.2.4 Discussion

3.2.4a

As suggested by field data (section 2.2.5), alteration of the Mamainse Point flows has produced new assemblages of minerals diagnostic of the prehnite-pumpellyite and zeolite facies. Epidote, pumpellyite and prehnite occur within the rock only in the lower part of the sequence, although they occur higher in the pile within amygdules. Stilbite occurs only in the upper part of the pile. This suggests that
alteration took place under a regional geotherm with higher temperatures at the base than at the top. Local deviations from the general geotherm occurred in fluid channel-ways allowing the higher temperature epidote, pumpellyite and prehnite to form higher in the pile. Parageneses within amygdules, coupled with the presence of laumontite-calcite veins in the lower zones, point to a progressive cooling with time.

The development of zoned zeolite and prehnite-pumpellyite facies assemblages is also observed in other Keweenawan sequences within Ontario (Wallace, 1972) and elsewhere (Stoiber and Davidson, 1959; Molly and Smith, 1972; Green, 1972a). These sequences are compared in Figure 3.2. All of them have been interpreted as resulting from burial metamorphism. The differences between them reflect their development in different basins within the Keweenawan Rift (section 2.1.4) with different geotherms, fluid compositions, lava compositions, etc.

3.2.4b

Estimates of the temperatures and pressures involved in the metamorphism at Mamainse Point are difficult to make with accuracy. The stratigraphic heights for the exposed sequence suggest minimum pressures of about 0.2 and 0.6 kbar
Figure 3.2 Comparison of Low-Grade Mineral Assemblages in Keweenawan Sequences

Depths in metres from top of exposed sequence.
All sections drawn to same scale except Shesheeb Bay (3 1/2 X expanded).

Sources of Information

Shesheeb Bay  Wallace (1972)
North Shore Volcanics  Green (1971, 1972a, 1972b),
           Author's observations
Portage Lake Lavas  Jolly and Smith (1972)
Mamainse Point  This work, Figure 2.7

Abbreviations used in diagram

Act  Actinolite
Epi, Epid  Epidote
Heul  Heulandite
Laum  Laumontite
Pr, Preq  Prehnite
Pu, Pump  Pumpellyite
Thom  Thomsonite
Stil  Stilbite
for the boundaries of the three zones, i.e. stilbite occurs below 0.2 Kb and epidote above 0.6 Kb. Pressures attained during metamorphism were probably higher due to an unknown amount of lava now beneath Lake Superior.

Temperature appears to be the most important factor controlling mineral formation in modern geothermal areas. In Iceland, stilbite develops over the range 50-120°C, with the main zone at 90-100°C, and laumontite appears at about 100°C (Kristmannsdottir and Tomasson, 1978). The zeolites disappear at about 130°C. Epidote first appears at 200°C, although the main development is above 260°C. Prehnite appears in the zone between the zeolite and epidote zones (Tomasson and Kristmannsdottir, 1972). Epidote appears at the same temperature (260°C) in the Broadlands field, but lower (220°C) in the Wairakei field (Tenn, 1971).

Experimental data relevant to low-grade rocks are summarised in Figure 3.3. No data are available for the lower stability limit of epidote, although Seki (1972) has estimated it to be 220 ± 50°C for $P_e = 1-6$ Kb. The experimental data help calibrate a P-T facies diagram (Figure 3.4) upon which an estimate of the conditions attained by the Mamainse Point sequence can be made.
Figure 3.3 Experimentally and Theoretically Determined Phase Equilibria in Low-Grade Rocks

1. Laum = Wt + 2H₂O (Liou, 1971a)
2. Laum = Lw + 2Qt + H₂O (Liou, 1971a)
3. Stil = Laum + 3Qt + 3H₂O (Liou, 1971b)
4. 5 Preh = 2Zoi + 2Gros + 3Qt + 4H₂O (Liou, 1971c)
5. and 6. Boundaries of stability fields for designated assemblages (Nitsch, 1971)
6. Wr = An + 2Qt + 2H₂O (Liou, 1970)
7. Cct + Ep + Qt + Chlor = Pump + Act + H₂O + CO₂ (Brown, 1977)
8. Act + Hem + Alb + Chl + H₂O = Cross + Ep + Qt (Brown, 1977)
9. Possible lower stability limit of epidote (Seki, 1972)

Abbreviations used in diagram

Stil  Stilbite  Chl  Chlorite
Im  Laumontite  Pump  Pumpellyite
Wr  Wairakite  Qt  Quartz
An  Anorthite  Act  Actinolite
Lw  Lawsonite  Epid  Epidote
Pr, Preh  Prehnite
Zo  Zoisite
Figure 3.4  Low Grade Metamorphic Facies

Shaded area - approximate conditions during metamorphism of the Mamainse Point Formation.

Abbreviations

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<td>Pmp</td>
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3.2.4c

The application of the experimental data to the natural assemblage at Mamainse Point is, however, not without difficulties. Even if equilibrium is demonstrated in experiments, this may not be so in the natural assemblages (Zen, 1974). All the experimental data were obtained under conditions of $P_t = P_f$. However, this was undoubtedly not the case in the natural situation, as suggested by the abundance of channel-ways available to the fluids, the consumption of water to form hydrous minerals and the variation of alteration away from channel-ways. The condition $P_f < P_t$ results in a change of slope; from positive to negative, for the hydration reactions in a $P_t$-T projection and also a lowering of temperatures at which hydrous minerals form (Coombs, 1971). Further reduction in $f_{H_2O}$ is effected by the addition of other components to the fluid, such as dissolved salts, $SO_2$, $CO_2$, etc. (Liou, 1971a). The estimated conditions in Figure 3.4 are thus to be regarded as maxima, more exact estimates requiring further studies, e.g. fluid inclusion, etc.

The occurrence of calcite in the Mamainse Point assemblages shows the presence of $CO_2$ in the fluid phase. Experimental, theoretical and natural observations show that $f_{CO_2}$ has a profound influence on the stability of many
minerals in low-grade conditions. Glassley (1974), using thermodynamic data, showed that the prehnite-pumpellyite facies was limited to conditions where $X_{CO_2} < 0.2$ at $P_t = 1$ Kb. Lower $CO_2$ contents would be required at higher $P_t$. Ivanov and Gurevich (1975) experimentally and thermodynamically found the boundaries of the zeolite facies to be a temperature range of 200-270°C, $P_t < 2.5$ Kb and $P_{CO_2} < 40$ b. These data confirm the earlier calculations of Thompson (1971) that zeolites were stable with respect to calcite and clays if $X_{CO_2} < 0.0075$, at $P_t = P_f = 2$ Kb. The equilibrium $P_{CO_2}$ for the reaction

$$Laum + cct = preh + qz + 3H_2O + CO_2$$

was calculated to be 30-40 b at $P_f = 2$ Kb (Thompson, 1970). Sphene is also unstable in the presence of high $CO_2$ and the reaction

$$cct + qz + rut = sph + CO_2$$

gives a maximum $P_{CO_2}$ of 25-30 b at 300°C and 45-50 b at 340°C (Schuiling and Vink, 1967). All these data suggest a limiting value for $P_{CO_2}$ of about 30 b for $P_t = 1-2$ Kb, in assemblages such as that at Mamainse Point.

The alteration of magnetite to hematite in the Mamainse Point sequence indicates that fluids were oxidising.
This may have an effect on the stability of such Fe-bearing minerals as epidote and pumpellyite. Liou (1973) showed that the stability field for epidote widens with increasing $f_{O_2}$ at both high and low temperatures. Thus pistacitic epidote may occur down to 200-300°C (c.f. data from natural geothermal areas). The pumpellyite field, however, may be suppressed in favour of pistacite (Jolly and Smith, 1972):

$$2Ca_4Al_4Fe^{3+}Fe^{2+}Si_6O_{23}(OH)_3 \cdot 3H_2O + 0.5O_2$$

pumpellyite

$$- 2Ca_4Al_4Fe_2^{3+}Si_6O_{24}(OH)_{24} + 5H_2O$$

epidote

This sort of reaction may explain the failure to develop a distinct pumpellyite zone in the Mamainse Point sequence compared to Shesheeb Bay or Keweenaw Peninsula, although the reaction will also depend upon $T$ and $P_{H_2O}$.

3.2.4d

In conclusion, the mineralogical evidence coupled with available experimental and theoretical data, suggest that the Mamainse Point Formation has suffered low-grade
burial metamorphism in the zeolite and prehnite-pumpellylite facies. Temperatures and total pressures probably rose to about 300°C and 2-2.5 Kb near the base of the pile. Fluid pressures were probably lower than lithostatic.

The fluid involved was oxidising and CO₂-bearing, although P_{CO₂} <30-40 b. The presence of calcite-laumontite veins in the epidote zone indicates that cooling took place from 300°C to about 200°C or less. Whether the calcite-laumontite assemblage represents equilibrium or some disequilibrium precipitation mechanism is not certain (Thompson, 1970) and possible increase in P_{CO₂} with time is conjectured.

The average geothermal gradient envisioned during the peak of the metamorphism was 'probably about 40 50°C km'. This is lower than that found in modern geothermal areas, but higher than that found in the Lake Superior area as present (20°C km; Birch, 1954). The heat was supplied to the system by circulating fluids and ultimately derived from the heightened heat flow connected with extensive volcanism.
CHAPTER 4

GEOCHEMICAL EFFECTS OF ALTERATION

"... which me will survive all these liberations"

Audre Lorde, "From a land where other people live", 1975

4.1 INTRODUCTION

Eighty-nine samples were crushed and analysed by the author for major-, minor-, and trace elements by XRF, AAS, INAA, and wet chemical techniques. Details of procedures, accuracy and precision are presented in Appendix I. U and Th determinations were carried out by Dr. E.L. Hoffmann of Nuclear Activation Services on contract; details are also included in Appendices I and II. 

Most of the samples represent centres of flows but three flow-tops were also analysed, along with eight dykes, ten samples from two heterogeneous flows and five samples from two fracture zones. Three samples from different lithologies in the
glomeroporphyritic "Daisy Stone" flow were also analysed. Sample locations are indicated on Figure 4.1.

Geochemical variability in the samples result from two superimposed processes. Primary variation, resulting from partial melting and crystal fractionation, has been obscured or complicated by later adjustments in chemistry that accompanied burial metamorphism. The latter effects can be seen not only in the heterogeneous and fractured flows, but also in the total sample population.

4.2. HETEROGENEOUS FLOWS

4.2.1

Two flows, from the zone of heterogeneity, developed just beneath the Lower Conglomerate, were sampled from base or top to the centre. It was hoped that this would yield information about element mobility that would help in the interpretation of the rest of the data set. The flows selected were thin (< 4 m) thus minimizing in-situ fractionation effects, so that geochemical variability could be ascribed to alteration processes.
Figure 4.1 Sample Locations

Closed Circles  Flows
Open Circles    Dykes
Dashed-Dotted Line Boundary of Keweenawan
HBF             Hibbard Bay Fault
GC               Great Conglomerate
LC               Lower Conglomerate
4.2.2

Flow 16-76 shows a well developed vesicular zone at its base with pipe vesicles up to 8-10 cm long. Chlorite, epidote, laumontite, and calcite are common in round vesicles, laumontite and calcite in the pipe vesicles. The basal zone is succeeded by a homogeneous layer with minor vesicles and chlorite-epidote veining. This passes up into a zone with well developed epidote metadomains in a grey matrix. Chlorite-laumontite-calcite occur in vesicles, and chlorite-epidote in veins. The central part of the flow is homogeneous feldspar phytic metaphyre with some chlorite-epidote veins. The top of the flow is not well exposed. The lithologic variation and sampling are shown in Figure 4.2 along with the element distributions. Fe, Mn and Bb were omitted due to their low values and lack of variation.

From comparing element distributions within the flow, it can be seen that MgO, SiO₂, Na₂O, H₂O+, Li, Ni, Cr and Zn show similar patterns of variation. TiO₂, Fe₂O₃ and Al₂O₃ are somewhat similar to these although more subdued. CaO, CO₂, Sr, Ox and U show patterns that are antipathetic to those of the first group of elements. This antipathy of MgO, Na and H₂O to CaO and CO₂ could arise from the varying proportions of chlorite-albite-magnetite on the one hand and calcite-hematite on the other. This would suggest perhaps that two geochemical-
Figure 4.2 Geochemical Variation in Heterogeneous Flow 16-76

All major element oxides in wt%, trace elements in ppm

$\text{Ox} = \text{Fe}_2\text{O}_3, \quad \text{Fe}_2\text{O}_3 - \text{Fe}^3+$
Heteroflow 16.76

\[
\begin{align*}
\text{Homogeneous} & : 35 \\
\text{Fsp-phyrk} & : 34 \\
\text{Basalt} & : 33 \\
\text{Epidote} & : 32 \\
\text{Melodomains} & : 31 \\
\text{Vesicular Homogeneous} & : 30 \\
\text{Vesicular, Base} & \\
\end{align*}
\]

\[
\begin{align*}
\text{SiO}_2 & : 5 \quad 10 \quad 15 \quad 20 \quad 25 \\
\text{TiO}_2 & : 5 \quad 10 \quad 15 \quad 20 \quad 25 \\
\text{Al}_2\text{O}_3 & : 5 \quad 10 \quad 15 \quad 20 \quad 25 \\
\text{FeO} & : 5 \quad 10 \quad 15 \quad 20 \quad 25 \\
\text{MgO} & : 5 \quad 10 \quad 15 \quad 20 \quad 25 \\
\text{CaO} & : 5 \quad 10 \quad 15 \quad 20 \quad 25 \\
\text{Na}_2\text{O} & : 5 \quad 10 \quad 15 \quad 20 \quad 25 \\
\text{K}_2\text{O} & : 5 \quad 10 \quad 15 \quad 20 \quad 25 \\
\end{align*}
\]
metamorphic events have taken place. The first resulted in hydration of the rocks plus some addition of alkalis (Na + Li) and some oxidation of Fe. This accompanied the development of epidote-chlorite-albite assemblages. The second event resulted in the development of clacite-laumontite, with the mobilization of Ca and Sr. The fluids involved in the latter were fairly oxidizing, causing further oxidation of Fe and addition of U. The petrographic and field evidence would support this double event theory, with the pervasive calcite-laumontite veining in the pile cross-cutting earlier, higher temperature metamorphic assemblages (see 3.2).

K and Ba show generally low values, except in the lower vesicular zone. Rb shows a high value for this zone, although other samples are below detection limit. This may suggest that K, Rb and Ba are added to the flow in the vicinity of channelways (the vesicle zone). The very low values in the central parts may even suggest some depletion also occurs. Relationships to other elements are obscure.

Y, Zr and Nb are normally considered to be immobile elements in low-grade alteration (Pearce and Cann, 1971, 1973) and to behave like Ti. Y and Zr, however, show increases towards the centre not seen in TiO₂. Nb on the other hand shows a decreasing trend with a peak in the vesicular zone (as for K and Ba). These trends may reflect original intra-flow
variation produced by differentiation during cooling, although
the flow is not very thick (max 4-5 m).

4.2.3

Flow 18c-76 shows a heavily reddened, hematized flow
top that passes down into a zone of chlorite metadomains.
Vesicles are abundant and infilled with epidote, chlorite and
calcite. Epidote veining is seen in the lower part of this
zone. This passes into a grey feldspar-phyrnic zone with
abundant vesicles. Chlorite, calcite, laumontite, chalcedony
and occasional prehnite occur in vesicles. Vesicles decrease
in number towards the centre of the flow and are replaced by
larger vugs infilled with quartz, laumontite, chlorite and minor
epidote.

MgO, H₂O⁺, Li, Ni and Cr again show similar distribution
(Fig 4.3), accompanied by TiO₂, Y, Zr and Nb on a more subdued
level. Sr appears to be opposed to this trend, but CaO and CO₂
show a stepped pattern with much higher levels in the marginal
zones. K, Ba (and Rb) show the reverse with very low levels in
the marginal zones and higher levels in the centre. Other
elements show distributions that are not easily related to other
patterns, although SiO₂-Al₂O₃ and Co-Cu seem to be related pairs.

The element patterns are less easy to explain than for
Figure 4.3 Geochemical Variation in Heterogeneous Flow 18c-76

All major element oxides in wt%, trace elements in ppm

Ox = Fe₂O₃ / (Fe₂O₃ + FeO)
16-76, which may reflect differences in style of heterogeneity and also sampling differences. A hydration event producing chlorite is suggested by the correlation of MgO, H$_2$O$^+$, Ni, Cr and Li. This may have been accompanied by the addition of K, Rb and Ba also. The carbonate elements -Ca, Sr, CO$_2^-$ are somewhat antipathetic to the hydrous group, but not in as clear cut a manner as in the case of 16-76.

4.2.4

The lava flows appear to have suffered two geochemical-metamorphic events. An initial hydration, probably accompanied by addition of alkalis (Li, Na, K, Rb and Ba), and a later carbonate-laumontite event with mobilization of Ca and Sr. Oxidation of Fe probably occurred in both stages, but shows good correlation with the carbonate event. U, which is more soluble in oxidizing fluids, also appears to have been mobilized during the later event. The time interval between the two events is unknown, though it is within the time-span of the whole igneous-metamorphic event, and may be quite short depending upon whether the fluids had separate origins or were different evolutionary stages of the same fluid.
4.3 OTHER SAMPLES

4.3.1.

Further evidence of the geochemical effects of the alteration can be gleaned by considering other altered samples from fracture zones and flow top-centre pairs, along with the two heterogeneous flows, and data from the whole of the pile (dominantly flow centres).

4.3.2 The Alkali Elements, Including Ba

The alkali elements are notoriously mobile in altered mafic rocks and the Mamainse Point sequence is no exception. $K_2O$ shows a range of values from 0.2 to 4.0%, much higher than expected for tholeiites. Although the presence of very low $K_2O$ (< 0.10%) and Ba (< 80 ppm) is some of the most altered samples (Figs 4.4a and 4.6a) may suggest that they have been leached from some lavas, the general trend appears to be of addition resulting in high $K_2O$ (> 1.0%). This is reflected in Figure 4.4, in which $K_2O$ is plotted against $TiO_2$. A lot of scatter is seen in the data with no overall trend. Lava's from the lower part of the pile show almost vertical trends with about 10x change in $K_2O$ for 1-2x change in $TiO_2$. This is much higher than can be explained by fractionation or melting effects.
Figure 4.4 $K_2O$ (%) vs $TiO_2$ (%)

a) Most altered samples
   - Heteroflow 16-76
   - Heteroflow 18-76
   - Flow top – centre pairs
   - Fracture zones

b) Other data
   - Lower flows (below the "Great Conglomerate")
   - Upper flows (above the "Great Conglomerate")
(Chapter 6) and must have resulted from addition of K$_2$O during alteration. Rb (Fig 4.5) and Ba (Fig. 4.6) are also added and show fairly good correlation with K$_2$O. The most altered samples also show a decrease in K/Rb with increasing K$_2$O (Fig. 4.5a), although this is not so apparent in the main data set (Fig 4.5b), nor is there any clear change in the K/Ba (Fig. 4.6).

Alteration of Na contents has also taken place in many samples, although rarely to the same extent as K. Thus increases in the total alkalis are accompanied by increases in K$_2$O/K$_2$O + Na$_2$O (Fig. 4.7). This results in a wide scatter of the sample points within Hughes' (1972) 'Igneous spectrum', and even a shift to the K-rich field. Few points fall within the designated spilite field, despite the presence of spilitic mineral assemblages (albite + chlorite + epidote + hematite + calcite) (Smith, 1972).

Li contents of many samples analysed are higher than expected for fresh basalts, which show a range up to ~20 ppm. Li has been found to be enriched in palagonites (Frey et al., 1974), spilites and Precambrian diabases (Shaw et al., 1977). The Mamainse Point samples fall in both the spilite and basalt fields on the Li vs CaO/Al$_2$O$_3$ plot of Shaw et al. (1977) (Fig 4.8), illustrating the variability of alteration in the
Figure 4.5  Rb (ppm) vs K$_2$O (%)  

a) Most altered samples  
    As for Figure 4.4  

b) Other data  

- Flows  
- Dykes  

Samples below Rb detection limit are omitted. Labelled lines are reference K/Rb ratios.
Figure 4.6  Ba (ppm) vs K₂O (%) 

a) Most altered flows 

b) Other data 

Symbols as in Figure 4.5

Labelled lines are reference K/Ba ratios.
Figure 4.7 $\text{Na}_2\text{O} + \text{K}_2\text{O}$ vs $\text{K}_2\text{O} / (\text{Na}_2\text{O} + \text{K}_2\text{O})$

a) Most altered samples

b) Other data

Symbols as in Figure 4.5

Field IS is Hughes' (1972) 'Igneous Spectrum', and represents the field occupied by the majority of igneous rocks.
Figure 4.8 Li vs CaO/Al$_2$O$_3$

a) Most altered samples

b) Other data

Symbols as in Figure 4.5

S = Spilites
B = Fresh Basalts

After Shaw et al. (1977)
considered significant as the resultant groups are not related to vertical position in the pile, content of other alkalis, etc. The Li values correlate well with $\text{H}_2\text{O}^+$ (Fig 4.9) suggesting addition during the hydration event. Its correlation with Mg in heterogeneous flows also suggest its presence in chlorite in agreement with Floyd (1974) who found enhanced Li levels in chloritic patches in spilites of S.W. England.

4.3.3 Ca and Sr

The data from the heterogeneous flows suggest that both Ca and Sr are mobile elements, a phenomenon reflected mineralogically by the presence in vesicles, etc. of secondary Ca-silicates such as epidote and laumontite, as well as calcite. Ca shows good correlation with $\text{CO}_2$ (Fig. 4.10b) although not uniformly in one direction. Up to levels of about $1 - 1\frac{1}{2}$ % $\text{CO}_2$, Ca appears to have been leached from the lavas. Above $1\frac{1}{2}$ % $\text{CO}_2$, Ca shows a good positive correlation on a trend that would project through the composition of pure calcite. This latter trend also is seen in the more altered flows (Fig. 4.10a). Thus Ca appears to have been leached from some flows and added to others as calcite. This may suggest that Ca mobility, results from the second of the two postulated
Figure 4.9 Li (ppm) vs $H_2O+($)

a) Most altered samples

b) Other data

Symbols as in Figure 4.5
Figure 4.10  CaO (%) vs CO₂ (%)

a) Most altered samples
b) Other data

Symbols as in Figure 4.5

Oct       pure calcite

Note: Samples with CO₂ < .1%, plotted at .1%.
geochemical-metamorphic events, and only local variation accompanied the hydration event.

Sr is not so well correlated with CO$_2$ (Fig. 4.11). Below 1% CO$_2$, Sr is fairly constant in the range 200-300 ppm (Fig. 4.11b). Above 1% CO$_2$, a tendency for Sr to be negatively correlated with CO$_2$ is seen, although many values still fall in the 200 ppm range. The highest Sr values occur in low-CO$_2$ bearing rocks. Conflicting tendencies are observed in the more altered flows (Fig. 4.11a), one heterogeneous flow and one flow top-centre pair showing positive correlation and the other samples poor or negative correlations. It thus appears that Sr has been mobilized differently than Ca, and in fact has been depleted in many samples where Ca has been enriched. This latter may result as much by dilution of Sr contents by low-strontian calcite, as much as by active leaching. The small variation seen at low-CO$_2$ contents probably reflects control of Sr by silicate phases like relict plagioclase and secondary epidote, prehnite, pumpellyite, etc.

4.3.4 Mg, Fe and Other Transition Elements

Nearly all samples show high contents of Fe$_2$O$_3$, often in excess of FeO, in contrast to fresh basalts which have Fe$_2$O$_3$ = 15-20% of total Fe. The oxidation of Fe has been variable, however, resulting in a range of oxidation ratios
Figure 4.11 Sr (ppm) vs CO$_2$ (%)

a) Most altered samples

b) Other data

Symbols as in Figure 4.5

Note: Samples with CO$_2$ < .1%, plotted at .1%. 
(Ox = Fe$_2$O$_3$/Fe$_2$O$_3$ + FeO) from .3 - .9. This variability is not simply related to H$_2$O + (Fig. 4.12) or CO$_2$ (Fig. 4.13). It results from a complex of processes involving alteration and oxidation of Fe in glass and mafic phases (olivine and augite) as well as in magnetite. Oxidation is thus subject to controls set by several solid-fluid reactions, which may not reach equilibrium, as well as characteristics of the fluids themselves.

Whether Fe has suffered any change other than oxidation can only be tested by reference to a second element that can be taken to be immobile. The lack of correlation with suitable indicators of alteration such as Li, H$_2$O +, CO$_2$, etc., does not itself preclude the possibility of alteration controlled by some complex reaction, or set of reactions, as for Ox. Ti has often been cited as an immobile element in low-grade metamorphic rocks (Pearce and Cann, 1971, 1973; Floyd and Winchester, 1975). The presence of small secondary sphene grains in altered matrix within flows, may suggest that TiO$_2$, released by alteration of magnetite and glass, has not moved more than millimetres and could be considered immobile on the scale of a hand sample. Coherent covariance of another element with TiO$_2$ may thus suggest that it also is immobile and subject only to variation due to dilution with mobile components, principally volatiles. The coherent behaviour of TiO$_2$ with elements of differing geochemical behaviour, e.g. Fe, P, Al, will also
Figure 4.12 Ox vs $H_2O^+$

$$Ox = \frac{Fe_2O_3}{Fe_2O_3 + FeO^*}$$

Symbols as in Figure 4.5b
Figure 4.13 Ox vs CO₂

\[ \text{Ox} = \frac{\text{Fe}_2\text{O}_3}{\text{Fe}_2\text{O}_3 + \text{FeO}} \]

Symbols as in Figure 4.5b
help confirm the original assumption that it is immobile. Using the TiO₂ variation diagram as a screen, leads to the conclusion that FeOₓ is essentially immobile (see Fig. 6.3) although some addition of Fe may have taken place in severely hematized samples. Ni, Cr, Co also appear essentially unaffected by the alteration (see Figs. 6.9 - 6.11), in contrast to MgO (Fig. 4.14) which shows greater variability although retaining some relics of the original trends. The alteration of MgO is less severe though than that seen already in CaO, K₂O, etc., and is reflected mineralogically in chlorite replacement of glass and feldspars, plus vesicle infillings.

Zn shows fairly good correlation with TiO₂ (see Fig. 6-20) although some alteration effects are seen in the lower lavas resulting in enrichments. Otherwise Zn mimics the FeOₓ pattern reflecting control by Fe-bearing phases. Cu abundance, however, is severely altered, its mobility being reflected in the native copper and chalcocite developed in vesicles and fractures. It shows a fairly good negative correlation with H₂O + (Fig. 4.15b) perhaps suggesting that low values result from leaching during the hydration event, and higher values reflect deposition with changing stability due to changes of temperature or fluid chemistry (Crisar and Barnes, 1976).
Figure 4.14  MgO (%) vs TiO$_2$ (%)  

Symbols as in Figure 4.5b
Figure 4.15 Cu (ppm) vs $\text{H}_2\text{O}^+$ (%)  

a) Most altered samples  
b) Other data  

Symbols as in Figure 4.5
However, a significant number of samples with less than 7% H₂O show low Cu contents also. A more complex relationship between Cu and H₂O + is shown in the most altered samples (Fig. 4.15a) where possible positive correlations can be seen. Jolly (1974) has suggested that dehydration of Michigan Keweenawan lavas has resulted also in the loss of Cu. This type of process may explain the anomalous samples here, although the variability of this dehydration between samples of similar position in the pile is problematical. It may be that these samples are just less altered (hence the low H₂O +) and are recording more or less primary Cu contents.

4.3.5 Other Elements

Of the other major-elements, Al₂O₃ (Fig. 6.4) and P₂O₅ (Fig. 6.2) appear to be essentially immobile on the scale of hand samples, although some redistribution of Al on the mineralogical scale is required for the alteration of plagioclase to albite and the formation of epidote and laumontite in vesicles. SiO₂ on the other hand appears to be remobilized on a more extensive scale (Fig. 4.16) producing secondary quartz and agate, as well as silicates, in vesicles and fractures.

Zr, Y and Nb are grouped with Ti and P as immobile elements in low-grade metamorphism, which seems to be the case
Figure 4.16 $\text{SiO}_2$ (%) vs $\text{TiO}_2$ (%)

Symbols as in Figure 4.5b
for the Maminase Point lavas (see Figs. 6.12, 6.14 and 6.15). This also seems to apply to Hf, Ta, Th and the REE's although this is based on a smaller number of samples (see Figs. 6.13, 6.16, 6.17, 6.18). Possible enrichment of the LREE during alteration is suggested by sample R37 (see Fig. 5.8), which lacks any sign of crustal contamination, as in R51 (see 6.3), that may otherwise explain the enrichment. It also occurs within the zone of heterogeneity that marks the most extreme readjustments during metamorphism. Without more data on heterogeneous and other flows, no further comments can be made except that alteration of REE's is generally not observed.

U appears to be subject to some modification by alteration, but retains moderately good correlation with TiO₂ (Fig. 6.18b) and Th (Fig. 6.19). The data from the heterogeneous flows (see 4.2 above) pointed to the possibility of U enrichment during the carbonation event, accompanying oxidation of Fe. No clearcut relationship between U and Oₓ is observed, however, in other altered samples (4.17a), or other flows generally (4.17b), reflecting its only partial alteration.

4.3.6

In summary, geochemical readjustments accompanying low-grade metamorphism have resulted in addition of K, Rb, Li, Ba, H₂O +, CO₂, and oxidation of Fe. Ca, Sr and Si have been
Figure 4.17 Ox vs U

\[ Ox = \frac{Fe_2O_3}{Fe_2O_3 + FeO} \]

a) Most altered samples
b) Other data

Symbols as in Figure 4.5
variously added or depleted, as have Mg and U to smaller degrees. FeO, Al₂O₃, TiO₂, P₂O₅, Zr, Y, Nb, Hf, Ta, Th and REE's, all appear to have been essentially immobile and to have retained covariant behaviour inherited from primary processes. Similar additions of K₂O, H₂O +, CO₂ and Li with variable CaO, Na₂O, Ba and Rb have also been recorded for the Mamainse Point felsites (Jackson, 1977; Jackson et al., 1978).

There appears from field evidence to have been two episodes of alteration — an initial period producing assemblages up to the epidote grade in lower parts of the pile, and a later calcite-lauomontite event. The latter would be at a lower temperature than the epidote-producing phase and probably represents a waning of the burial metamorphism, rather than a separate, discrete event. The mobilities of certain elements appear to have been produced dominantly by one or other of the two events, e.g. Li added during hydration; Ca mobilized during carbonation; but some elements have been affected by both events in a complex manner not readily understandable with the present data. Where additions of material can be demonstrated, as with the alkalis, these appear to have come in with the earlier hydration event and were derived from outside the pile. Other elements such as Cu in the hydration event, and Ca in the carbonation event appear to be explicable in terms of redistribution within the pile although external sources, at
least in part, cannot be ruled out.

The nature of the fluids involved in the alteration can only be guessed at this stage. The initial fluids appear to have been CO₂-poor waters, carrying alkalis in solution, and probably Cl⁻ to allow leaching and complexing of Cu. The subaerial nature of the sequence excludes the possibility of sea water being involved. However, briney subsurface waters may be expected in the region at the time due to the semi-arid climate and possible internal drainage into the rift valley. These subsurface brines would combine with any hydrothermal waters accompanying volcanism. With time these fluids evolved to more CO₂-enriched waters allowing the mobilization of Ca. The CO₂ content of the waters was still not excessive, however, as zeolites were precipitated (see 3.2.4c). Oxidation accompanied all stages of alteration suggesting the fluids were oxidative. The pH of the fluids cannot be satisfactorily estimated without more detailed knowledge of the alteration reactions, etc., although they were probably alkaline during the later stages, being buffered by calcite deposition.
4.4 COMPARISON WITH OTHER ALTERED BASALTS

4.4.1 Other Keweenawan Areas

Detailed studies of the geochemical effects of alteration accompanying low-grade metamorphism of Keweenawan sequences are limited to the Keweenawan Peninsula, Michigan, where they were initiated as contributions towards understanding the genesis of the extensive copper mineralization (Jolly and Smith, 1972; Jolly, 1972, 1974; Stoiber and Davidson, 1959; Scofield, 1976). The effects of alteration are to be seen elsewhere in the Keweenawan causing mobilization of alkalis, oxidation of Fe and additions of volatiles (Wallace, 1972; Annells, 1974).

Jolly and Smith (1972) asserted that the Michigan lavas suffered an initial hydration during early diagenesis of the flows near the surface. With burial, metamorphism produced a progressive dehydration-hydration regime with chemical and mineralogical readjustments, particularly in flow tops. Calculation of the bulk major-element composition of the altered flow tops showed them to be similar to the unaltered flows, suggesting that chemical variation resulted from redistribution of Na, Ca, Si, etc. within the pile, requiring no material to be brought in or carried out. Only K_2O appeared to be significantly altered, being leached out of altered flow tops compared to unaltered flows. This is in contrast to the
addition of K$_2$O found in many Mamainse Point lavas, although some leaching may be indicated by the very low contents in the heterogeneous flows. Jolly (1974) also reported that Ni was unaffected by the alteration, but that Cu had been leached out of the dehydrated zones and enriched in the hydrated zones. Zn had been leached out of all altered parts and removed from the pile. This behaviour also contrasts with Mamainse Point where Cu shows a fairly good negative correlation with H$_2$O + in most samples, thus being leached out of the most hydrated samples and enriched in less hydrous areas. Zn also appears to be less mobile than Cu, only showing significant alteration in the lower parts of the pile.

Scofield (1976) confirmed that there was much mobility of Ca, Mg, Na, etc., in the Michigan lavas, but that this was essentially within flow with no net gains or losses, even at the scale of thin flows. Some addition of Mg, K and Na and loss of Ca were observed in parts of the thick Scales Creek Flow; however, K was lost from the altered thin flows, perhaps providing a source for the K added to the Scales Creek Flow. Cu abundances were found to be erratic within and between flows. It was concentrated in primary Fe-Ti oxides and Fe-silicates (olivine and augite) and was released during oxidation and alteration. No external source of Cu is necessary to explain the mineralization in other parts of the sequence.
Several differences exist between the effects of alteration in the Mamainse Point Formation and in the Portage Lake Lavas of Michigan. Although much of the variation within both sequences represents within-pile mobilization, some elements such as K, Ba, Rb and Li have been added to the Mamainse Point lavas along with the volatiles. The Portage Lake Lavas appear to have lost K, however, and Zn. The differences probably reflect differences in the compositions of fluids, temperature gradients, etc. Differences in metamorphic zonation (see Fig. 2.6) may point also to different mineralogical controls on geochemical variations. Both sequences involve two events, however, although the initial hydration is believed by Jolly and Smith (1972) to be diagenetic and before development of zeolite and prehnite-pumpellyite facies assemblages. A carbonation event occurs as a later stage.

4.4.2 Other Altered Basalts

Gottfried et al. (1979) described alteration effects in basalts recovered from a deep borehole in South Carolina. These basalts are related spatially, temporally and geochemically to the Late Triassic - Early Jurassic tholeiitic province of eastern North America. They are believed to have developed in an extensional tectonic regime related to early opening of the
Atlantic, and may be analogous to the Keweenawan volcanics. Alteration has most affected the margins of flows producing amygdule assemblages of laumontite-calcite-chlorite. Concentrations of K, Rb, Ba and Sr are highly variable indicating enrichments and depletions compared to other less altered samples. Pb and Ca are less variable and Ti, P, Zr, Nb and REE's appear to be immobile. Many similarities thus exist with the Mamainse Point Formation, but further comparison is not warranted at this time due to the small data base from only 42 m of penetrated basalts.

Successful recovery of ocean-floor basalts by dredging, drilling and submersibles has led to the recognition of alteration processes in the oceanic crust. A spectrum of processes is recognized from low-temperature weathering or halmyrolysis, through zeolite- and greenschist-facies metamorphism to higher-temperature hydrothermal systems, which may be associated with mineralization. Similar processes are believed to have affected spilites (Vallance, 1969) and ophiolitic basalts (Liou and Ernst, 1979). The chemical effects of these processes are summarized in Table 4.1 and compared to experimental seawater-basalt systems and the Mamainse Point sequence. Some similarities exist between all the alteration processes, e.g. the enrichment of alkalis, the immobility of Ti, Zr, Y, Nb, Al and Cr; but some important differences also
<table>
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<th>Enriched</th>
<th>Halmyrolysis</th>
<th>Ocean-floor Metamorphism</th>
<th>Experimental Systems</th>
<th>Mamainsee Point</th>
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<td>$H_2O^+, Fe_{III}, K, Rb, Cs, Mn, Pb, U, Li, REE, S^{15}, Sr^{87/86}$</td>
<td>$H_2O^+, Fe_{III}, EFe, Na, Mg, S^{2-}, Na, Mg, K, ?Rb, Sr^{87/86}$</td>
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<td>$Cu, Zn, K, Rb, S^{2-}$</td>
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<tr>
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**TABLE 4.1 VARIATION IN CHEMISTRY OF LOW-GRADE METABASITES**
18. MacDougall (1973) EOS, 54(11), 988.
exist, e.g. the variable behaviour of Mg and REEs between halmyrolysis and the higher-temperature alterations. In general there are many similarities between the Mamainse Point alteration and ocean-floor metamorphism despite the involvement of different fluids (although both probably brines). The differences that exist reflect the very different rock-water ratios, mineralogical controls, etc.

4.5 CONCLUSIONS

Geochemical readjustments accompanying burial metamorphism have led to the mobility of many major- and trace-elements. In particular, additions of H$_2$O +, CO$_2$, the alkalis and the oxidation of Fe have occurred, with variable addition or depletion of Si, Mg, Ca, Sr, Cu and ?U. Fluids involved in the alteration appear to have evolved from CO$_2$-poor to more CO$_2$-rich with time. A large group of elements appear to have been essentially immobile, at least at the scale of sample-size used, and these elements - Al, Fe, Ti, P, Zr, Y, Nb, REE, Ni, Cr, Co, Hf, Th and Ta - should have retained primary petrogenetic information.
CHAPTER 5

GEOCHEMISTRY AND CLASSIFICATION OF THE
MAMAINSE POINT BASALTS

"Who hath ... comprehended the
dust of the earth in a measure,
and weighed the mountains in
scales, and the hills in a
balance?"

Isaiah 40:12

5.1 GEOCHEMICAL VARIATION

5.1.1 Introduction

The geochemical data for most elements are presented
in stratigraphic plots in Figures 5.1 to 5.3. Omitted from these,
are the data from the altered rocks of the heterogeneous flows
and fractures zones, the dykes and the flows from the Alona
Bay section whose exact stratigraphic relation to the Mamainse
Point rocks is unknown. The average one-sigma error, based on
the precision monitors, is contained within the size of the dot
Figure 5.1 Stratigraphic Variation of Major Elements

All data in wt% hydrous.

Paleomagnetic stratigraphy from Palmer (1970)

LC Lower Conglomerate
GC Great Conglomerate
HBF Hibbard Bay Fault
Figure 5.2 Stratigraphic Variation of Trace Elements and FeO$_x$/MgO

All data (except FeO$_x$/MgO) in ppm

Paleomagnetic stratigraphy from Palmer (1970)
Figure 5.3  Stratigraphic Variation of Y, Zr, Nb, P₂O₅, and TiO₂

Y, Zr, Nb in ppm; P₂O₅, TiO₂ in wt% hydrous

Paleomagnetic stratigraphy from Palmer (1970)

Note: Division into series shown on the right hand side.
Samples R94 and R95 are distinguished by ◇ in the TiO₂ plot
(see text).
for most elements.

Three gaps in the stratigraphic sequence are apparent. The lower two result from the presence of the Lower and Great Conglomerates, and the upper, from poor exposure in the area just west of the Hibbard Bay Fault (see Fig. 4.1).

5.1.2 Structural Effects

As folding is absent in the Mamainse Point section (2.2.4), the major structural effect on the stratigraphic-geochemical plots is faulting, causing repetitions or omissions. Three parts of the section are of interest here:

1. 1750-1800 m from the base. A fault has been postulated here to explain the triple reversal in the palaeomagnetic sequence, compared to the normal single reversal in other Keweenawan sequences (Palmer, 1970; Robertson, 1973). There is, however, no geological evidence to support this hypothesis. Also the flows on either side of the postulated fault seem to be similar in chemistry. They are distinguished from their supposed correlatives by lower contents of Ti, P, Y, Zr and Nb. The present author (Massey, 1979) has thus suggested that the triple reversal at Mamainse Point is real and unrecorded in other Keweenawan sequences where stratigraphic breaks
occur with the reversal. Mixed polarity rocks from
the Dora Sandstone, Arizona (Elston and Grömpü, 1979),
correlate with the Keweenawan lavas and would support
this interpretation.

b) 3100 m. Block faulting is common in the Mamainse
Point-Hibbard Bay area (Fig. 2.4) and may have given
rise to repetitions of strata which were unnoted in
the field, due to lack of distinct marker horizons.
The faulting also gives rise to some uncertainties in
the estimation of the stratigraphic height of samples,
although they are believed to be correct to 50-100 m,
which would not alter any of the interpretations
presented below.

c) 3400 m. The Hibbard Bay Fault was interpreted by
Giblin based on geomorphic and aerial photographic
evidence (Giblin, pers. comm.). It is not exposed on
the ground and its effects on the stratigraphy are
unknown. Poor exposure in the Hibbard Bay area compounds
the problem.

5.1.3 Geochemical Subdivision of the Mamainse Point
Formation

From an inspection of the immobile elements, e.g., TiO₂,
Ni, Zr, etc., certain changing distributions with height can be
discerned. These trends presumably result from eruption of magma undergoing differentiation with time (= height in the pile). The trends show some stepwise cyclicity with inflexions and breaks, suggesting that either periodic recharge of the magma chamber took place or that more than one magma chamber erupted.

The inflexions and breaks in the patterns of the immobile incompatible elements (Ti, P, Y, Zr, Nb) allow the Mamainse Point sequence to be subdivided into five series (Fig. 5.3). Series I consists of the basal olivine-phryic flows, which show increasing Ti, etc., with height. The three 'Daisy Stone Flow' samples have been excluded because of the effects of in situ differentiation that in part led to the development of lithologic variation in the flow. Series II consists of the rest of the flows below the Lower Conglomerate. They are distinguished from series I by their being feldspar-phryic. They are also marked by an inflexion in the chemical trends, e.g., Ti, P. Series III consists of the flows between the Lower and Great Conglomerates. They are marked by low contents of incompatible elements (e.g., TiO₂ usually less than 1%, with only a slight increase with height).

Series IV flows occur between the Great Conglomerate and the Hibbard Bay Fault. They generally have high contents of the incompatible elements with a tendency to increase with
height although in a complex way. Series V flows occur above the Hibbard Bay Fault, but include three flows below, that overlap with the series IV. They are marked from the series IV by a sudden drop in the incompatible element contents, which then increase. The overlap between series IV and V may be due to either of two causes:

a) Interbedding of the lavas (Fig. 5.4b). The differences in chemistry imply that two different magma chambers are being tapped at the same time, the older series IV chamber being more fractionated than the newly-erupting series V chamber.

b) Fault repetition (Fig. 5.4a). The block faulting common to this area of outcrop, may have caused repetition of the series IV/series V boundary which was unnoticed during sampling. The respective similarity of the two series IV flows (R81 and R87) and of the three series V flows (R82, R84, and R89) in the region of overlap may suggest the repeated sampling of the same two flows, although this cannot be easily proved.

The heterogeneous flows discussed in the previous chapter occur in series II and show similar levels of immobile elements as the samples used to define the series. They have not been included with the series II flows, however, because of
Figure 5.4 Interpretation of Series IV/Series V Overlap

a) Fault Repetition of Series IV/Series V contact
b) Interbedding of Series IV and V, faulting has little effect
c) Identification of sample points on Figures 5.1 to 5.3 (based on TiO$_2$ plot)

Maps are based on Giblin (1969b) except for fault in (a)

F - felsen intrusion

Further explanation is to be found in the text.
their marked heterogeneity.

Alona Bay flows are olivine-phyric and show similar ranges of composition to the series I lavas (see Appendix II). Although they are discriminated from the series I flows in many of the figures which follow, they generally behave similarly and are described together under the general description 'Olivine-phyric flows'.

The dykes are not easily related to any of the lava series. As a group they show high contents of incompatible elements (Ti, P, Y, Zr, Nb, U, Th, see Appendix II) although some variability exists, e.g., TiO₂ varies from 1.18 (P25) to 3.87 (R91). They are distinguished from the series IV flows, which also show high incompatible element contents, by different ratios of those elements, in particular TiO₂/P₂O₅ (see Fig. 6.2) and Ti/Zr (Fig. 5.12). The two flows R 94 and R 95 are separated from series V lavas in Figure 5.3 (TiO₂). These two flows show analyses similar to some of the dykes, and have been included with the dykes in all subsequent plots. The differences between the lava series and the dykes suggests that few, if any of the dykes were feeders to the lavas, and the dykes thus sample a distinct magma type, which existed contemporaneously at least with the series V magma due to the interbedding of R94 and R95 with the series V flows.
5.1.4 Rare-Earth Element Patterns

Thirteen samples were analysed by Instrumental Neutron Activation Analysis (INAA) to determine REE's, Hf, Ta and Th. These consisted of one Alona Bay flow and twelve Mamainse Point flows, including the dyke-related flow R95. Results are presented in Appendix II (Tables AII.2 and AII.3). When plotted on Masuda-Coryell chondrite normalized plots, three types of patterns can be distinguished:

**Type A** (Fig. 5.5): a stepped pattern, marked by flat to slightly inclined LREE's and a marked LREE/HREE enrichment. \((\text{La/Sm})_N\) varies from 1.02 to 1.47, and \((\text{Sm/Lu})_N\) from 1.70 to 3.38. This pattern is present in lavas from Alona Bay (R105), series I (R14, R19), series IV (R67, R72, R78) and one of the series II flows (R28).

**Type B** (Fig. 5.6): a regularly inclined pattern with moderate LREE enrichment. \((\text{La/Sm})_N\) is about 1.45 and \((\text{La/Lu})_N\) 2.40. This pattern is found in flows from series V (R93) and series II (R37). The latter shows higher La, Ce and Nd values compared to R93, values which deviate from the good covariance with TiO₂ found for other samples (see Fig. 6.16) and which may reflect the effects of alteration (see 4.3.5).
Figure 5.5 Type A REF Pattern

Estimated analytical uncertainties shown on sample page 77.
Figure 5.6 Type B REE Patterns

Estimated analytical uncertainties indicated on both samples.
Type C (Fig. 5.7): a flat to slightly U-shaped pattern with \((\text{La/Sm})_N\) about 1.40, \((\text{La/Lu})_N\) about 1.30 and \((\text{Sm/Lu})_N\) about .9. This pattern is shown by flows from series III (R57, R63). R51 is similar to other series III flows except for the LREE. This sample also shows deviations from other series III flows with respect to other elements, e.g., Zr, Y, Nb, U, etc., which are believed to reflect crustal contamination (see 6.3).

Sample R95, a flow similar in chemistry to the dykes, shows a different pattern to any of the normal flows (Fig. 5.8). It shows a fairly LREE-enriched pattern with \((\text{La/Lu})_N\) of 6.54. This again suggests that the dykes were different to any of the lava series in the Mamainse Point sequence.

5.1.5 Comparison with Previous Analyses

Annells (1973) presented analyses for major- and trace-elements for twenty-nine mafic flows and three dykes from the Mamainse Point area. The sampling was too small, however, for him to recognize the existence of more than one lava series, and he consequently treated the whole data set as a single group. Comparison of his data to that presented here, shows good agreement (see Fig. 5.9), which may be expected as often
Figure 5.7 Type C REE Patterns

Estimated analytical uncertainties indicated for all samples.
Figure 5.8  REE Pattern for Lakes

Estimated analytical uncertainties as indicated.
Figure 5.9  Comparison of Sample Analyses from this Work and from Annells (1973), for selected immobile elements

Circles  This Work
Triangle  Annells (1973)

Half filled symbols are transitional basalts (dyke-like flows).
the same outcrops were sampled. Differences in stratigraphic trends for some elements result from variability due to alteration or systematic differences between analytical methods and laboratories. The near absence of series II samples in Annells' data probably reflects his avoidance of the altered flows in this heterogeneous zone.

Annells also failed to recognize the dykes as being distinctive in composition, again a function of numbers of samples. Of interest here are his lava samples 604, 707, and 725 (see Table 5.1). 707 is from the same outcrop area as R94 and R93, while 725 is from further east, possibly along strike. They both have similar composition to R94 and R95, confirming the existence of this dyke-like magma in an extrusive form. 604 was collected from about the middle of series III, but differs markedly from series III analyses, either those presented here or their equivalents given by Annells (see Fig. 5.9). The low TiO$_2$/P$_2$O$_5$ (5.9) and Ti/Zr (68) suggest affinities to the dykes and, if this sample really is extrusive, may point to the long-term existence of the dyke magma-type.

Annell's analyses are thus complementary to those presented here, and can be interpreted the same way. However, differences in analytical techniques, particularly for trace-elements, prevent the inclusion of this data in the rest of the study.
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<th>This Work</th>
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<td>Cr</td>
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5.2 CLASSIFICATION OF THE LAVAS AND DYKES

5.2.1 Norm Calculations and Classifications

Although ideally the classification of volcanic rocks, like plutonic rocks, should be based on modal mineralogy (Streckeisen, 1979), this is often not feasible because of microcrystalline or glassy textures. It has thus become customary for petrologists to use chemical criteria in the classification of volcanic rocks. In particular, the rock analysis can be recalculated to a norm as an estimate of the ideal mineralogy of the rock. The normative minerals can then be used in a classification scheme such as that of Yoder and Tilley (1962) for mafic volcanics. Such a procedure is appropriate for the Mamainse Point Formation which show relict glassy textures.

However, the application of the norm calculation to the analyses of the Mamainse Point Formation lavas and dykes is not without difficulty. These rocks have suffered variable alteration, at least with increases in the oxidation of iron and the addition of volatile components, and probably in the mobility of some other components. If the norm is to mean anything, it should be calculated on the original chemistry. Thus corrections have to be made to the chemical analyses. Realistic adjustments, however, can only be made for the
oxidation ratio of iron and the volatile content. Other mobile components such as SiO₂, Na₂O, K₂O, CaO, etc., can only be corrected by use of complex procedures such as suggested by Beswick and Soucie (1978), raising doubts as to the meaning of the norm following from such extensive numerical manipulation.

The Fe₂O₃/FeO ratio of an analysis has a serious effect on the norm calculation (Le Maitre, 1976) and its correct adjustment can be critical. Various procedures have been suggested in the literature (e.g. Coombs, 1963; Irving and Baragar, 1971; Hughes and Hussey, 1976; Le Maitre, 1976) but no universally accepted practice has yet emerged. The present author has elected to follow the procedure of Irving and Baragar (1971) —

\[ \% \text{Fe}_2\text{O}_3 = \% \text{TiO}_2 + 1.5 \] excess Fe₂O₃ being converted to FeO.

This correction is perhaps the most widely used in Canada and the differences compared to other procedures are expected to be small, especially in relation to the difference between corrected and uncorrected analysis.

Both CIPW and Barth-Niggli norm calculations determine anhydrous minerals and thus ignore H₂O + CO₂, however, is calculated as calcite. This can have an effect on the other normative minerals by reducing the CaO available to calculate An and Wo. From petrographic evidence and inspection of the
raw analyses (4.3.3) it seems likely that at least some, if not all, of the CaO present in modal calcite was derived from the alteration of original minerals, i.e., it was already present and not brought in with CO₂ in the fluid phase. Thus, in an attempt to take account of this, CO₂ was ignored in the norm calculations.

The effects of these two corrections on the norm can be seen in Table 5.2. CIPW norms have been calculated for five samples before and after applying the corrections. The original, uncorrected norm can be seen to be Co-, Hem- and Qz-bearing in most cases. Di is usually absent. The iron correction results in elimination of Hem and a reduction of Qz, with an increase in Fs (or Fa). The omission of CO₂ results in more CaO being calculated as An and Wo. This further reduces or eliminates Qz and Co and generates Di and O1 in the norm.

The resulting norm (C) is more typical of mafic volcanics and, although there is some evidence that individual samples still are anomalous due to under- or over-corrections, as a whole the norms are a reasonable estimate of original compositions. Abbreviated CIPW norms, listing those minerals most used in classification of mafic rocks, are tabulated in Appendix III. Using the scheme of Yoder and Tilley (1962) the majority of the Mamainse Point Formation classifies (using norm C) as olivine-tholeiite, except for the series IV lavas and
### Table 5.2 Effect of Corrections on CPW Norms

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A = Uncorrected  
B = Fe corrected, CO₂ included  
C = Fe corrected, CO₂ omitted  

All calculations summed to 100% anhydrous.
the dykes which classify as quartz-tholeiites. The absence of
Ny and the presence of Ne, Co and Wo in the norms of anomalous
samples, reflects more extreme alteration which has not been
properly corrected.

The normative An content of plagioclase is not listed
in Appendix III, as it is subject to uncertainty due to
uncorrected Na- and Ca-metasomatism. It shows a range of 30-98.
most of the rock falling in the narrower range 40-62,
more typical for mafic rocks.

5.2.2 Elemental Classification Schemes

5.2.2a Classical Schemes

Several chemical classification schemes have entered
into regular petrological practice. These entail a binary
or ternary plot of selected elements or combinations of
elements, e.g. the alkali-silica diagram (Kuno, 1956), MgO vs
Al$_2$O$_3$/SiO$_2$ (Murata, 1960), the AFM triangular plot. They are
of limited or doubtful application to rocks which have
suffered variable alteration involving mobility of cations
such as Na$_2$O, K$_2$O, CaO, SiO$_2$, as well as hydration and
carbonation. Some results of this are seen in the AFM plot
in Figure 5.10 where addition of alkalis has resulted in
displacement of points towards the A-apex away from an original
Figure 5.10  AFM Plot for Mamainse Point Formation Flows and Dykes

Series I to V as defined in Figure 5.3

The dividing line between tholeiitic (Th) and calcalkaline (Ca) basalts is that of Irvine and Baragar (1971).
smooth trend. However, the original trend can still be
discerned, running from the M- to the F-apex, suggesting the
rocks are tholeiitic in character, agreeing with the
petrographic and norm-based conclusions.

5.2.2b Immobile Element Schemes

Studies in metamorphosed terrains and on altered
ophiolitic rocks in the last decade have resulted in the
promulgation of new classification schemes for basaltic rocks
based on minor- and trace-elements which are less susceptible
to alteration. These schemes aim to discriminate both the
petrochemical character of the basalt and the petroTECTONIC
environment of eruption.

Floyd and Winchester's (1975) plot of Nb/Y vs Zr/P₂O₅
(Fig. 5.11) shows the Mamainse Point Formation flows to be
tholeiitic in character. The dykes, however, show a tendency
to be transitional to alkalic. Similar results are found in
the TiO₂ vs Zr/P₂O₅ plot (Fig. 5.12). It is not possible on
these diagrams to discriminate the tectonic environment of
generation of the volcanics.

Mamainse Point and Alona Bay flows define a good
linear trend in the TiO₂-K₂O-P₂O₅ plot (Pearce et al., 1975),
which crosses the oceanic-nonoceanic dividing line (Fig. 5.13).
Figure 5.11. Nb/Y vs Zr/P2O5

Symbols as in Figure 5.10
Boundaries after Floyd and Winchester (1975)

Solid lines        Continental
Dotted lines       Oceanic
Alk                Alkalic basalts
Th                 Tholeiitic basalts
Figure 5.12  TiO$_2$ vs Zr/P$_2$O$_5$.

Symbols as in Figure 5.10

Boundaries after Floyd and Winchester (1975)

Solid lines    Continental
Dotted lines   Oceanic

Alk            Alkaline basalts
Th             Tholeiitic basalts
Figure 5.13  \( \text{TiO}_2 - \text{K}_2\text{O} - \text{P}_2\text{O}_5 \)

Symbols as in Figure 5.10

Upper plot  Series I, II, Alona Bay and the Dykes
Lower plot  Series III, IV and V

Oceanic/Nonoceanic boundary after Pearce et al. (1975).
Reference lines are of constant \( \text{TiO}_2/\text{P}_2\text{O}_5 \) ratios.
A. Oceanic
B. Non-Oceanic
This trend is interpreted as resulting from the effects of K-metasomatism during alteration which moves points out of the oceanic field towards the K₂O-corner, without affecting the TiO₂/P₂O₅ ratio. This is seen most effectively in the lower lavas (series I, II and III and the Alona Bay flows), whereas the less altered upper lavas (series IV and V) remain in the oceanic field. The dykes form a distinct trend with a different TiO₂/P₂O₅ ratio to the flows. It is not clear if the dykes are oceanic in character or not.

The Ti-Zr-Y plot (Fig. 5.14) of Pearce and Cann (1971, 1973) further suggests an oceanic affinity for most of the lavas. The lowest lavas (series I and II and the Alona Bay flows) show scatter but appear to be transitional between within-plate basalt (WPB) and ocean-floor (OFB). The upper lavas (series III - V) are more clearly OFB-like. The ambiguity in classification of the lower lavas reflects the ambiguity in the tectonic environment in which they developed. It is probably to be expected that in an immature rift such as the Keweenawan, the initial flows should show some characteristics of WPB, becoming more OFB-like as the rift evolves and simatic crust is created. Such behaviour is also seen in the lavas of the Tertiary Volcanic Province of Baffin Bay and Western Greenland (Clarke, 1977). Some of the ambiguity also results from the choice of samples used to erect the boundary
Figure 5.14. Ti - Zr - Y

Symbols as in Figure 5.10

Upper plot  Series I, II, Alona Bay and Dykes
Lower plot  Series III, IV, and V

Boundaries are after Pearce and Cann (1971, 1973)

LKT Low potassium (Island Arc) tholeiites
WPB Within plate basalts
CAB Calc-alkaline basalts
OFB Ocean floor basalts (plus some low potassium tholeiites)
lines in the diagram. Samples from DSDP leg 49 (IPOD 1) show closely defined fields for each unit, but many fall outside the limits of the MORB field (Tarney et al., 1979). Dykes from Mamainse Point are distinct from the flows, plotting as WPB, further attesting to the complexity and transitional nature of such an immature rift.

5.2.3. Conclusions

Flows from the Mamainse Point and Alona Bay areas are tholeiitic in character, being predominantly olivine-tholeiites except for series IV flows which are quartz-tholeiites, representing more advanced fractionation. The immobile elements confirm the tholeiitic character and suggest an affinity with oceanic rocks in an environment transitional between within-plate and ocean-floor, in agreement with geological and geophysical evidence (see 2.1).

The dykes which intrude the Mamainse Point Formation are quartz-tholeiites with within-plate affinity. They also show some alkaline characteristics, distinguishing them from the flows and are hence termed transitional basalts. They must represent a different magma type and are not feeders for the lavas.
5.3 COMPARISON TO OTHER BASALT SUITES

5.3.1 Introduction

Comparison of the Mamainse Point flows and dykes with other rocks is, of course, implicit in the discriminant diagrams used above, e.g., Figure 5.14, but these graphical comparisons are limited to only small percentages of the total analyses. To allow comparison with other suites, average compositions for olivine-phyric (Alona - Bay and series I) and feldspar-phyric (series II, IV and V) flows have been calculated (Table 5.3). The series III flows have been separated from other feldspar-phyric flows because of their lower contents of Fe, Ti, P, Zr, Y, etc. An average for the dykes is also listed. The meaningfulness of these averages is limited due to the suppression of important petrochemical trends, the variable effects of alteration, etc. Also, comparison to average values from other areas is subject to limitations of sample sizes, etc.

5.3.2 Other Keweenawan Sequences

The Mamainse Point flows in general resemble other Keweenawan tholeiites (Table 5.4) with a tendency, particularly in the olivine-phyric group, to show higher MgO and FeO and
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¹ Major elements summed to 100% anhydrous
KEY TO TABLE 5:4

1. Weighted average Greenstone Flow (12) (Broderick, 1935)
2. Weighted average Kearsage Flow (7) (Broderick, 1935)
3. Average olivine-tholeiite, North Shore Volcanics (4) (Green, 1972a)
4. Plagioclase-phyric, olivine-tholeiite, North Shore Volcanics (1) (Green, 1972a)
5. Average quartz-tholeiite, North Shore Volcanics (4) (Green, 1972a)
6. Average Osler Formation, Shesheeb Bay (26) (Wallace, 1972)
7. Average ophitic olivine-basalt, Mamainse Point Formation, Michipicoten Island (5) (Annells, 1974)
8. Average alkalic basalt, Ely's Peak, Minnesota (4) (Kilburg, 1972)
9. Average alkali-olivine basalt, Kallender Creek Formation, Wisconsin (5) (Cooper, 1973)

Note: analyses 3 - 5 have Fe recalculated to give \( \frac{Fe^{3+}}{Fe^{2+}} = .25 \)
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lower $\text{Al}_2\text{O}_3$. Higher $\text{K}_2\text{O}$ values in the Mamainse Point flows probably reflect differences in alteration. The series III flows are more similar to other Keweenawan tholéiites except for lower $\text{TiO}_2$ and $\text{P}_2\text{O}_5$. Few analyses of other Keweenawan dykes are available for comparison with the Mamainse Point dykes. The latter appear, however, to be intermediate between the average Minnesotan quartz-tholeiite (col. 5) and the average alkalic basalt (col. 7 and 8) confirming their transitional nature.

5.3.3 Other Continental Basalts

The average compositions of other plateau basalt or continental intrusive provinces (Table 5.5, cols. 1-5, 8-12) show a range in values that encompasses those of the Mamainse Point flows. The feldspar-phric flows show fairly good comparison to the Seal Lake Group (col. 2) although having lower $\text{Al}_2\text{O}_3$ and MgO and higher CaO. It is very doubtful, however, if this can be taken as supporting any possible correlation as suggested by Baragar (1977) (see Fig. 2.3c). There is little similarity between the other Mamainse Point averages and the plateau basalts, or between the plateau basalt provinces themselves, perhaps indicating that each province possesses its own unique chemistry resulting from
KEY TO TABLE 5.5

1. Coppermine River Basalts (169) (Baragar, 1969)
2. Seal Lake Group (130) (Baragar, 1977)
3. Triassic of Nova Scotia (65) (Baragar, 1977)
4. Deccan Trap (10) (Sukheswalla and Poldervaart, 1958)
5. Drakensberg Basalt (Karoo), South Africa (4) (Walker and Poldervaart, 1949)
6. Average Continental Tholeiite (946) (Manson, 1968)
7. Average Continental Basalt (75) (Pearce, 1976)
8. Tasmania Mesozoic Tholeiites (Edwards, 1942)
10. East North America, High-Fe Qz-Tholeiite (Weigand and Ragland, 1970)
11. East North America, Low-Ti Qz-Tholeiite (Weigand and Ragland, 1970)
12. East North America, Olivine Tholeiite (Weigand and Ragland, 1970)
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<td>5.98</td>
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<td>.95</td>
<td>.91</td>
<td>.64</td>
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<td>.15</td>
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<td>-</td>
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<td>10.4</td>
<td>12.5</td>
<td>10.6</td>
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</table>
differences in petrogenetic processes - fractional crystallization, partial fusion, etc.

The eastern North America dykes (cols. 9-12) developed in an extensional regime that led to the opening of the North Atlantic Ocean; a rifting environment similar to the Keweenawan. There is little similarity in any of the average analyses, however, the Mamainse Point sequence generally showing higher TiO₂ (except series III), and lower SiO₂ and CaO.

There thus seems to be a lot of variability in the analyses of continental basalts but, although the Mamainse Point rocks show little direct comparison to any of the other provinces, they do fall within the general range of compositions. Compared to Manson's average continental tholeiite (col. 6), the Mamainse Point rocks show lower Al₂O₃ and higher FeO⁴ TiO₂ and MgO, with perhaps the series III flows being closest in composition. The dykes show higher SiO₂ and lower CaO than Pearces' average continental basalt, but otherwise compare favourably. This latter average includes tholeiitic as well as alkaline rocks and as such should compare to transitional basalts such as the dykes, but show marked differences to the strict tholeiites.
5.3.4 Oceanic Basalts

Some comparison to oceanic basalts has already been implied in the petrologic classification schemes above (5.2.2). The major-element variations in ocean-floor basalts are also apparently controlled by an olivine-plagioclase cotectic (Shido et al., 1974; Bryan, 1979) similar to the Mamainse Point sequence. The averages listed in Table 5.6 show similar characteristics in all the ocean-floor basalts. Higher K<sub>2</sub>O in the Mamainse Point flows may partly be due to alteration processes. The olivine-phryic rocks also show higher MgO and lower Al<sub>2</sub>O<sub>3</sub>, and the series III flows lower TiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub>. Better agreement is found with the intra-plate basalts, with the exception of TiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub>. The dykes also show similarities to those with lower MgO and CaO and higher SiO<sub>2</sub> perhaps reflecting more advanced fractionation.

5.3.5 Trace-Element Data

Comparisons can be made of the REE patterns in the Mamainse Point Formation with other suites, continental and oceanic. Basalts from the North Shore Volcanics of Minnesota show LREE-enriched patterns with fairly constant slope (Fig. 5.15a). These are slightly more enriched than the type B, Mamainse Point patterns, but lack the stepped
KEY TO TABLE 5.6

1. Mid-Indian Ocean-ridge basalts (68)

2. Intra-plate ("basin") ocean-floor basalt, Indian Ocean (51)

3. Aseismic ridges, seamounts and intra-plate "hot spots",
   Indian Ocean (48). 1-3 from Subbarao et al. (1979) after
   sources in Kempe (1975)

4. Alkali basalts from islands in the Indian Ocean (42)
   (Engel et al., 1965)

5. Atlantic Ocean basalt glass (206) (Melson et al., 1976,
   Bryan et al., 1976)

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

7. Average ocean-floor basalt (94) (Cann, 1971)
<table>
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</table>
pattern of type A. None of the published Minnesotan basalt analyses are as flat as the type C or as enriched as the transitional basalt.

LREE-enriched patterns are typical of other continental tholeiites, many having \((\text{La/Sm})_N > 1.4\) (Leeman, 1977b). Plateau basalts from the Deccan (Fig. 5.15b) and other provinces (Fig. 5.15c) exhibit good linearity, similar to the North Shore Volcanics, but are more enriched than the Mamainse Point flows with none of them showing the stepped type A pattern. The transitional basalts, however, are similar to the Dhandhuka basalts (Fig. 5.15b), although more enriched than other patterns. REE data from the eastern North America Mesozoic intrusions (Fig. 5.16a) show less enriched patterns which compare favourable with the Mamainse Point types B and C. The more LREE-enriched patterns, however, show \((\text{La/Sm})_N\) higher than the type A patterns. Stepped patterns are found in the tholeiitic Fairy Bridge magma-type in the Tertiary Hebridean province (Fig. 5.16b) where they occur with more LREE-enriched and LREE-depleted types.

Basaltic rocks from oceanic islands and aseismic ridges, like continental basalts, usually show LREE-enriched patterns (Fig. 5.17). They also commonly show good linearity, but may have flattened LREE's, e.g., Mauna Loa and DSDP site 254 basalts (Fig. 5.16c, 5.16d), like the Mamainse-type A
Figure 5.15  REE Patterns of Selected Continental Basalts

a) Keweenawan volcanics of the North Shore Group, Minnesota
   (from Haskin, 1979)

b) Average patterns for three rock-types from Dhandhuka
   Borehole, Deccan basalts, India
   \[ B = \text{Basalts} \]
   \[ TPB = \text{Three-phenocryst basalts} \]
   \[ PB = \text{Picrite basalt} \]
   (from Alexander, 1979)

c) Selected plateau basalts
   Average Deccan trap, Mahabaleshwar area
   (Nakamura and Masuda, 1971)

   Columbia plateau basalts (Schmitt and O'Leary, 1964)
   Siberian platform (Balashor and Nestereenko, 1966)
   Deccan basalt (Frey et al., 1968)
   (Figure from Nakamura and Masuda, 1971)
Figure 5.16 REE Patterns from Rifted Continental Margin Regimes

a) Eastern USA (Philpotts and Schnetzler, 1968; Ragland et al., 1971)

Upper
1. Olivine-normative diabase
2. Low Ti, quartz-normative diabase
3. High Ti, quartz-normative diabase
4. Palisade sill

Lower DSDP, Leg 11 (Bryan et al., 1977)
1. Site 100
2. Site 105

b) Skye, NW Scotland (Matley et al., 1977)

□ Transitional basalts, Skye Main Lava Series
★ Tholeiites, Fairy Bridge magma type
● High calcium, low alkali tholeiites, Preshal Mhor magma type
Figure 5.17 REE Patterns from Within-Plate, Oceanic Regimes

a) Hawaii summit lavas (from Leeman et al., 1977)

- Mauna Loa
- Kilauea

b) Ninetyeast Ridge, Indian Ocean (from Subbarao et al., 1979)
(a)

(b)
patterns. Mid-ocean ridge basalts are usually characterized by LREE-depleted patterns (e.g., leg 11, Fig. 5-16a) which contrast markedly with continental basalts. Some ridge segments, however, have been shown to be anomalous displaying LREE-enriched patterns similar to the oceanic islands, or transitional between the two types (Sun et al., 1979; Wood, 1979a). A spectrum of results may even be found within one place on the ridge, e.g., 36°N, Mid-Atlantic Ridge (411, 413 Fig. 5.18b) which range from LREE-enriched (413 - 1) to LREE-depleted (413 - 2). Some sites even show stepped patterns as in Mamainse Point (e.g. 408, 607 - 4, Fig. 5.18a).

The REE-patterns found in Mamainse Point rocks are LREE-enriched to varying degrees similar to continental, oceanic island, or enriched MOR basalts. The lavas differ, however, in being less enriched than most continental rocks and also some of them showing flat LREE's to give a stepped pattern (type A). The suites most similar are the eastern North America Mesozoic intrusions and the Tertiary Hebridean Province, both of which represent dilation and break-up of continental crust during initial stages of the opening of the Atlantic Ocean. Similar patterns can also be seen in some modern Mid-Atlantic Ridge basalts.

Other trace-elements are more difficult to compare to other basaltic suites. Often suitable data has not been
Figure 5.18  REE and Nb-Zr Data, Mid-Atlantic Ridge (from Wood et al., 1979b)

a) REE's from 63°N

b) REE's from 36°N (411, 413) and 45°N (410)

c) Nb vs Zr for DSDP Leg 49 Basalts (36°N, 45°N and 63°N) and representative 22°N basalts (Legs 45 and 46). Data from unit 410-2 (arrowed) are plotted half scale.
published or is only available for elements such as Rb, Ba, and Sr, which have been subject to alteration, ruling out meaningful comparisons. Nevertheless, oceanic basalts have been extensively studied since the initiation of the Deep Sea Drilling Project, and a lot of data are available. As with the REE's, the incompatible elements show a range of contents and ratios (Fig. 5.18c) which envelope the Mamainse Point rocks.

Several authors have suggested a subdivision of mid-ocean ridge basalts into normal (N), transitional (T) and enriched (E) types based on normalized trace-element patterns (Sun et al., 1979, Wood, 1979a). Figures 5.19 - 5.24 present the Mamainse Point data normalized to Wood's estimated primordial mantle (Table 5.7). In general, the patterns show a decrease from Ta + Nb to Lu. U and Th values suggest a decreasing trend from Nb to Rb also, but this is not very clear because of the effects of alteration on K, Ba and Rb.

Compared to the oceanic rocks, the Mamainse Point lavas are similar to E- and T-type tholeiites, e.g., Askja, Iceland, Figure 5.25b. The dykes are more enriched and closer to E-type alakaline and transitional basalts.
<table>
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<td>Ba</td>
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<td>Th</td>
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<tr>
<td>U</td>
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<td>K</td>
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<td>Tm</td>
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<td>La</td>
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<tr>
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<tr>
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<tr>
<td>Yb(^1)</td>
<td>0.422</td>
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<tr>
<td>Lu(^1)</td>
<td>0.072</td>
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</table>

\(^1\) Estimated by the author, based on relative chondritic pattern for the REE's.
Figures 5.19 to 5.24 Incompatible Element Patterns for the Mamainse Point Rocks

\[(EL)_{PM} = \text{element abundance normalized to primordial mantle (Wood, 1979; see Table 5.7)}\]

Ranges of abundances are indicated for elements which were analysed in all samples of the series.

Dashed lines (Rb and Nb) indicate some samples have abundances below the detection limit.
Figure 5.25  Selected Alakalic Basalts, E-Type and N-Type MORB
(after Wood, 1979a)
A. Melilitite 2327 (○) and basanite 3679 (★), both from southeastern Australia (Frey and others, 1978); alkali basalts ISL 79 (□, T-Z (x), and Ch30 (△) from Eldgíð (Iceland), Terceira (Azores), and Etta Ale (Afar; Fleur and Joron, 1975), respectively; representative MORB from lat 63°N (•) and lat 25°N (○) in the North Atlantic Ocean (Wood and others, 1979; Joron and others, 1978); average N-type MORB (★).

B. E-type MORB from lat 45°N (○) and lat 36°N (✓) in the North Atlantic Ocean (Wood and others, 1979); tholeite ISL 28 (★) from Askja, Iceland; N-type MORB (○) from the Faeroe-Iceland Ridge.
5.4 CONCLUSIONS

Mamainse Point flows were olivine- and quartz-normative tholeiites similar to other Keweenawan lavas. Despite the chemical readjustment during burial metamorphism, the lavas show variation of chemistry with stratigraphy, producing a step-wise cyclicity. This suggests that the sequence underwent fractionation with either periodic recharge of the magma chamber or successive tapping of new magma chambers. Trace-element data point to the lavas evolving in a petrogeologic environment transitional between within-plate and ocean-floor. REE-patterns are LREE-enriched, and show similarities to patterns found in other tensional regimes that developed during initiation of ocean development, or in anomalous sections of modern ocean ridges.

The dykes are quartz-tholeiites appearing to have compositions transitional to alkalic basalts. Trace-element data suggest they are of within-plate affinity although it is not clear whether continental or oceanic. REE patterns are similar to other continental basalts or oceanic islands. It is thus doubtful that the dykes were feeders for the flows, although two flows (R94 and R95) share similar chemistry. The dykes point to the existence of two different magma-types in the area, at the same time, a situation also reported in the
modern oceans (Johnson, 1979), the Tertiary Hebridean Province (Mattey et al., 1979; Beckinsale et al., 1978) and the eo-Appalachian Rift (Kumarapeli, 1978).
CHAPTER 6

PETROGENESIS OF THE MAMAINSE POINT FORMATION

"What stuff 'tis made of, whereof it is born, I am to learn."

Merchant of Venice (Act I, Scene 1)

6.1 FRACTIONAL CRYSTALLIZATION

6.1.1 Introduction

The field and petrographic evidence presented above (Chapters 2 and 3) show that the Mamainse Point sequence passes from basal olivine-phyric to overlying feldspar-phyric flows. The presence of even small proportions of olivine and plagioclase phenocrysts points to possible fractional crystallization before eruption of the lavas. The quartz-normative series IV flows also suggest extensive olivine fractionation of the olivine-tholeiites took place (O'Hara, 1968). Fractionation is again suggested by the stratigraphic
variations in major- and trace-element chemistry, although the breaks and steps in the sequence point to a more complex model than one simple fractionating magma-chamber. Either periodic recharge of the chamber or successive tapping of more than one chamber is suggested.

6.1.2 Major-Element Evidence

6.1.2a

Most of the commonly used petrogenetic indices of differentiation rely on combinations of major-elements, in particular SiO₂, CaO, Na₂O and K₂O. These elements have suffered alteration and the application of such petrogenetic indices to the Mamainse Point Formation is limited. Similarly norms have to be treated with care, even after making suitable corrections for oxidation of iron and addition of volatiles (see 5.2.1). However, some information is still retained, as seen in Figure 6.1 in which some of the samples plot on or close to the olivine-plagioclase cotectic. Some of the olivine-phyrstic samples plot within the olivine field, perhaps due to the addition of cumulate olivine.

6.1.2b

Certain of the major- and minor-elements appear to be relatively immobile and to retain coherent variation patterns.
Figure 6.1 Di - Ol - Plag Face of the Normative Basalt
Tetrahedron

Note:  Hyp is recalculated to Ol + Qz

Dotted lines are the pseudo-univariant equilibria in the
natural basalt system Oliv - Cpx - Plag - Qz (Clarke, 1970)

Symbols (as in Figure 5.10, etc.)

- Series I
- Series II
- Series III
- Series IV
- Series V
- Alona Bay
- Transitional Basalts
TiO₂ and P₂O₅ are examples of this behaviour (Fig. 6.2). The Mamainse Point lavas define a good linear trend with a constant ratio of 10. The dykes may also show a linear trend, although with a smaller TiO₂/P₂O₅ of 7. The constancy of this ratio in the lavas shows that both Ti and P are behaving incompatibly and not being removed by crystal fractionation. This suggests that Ti-bearing phases, such as clinopyroxenes or Fe-Ti oxides, are not involved in the fractional crystallization. Separation of clinopyroxene from the melt in the magma chamber would result in the removal of Ti but not P, thus causing a gradual change in the TiO₂/P₂O₅. Clinopyroxene never occurs as phenocrysts within the flows, but usually as ophitic overgrowths or interstitial granules, pointing to its probable post-extrusive formation.

P₂O₅ has been proposed as a good index of differentiation for basaltic rocks due to its incompatibility with the normal fractionating minerals (Anderson and Greenland, 1969). By analogy TiO₂ can be used for the Mamainse Point rocks, with increasing TiO₂ being indicative of increasing fractionation in a series. This procedure has been followed in this section, TiO₂ being preferred to P₂O₅ as it enjoys better analytical precision, particularly for the lowest contents observed.

FeOₜ (total Fe as FeO) shows a good positive linear trend with TiO₂ on a log-log plot, although not at constant
Figure 6.2 $P_2O_5$-TiO$_2$ Variation Diagram

Symbols as in Figure 6.1

Solid lines are lines of constant TiO$_2/P_2O_5$ ratio. Error bars on points near axes show the 2σ error estimated from the precision monitors (see Appendix I).
ratio (Fig. 6.3). This confirms the Fe-enrichment trend observed in the AFM diagram (Fig. 5.10). That Fe is, however, being removed in the fractionating assemblage is apparent in the non-unity slope of the trend, i.e. decreasing FeO/TiO₂ with increasing TiO₂, indicating a mafic phase such as olivine or chromite being present in all series. The displacement of the series III lavas from the other series may reflect differences in the Fe content of the parental magmas.

In contrast to FeO, Al₂O₃ only shows enrichment in the olivine-phryic (Aloha Bay and series I) and series III lavas (Fig. 6.4), with depletion in other series. This may suggest a difference in mineral proportions between more, and less plagioclase-dominant assemblages. Plagioclase is still required to be a part of even the olivine-phryic fractionating assemblage due to the decrease in Al₂O₃/TiO₂ with fractionation.

The relative behaviour of Al and Fe can be seen in Figure 6.5, which confirms the presence of plagioclase in all fractionating assemblages. The normalization to TiO₂ used in this diagram eliminates differential dilution effects due to variable addition of volatiles, etc., during alteration, and also yields the true relationship between the variables (Pearce, 1968). Each series can be seen to form a different trend in Figure 6.5b. The variation in slopes of these trends reflects the different proportions of olivine and
Figure 6.3  FeO₂⁻TiO₂ Variation Diagram

Symbols as in Figure 6.1.

Error bars on points near axes show the 2σ error estimated from the precision monitor (see Appendix I).
Figure 6.4  $\text{Al}_2\text{O}_3 - \text{TiO}_2$ Variation Diagram

Symbols as in Figure 6.1

Error bars on points near axes represent the $2\sigma$ error estimated from the precision monitor (see Appendix I). Trend lines for each series are labelled.
Figure 6.5 $\text{Al}_2\text{O}_3/\text{TiO}_2$ vs $\text{FeO}_x/\text{TiO}_2$

a) Data points. Symbols as in Figure 6.1. Effect of olivine and plagioclase fractionation are indicated by the labelled arrows.

b) Interpretation, with labelled trend lines for each series.
plagioclase in the fractionating assemblages. The variation in position of the trends may be due to differences in the composition of parental magmas, which later, in turn, result from differences in primary magma composition and possible unsampled fractionation events. The differences are also seen when Al and Mg are compared (Fig. 6.6), although the slight mobility of MgO results in some anomalous samples. The olivine-phyric samples (series I and Alona Bay) show the combined effects of fractional crystallization and variable addition of cumulate olivine (Fig. 6.6b).

The plot of molar MgO and FeO allows comparison with the melting models of Hanson and Langmuir (1978) (Fig. 6.7). All the samples fall outside the field of possible mantle melts. Thus, none of them can be considered primary and all have undergone some degree of fractionation. This conclusion holds even allowing for the difference between the use of total Fe in the samples instead of FeO s.s. in Hanson and Langmuir's work. Making reasonable allowances for Fe₂O₃ in the samples would move the data points to the left by 15-20% at most, still outside the field of permissible melts. This plot also illustrates the usual J-shaped fractionation patterns for tholeiites and the displacement of some olivine-phyric samples due to the addition of cumulate olivine.
Figure 6.6 $\text{Al}_2\text{O}_3/\text{TiO}_2$ vs $\text{MgO}/\text{TiO}_2$

a) Data points. Symbols as in Figure 6.1
Effects of olivine and plagioclase fractionation are indicated by the labelled arrows.

b) Interpretation, with labelled trend lines for each series. The effects of olivine accumulation on the series I flows are also shown.
Figure 6.7 Molar MgO - FeO Variation Diagram

Symbols as in Figure 6.1

Field of model mantle melts from Hanson and Langmuir (1978). Fractionation trend lines for each series as shown are solid lines and labelled. The effect of olivine accumulation on olivine-phyric flows is also indicated.
6.1.2c

Variation of the major- and minor-elements Al, Fe, Mg, Ti and F thus shows that the Mamainse Point Formation lavas have suffered crystal fractionation of olivine-plagioclase assemblages. No clinopyroxene appears to be involved. Each of the recognized series shows slight differences in starting compositions and proportions of fractionating phases, reflecting differences in primary melt compositions coupled with differences in pressure, temperature, etc. This may indicate that more than one magma chamber was operative during formation of the lava pile.

The actual proportions of the crystallizing phases cannot be calculated without making assumptions about their compositions. Due to the lack of controls, such as compositions of fresh phenocrysts, etc., this has not been attempted at this stage.

6.1.3 Trace-Element Evidence

6.1.3a The Transition Metals Ni, Cr and Co

The trace-elements Ni, Cr and Co are very sensitive to fractional crystallization of mafic phases, such as olivine, pyroxene and spinel (chromite), being rapidly depleted, whereas they vary very little during partial melting of mantle sources.
(Minster and Allègre, 1978; Bougault et al., 1979). Indeed, the Ni and Cr content of a flow has been used as one of the geochemical criteria suggestive of possible primary mantle melts (Bender et al., 1978). All the feldspar-phyril flows contain 200 ppm Ni or less, indicating that fractionation has been operative, in support of the major-element evidence. Some of the olivine-phyril flows show higher Ni and Cr than expected for normal mantle melts and suggest that earlier formed Ni-rich olivine may have been incorporated into more fractionated magma.

The Ni-Cr plot (Fig. 6.9) shows fairly good correlation between the two elements, both being depleted with fractionation. The olivine-phyril series are discriminated from the feldspar-phyril series by higher Cr as well as Ni. The reference lines shown for each group of rocks demonstrate that the Ni/Cr is not constant during fractionation, but decreases steadily.

As shown above (6.1.2b), Ti behaves as a hygromagnatomophile element during differentiation of the Mamainse Point Formation lavas. Thus Ni-TiO₂ (Fig. 6.9) and Cr-TiO₂ (Fig. 6.10) plots can be used to estimate the bulk partition coefficients (D) for Ni and Cr for the various series (Treuil and Joron, 1976; Allègre et al., 1977). In turn, the proportions of fractionating phases can also be derived from these estimates, assuming appropriate mineral phases. Details of the procedure
Figure 6.8 Ni-Cr Variation Diagram

Symbols as in Figure 6.1

Reference lines for olivine-phyric and feldspar-phyric flows are shown. Error bars on points near axes show the 2σ analytical error estimated from precision monitors (see Appendix I).
Figure 6.9 Ni-TiO₂ Variation Diagram

Symbols as in Figure 6.1

Labelled fractionation trends shown for each series except II. Error bars on points near axes show 2σ analytical error estimated from precision monitors (see Appendix I).
Figure 6.10 Cr-TiO₂ Variation Diagram

Symbols as in Figure 6.1

Labelled fractionation trends are shown for each series except II. Error bars on points near axes show the 2σ analytical error estimated from precision monitors (see Appendix I).
are included in Appendix IV.

In both plots, all the series fall on trends of negative slope confirming the presence of a mafic phase like olivine in the fractionating assemblages. These trends are not fitted in any statistical sense and so the estimated $D$-values are subject to some uncertainty. However, this uncertainty is considered to be less than the uncertainties in the selected mineral-melt partition coefficients (Table 6.1) and thus will still allow semi-quantitative estimates, at least, of the fractionating assemblages to be made.

Series IV samples yield $\bar{D}_{Ni} = 4.4$ and series V lavas a value $= 2.7$. The series II flows split into two groups which are difficult to interpret due to the small number of samples involved. The olivine-phyric and series III flows do not show such good linear trends as the series IV and V, and are thus subject to more error in the estimates of $\bar{D}_{Ni}$. Their slopes appear to be slightly steeper than the other series suggesting a higher $\bar{D}_{Ni} = 5.6$. Series V flows yield a lower $\bar{D}_{Cr}$ of $= 1.6$ compared to $= 6.7$ for the other series. Again series II flows do not yield an easily interpretable pattern.

The estimated $\bar{D}_{Ni}$ values are lower than those determined for olivine under conditions similar to shallow-level fractionation ($10 - 29$ for $T = 1250 - 1100^\circ C$, Leeman and Lindstrom, 1978). This results from the diluting effect of plagioclase in the
fractionating assemblages. Higher proportions of plagioclase are indicated for series V than for series IV, and in turn, for series IV than for series I and III. $\delta_{Cr}$ estimates for all except the series IV lavas are higher than expected for olivine (Table 6.1). As clinopyroxene is apparently absent from the liquidus for these lavas, this Cr depletion must result from the presence of small amounts of chromite. A three-mineral liquidus assemblage is thus suggested for all the series.

To further constrain the calculations of the proportions of these three phases, a third element is required. Co would also be depleted by crystallization of olivine and chromite but not plagioclase. Its minor depletion during the fractionation of the Mamainse Point flows (Fig. 6.11) suggests a $\delta_{Co} = 1.2$ and implies that plagioclase must be the dominant phase in all assemblages.

The relative proportions of possible assemblages are tabulated in Table 6.1, and their calculated bulk partition coefficients compared to the estimates made above. The results demonstrate, at least semi-quantitatively, that all series probably had the same minerals present in their fractionating assemblages but that there were differences in their relative proportions. This supports the general findings of petrography and major-element variation. Better estimates of the fractionating mineral proportions will depend upon obtaining
Figure 6.11 Co-TiO\textsubscript{2} Variation Diagram

Symbols as in Figure 6.1

One fractionation trend is drawn for all the data points. Error bars on points near axes show the 2\sigma analytical error as estimated from precision monitors (see Appendix I).
### Table 6.1: Estimated Proportions in Fractionating Assemblages

<table>
<thead>
<tr>
<th>Series</th>
<th>Plag</th>
<th>Ol</th>
<th>Chrom</th>
<th>$D_{\text{Ni}}$</th>
<th>$D_{\text{Cr}}$</th>
<th>$D_{\text{Co}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>A</td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>I &amp; III</td>
<td>5</td>
<td>3</td>
<td>.075</td>
<td>5.1</td>
<td>5.5</td>
<td>6.3</td>
</tr>
<tr>
<td>IV</td>
<td>2</td>
<td>1</td>
<td>.030</td>
<td>4.6</td>
<td>4.8</td>
<td>6.6</td>
</tr>
<tr>
<td>V</td>
<td>4</td>
<td>1</td>
<td>.012</td>
<td>2.8</td>
<td>2.7</td>
<td>1.8</td>
</tr>
</tbody>
</table>

A Calculated bulk partition coefficients
B Estimates from Figures 6.9 - 6.11 (see Appendix IV)

Calculations were based on the following mineral-melt partition coefficients from Allègre et al. (1970)

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Cr</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>olivine</td>
<td>13</td>
<td>1.8</td>
<td>3.8</td>
</tr>
<tr>
<td>plagioclase</td>
<td>.26</td>
<td>.04</td>
<td>.1</td>
</tr>
<tr>
<td>chromite</td>
<td>16</td>
<td>600</td>
<td>40</td>
</tr>
</tbody>
</table>
statistically fitted trends for Figures 6.9 - 6.12. Removing some of the uncertainty in the mineral-melt partition coefficients; and also using elements that actively partition into plagioclase, but which, unlike Sr, are not subject to alteration effects.

6.1.3b. The Incompatible Elements Zr, Nb, Y, REE's, Th, U, Ta, Hf

Hygromagmatophile elements should plot on lines of unit positive slope on log-log plots against other hygromagmatophile elements (Allègre et al., 1977; see Appendix IV). A plot of Zr-TiO₂ in part confirms this relationship (Fig. 6.12) with many of the flows falling on a line of average Ti/Zr ≈ 34. Three series III samples (P51, P52 and P54) show deviation from this behaviour tending to define a trend almost at right angles to the rest of the flows. This effect is seen in some other elements, e.g., Y, Nb, REE's, and is discussed in more detail in 6.3. Hf show similar behaviour to Zr (Fig. 6.13).

Ti-Y relations are not so simple, however. In Figure 6.14a all the sample data are presented. They appear to fall on a line of slope ≈ 35°, suggesting that Y may have behaved less incompatibly than Zr and Ti, and was being extracted by a crystallizing phase such as clinopyroxene. This would appear to contradict the interpretation of Ni-Cr-Co data which suggest
Figure 6.12 Zr-TiO₂ Variation Diagram

Symbols as in Figure 6.1

Labelled lines are of average Ti/Zr ratio for the lavas and the dykes. Anomalous series III trend is indicated by the dotted lines (see Figure 6.3). Errors on points near axes show the 2σ analytical error as estimated from precision monitor (see Appendix 1).
Figure 6.13 Hf-TiO₂ Variation Diagram

Symbols as in Figure 6.1

Line of constant Ti/Hf ratio shown. Errors are points near the axes are the estimated 2σ errors from precision monitors (see Appendix I).
Figure 6.14  Y-TiO$_2$ Variation Diagram

$Y$ in ppm           TiO$_2$ in wt%

a) All data. Possible fractionation trend indicated by dashed line.

b) Series III, IV and V. Labelled lines are of constant Ti/Y. Anomalous series III trend is indicated by a dotted line (see 6.3).

Symbols as in Figure 6.1

Error bars on points near axes in (a) are the estimated 2σ analytical error based on precision monitors (see Appendix I).
only olivine-plagioclase-chromite assemblages. Upon close
inspection, however, it can be seen that each lava series does
indeed fall on a 45°-slope line, but that a different trend
and hence a different Ti/Y is found for each series. The
upper three series are illustrated in Figure 6.14b as examples
of this. Application of a statistical test of significance
to the mean Ti/Y for the three series suggests that they are
significantly different at the 99% confidence level (see Table
6.2). This supports the qualitative assessment made in Figure
6.14b. The olivine-phyric flows show some scatter, partially
due to analytical error in Y, and perhaps also to their non-
aphyric character, but generally fall on or close to the
series IV trend (Ti/Y = 400). Series II flows split into two
groups with some close to the series IV line and some at
higher Ti/Y (~ 500), although only a small number of samples
(6) make up this series, thus limiting interpretation.
Because fractionation produced no change in the Ti/Y of a
series, and all series have olivine-plagioclase-chromite
liquidus assemblages, it follows that the differing ratios must
reflect original characteristics of their respective parental
magmas and these cannot be derived from one another by shallow-
level fractionation.

A similar interpretation is possible for the Nb data
(Fig. 6.15) although considerably more scatter is seen here due
TABLE 6.2  STATISTICAL TEST OF SIGNIFICANCE FOR DIFFERENCES IN
TI/Y, AND TI/Nb BETWEEN SERIES III-V

<table>
<thead>
<tr>
<th></th>
<th>Ti/Y</th>
<th></th>
<th>Ti/Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>z</td>
<td>d</td>
<td>T.99</td>
</tr>
<tr>
<td>IV - V</td>
<td>22</td>
<td>4.40</td>
<td>2.51</td>
</tr>
<tr>
<td>V - III</td>
<td>11</td>
<td>5.83</td>
<td>2.72</td>
</tr>
</tbody>
</table>

H₀ : \( \bar{x}_1 = \bar{x}_2 \)
H₁ : \( \bar{x}_1 > \bar{x}_2 \)

\[ d = \frac{\bar{x}_1 - \bar{x}_2}{\sqrt{\frac{S_1^2}{n_1} + \frac{S_2^2}{n_2}}} \]

which is distributed similarly to Student's "t" with \( f \) degrees of freedom.

where \[ f = \frac{1}{\frac{u^2}{n_1 - 1} + \frac{(1 - u)^2}{n_2 - 1}} \]
\[ u = \frac{S_2^2/n_2}{S_1^2/n_1 + S_2^2/n_2} \]

\( T.99 \) are 99-percentile values for Student's t, with \( f \) degrees of freedom (from Appendix D, Spiegel, 1976).
Figure 6.15 Nb-TiO₂ Variation Diagram

Nb in ppm  TiO₂ in wt%

a) All data. Possible fractionation trends shown for the lavas and the dykes.

b) Series III, IV and V. Labelled lines are of constant Ti/Nb. Anomalous series III trend is indicated by the dotted line (see 6.3).

Symbols as in Figure 6.1

Error bars on points near axes in (a) are the estimated 2σ errors from precision monitors (see Appendix I).
to the higher analytical uncertainty in Nb. Some statistical support for the interpretation is provided in Table 6.2, where the Ti/Nb for the three series are tested.

The results from REE analysis of twelve tholeiite flows and one transitional-basalt flow are presented in Figure 6.16. The LREE's (La, Ce, Nd and Sm) in the tholeiites can be interpreted as defining single trends of constant ratio similar to those found for Zr. The scatter in the Nd data appears to be due to analytical uncertainties (see Appendix I). The irregular series III sample is R51 and is comparable to the behaviour it shows in Zr, Y and Nb. Eu defines a good linear trend of slope ~38° yielding an apparent δ-value of ~2. Depletion of Eu is to be expected during fractional crystallization of plagioclase-rich assemblages, although it is more apparent here than would be suggested by the Eu/Eu* determined in the samples (see Table 2.3). Interpreting the Eu anomaly as due to redox effects in the magma chamber, leads to an estimate of $f_{O_2} = 10^{-6}$ (Drake and Weill, 1975), very much higher than estimated for normal basaltic systems which show a range from $10^{-8.5}$ to $10^{-13.5}$ (Carmichael et al., 1974; Fig. 6.13; Sun et al., 1974). This estimate is thus very much in doubt, and without other constraints on temperature, etc., cannot be taken too seriously. The anomaly may, however, suggest that the fractionating plagioclase was fairly calcic
Figure 6.16 REE, Y-TiO$_2$ Variation Diagram

REE, Y in ppm \hspace{1cm} TiO$_2$ in wt%

All lines are of constant ratio except for Eu, which shows possible fractionation trend. Y-TiO$_2$ is the same as Figure 6.14b.

Symbols as in Figure 6.1, except
© Anomalous series III samples (see 6.3)

Error bars on points near axes are the estimated analytical errors from duplicates of W-1 or precision monitors (see Appendix I).

Linear regression for Eu - TiO$_2$ yields line of equation:
\[
\log \text{Eu (ppm)} = .793 \log \text{TiO}_2 (\%) - .042
\]
from which $\bar{D}_{\text{Eu}} = .207$

(see Appendix AIV.1)
An80 (Zielinski, 1975, Fig. 4), similar to the bytownite xenocrysts seen in sample R63 (see 3.1.2a above).

The HREE's (Tb, Yb and Lu) do not display easily interpretable trends, failing to fall on a single line. By analogy to Y, which behaves similarly to the HREE's (Herrmann, 1970), the latter could possibly be interpreted as lying on 45° lines, but with different lines for each series. The Y data for the upper three series are also shown in Figure 6.16 for comparison. Less data points are available for the HREE's than for Y, however, and although the Y interpretation is not inconsistent with the HREE data, the interpretation of the latter is still uncertain.

Ta, Th and U also show complex relationships with TiO2 (Figs. 6.17 and 6.18). Some of the complexity of the TiO2 plot is due to alteration effects. However, some coherence is retained and is revealed by considering each series separately (Fig. 6.18b). Each series appears to have originally fitted a line of unit slope although this is now obscured somewhat by enrichment of U in some samples during alteration. Each series may have had a different Ti/U ratio. Series II samples split into two groups as with other elements and have been omitted from Figure 6.18b. Ta can be interpreted similarly to Nb, to which it behaves similarly geochemically, although there are differences in the series II and Alona Bay samples. Th seems to divide into two
Figure 6.17 Ta, Th-TiO₂ Variation Diagram

Symbols as in Figure 6.1

All lines are of constant ratio.

Error bars on points near axes are estimated analytical errors from repeats of W-1 or precision monitor (see Appendix I).
Figure 6.18 U-TiO₂ Variation Diagram

a) All data for lavas

b) Fields occupied by the various series, except II, with possible fractionation trend of constant Ti/U ratio.

Symbols as in Figure 6.1

Error bars on points near axes show estimated 2σ errors from count data on precision monitor (see Appendix I).
groupings with the Alona Bay, series II and III samples having higher Ti/Th than the series I, series IV and series V samples. The limited data for Ta and Th makes further interpretation hazardous. A similar Th/U ratio is indicated in Figure 6.19 for all samples except series IV and V which have higher U contents and thus lower Th/U.

As would be expected, fractionation has resulted in increases in the absolute abundances of hygromagmatophile elements without changing their relative abundances within a series. Differences in element ratios between series must be a characteristic of the parental magmas and result from processes operating in the mantle during their genesis. The non-depletion of Y and HREE's during fractionation supports the major- and other trace-element data in ruling out clinopyroxene as a liquidus phase.

6.1.3c Other Trace-Elements

Most of the other trace-elements (Ba, Sr, Rb, Li, Cu) have been subject to alteration effects, particularly in the lower parts of the pile. Some of them may show fairly good trends for the upper series of flows, though, e.g. Zn (Fig. 6.20). Possible alteration effects are seen in the olivine-phyric flows producing a negative slope. A similar trend is also found in
Figure 6.19 U-Th Variation Diagram

Labelled lines are of constant Th/U ratio.

A Series I, II, III, Alona Bay and the dykes
B Series IV and V

Symbols as in Figure 6.1
Figure 6.20 Zn-TiO$_2$ Variation Diagram

Lines represent possible fractionation trends from the series III flows and the other flows.

Symbols as in Figure 6.1

Error bars on points near axes are the estimated 2σ analytical errors based on precision monitors (see Appendix I).
some of the series III flows. Unaltered series III and series IV and V flows, however, show positive slopes which compare to the variation of FeO$_c$ (Fig. 6.3). Zn is also enriched in series III compared to other series, as is FeO$_c$. The estimated 5-value for Zn from Figure 6.20 rules out the presence of sulphide phases during fractionation, but the absence of well-determined partition coefficients for Zn precludes further discussion.

6.1.4 Conclusions

Though geochemical data has survived the effects of alteration to allow the recognition of fractionating olivine-plagioclase-chromite assemblages, none of the samples can be considered primary magmas and all have suffered some degree of fractional crystallization. Differences in variations of Al, Fe, Mg, Si, Cr and Co can be ascribed to varying proportions of the liquidus phases. Immobile, incompatible trace-elements, although increasing in absolute abundances during fractionation, do not change in relative abundance. Differences in ratios cannot thus be ascribed to shallow-level fractionation, but must reflect original differences in the parental magmas.
6.2 PARTIAL MELTING OF THE MANTLE

6.2.1 Rare Earth Data

6.2.1a Introduction

During fractional crystallization of olivine and olivine-plagioclase assemblages, REE's behave as hygromagmatophile elements (see above 6.1.3). Consequently the only effect on the chondrite normalized pattern is to raise its position but not to alter its shape. By modelling of the REE-pattern shapes, it may thus be possible to estimate the melting conditions and source characteristics of the flows, even though primary magmas are not seen in the sequence.

6.2.1b Modelling of REE-Patterns

Application of the theory of trace element behaviour to the problem of anatexis has led in recent years to the publication of variously complex quantitative models of both crustal and mantle melting (Schilling and Winchester, 1967; Gast, 1968; Shaw, 1970; Hertogen and Gijbels, 1976; Langmuir et al., 1977). A review of the problems and constraints on these models and the development of a generalized theory are presented by Shaw (1977). Modelling equations used in this study are presented in Appendix IV.
Fractional fusion, involving the instantaneous fusion and removal of melt, is improbable for the production of tholeiitic melts requiring large percentages of melting (Mysen and Kushiro, 1977) and has been discounted. The equilibrium batch melting model has been used for most of the calculations below. Before applying the model, however, various assumptions have to be made about the source materials, modality of melting, initial concentrations of REE's, partition coefficients, etc. These assumptions will constrain the model and limit its application, but by careful choice reasonable success should result.

The light rare earth enrichment found in most of the samples, suggests the involvement in melting of a phase such as clinopyroxene or garnet, which strongly fractionates the LREE's. Olivine and orthopyroxene, as common mantle phases, will also be involved. Iherzolite and garnet-Iherzolite starting materials were thus selected (see Table 6.3). Non-modal melting was assumed, with the melting proportions being selected to approximate the invariant points in simple mantle systems (Leeman et al., 1977). It should be noted, however, that due to the large differences in 5-values between Cpx and Gnt on the one hand and Ol and Cpx on the other, the major effect of altering the melting proportions is to change the degree of melting (F) needed to produce a pattern and large uncertainties
<table>
<thead>
<tr>
<th></th>
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<th></th>
<th>Garnet lherzolite</th>
<th></th>
</tr>
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<tr>
<td></td>
<td>source</td>
<td>melt</td>
<td>source</td>
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</tr>
<tr>
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<td>--</td>
<td>--</td>
<td>10</td>
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</tr>
</tbody>
</table>
in these proportions can be tolerated.

It is also assumed that melting was essentially dry and no separate vapour phase existed. The volatile content of the mantle can be considered so small, that for the amounts of fusion required to produce tholeiitic melts, any melt would be undersaturated and anhydrous melting is thus a reasonable approximation (Presnall et al., 1977).

Perhaps the major error in modelling equations comes from the uncertainties in the mineral-melt partition coefficients. The REE's are generally better known than any other group of trace-elements but quite large ranges of partition coefficients have been reported (Arth, 1976). This variability reflects not only analytical uncertainties and differences in methodology (e.g. natural phenocryst-matrix determinations versus experimental mineral-vapour or mineral-melt determinations), but also real variations with temperature, pressure and composition of mineral and melt. Where the D-values are sufficiently low, as for $D_\text{REE}$ in olivine and orthopyroxene, even gross uncertainties have only limited effect on the model results. Where the D-values are high, however, then care is needed in their selection and the interpretation of results. This will primarily affect the HREE's in clinopyroxene and garnet. Values selected for the calculations (Table 6.4) were determined for mafic compositions at temperatures and/or pressures applicable
<table>
<thead>
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<td>.027</td>
<td>(.20)</td>
<td>(.20)</td>
<td>(4.0)</td>
<td>10.5</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Brackets refer to estimated values (after Wood, 1979)

Sources:
5. Philpotts et al. (1972), sample GSFC-21
6. Mixed 4 and 5
to mantle melting. Two sets of garnet partition coefficients were tested in preliminary model calculations (Cols. 4 and 5). The results obtained agreed for the LREE's but showed differences for Tb, Yb and Lu. Differences of the same order can be produced in model results from either set of D-values by varying the garnet content of the source rock. As there was little difference between the results for the LREE's, and these provided the major constraint on the models selected and their interpretation, a mixed set of garnet partition coefficients, which gave a better fit to the sample data, was used (Col. 6). All D-values are assumed to remain constant during melting.

The present consensus of opinion is that primitive mantle sources have REE abundance patterns that are relatively chondritic but 2-3x the average carbonaceous chondrite in absolute abundance (Frey and Green, 1974; Doubet et al., 1975; Ringwood, 1975). Thus a 2x chondrite pattern has been selected as the source composition in the models. Melt compositions ($C_\text{p}$) can now be calculated for varying degrees of melting ($P$). All calculations were made using a 'FORTRAN IV computer program (FUSION) written by the author.
6.2.1c Results of Modelling

REE-patterns produced by partial batch-melting of lherzolite and garnet-lherzolite sources are presented in Figures 6.21 and 6.22. Low degrees of melting result in LREE-enriched patterns with the garnet-bearing residue producing the greater enrichment. The enrichment decreases with increased melting until at high degrees of melting the patterns are essentially flat and mimic the initial pattern in the mantle source. Beyond F = .25, garnet is eliminated from the garnet lherzolite and the two models converge to yield similar patterns. The effect of reducing the proportion of garnet in the original mantle source is to reduce the percentage of melting needed to produce any particular pattern. The minimum amount of garnet in the mantle source is constrained somewhat by the need to produce an olivine tholeiite melt. The experimental data of Mysen and Kushiro (1977) suggest that this requires in the range of 5-30% melting of a garnet peridotite. Fitting the model curves to the sample data leads to the interpretation of Types B and C as being 14% and 25% melts of the 10% garnet lherzolite respectively (Figs. 6.23 and 6.24). These F-values will be decreased to about 8% and 13+% respectively for a 5% garnet lherzolite source. These are close to the minimal amounts that still allow the melts to be olivine tholeiites. Type C patterns are, of course, not dependent on
Figure 6.21  Equilibrium, Batch-Melting of Lherzolite Source

\[ C_o \] Initial concentration

\[ C_L \] Concentration in liquid at given percent melting

\[ C_s \] Concentration in residue at given percent melting

\[ \text{REE}_N \] Chondrite normalized abundances
Mantle 50 Ol : 25 Opx : 25 Cpx
Melt 15 Ol : 35 Opx : 50 Cpx

REE_N

La Ce Nd Sm Eu Tb Yb Lu

C_L
C_D
C_S
Figure 6.22  Equilibrium, Batch-Melting of a 10% Garnet Lherzolite Source

\( C_0, C_L, C_s \) as in Figure 6.21
Figure 6.23 Model Fit to Type B REE-Patterns

Sample data are numbered

$C_O$, $C_L$, and $C_S$ as in Figure 6.21
Figure 6.24 Model Fit to Type C REE-Patterns

Sample data are numbered

$C_0$, $C_L$, and $C_S$ as in Figure 6.21
Type C

REE_{N}

F = 25%

C_L

C_B

C_S

La Ce Nd Sm Eu Tb Yb Lu
the amount of garnet in the source as they are produced after elimination of the garnet and are controlled only by the olivine-orthopyroxene-clinopyroxene residue.

Using the initial REE concentrations selected, it is not possible to successfully reproduce the Type A pattern shown by the majority of samples. Fitting the HREE end of the patterns suggests 8-10% melting but the LREE are flatter in shape and significantly less abundant than those produced by the model. This points to a source which originally had a LREE-depleted pattern. The calculations were thus repeated with such a source and the results are shown in Figure 6.25, where a 8-10% melt can be seen to be a reasonable fit to the Type A step-pattern (Fig. 6.26). The slight differences between series I and IV patterns, particularly the La/Ce ratios, can be explained by slight differences in the relative depletion of these elements in the source rock. R28, however, deviates from the 8-10% melt model. The inclination of the LREE's and the larger LREE to HREE enrichment suggests a smaller degree of melting may be involved, and indeed a 5% melt fits this sample except for Tb.

Reducing the proportion of garnet in the source rock would reduce the F-values of Type A patterns to levels below than necessary for the production of an olivine tholeiite. Thus a source is required possessing in the order of 10% garnet.
Figure 6.25  Equilibrium, Batch-Melting of a 10% Garnet
Lherzolite Source with Initial LREE-Depletion

$C_0$ and $C_L$ as in Figure 6.21
Mantle  50 Ol: 23 Opx: 17 Cpx: 10 Gn
Melt 10 Ol: 15 Opx: 35 Cpx: 40 Gn
Figure 6.26 Model Fit to Type A REB-Patterns

Sample data occupy hachured field. R28 shown separately.

$C_o$ and $C_L$ as in Figure 6.21
The occurrence of Type A-like patterns in oceanic (e.g. Hawaii, Fig. 5.17a, 63°N'N'AR Fig. 5.18a) or rifted continental margin regimes (e.g. Skye, Fig. 5.16b), where LREE-depleted patterns are also observed, provides supporting evidence for their derivation from LREE-depleted sources.

6.2.1d Incongruent Melting

All the modelling results above are based essentially on congruent invariant melting and take no account of possible mineral reactions during melting. Harrison (1979) suggested that the variability of experimentally determined REE abundances in melts from a garnet peridotite can be explained by the reaction:

\[ \text{Garnet} + 0.67 \text{Diopside} + 0.14 \text{Enstatite} = 0.22 \text{Forsterite} + 1.61 \text{Liquid} \]

Equilibrium partial melting models of this reaction yield similar results to those already obtained, except that the degree of melting needed to produce a given pattern is lowered. The effect is similar to that of lowering the garnet content of the initial source rock in the models already presented. However, the need for two different sources for the various REE patterns is not changed.
6.2.1e Eclogite Fractionation

An alternative to the derivation of type A patterns by partial melting processes is that they result from high-pressure fractionation of an eclogite assemblage from a type B or C primitive magma. Eclogite fractionation has been proposed to explain some of the variation of K contents of tholeiites (Jamieson and Clarke, 1970), and can indeed produce a stepped, type A pattern from an original flat type C pattern (Fig. 6.27), although Th is less depleted than in the sample patterns. Quite extensive fractionation is required, however, up to 50%, and it is doubtful that the residual liquid would resemble a basalt, but some highly undersaturated melt like a kimberlite or alnöite (O'Hara, 1968). Eclogite fractionation can thus be ruled out as a viable process in the petrogeneses of the Mamainse Point flows, and differences in REE chemistry can be ascribed to melting processes and source composition.

6.2.1f Discussion

The results of the equilibrium batch-melting models are summarized in Figure 6.28 in which the REE pattern of the samples, the initial mantle source pattern and degrees of melting of the source to produce the sample pattern are indicated against the approximate stratigraphic height in the sequence. This suggests
Figure 6.27  Eclogite Fractionation Model

\( F = \text{mass fraction of liquid remaining} \)
Figure 6.28 Summary Stratigraphic Diagram of REE-Patterns in Lava Series and Their Model Mantle Sources
(Not to Scale)

Numbers on mantle patterns indicate percent melting required to generate the corresponding lava pattern.
the tapping of sources which are successively depleted, flat, depleted and flat. This alternation of patterns also indicates that more than one magma chamber was involved in eruption (each chamber perhaps being tapped in turn) with little or no mixing of new magmas with residual melt. At least two sources are required raising important questions about the homogeneity of the mantle beneath the Keweenawan Rift. Two interpretations are possible:

a) Mantle heterogeneity. The mantle beneath the Keweenawan Rift was heterogeneous with the presence of normal, flat chondritic and LREE-depleted sources. The close proximity of modern MORB with distinctly different incompatible elements and isotopic ratios has been interpreted as resulting from different mantle sources which may be depleted, flat or enriched (Sun et al., 1979; Wood, 1979a; Schilling, 1973, 1975a, 1975b; Gast, 1968; Hart et al., 1973, Batiza, 1977). The heterogeneities appear to be large-scale features, perhaps best explained by a layered-mantle model (Hofmann et al., 1978) Differences have also been noted between the subcontinental and sub-oceanic mantles generally (Leeman, 1977b; De Paolo and Wasserburg, 1977), although LREE-depleted ocean-like mantle has been suggested in some continental areas (Stosch, 1979).
b) Evolving homogeneous mantle. Extraction of even moderately to slightly LREE-enriched liquids, such as types B and C, will result in a LREE-depleted mantle which could serve as the source for subsequent melts. The residues remaining from type B or C melts are too depleted, both absolutely (i.e. the abundances are too low) and relatively (i.e. LREE to HREE) to be of themselves sources of the type A melts (see Figs. 6.23 and 6.24). However, if the melt is incompletely separated and some remains with the residue, the resultant mix may be a suitable source. Calculation of this is possible using an incremental or continuous melting model (Langmuir et al., 1977; Wood, 1979b). Possible models are presented in Figure 6.29 for the various type A patterns. These results are not unique, however, as other combinations of the variable Fl, I and Q can produce similar patterns, but this does not negate the basic idea that these patterns can be generated by an incremental melting process of an originally flat chondritic mantle source.

Both of the above explanations are feasible but it is not possible to distinguish between them on REE data alone. Other trace-elements may give some indications one way or the
Figure 6.29  Continuous Melting Model of a 10% Garnet Lherzolite, with an Initial Chondritic REE-Pattern

Variables in the model as indicated (see Appendix IV).

Cl pattern 6 is the REE pattern in the melt produced by the initial 6% melting.

1, 3, 4 patterns refer to the first, third and fourth increments of melting after the initial melting.

Fits to the Type A REE-Patterns are indicated.
other but perhaps only isotope evidence (e.g. $^{143}\text{Nd}/^{144}\text{Nd}$) can really decide.

6.2.2 Other Trace Elements

Hygromagmatophile element ratios, e.g. $\text{Ti}/\text{Zr}$, have not been affected by fractional crystallization and these ratios will thus be characteristic of the parental magmas for the various series. Table 6.5 lists several of these ratios for the Mamainse Point lava series. Series II has been subdivided into two based on the REE patterns and $\text{TiO}_2$ content. Series IIa consists of four samples and IIb of only two, and their average ratios are thus not as well determined as the other series.

For elements which have very similar bulk partition coefficients in mantle-liquid systems, such as $\text{Ti}-\text{P}$, $\text{Ti}-\text{Zr}$, $\text{Zr}-\text{Hf}$, these ratios are essentially the same for all series, and thus probably reflect the ratios found in the source material. Where elements differ somewhat in $\bar{g}$-values, such as $\text{Ti}-\text{Y}$, $\text{Ti}-\text{Nb}$, different ratios are found for the different series. The different ratios must be produced by the melting event as fractional crystallization has been shown to have no effect (6.1).

$\text{Ti}/\text{Y}$ and $\text{Zr}/\text{Y}$ correlate very well with $(\text{Sm}/\text{Lu})_N$, as may be expected from the similarities in $\bar{g}$-ratios of $\text{Y}$ and NREE's on the one hand, and Ti, Zr and the NREE's on the other. The
<table>
<thead>
<tr>
<th></th>
<th>TiO$_2$/P$_2$O$_5$</th>
<th>Ti/Zr</th>
<th>Ti/Y</th>
<th>Ti/Hf</th>
<th>Zr/Y</th>
<th>Zr/Hf</th>
<th>Th/U</th>
<th>(La/Sm)$_N$</th>
<th>(Sm/Lu)$_N$</th>
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<tr>
<td>A B</td>
<td>10.2</td>
<td>69</td>
<td>373</td>
<td>626</td>
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<td>434</td>
<td>641</td>
<td>5.1</td>
<td>7.5</td>
<td>39</td>
<td>47</td>
<td>3.4, 4.7</td>
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<tr>
<td>IIa</td>
<td>10.0</td>
<td>90</td>
<td>476</td>
<td>869</td>
<td>5.3</td>
<td>9.7</td>
<td>40</td>
<td>4.0</td>
<td>1.47</td>
</tr>
<tr>
<td>IIIa</td>
<td>10.0</td>
<td>77</td>
<td>313</td>
<td>514</td>
<td>4.1</td>
<td>6.7</td>
<td>40</td>
<td>3.4</td>
<td>2.97</td>
</tr>
<tr>
<td>III</td>
<td>10.3</td>
<td>84</td>
<td>217</td>
<td>446</td>
<td>2.6</td>
<td>5.3</td>
<td>31</td>
<td>49</td>
<td>3.8, 3.9</td>
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<td></td>
<td></td>
<td>95</td>
<td>5.0</td>
<td>1.55</td>
</tr>
<tr>
<td>IV</td>
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<td>84</td>
<td>384</td>
<td>948</td>
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<td>11.2</td>
<td>44</td>
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<td>1.9, 3.1</td>
</tr>
<tr>
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<td>90</td>
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<td>707</td>
<td>3.6</td>
<td>7.0</td>
<td>47</td>
<td>2.3</td>
<td>1.45</td>
</tr>
</tbody>
</table>

Chondrite$^1$ 10 110 250-310 1600-1800 2.5-3.0, 16 44 3.1

$^1$ (Sun et al., 1979; Frey et al., 1978)
variations in the Ti/Y and Zr/Y thus probably result from the same processes as produce the variations in the REE patterns, as can be guessed from the possible similarities of Ti-Y and Ti-REE plots (Fig. 6.16), with high ratios from smaller degrees of melting (cf. type A patterns) and low ratios from the higher degrees of melting (cf. type C patterns).

A similar correlation is found for Ti/Nb and Zr/Nb, with (Sm/Lu)₉. This is unexpected as Nb usually shows 5 < Ti, Zr and the Ti/Nb ratio should thus be lower for small degrees of melting and higher for large degrees of melting. However, the type A REE-patterns require a LREE-depleted source and it might be reasonably expected that whatever process caused this depletion would have depleted Nb, Ta, U, Th, etc., as well. Such a source would have higher Ti/Nb than the type C source and could generate partial melts with higher Ti/Nb. This is exactly what is observed in the Mamainse Point sequence with the highest Ti/Nb and Zr/Nb being found in series I, IIa and IV flows which all show stepped, type A patterns. Unfortunately, good quality determinations of partition coefficients for Ti and Nb are lacking or non-existent, particularly under mantle conditions and for mantle minerals. A quantitative assessment of this explanation thus could not be undertaken.

Similar behaviour to Ti-Nb is observed in the Ti-U, Ti-Th and Ti-Ta pairs (Figs. 6.17 and 6.18). It may perhaps be
expected in Ti-La or Ti-Ce as well, but presumably the extent of depletion and the differences in partition coefficients are smaller for these and the resultant effect is subordinate to scatter from analytical error (Fig. 6.16).

6.3 CRUSTAL CONTAMINATION AND THE ORIGIN OF THE TRANSITIONAL BASALTS AND ANOMALOUS SERIES III FLOWS

6.3.1

The transitional basalt dykes and flows are characterized by generally high levels of incompatible elements compared to the tholeiitic flows. These higher values are coupled with lower TiO$_2$/P$_2$O$_5$ and Ti/Zr. REE data from R95 point towards a lower degree of melting than the tholeiites, but no good fit with model results could be found. A certain amount of variability is found amongst the transitional basalts with a wider range of Ti/Y, Ti/Nb and even Ti/Zr, than in any of the lava series (Figs. 6.30-6.33). Processes other than fractionation and partial melting have thus played a part in producing this variation.
Figure 6.30  \( \text{TiO}_2 - \text{Zr} \) Plot for Transitional Basalts (\( \bigcirc \)) and Series III Lavas (\( \bigcirc \)).

Field occupied by Mamainse Point felsic rocks as indicated.

Dashed line indicates correlation found in normal lavas (see Figure 6.12).

Arrows demonstrate the effect of contamination by felsic material.
Figure 6.31 TiO$_2$-Y Plot for Transitional Basalts (○) and Series III Lavas (○)

As for Figure 6.30, except that dashed line applies only to the "normal" series III lavas.
Figure 6.32 TiO$_2$-Nb Plot for Transitional Basalts (○) and Series III Lavas (○)

As for Figure 6.31
Figure 6.33 TiO$_2$–U Plot for Transitional Basalts (◊) and Series III Lavas (○)

As for Figure 6.31, except that Felsite field is hypothetical.
Variability in Zr, Y, Nb, U, LREE's, ?Zn, etc., is also found in the series III lavas. The majority of these flows behave normally, with uniform Ti/Zr, etc., but three samples, R51, R52 and R54 all show deviations to lower Ti/Zr, Ti/Y, Ti/Nb and Ti/U (Figs. 6.30-6.33). These samples contain feldspar xenocrysts that appear to be partially resorbed with many ?glassy inclusions, in contrast to the clear plagioclase phenocrysts in these samples. They also contain rounded blebs of glass that bear some similarity to the glass globules in some of the dykes, but which do not occur in any of the other flows. These features are believed to result from the incorporation into the ascending magmas of crustal material, which was partially melted and mixed in. The types of glass occurrence in the dykes would suggest that such mixing was not always complete, ranging from pseudo-immiscibility to almost complete homogeneity.

Felsites that occur within the Mamainse Point sequence are probably good analogues for the contaminating material. These felsites are a fairly heterogeneous group chemically, with low TiO₂ and P₂O₅ (Jackson, 1977), but relatively high, though variable, Zr, Y and Nb. They cannot be derived in any simple way by the differentiation of the mafic lava series, and are
more likely the products of partial melting of a variable sialic crust. In Figures 6.30 to 6.32 the felsites occupy a large field at the end of possible mixing lines with the transitional basalts and series III lavas. No U data are available for the felsites but high contents are normal for acidic rocks generally, and a similar relationship is to be expected in 6.33 as in 6.30 to 6.32.

It thus appears that crustal contamination is responsible for some of the chemical variability of the transitional basalts and the anomalous series III lavas. As not all the series III flows are affected, the contamination presumably took place during ascent of the magma rather than in the magma chamber. This may also be true for the dykes. It is not, however, clear at what stage the transitional dykes were generated. The interbedding of transitional basalts and series V tholeiites gives a minimum age, but Annells' sample 604 (see 5.1) may point to earlier generation. The possibility of more than one period of generation of transitional basalt, particularly within a dynamic melting model, cannot be ruled out.
6.4.1

The REE modelling above has assumed either a relatively flat chondritic source or a regularly depleted pattern. Inspection of Table 6.4 reveals that this may not be strictly correct. Series III flows probably represent the highest degrees of melting and should have incompatible ratios close to those of the supposed chondritic mantle source. This is true for Zr/Y, Zr/Hf and Th/U but not for other ratios. Ti/Zr and Ti/Y are both less than chondritic, implying that Ti is slightly depleted. P must also be depleted to maintain $\text{TiO}_2/\text{P}_2\text{O}_5$ equal to chondritic. Enrichment of Nb is suggested by the low Zr/Nb which is much less than chondritic. These effects are visible in Figure 5.21, in which the incompatible elements are shown normalized to an estimated primordial mantle. A flat to slightly enriched pattern is found with a strong peak for Nb + Ta and troughs for P and Ti.

The Ti and P depletions are probably real features of the mantle source and not due to retention in residual mantle phases. Both Ti and P may be taken up by garnet under mantle conditions, but modelling of the REE's requires exhaustion of garnet and an olivine-orthopyroxene-clinopyroxene residue for the series III magma. It is also unlikely that other accessory
phases would retain Ti and not Zr, nor take in P without affecting the REE's.

Nb appears to be enriched, showing a pronounced peak. This is also a common feature of alkalic basalts and E-type MORB (Fig. 5.25), and one or two otherwise depleted N-type MORB. This may arise from using too small a normalizing value, suggesting that the primordial mantle was enriched in Nb relative to other refractory elements like Zr. However, the common occurrence of chondritic Zr/Nb in Archaean tholéitic and ultramafic flows (Nesbitt and Sun, 1976, Sun and Nesbitt, 1977) would point against this. Also many of the N-type MORBs possess smooth patterns and changing the normalizing value for Nb would result in a depletion in these patterns, creating a new problem for interpretation. Thus the Nb enrichment appears to be a real feature.

6.4.2

Two other features of the trace-element patterns are worthy of note. The HREE's in the series III flows may show a slight enrichment resulting in a shallow U-shaped REE-pattern with $(\text{Sm/Lu})_N < 1$. U-shaped REE-patterns have been reported from ophiolitic lavas (Coish, 1979), but these are usually more severe than the Mamainse Point series III. The average
(Sm/Lu)$_N^* = .9$ and, given the analytical uncertainties, may not be different to 1.0. Even if real, this HREE-enrichment will not affect the applicability of the REE models due to the uncertainties in $D_{REE}$ for garnet (see 6.2.1b).

In all incompatible trace-element patterns (Figs. 5.19-5.23), U is comparable in relative abundance to La, but Th is variable. Series I, II and III have Th $>$ U, whereas series IV and V have Th $<$ U. This is reflected in lower Th/U for series IV and V than for other series (Table 6.4, Fig. 5.19). There may thus be differences in the mantle source for series IV and V compared to series I-III, Th/U, like Zr/Hf, Ti/P, etc., not being readily fractionated during melting. Coupling this with differences in the REE patterns of sources between IV and V, and I, IIa and IIb, III, may suggest up to four differing mantle sources for the lavas characterized as in Table 6.6.

The dynamic melting model, however, reduces this requirement to two with the lower lavas I-III being derived from one source and IV-V from another. The two mantle sources are characterized by differing Th/U, and perhaps Nb abundances to give differing Ti/Nb in series III and IV. The REE patterns then result from incremental melting effects within each mantle "blob". Within each group there is an inversion of sequence from the more complexly derived parental magmas, requiring incremental melting products, at the base, to simpler batch-melting
TABLE 6.6  CHARACTERISTICS OF MANTLE SOURCES FOR PARENTAL MAGMAS

<table>
<thead>
<tr>
<th>Series</th>
<th>REE Pattern</th>
<th>Th/U</th>
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<tr>
<td>I, IIa</td>
<td>LREE depleted</td>
<td>chondritic</td>
</tr>
<tr>
<td>IIb, III</td>
<td>chondritic</td>
<td>chondritic</td>
</tr>
<tr>
<td>IV</td>
<td>LREE depleted</td>
<td>depleted</td>
</tr>
<tr>
<td>V</td>
<td>chondritic</td>
<td>depleted</td>
</tr>
</tbody>
</table>
products above these. This inversion of sequence was suggested by Wood (1979) as being characteristic of dynamic melting, and it may point to an evolutionary history of melting in ascending mantle diapirs. It is perhaps significant that there is a marked stratigraphic break -- the Great Conglomerate -- between the two groups of flows. This could mark a period of relative quiescence between the end of melting in the first mantle diapir (I-III) and the commencement of melting in the succeeding one (IV-V).

6.4.3

Regardless of whether two or four mantle sources are believed to have been tapped in the mantle, these sources show complex trace-element patterns that are markedly deviant from the model primordial mantle. Assuming that heterogeneous accretion of the earth is discounted, then multiple processing of the mantle must have taken place. The depletion of both Ti and P while maintaining a chondritic TiO₂/P₂O₅ probably resulted from a previous melting event, which would of course deplete all the other incompatible elements as well. At some later time, however, most of the other elements, and particularly Nb and Ta, were enriched, perhaps by veining of material (melt or metasomatic fluid) derived from some lower source (Prey and
Green, 1974; Wood, 1979). This enrichment process may not have been a singular event and was not regular, producing a relatively flat pattern in some parts but still slightly depleted in the more incompatible elements, e.g. Th, U, Nb in other parts. Thus local heterogeneities were formed which were not equilibrated during the Keweenawan melting.

The nature and timing of the enrichment are unknown. Wood (1979) has suggested that enrichments of Ta and Nb may result from recycling of subducted lithosphere with accessory rutile and sphene. Recycling of such material may decouple Nb and Ti, the latter behaving as a major-element so long as sphene is stable, producing possible enrichments of Nb relative to Ti; but it does not explain the coherence of Ti and P, nor the enrichment of Nb over Zr. That processing of the mantle in this region has taken place is indicated by volcanism during Archaean and Early Proterozoic times.

6.5 CONCLUSIONS

The Mamainse Point sequence has undergone shallow-level crystal fractionation involving olivine-plagioclase-chromite assemblages. Each series appears to have occupied a different magma chamber, with parental magmas derived by partial melting of a garnet-lherzolite mantle. Crustal contamination is
indicated for some samples but is limited.

Incompatible elements suggest that the parental magmas represent the products of differing degrees of melting of the mantle, with incremental and equilibrium batch-melting being involved. The mantle source shows signs of past processing involving depletions and variable enrichments, that left complex trace-element patterns and local heterogeneity. Several parental magmas may be derived by dynamic melting of a single rising mantle diapir, each diapir having a characteristic trace-element fingerprint, although the differences between diapirs are subtle and less than the common shared characteristics. Dykes may represent magmas from small degree of melting of the mantle prior to incremental melting in the dynamic melting model, although their ages relative to the lava series are not well known.
CHAPTER 7

CONCLUSIONS

"Diseased nature often times
breaks forth
In strange eruptions,..."

Henry IV, Part I
(3.1.27–28)

7.1 SUMMARY OF FINDINGS

The Mamainse Point Formation formed on the margins of
the Keweenawan Rift during the extensional stage that saw the
rupture of the Canadian Shield and the development of new dense
simatic crust. The lavas are olivine- and feldspar-phyric,
with a crystallization sequence suggestive of shallow-level
processes. They classify as olivine- and quartz-tholeiites.
No alkalic rocks are found. Dykes are also quartz-tholeiites,
although they show trace-element characteristics of alkalic
rocks and are better termed transitional basalts.

Formation of the pile has been accompanied by low-grade
burial metamorphism in the zeolite and prehnite-pumpellyite
facies. Flow-tops, coarse sedimentary layers and abundant fractures acted as channel-ways for fluids. A crude mineral zonation was developed from epidote at the base to stilbite at the top of the exposed section. Calcite-laumontite veins are ubiquitous and even cross-cut higher grade epidote-bearing rocks. This suggests that the metamorphism may have been in two stages: the second at a lower temperature. Geochemical evidence may support this interpretation and also suggests that the fluid composition changed. The initial hydration event established the mineral zonation and resulted in addition of $H_2O^+$ and alkalis to the rocks. Fluids evolved to more carbonate-rich compositions and a carbonation event ensued, with the development of abundant calcite, the addition of $CO_2$ and mobilisation of Ca and Sr.

Enough elements appear to have survived the alteration processes accompanying alteration to allow petrogenetic inferences to be made. The stratigraphic variation of "immobile" elements allows the subdivision of the lavas into five series. These series are not lithologically controlled, each series containing ophiolites and melaphyres. Variation trends for $Al_2O_3$, $FeO^+$, $MgO$, $TiO_2$, $Ni$, $Cr$, and $Co$ suggest that shallow-level fractionation of the magma can account for most of the variation seen. Fractionating assemblages of olivine-plagioclase-chromite are required for all five series, although in slightly
differing proportions. Clinopyroxene and Fe-Ti oxides crystallized only after extrusion of the lava. Fractional crystallization of olivine-plagioclase-chromite assemblages increases the abundances of incompatible elements but does not change their relative abundances to each other. Variations in incompatible element ratios thus have resulted from earlier stages in their evolution, either from the melting process or source heterogeneities.

Modelling of REE patterns requires varying degrees of melting of a garnet lherzolite mantle. However, two source compositions are indicated by initial REE concentrations, one containing a flat chondritic pattern and the other a LREE-depleted pattern. Other incompatible trace-element variations; e.g. Ti/Y, etc., appear to be consistent with this modelling although Th and U abundances may point to further, perhaps local-scale, heterogeneities in the mantle sources.

7.2 DISCUSSION AND FURTHER SPECULATION

7.2.1 Mantle Models

The incompatible element data suggest that heterogeneities existed in the mantle source for the Mamainse Point Formation. Two models can be appealed to:
a) A heterogeneous mantle with heterogeneities on both the large-scale (flat REE vs LREE-depleted) and the more local-scale (Th/U). Simple batch-melting of this complex mantle can produce all the variation seen.

b) A similar mantle with only local-scale heterogeneities. (Th/U). Other incompatible element variations would be produced by dynamic melting within rising mantle diapirs. Thus series I-III formed from one diapir and series IV-V from another, each labelled with slightly different Th/U (see Fig. 7.1).

Choosing between the two models is difficult, and with the present data can probably only reflect the interpreter's biases. Model b appears to allow a more self-consistent, harmonious interpretation with the minimum of complexity in the mantle, the least understood part of the models. The dynamic melting model, although complex and possibly unprovable, is geologically reasonable in its assumptions and workings and allows the explanation of a group of series by one origin. Even the transitional basalts fit the model as representatives of the initial low degree melt in the incremental melting scheme, although whether they are related to both diapirs or just the second is not certain.

The heterogeneous mantle model requires the melting of at least four sources, when both large-scale and local-scale
Figure 7.1 Summary Stratigraphic Diagram Illustrating the Dynamic Partial Melting Model

As Figure 6.28 (with REE patterns of the lava series and their mantle sources based on equilibrium batch melting) with the addition of U/Th data and the possible division into two groups A and B (see Figure 6.19). Within each group, lava series are related by differing melting processes operating in the same mantle diapir.

(U/Th)$_{PM}$ U/Th normalized to primordial mantle (Wood, 1979b)

$F_l$ Initial melt in the incremental melting model
heterogeneities are taken into account, all within a comparatively small volume of the earth. Irregularities in the primordial-mantle normalized, incompatible element patterns suggest that complex processing of the mantle may have preceded the Keweenawan melting event. This could have produced the required heterogeneities.

Isotope data could provide a good test of the two hypotheses, particularly $^{143}\text{Nd}/^{144}\text{Nd}$, as the REEs appear to be unaffected by the alteration processes, unlike Rb/Sr. In the first model suggested above, the large-scale heterogeneities in the incompatible elements would be accompanied by variations in Sm/Nd. Given enough time between the generation of these heterogeneities and partial melting in the Keweenawan, there will thus be differences in the $^{143}\text{Nd}/^{144}\text{Nd}$ of the lavas, the ratio being higher in those derived from the LREE-depleted source than those from the flat source. No differences would be expected if the second model was operative.

7.2.2 Keweenawan Geotectonics

The geochemistry of the Mamainse Point Formation, along with geophysical and geological evidence, suggests that the Keweenawan Rift was a proto-ocean. New simatic crust formed and extensive extrusive activities overlapped onto the margins of the rift. The lavas in the eastern rift are tholeiitic,
although somewhat enriched in incompatible elements, but become more alkalic in the west with trachybasalts and trachyandesites developed in the North Shore Volcanics of Minnesota (Green, 1972). This may be analogous to the changes in composition observed in the transition from oceanic to continental rift within the Afar region (Barberi and Varet, 1978). Crustal separation stopped at the end of the Middle Keweenawan (1100-1080 Ma). This may have resulted from lithospheric adjustments accompanying the Grenville collision to the east. A compressional phase in the rift, particularly well developed in the western part of the rift which parallels the Grenville Front, represents further effects of the continuing Grenville Orogeny. Infilling of the rift by sediments ensued, with isostatic sinking of the mafic crust, in the centre of the rift, causing widening of the basin and overlapping of the sediments onto the craton margins.

The enriched incompatible element patterns found in the Mamainse Point Formation are similar to those observed in lavas from "hot spots" in modern oceans, e.g. Iceland, Azores, etc. This may provide support for the suggested triple junction in this area (Burke and Dewey, 1973; Sawkins, 1976a). However, the geometry of the eastern part of the rift is poorly understood at the moment, and may involve transform offsets of the ridge rather than a triple junction (Norman, 1978). The Mamainse Point data do not negate the presence of a triple junction near
the Black Bay Peninsula (McIlwaine et al., 1974) nor anywhere else along the rift (O'Hara, 1978).

The intersection of the Keweenawan Rift and the Grenville Front is not exposed at the surface but is buried beneath Palaeozoic sediments. This adds to the confusion about the relationships of the Grenville Orogeny and the Keweenawan Rift. Geophysical expressions of possible extensions of the Keweenawan Rift east of the Grenville Front have also not been identified. The detection of suture lines within the Grenville Province is made difficult by polyphase deformation and high-grade metamorphism. Volcanic sequences to the east of the Elzevir Batholith in eastern Ontario contain a calc-alkalic sequence on older submarine tholeiites (Morton and Moores, 1978), which at least points to a continental margin being preserved in places, although the ages of these suites and their geographical extensions northeast or southwest are not known. Thus, although the available data for the Keweenawan Rift can best be explained by a model involving proto-oceanic rifting before the Grenville Collision event, it is still only a tenuous interpretation and must await the results of further geological and geochronological studies, particularly in the Grenville Province, for confirmation.
7.3 SUGGESTIONS FOR FURTHER STUDIES

7.3.1. Palaeomagnetics

The need to interpret the Mamainse Point triple reversal (R-N-R-N) as due to faulting rests mainly on the 30° pole shift between reverse and normal poles. This pole shift is recorded in other Keweenawan sequences and is not due to secondary magnetizations (Pessonsen and Hall, 1979). This pole shift has been interpreted as due to continental drift. Even allowing for a break of 10-20 Ma between Lower and Middle Keweenawan lavas, this requires plate motions of the order 10-30 cm/year, much more rapid than presently observed. The actual time involved was probably shorter, requiring even faster plate motions. This seems unreasonable in the light of our present knowledge. If the Mamainse Point sequence really records a triple reversal, the pole shift may be apparent and result perhaps from some long-term non-dipole component or other aberration of the geomagnetic field at the time. Careful study of other Keweenawan sequences may reveal similar reversals. Also other sequences of similar age in North America and elsewhere may reveal reversals and contribute to modelling of the geomagnetic field at the time, e.g. Arizona (Elston and Grommé, 1979).
7.3.2 Alteration and Burial Metamorphism

Secondary minerals formed in vesicles and veins may contain fluid inclusions whose study would provide valuable data on temperatures of formation and fluid compositions. These data along with more detailed studies of mineral parageneses would provide a good test for the ideas presented here in Chapter 4 concerning two different geochemical-metamorphic events. The study should also extend to mineralized veins to check their relationship to the metamorphism.

7.3.3 Other Geochemical and Isotopic Studies

Analytical data for trace-elements that are both immobile and specific for plagioclase, e.g. Ga, and clinopyroxene, e.g. Sc, ?V, would help confirm the fractionation assemblages suggested in Chapter 6. However, these data may not be readily obtained with high enough precision by rapid or inexpensive methods. Determinations of La, Ce and possibly Nd, may be possible by XRF, and coupled with Y as a surrogate HREE, could confirm the findings of the limited, though more detailed, REE determinations presented here.

Microprobe analyses of plagioclase xenocrysts, glass globules and irregular glass patches in the anomalous series III lavas and the dykes would test the suggestion advanced in
6.3 that they are derived from contamination of the mafic magmas with more felsic crustal material. U and REE analyses of Mamainse Point felsites may support them as possible analogues for contaminants, as well as allowing inferences for their own origins.

Nd isotopes would provide a good test of the two possible mantle models outlined above in 7.2.1. The Sm/Nd system may also provide a reliable dating method not reset by the alteration processes, although 1100 Ma may be close to the lower limit of its application. The efficacy of the Rb/Sr and U/Pb systems is doubtful due to alteration effects.

7.3.4 Regional Studies

Application of similar major- and trace-element geochemistry to other lava plateaus in the Keweenawan sequence, could provide much useful information. They would allow some checks to be made on some of the conclusions drawn here, as well as allowing study of regional variations of chemistry, etc., in the rift. The North Shore Volcanics of Minnesota contain alkalic as well as tholeiitic rocks, unlike other sequences. This suggests one or more of: differing mantle processes, different fractionation schemes, regional variation in the mantle composition, etc., all of which may reflect some large geotectonic variation from
proto-oceanic to continental conditions within the rift.

The geochemistry and geochronology of Lower Keweenawan dykes marginal to the rift would be valuable constraints on the modelling of the evolution of the rift and its magmatic products. Any studies that lead to a better understanding of the evolution of the Grenville Province will have obvious importance in solving the problems of the relationship of the Keweenawan Rift to the Grenville.
APPENDIX I

ANALYTICAL PROCEDURES

AI.1 X-Ray Fluorescence Spectrometry

AI.1.1 Major Elements

Major elements were determined by XRF using a fused glass bead procedure. 500 mg of sample powder were mixed with 3.00 g of lithium metaborate-tetraborate (1:1) flux. This mixture was fused in a platinum crucible over a hot burner and cast in a platinum mould. A numbered self-adhesive label was placed on the upper curved surface for identification. Pellets were stored in open trays lined with soft Kleenex tissue. Similar glass pellets were prepared from standard rock powders by C. Mudroch and the author, and stored in a dessicator. Sample homogeneity and pellet-making ability were tested by preparing six pellets from the same sample powder (R66). The variability in results from the different pellets were compared to the variability in replicate analysis of the same pellet (Table AI.1). The results show good agreement.

Analysis were made on a Phillips PW 1650 automatic sequential machine. Conditions used for the element determinations are summarized in Table AI.2. Six standard rocks were chosen to form the calibration curves. Three
### Table AII.1 Variability of major elements due to sample powder heterogeneity

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
</tr>
</thead>
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<tr>
<td></td>
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<tr>
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</tr>
<tr>
<td>Fe$_2$O$_3$</td>
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<td>.08</td>
</tr>
<tr>
<td>MgO</td>
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<td>.12</td>
</tr>
<tr>
<td>CuO</td>
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<td>.03</td>
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<tr>
<td>Na$_2$O</td>
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<td>.14</td>
</tr>
<tr>
<td>K$_2$O</td>
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<td>.01</td>
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<tr>
<td>P$_2$O$_5$</td>
<td>.33</td>
<td>.01</td>
</tr>
</tbody>
</table>

A - six repeats of the same pellet (R66-1)

B - five different pellets made from the same powder (R66-2, to R66-6)

(Note: Counts were compared to B1 by a single standard program supplied to McMaster by B.M. Gunn, and not determined by calibration curve method.)
<table>
<thead>
<tr>
<th>Element</th>
<th>Pellet type</th>
<th>X-ray tube</th>
<th>K/v mA</th>
<th>Analysing crystal</th>
<th>Collimator</th>
<th>Counter</th>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td>C</td>
</tr>
<tr>
<td>Fe</td>
<td></td>
<td></td>
<td></td>
<td>LiF200</td>
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<td>F</td>
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<td></td>
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<td>ADP</td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Cu</td>
<td>Glass bead</td>
<td>Chromium</td>
<td>50/50</td>
<td>LiF200</td>
<td></td>
<td>F</td>
</tr>
<tr>
<td>Na</td>
<td></td>
<td></td>
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<td>C</td>
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<tr>
<td>K</td>
<td></td>
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<td>F</td>
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<td>Mn</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>TLAP</td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Na</td>
<td>Powder</td>
<td>Chromium</td>
<td>50/50</td>
<td>TLAP</td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Rb, Sr</td>
<td>Powder</td>
<td>Molybdenum</td>
<td>80/30</td>
<td>LiF200</td>
<td></td>
<td>F</td>
</tr>
<tr>
<td>Y, Zr, Nb</td>
<td>Powder</td>
<td>Chromium</td>
<td>50/50</td>
<td>LiF200</td>
<td></td>
<td>F</td>
</tr>
<tr>
<td>Ni</td>
<td>Powder</td>
<td>Chromium</td>
<td>50/50</td>
<td>LiF200</td>
<td></td>
<td>F + S</td>
</tr>
</tbody>
</table>

1 C = coarse, F = fine
2 F = flow counter, S = scintillation counter
other standard rocks were run as unknowns to test for
accuracy (Table AI.3). The standards in the calibration
curve were run with each day's batch of samples to ensure
similarity of run conditions. Count data were processed by
FORTRAN IV programs written by O. Mudroch using least-squares-
fit calibration curves for each element. Mass absorption
corrections were then applied, and the total resummed to
100%. The mean values for standards NIMN, JBl, and DRN show
good agreement with the recommended values - usually within
one standard deviation. Precision is better than 1% for most
elements (1; level) except for MgO and Na₂O whose lower
count-rates lead to poorer statistics.

In later runs, Na₂O values were found to be inaccurate
and imprecise, due to the low counting rate from the glass
bead. New determinations were made using a powder pellet
program. Accuracy and precision data are included in Tabl
AI.3.
Table A1.3 Accuracy and precision for major elements by XRF

<table>
<thead>
<tr>
<th></th>
<th>NIMN 10 (6)</th>
<th></th>
<th>JBI 13 (9)</th>
<th></th>
<th>DRN 13 (9)</th>
</tr>
</thead>
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<tr>
<td></td>
<td>( \bar{x} )</td>
<td>( s )</td>
<td>( \bar{x} )</td>
<td>( s )</td>
<td>( \bar{x} )</td>
</tr>
<tr>
<td>SiO₂</td>
<td>52.47</td>
<td>.25</td>
<td>52.89</td>
<td>.30</td>
<td>53.14</td>
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<tr>
<td>TiO₂</td>
<td>.19</td>
<td>.01</td>
<td>.20</td>
<td>1.30</td>
<td>.01</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>16.36</td>
<td>.09</td>
<td>16.64</td>
<td>14.63</td>
<td>.08</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>8.89</td>
<td>.12</td>
<td>8.97</td>
<td>.08</td>
<td>9.10</td>
</tr>
<tr>
<td>MnO</td>
<td>.18</td>
<td>.01</td>
<td>.18</td>
<td>.15</td>
<td>.01</td>
</tr>
<tr>
<td>MgO</td>
<td>7.69</td>
<td>.16</td>
<td>7.53</td>
<td>8.01</td>
<td>.14</td>
</tr>
<tr>
<td>CaO</td>
<td>11.55</td>
<td>.10</td>
<td>11.53</td>
<td>9.29</td>
<td>.10</td>
</tr>
<tr>
<td>Na₂O</td>
<td>(1) 2.41</td>
<td>.11</td>
<td>2.78</td>
<td>.11</td>
<td>3.01</td>
</tr>
<tr>
<td></td>
<td>(2) 2.49</td>
<td>.01</td>
<td>2.53</td>
<td>.03</td>
<td>2.82</td>
</tr>
<tr>
<td>K₂O</td>
<td>.28</td>
<td>.04</td>
<td>.25</td>
<td>.13</td>
<td>.03</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>.00</td>
<td>.01</td>
<td>.03</td>
<td>.27</td>
<td>.01</td>
</tr>
</tbody>
</table>

1 Fused pellets
2 Powder Pellets, \( n = 5 \)
3 Number in brackets for Na by fused pellets
4 Abbey (1977), normalized to 100
AI.1.2 Trace-elements

Trace-element (Rb, Sr, Y, Zr, Nb, Ni) determinations were made using compressed powder pellets. Sample powder was mixed with a few drops of Mowiol binder (Marchand 1973) in a disposable plastic beaker and then transferred to a Chemplex aluminium pellet cup. This was compressed at about 17 tons/in² for about 5 minutes. Sample numbers were marked on the backs of the cups and the pellets stored in open trays lined with Kleenex tissue. Sample homogeneity and pellet making ability were tested by preparing six pellets from sample R16.

Conditions used in the various programs are incorporated in Table AI.2. As with the major-elements, standard rocks were used for calibration and also run as unknowns to check for accuracy and precision. Count data were processed in FORTRAN IV programs written by M. Marchand and O. Mudrock, with minor corrections by the author. Mass absorption corrections were made using the major-element data or the scattering of the Mo-Compton peak (Rb, Sr). Detection limits were calculated by the method of Jenkins and de Vries (1970) and are listed in Table AI.4.

The variability of analysis from one pellet (R16-1) was compared to that between other pellets of the same sample (R16-2 to R16-6). The results (Table AI.5) show good agreement for all elements although higher coefficients of variance were
Table AI.4 Calculated detection limits for trace-elements, XRF (ppm)

<table>
<thead>
<tr>
<th>Element</th>
<th>Detection Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rb</td>
<td>6</td>
</tr>
<tr>
<td>Sr</td>
<td>5</td>
</tr>
<tr>
<td>Y</td>
<td>4</td>
</tr>
<tr>
<td>Zr</td>
<td>10</td>
</tr>
<tr>
<td>Nb</td>
<td>5</td>
</tr>
<tr>
<td>Ni</td>
<td>4</td>
</tr>
</tbody>
</table>

Calculated using equation of Jenkins and de Vries (1970)

\[
\text{Detection Limit} = \frac{2\sqrt{T}}{m} \sqrt{\frac{Rb}{T}}
\]

- \(m\) = counts/sec/ppm
- \(Rb\) = counts/sec for background
- \(T\) = total analysis time
Table AI.5  Variability of trace elements due to sample powder heterogeneity (ppm)

<table>
<thead>
<tr>
<th>Element</th>
<th>Repeat of One Pellet 1</th>
<th>Different pellets of same sample 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n  X       s  c%</td>
<td>n  X   s  c%</td>
</tr>
<tr>
<td>Rb</td>
<td>8  28  .5  1.9</td>
<td>5  26  .4  1.3</td>
</tr>
<tr>
<td>Sr</td>
<td>8  334  1.8  .5</td>
<td>5  334  1.8  .5</td>
</tr>
<tr>
<td>Y</td>
<td>6  31  1.2  3.9</td>
<td>5  33  3.4  10.3</td>
</tr>
<tr>
<td>Nb</td>
<td>6  .10  1.3  13.0</td>
<td>5  10  2.3  22.1</td>
</tr>
<tr>
<td>Zr</td>
<td>6  144  10.3  7.2</td>
<td>5  150  7.3  4.9</td>
</tr>
<tr>
<td>Ni</td>
<td>8  191  4.3  2.2</td>
<td>5  195  5.8  3.0</td>
</tr>
</tbody>
</table>

1 R16-1
2 R16-2, -3, -4, -5, -6  All data run on same day under similar conditions
found for Y and Nb within the group of different pellets. The other elements suggest that sample preparation has resulted in homogeneous pellets. R16-1 was run along with standard rocks in all batches of samples to check for precision (Tables A1.6 - A1.8).

In general the precision data for R16-1 are good, with one sigma errors being <5% for Rb, Sr, Ni and <10% for Y and Zr. The high coefficient of variation for Nb to some extent reflects the low count-rates for R16-1. Agreement between observed and recommended values is good where the latter are well known.
Table AI.6  Accuracy and precision data for Rb, Sr (ppm)

<table>
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<tr>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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<tbody>
<tr>
<td></td>
<td>n</td>
<td>x</td>
<td>s</td>
<td>c</td>
<td>Rec Val</td>
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<tr>
<td>n</td>
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<td>177</td>
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<td>185</td>
<td>181</td>
<td>1.6</td>
<td>0.9</td>
<td>185</td>
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<td>40</td>
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<td>451</td>
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<tr>
<td></td>
<td>22</td>
<td>30</td>
<td>1.2</td>
<td>4.2</td>
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<td>326</td>
<td>7.4</td>
<td>2.3</td>
<td>-</td>
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1 Abbey (1977)
2 J. Muysson (pers. comm.)
Table AI.7 Accuracy and precision data for Ni (ppm)

<table>
<thead>
<tr>
<th></th>
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<th>( \bar{x} )</th>
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<th>c3</th>
<th>Rec Val</th>
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<tr>
<td>B1</td>
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<td>64</td>
<td>7.9</td>
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<td>?62(^1)</td>
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<td>B2</td>
<td>8</td>
<td>50</td>
<td>6.3</td>
<td>12.6</td>
<td>?72(^1)</td>
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<tr>
<td>JBL</td>
<td>7</td>
<td>132</td>
<td>7.6</td>
<td>5.7</td>
<td>135(^2)</td>
</tr>
<tr>
<td>ON64</td>
<td>7</td>
<td>24</td>
<td>4.3</td>
<td>17.9</td>
<td>?26(^3)</td>
</tr>
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<td>R16</td>
<td>15</td>
<td>193</td>
<td>4.0</td>
<td>2.1</td>
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\(^1\) Abbey suggested values (1973)  
\(^2\) Abbey (1977)  
\(^3\) J. Muysson (pers. comm.)
Table AI.8 Accuracy and precision data for Y, Nb, Zr (ppm)

<table>
<thead>
<tr>
<th></th>
<th>Y</th>
<th></th>
<th></th>
<th></th>
<th>Nb</th>
<th></th>
<th></th>
<th></th>
<th>Zr</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>(\bar{x}) ppm</td>
<td>s ppm</td>
<td>c %</td>
<td>Rec (^1) ppm</td>
<td></td>
<td>(\bar{x}) ppm</td>
<td>s ppm</td>
<td>c %</td>
<td>Rec (^1) ppm</td>
<td></td>
<td>(\bar{x}) ppm</td>
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<tr>
<td>W1</td>
<td>10</td>
<td>27</td>
<td>1.4</td>
<td>5.2</td>
<td>25</td>
<td>12</td>
<td>2.4</td>
<td>20</td>
<td>79.5</td>
<td>96</td>
<td>16.1</td>
<td>16.7</td>
</tr>
<tr>
<td>NIMN</td>
<td>7</td>
<td>11</td>
<td>2.5</td>
<td>22.3</td>
<td>7</td>
<td>BDL(^2)</td>
<td>-</td>
<td>-</td>
<td>72</td>
<td>25</td>
<td>9.1</td>
<td>36.4</td>
</tr>
<tr>
<td>BR</td>
<td>8</td>
<td>35</td>
<td>2.3</td>
<td>6.6</td>
<td>30</td>
<td>75</td>
<td>8.3</td>
<td>11</td>
<td>210</td>
<td>246</td>
<td>9.2</td>
<td>3.7</td>
</tr>
<tr>
<td>RL6</td>
<td>16</td>
<td>32</td>
<td>2.2</td>
<td>7</td>
<td>-</td>
<td>13</td>
<td>2.7</td>
<td>21.3</td>
<td>-</td>
<td>155</td>
<td>15.4</td>
<td>9.9</td>
</tr>
</tbody>
</table>

\(^1\) Abbey (1977)

\(^2\) Below detection limit (= 5 ppm, see Table AI.4)
AI.2 Atomic Absorption Spectroscopy

Various trace-elements (Li, Cr, Co, Cu, Zn, Ba) were determined by the use of atomic absorption spectroscopy (AAS) using a Perkin-Elmer 603 AAS unit. Solutions were prepared by dissolving 1 g of sample powder in 25 ml of HF + HClO₄ (3:1) and 2 ml HNO₃, in a covered teflon crucible over a water bath. The solutions were evaporated to near-dryness and redissolved in HClO₄ and deionised distilled water.

Artificial standards were prepared from stock solutions with the addition of Al and Fe matrix and HClO₄. The artificial standards were used to calibrate the AAS unit, and artificial and natural rock standards were used to check for accuracy. One sample (R23) was run in all batches to obtain an estimate of total precision. Results of accuracy and precision are summarised in Table AI.9.

The coefficients of variation for all elements are better than 7%, this being a measure of total precision including variability due to differing dissolutions, etc. Accuracy is good except for Ba, and Cr and Co in in-house standard ON64. The recommended values for the latter are based on far fewer data than Li or Ba and so are not considered well established yet. The Ba results all appear high by about 15%. This may result from enhancements of the Ba absorption due to the presence of Ca in sample solutions which was not corrected for in the standard solutions. Although this raises doubts about the accuracy of the Ba
Table AI.9. Summary of accuracy and precision data, AAS (ppm)

<table>
<thead>
<tr>
<th>Sample</th>
<th>ON64</th>
<th>BR</th>
<th>BCR-1</th>
<th>DRN</th>
<th>R23</th>
</tr>
</thead>
<tbody>
<tr>
<td>n&lt;sup&gt;1&lt;/sup&gt;</td>
<td>3</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>Li</td>
<td>21</td>
<td>13</td>
<td>11</td>
<td>37</td>
<td>19 ± 4.3%&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>rec&lt;sup&gt;2&lt;/sup&gt;</td>
<td>21.8</td>
<td>13</td>
<td>13</td>
<td>45</td>
</tr>
<tr>
<td>Zn</td>
<td>105</td>
<td>77&lt;sup&gt;3&lt;/sup&gt;</td>
<td>128</td>
<td>164</td>
<td>109 ± 6.3%</td>
</tr>
<tr>
<td></td>
<td>rec&lt;sup&gt;2&lt;/sup&gt;</td>
<td>150</td>
<td>120</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>48</td>
<td>404</td>
<td>23</td>
<td>42</td>
<td>618 ± 2.9%</td>
</tr>
<tr>
<td></td>
<td>rec&lt;sup&gt;2&lt;/sup&gt;</td>
<td>380</td>
<td>16</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>43</td>
<td>58</td>
<td>37</td>
<td>41</td>
<td>68 ± 6.6%</td>
</tr>
<tr>
<td></td>
<td>rec&lt;sup&gt;2&lt;/sup&gt;</td>
<td>31</td>
<td>37</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>12</td>
<td>74&lt;sup&gt;3&lt;/sup&gt;</td>
<td>16</td>
<td>82</td>
<td>141 ± 6.6%</td>
</tr>
<tr>
<td></td>
<td>rec&lt;sup&gt;2&lt;/sup&gt;</td>
<td>72</td>
<td>19</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>302</td>
<td>1255</td>
<td>795</td>
<td>516</td>
<td>532 ± 5.8%</td>
</tr>
<tr>
<td></td>
<td>rec&lt;sup&gt;2&lt;/sup&gt;</td>
<td>280</td>
<td>1030</td>
<td>650</td>
<td>380</td>
</tr>
</tbody>
</table>

<sup>1</sup> number of determinations

<sup>2</sup> recommended values from Abbey (1977) except ON64 (J. Muyssen, pers. comm.)

<sup>3</sup> based on two determinations, other samples rejected due to contamination

<sup>4</sup> coefficient of variation
values for the samples, it should not detract from using the
data for comparisons between samples.

The Li value for BIA differs from Abbey's (1977) recommended value of 45 ppm, but is in agreement with values of 35, 36 and 37 obtained on the same sample split and values of 35 and 35 obtained on a different split supplied by Abbey (P. Fung, pers. comm.). The discrepancy remains unresolved.
AI.3 Volatiles and FeO

The volatiles ($H_2O^+$, $H_2O^-$, $CO_2$) and FeO were determined by standard wet chemical procedures, briefly summarized below:

a) Total $H_2O$ — a modified Penfield tube method, using a lead/lead chromate/calcium carbonate flux.

b) $H_2O^-$ — a gravimetric method, after overnight drying in an oven at 115°C.

c) $H_2O^+$ — the difference between a) and b).

d) $CO_2$ — the sample powder was reacted with HCl and the evolved $CO_2$ dried and collected in an absorption cell filled with Ascarite. The change in weight of the absorption cell equals the $CO_2$ evolved.

e) FeO — a titrimetric method using potassium dichromate as the titrant. The end point was determined with a Zeromatic pH meter using a calomel and a platinum electrode.

Accuracy and precision were assessed by repeat runs of in-house standard ON64 and some samples. Details are presented in Table AI.10.
Table AI.10  Precision data for wet chemical methods

<table>
<thead>
<tr>
<th>Element</th>
<th>Sample</th>
<th>n</th>
<th>$\bar{x}$</th>
<th>s</th>
<th>Rec</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO</td>
<td>ON64</td>
<td>16</td>
<td>6.74</td>
<td>.14</td>
<td>6.77</td>
</tr>
<tr>
<td>$\cdot H_2O\cdot$</td>
<td>RL7</td>
<td>4</td>
<td>3.87</td>
<td>.10</td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>R69</td>
<td>6</td>
<td>4.08</td>
<td>.05</td>
<td></td>
</tr>
<tr>
<td>Pure $CaCO_3$</td>
<td></td>
<td>2</td>
<td>44.73</td>
<td>.18</td>
<td>44.00 (\text{Theoretical yield})</td>
</tr>
<tr>
<td>$H_2O_T$</td>
<td>ON64</td>
<td>3</td>
<td>.54</td>
<td>.03</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\) J. Muysson, pers. comm.
AI.4 Instrumental Neutron Activation Analysis (INAA)

Thirteen samples were analysed for REE (La, Ce, Nd, Sm, Tb, Yb, Du), Ta, Th, and Hf by INAA. About 250 mg of dry sample powder were accurately weighed into a pure silica vial. The vials were numbered and sealed. Samples were irradiated in the McMaster Nuclear Reactor and counted on Li-drifted Ge-detectors. Two irradiations and counts were used due to the differing half-lives of the rare-earths:

i) 30 min irradiation at flux rate $1.3 \times 10^{13}$ n/cm$^2$/sec followed by 48 hours cooling and 1800 sec count. Only the peaks of interest were selected and peak intensities were calculated automatically by microprocessor or manually from the count data.

ii) 12 hour irradiation at flux rate $1.3$ n/cm$^2$/sec, 14 days cooling and 4000 sec count. The full spectrum from 35 to 370 KeV was reduced through the peak-fitting program SAMPO (Routti 1969).

In both cases, the multi-channel analysers were calibrated with commercially- and laboratory-prepared radioisotopes. Peak intensities were decay corrected and concentrations calculated relative to the standard BCR-1. Peak energies used are included in Table AI.11. W-1 was analysed as an unknown to check on accuracy and precision (Table AI.11). Precisions appear to be better than 5% for Ce, Lu, Tb, Hf and Th; better than 10% for Yb and Eu; 12% for Ta and 20% for Nd.
<table>
<thead>
<tr>
<th>Element</th>
<th>Peak KeV</th>
<th>Batch A</th>
<th>Batch B</th>
<th>Recommended</th>
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</thead>
<tbody>
<tr>
<td>La</td>
<td>1596.5</td>
<td>10.5</td>
<td></td>
<td>9.8</td>
</tr>
<tr>
<td>Ce</td>
<td>145.4</td>
<td>22</td>
<td>24</td>
<td>23</td>
</tr>
<tr>
<td>Nd</td>
<td>91.1</td>
<td>10</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Sm</td>
<td>103.2</td>
<td>2.87</td>
<td></td>
<td>3.33</td>
</tr>
<tr>
<td>Eu</td>
<td>344.4</td>
<td>1.14</td>
<td>?</td>
<td>.96</td>
</tr>
<tr>
<td>Tb</td>
<td>298.5</td>
<td>.62</td>
<td>.56</td>
<td>.65</td>
</tr>
<tr>
<td>Yb</td>
<td>198.0</td>
<td>2.1</td>
<td>2.4</td>
<td>2.1</td>
</tr>
<tr>
<td>Lu</td>
<td>208.4</td>
<td>.35</td>
<td>.34</td>
<td>.35</td>
</tr>
<tr>
<td>Ta</td>
<td>67.8</td>
<td>.44</td>
<td>.56</td>
<td>.50</td>
</tr>
<tr>
<td>Th</td>
<td>311.9</td>
<td>2.3</td>
<td>2.5</td>
<td>2.42</td>
</tr>
<tr>
<td>Hf</td>
<td>133.0</td>
<td>2.4</td>
<td>2.4</td>
<td>2.67</td>
</tr>
</tbody>
</table>

1 Flanagan (1973)
Estimates are not available for La and Sm as only one
determination was made. Accuracy appears good compared to
Flanagan's (1973) values, although Sm and Tb may be slightly
low and some Nd values from samples run in batch A may be
low.

AI.5  U and Th Determinations

Uranium and thorium analyses were carried out by Dr.
E. Hoffmann of Nuclear Activation Services by delayed neutron
counting and INAA respectively. Estimated counting errors
for U were 5% at the .20 ppm level and better for higher
levels (Hoffmann, pers. comm.). Detection limit for Th was
1 ppm and estimated counting errors were 100% at 1 ppm, 50%
at 3 ppm and 15% at 11 ppm. Results from standard rocks for
both U and Th are included in Table AI.12. U shows good
agreement for the low U standards which cover the range of
values found in the samples. Deviations in the higher
standards may reflect uncertainties in the recommended values.
Th values for the samples are low, with many below the
detection limit. Although the results are included in Table A2.1,
they have not been used in this study. Th results from the
REE-spectra (Table A2.2) were considered to be more
accurate, due to the longer irradiations and count times, plus
the processing of the spectra by least-squares techniques and
have been used for the discussion in the text.
Table AI.12  U and Th results for standard rocks (ppm)

<table>
<thead>
<tr>
<th></th>
<th>U</th>
<th>Th</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>found</td>
<td>Rec(^1)</td>
</tr>
<tr>
<td>NIMG</td>
<td>18.51</td>
<td>15</td>
</tr>
<tr>
<td>AGV-1</td>
<td>1.99</td>
<td>2.0</td>
</tr>
<tr>
<td>JG-1</td>
<td>4.21</td>
<td>3.3</td>
</tr>
<tr>
<td>NIM-N</td>
<td>.32</td>
<td>.4</td>
</tr>
<tr>
<td>JB-1</td>
<td>1.76</td>
<td>1.8</td>
</tr>
</tbody>
</table>

\(^1\) Abbey (1977)

\(^2\) Below detection limit (= 1 ppm)
APPENDIX II

COMPILATION OF RESULTS

Analytical results for major- and trace-elements and some element ratios are presented in Table AII.1. Samples are grouped into series based on the interpretation of stratigraphic variations of chemistry (see 5.2). Sample values below the detection limit for an element are represented by zero values, and similarly, ratios involving these elements are assigned zero values.

REE, Ta, Hf and Th values derived from INAA are presented in Table AII.2 along with some element ratios. Chondrite normalized element values and element ratios are presented in Table AII.3.
<table>
<thead>
<tr>
<th>Element</th>
<th>R14</th>
<th>R19</th>
<th>R28</th>
<th>R37</th>
<th>R51</th>
<th>R57</th>
<th>R63</th>
<th>R67</th>
<th>R72</th>
<th>R78</th>
<th>R93</th>
<th>R95</th>
<th>R105</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>6.9</td>
<td>8.2</td>
<td>14.9</td>
<td>14.5</td>
<td>16.2</td>
<td>5.1</td>
<td>4.8</td>
<td>11.8</td>
<td>16.2</td>
<td>11.4</td>
<td>8.2</td>
<td>38.5</td>
<td>6.9</td>
</tr>
<tr>
<td>Ce</td>
<td>21.4</td>
<td>24.5</td>
<td>37.5</td>
<td>22.3</td>
<td>44.5</td>
<td>13.3</td>
<td>9.3</td>
<td>27.0</td>
<td>39.7</td>
<td>29.2</td>
<td>19.4</td>
<td>11000</td>
<td>19.6</td>
</tr>
<tr>
<td>Nd</td>
<td>10.8</td>
<td>16.9</td>
<td>18.3</td>
<td>11.6</td>
<td>15.9</td>
<td>6.7</td>
<td>4.6</td>
<td>19.4</td>
<td>22.5</td>
<td>20.2</td>
<td>10.3</td>
<td>55.5</td>
<td>12.1</td>
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<tr>
<td>Sm</td>
<td>3.55</td>
<td>4.45</td>
<td>5.57</td>
<td>2.67</td>
<td>2.48</td>
<td>2.18</td>
<td>1.70</td>
<td>5.07</td>
<td>7.9</td>
<td>4.3</td>
<td>3.08</td>
<td>9.87</td>
<td>2.97</td>
</tr>
<tr>
<td>Eu</td>
<td>1.103</td>
<td>1.369</td>
<td>1.803</td>
<td>.961</td>
<td>.655</td>
<td>.825</td>
<td>.650</td>
<td>1.479</td>
<td>2.084</td>
<td>1.448</td>
<td>1.161</td>
<td>3.114</td>
<td>1.000</td>
</tr>
<tr>
<td>Yb</td>
<td>1.81</td>
<td>1.34</td>
<td>1.86</td>
<td>1.82</td>
<td>3.35</td>
<td>2.50</td>
<td>2.45</td>
<td>2.58</td>
<td>4.37</td>
<td>2.98</td>
<td>2.14</td>
<td>4.42</td>
<td>1.35</td>
</tr>
<tr>
<td>Lu</td>
<td>.319</td>
<td>.287</td>
<td>.311</td>
<td>.249</td>
<td>.562</td>
<td>.373</td>
<td>.367</td>
<td>.449</td>
<td>.747</td>
<td>.475</td>
<td>.347</td>
<td>.605</td>
<td>.271</td>
</tr>
<tr>
<td>Ta</td>
<td>.54</td>
<td>.62</td>
<td>1.71</td>
<td>.94</td>
<td>1.19</td>
<td>.45</td>
<td>.97</td>
<td>.89</td>
<td>1.11</td>
<td>92</td>
<td>1.16</td>
<td>6.34</td>
<td>.82</td>
</tr>
<tr>
<td>Hf</td>
<td>2.47</td>
<td>2.66</td>
<td>3.52</td>
<td>2.30</td>
<td>2.66</td>
<td>1.28</td>
<td>.78</td>
<td>2.98</td>
<td>4.52</td>
<td>2.87</td>
<td>2.11</td>
<td>7.18</td>
<td>2.42</td>
</tr>
<tr>
<td>Th</td>
<td>.68</td>
<td>1.26</td>
<td>2.25</td>
<td>1.31</td>
<td>11.56</td>
<td>1.48</td>
<td>.90</td>
<td>.89</td>
<td>1.90</td>
<td>1.17</td>
<td>.81</td>
<td>3.98</td>
<td>1.38</td>
</tr>
<tr>
<td>Zr/Hf</td>
<td>38.5</td>
<td>46.6</td>
<td>40.1</td>
<td>40.0</td>
<td>30.5</td>
<td>49.2</td>
<td>94.9</td>
<td>44.3</td>
<td>44.4</td>
<td>48.8</td>
<td>46.9</td>
<td>44.0</td>
<td>45.5</td>
</tr>
<tr>
<td>Zr/Ce</td>
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<td>5.1</td>
<td>3.8</td>
<td>4.1</td>
<td>1.8</td>
<td>4.7</td>
<td>8.0</td>
<td>4.9</td>
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<td>4.8</td>
<td>5.1</td>
<td>2.8</td>
<td>5.6</td>
</tr>
<tr>
<td>Th/U</td>
<td>3.4</td>
<td>4.7</td>
<td>4.0</td>
<td>3.4</td>
<td>3.8</td>
<td>3.9</td>
<td>5.0</td>
<td>1.9</td>
<td>3.1</td>
<td>2.7</td>
<td>2.3</td>
<td>4.7</td>
<td>6.8</td>
</tr>
</tbody>
</table>
Table AII.3  Chondrite normalized REE's and element ratios

<table>
<thead>
<tr>
<th>Element</th>
<th>Chondrite Values</th>
<th>R14</th>
<th>R19</th>
<th>R28</th>
<th>R37</th>
<th>R51</th>
<th>R57</th>
<th>R63</th>
<th>R67</th>
<th>R72</th>
<th>R78</th>
<th>R93</th>
<th>R95</th>
<th>R105</th>
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<tbody>
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<td>.33</td>
<td>21.1</td>
<td>25.0</td>
<td>45.3</td>
<td>44.0</td>
<td>49.0</td>
<td>15.6</td>
<td>14.6</td>
<td>35.9</td>
<td>49.0</td>
<td>34.6</td>
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<td>116.5</td>
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</tr>
<tr>
<td>Ce</td>
<td>.88</td>
<td>24.3</td>
<td>27.8</td>
<td>41.2</td>
<td>25.4</td>
<td>50.6</td>
<td>15.2</td>
<td>10.5</td>
<td>30.7</td>
<td>45.1</td>
<td>33.2</td>
<td>22.0</td>
<td>127.3</td>
<td>22.3</td>
</tr>
<tr>
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<td>.60</td>
<td>17.9</td>
<td>28.1</td>
<td>30.5</td>
<td>19.4</td>
<td>26.5</td>
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<td>37.6</td>
<td>33.6</td>
<td>17.2</td>
<td>92.5</td>
<td>20.2</td>
</tr>
<tr>
<td>Sm</td>
<td>.181</td>
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<td>24.6</td>
<td>30.0</td>
<td>14.8</td>
<td>13.7</td>
<td>12.0</td>
<td>9.4</td>
<td>28.0</td>
<td>43.8</td>
<td>23.8</td>
<td>17.0</td>
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<td>26.1</td>
<td>13.9</td>
<td>9.5</td>
<td>12.0</td>
<td>9.4</td>
<td>21.4</td>
<td>30.2</td>
<td>21.0</td>
<td>16.8</td>
<td>45.1</td>
<td>14.5</td>
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<td>16.0</td>
<td>12.7</td>
<td>11.0</td>
<td>15.0</td>
<td>10.9</td>
<td>9.0</td>
<td>16.4</td>
<td>31.0</td>
<td>14.9</td>
<td>13.9</td>
<td>30.6</td>
<td>11.2</td>
</tr>
<tr>
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1 Composite of 9 chondrites (Haskin et al 1968)
2 Eu* Expected Eu value, determined by interpolation between Sm and Tb
APPENDIX III
CIPW NORMS

CIPW norms were calculated for all samples after correcting for the oxidation of Fe and ignoring CO₂ and H₂O+ (see 5.3). Abbreviated versions of the norms are included in Table AIII.1, which lists normative plagioclase (Ab + An), quartz, olivine (Fo + Fa), hypersthene (En + Fs), and diopside (Wo + En + Fs) contents. The presence of nepheline, corundum or wollastonite is noted, indicating a failure to fully correct for alteration processes. Norms also contained Ilm, Mt, Ap and Or. Samples are grouped in series as in Table AIII.1. Heterogeneous flows and fracture zone samples are omitted.
Table AIII.1 Abbreviated CIPW Norms

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APPENDIX IV
MODEL EQUATIONS

AIV.1 Fractional Crystallization

Fractional crystallization can be modelled assuming either:

i) equilibrium between crystals and melt is maintained at crystal surfaces only, or crystals are removed from the melt immediately they form, ie Rayleigh-type fractionation

ii) equilibrium between crystals and melt is maintained throughout the crystallizing interval, ie Equilibrium crystallization

iii) a portion of crystals are formed in equilibrium (as in ii) but are then removed from the melt before further crystallization, ie Incremental crystallization

Rayleigh and equilibrium crystallization models represent the two extremes, with incremental crystallization models being intermediate. Under natural conditions, with gravitational settling of crystals in a magma chamber, equilibrium crystallization may not be applicable. Consequently,
Rayleigh fractionation, or the more complex incremental crystallization, may serve as a better model.

Following the Rayleigh law:

$$C_1 = C_0 F (D - 1)$$  \hspace{1cm} (1) \hspace{1cm} (Neumann et al. 1954)

where

- $C_1$ = trace element concentration in the fractionated liquid
- $C_0$ = trace element concentration in the initial liquid
- $F$ = mass fraction of residual liquid
- $D$ = bulk partition coefficient for the trace element

if $D << 1$ i.e. the element is hygromagnatophile ($H$-element)

then

$$C_1^H = C_0^H / F$$  \hspace{1cm} (2)

or

$$F = C_0^H / C_1^H$$  \hspace{1cm} (2a) \hspace{1cm} (Treuil and Varet 1973)

Thus by substituting for $F$ in (1), the Rayleigh law for a non-$H$ or less-$H$ element can be written:

$$C_1^i = C_0^i \frac{C_0^H}{C_1^H} (D_i - 1)$$  \hspace{1cm} (3) \hspace{1cm} (Treuil and Varet 1973)

and thus:

$$\log C_1^i = \log C_0^i + (D_i - 1) \log C_0^H - (D_i - 1) \log C_1^H$$  \hspace{1cm} (4)
Plotting log $C_i^1$ vs log $C_i^R$ will produce a straight line with slope $(1 - \overline{D}_i)$, allowing the estimation of $\overline{D}_i$ for any element, given a suitable H-element to compare it with, e.g. Th, Ta, or for this study TiO$_2$. Changes of $\overline{D}_i$ with temperature or composition will produce curving of the line on the log-log plot. Changes of $\overline{D}_i$ due to changes in mineral assemblage will result in sharp changes of slope, with a new line for the new assemblage.

If $\overline{D}_i$ can be estimated in this way, then estimates of the mineral percentages in the crystallizing assemblage can be made from the relationship:

$$\overline{D}_i = \overline{D}^a_i x_a + \overline{D}^b_i x_b + \ldots \ldots \text{ etc.} \quad (5)$$

where $\overline{D}^a_i = \text{the mineral-melt partition coefficient}$

$x_a^i = \text{the mass fraction of the phase a in the crystallizing assemblage}$

At least as many $\overline{D}_i$'s as minerals are needed to solve the equations, however.

The above procedure has been followed in 6.1, although it should be noted that it is dependent upon the assumptions that:

a) $\overline{D}_i$ does not vary with $F$

b) The erupted lavas are representative samples of the liquid at the time of eruption

c) The mineral-melt partition coefficients are known.
All these assumptions are subject to uncertainty.

AIV.2 Partial Melting Models

AIV.2.1

As with crystallization, melting processes can be modelled assuming Rayleigh-type, equilibrium or incremental melting. Unlike crystallization, however, & particularly for high degrees of melting, Rayleigh-type models are not geologically sound. Modelling has thus followed either the equilibrium or incremental melting models.

AIV.2.2 Equilibrium Batch Melting

The concentration of a trace element in a melt can be calculated thus:

\[ C_L = \frac{C_0}{D + F (1 - D)} \]  

(6) (Gast 1968, Shaw 1970)

where

- \( C_L \) = the concentration in the melt
- \( C_0 \) = the initial concentration in the solid
- \( D \) = the bulk partition coefficient of the solid
- \( F \) = the mass fraction of melt produced

or for the more geologically reasonable non-modal melting
\[ C_L = \frac{C_0}{D_0 + P (1 - P)} \]  

where \[ D_0 = \sum_n x_n D_n \]

- \( x_n \) = the mass fraction of mineral \( n \) in the initial solid
- \( D_n \) = the mineral-melt partition coefficient
- \( P = \sum_n P_n D_n \)

- \( n \) = the mass fractions of minerals going into the melt

Melting ceases when one of the phases is exhausted (Presnall 1969, Shaw 1977) and thus \( P \) is restricted to values less than \( x_a / P_a \), where \( a \) is the exhausted phase. Further melting can be modelled by resetting the mineral proportions involved.

Modelling according to eqn 7, as in 6.2, assumes that \( D_n \) and \( P_n \) remain constant during melting. It is also assumed that a vapour phase is absent.

AIV.2.3 Incremental or Continuous Partial Melting

Incremental melting models assume that equilibrium batch-melting applies, but that at the end of melting, the melt is removed before the next increment of melting. Thus:
\[
\frac{\left(C_L\right)_R}{C_0} = \frac{\left(C_s\right)_R - 1}{I + D_R (1 - I)} \quad \text{(8): (Wood 1979b)}
\]

where \( R \) = the number of the melting increment
\( \left(C_s\right)_{R-1} \) = the concentration of the trace element in the residue from the previous melting increment
\( I \) = the mass fraction of the liquid phase in each increment
\( D_R \) = the bulk partition coefficient for the melting increment

If some of the melt produced remains with the residue, however, eqn 8 becomes

\[
\frac{\left(C_L\right)}{C_0} = \frac{\left(C_s\right)_{R-1}}{(Q + I) + D_R (1 - (Q + I))} \quad \text{(9): (Langmuir et al. 1977; Wood 1979b)}
\]

where \( Q \) = the mass fraction of liquid remaining with the residue
\( \left(C_s\right)_{R-1} \) = the concentration of the trace element in the residue, including the irrempovable liquid

\( \left(C_s\right)_{R-1} \) is evaluated thus:
\[
\frac{(C'_s)_{R}}{C_0} = \frac{(C_L)_{R}}{C_0} \left( Q + D_R - D_R Q \right) \tag{10}
\]

and \( D_R = x_{Rn} D_n \) \tag{11}

where \( x_{Rn} = (x_n - P_n (F_R - F_1)) A \)

\( F_R = \) the total fraction of liquid produced at the end of the \( R \)th increment

\( F_1 = \) the mass fraction of liquid in the first melting increment

\( A = \) the normalizing factor

\( 1/(1 - (F_R - F_1)) \)

other symbols as defined above.

Application of the incremental models is subject to the same constraints as the equilibrium models.
BIBLIOGRAPHY


Alexander P O (1979) Rare earth elements in Dhandhuka Bore Hole suite Deccan Basalts, western India. J Geol Soc India 20, 73-82.


(1977) The Grenville Province as a shear zone.

Nature 267, 337-338.


Burke K C and Dewey J F (1973) Plume generated triple junctions: Key indicators in applying plate tectonics to old rocks. Geol 81, 406-433.


Coish R A (1979) Rare earth geochemistry of basalts from the Betts Cover ophiolite, Newfoundland. Geol Soc Amer, Abstr with Prog 11, 403.


in Chemistry Series 101, 317-327.
Crerar D A and Barnes H L (1976) Ore solution chemistry V: solubilities of chalcopyrite and chalcocite assemblages in hydrothermal solutions at 200° to 350°C. Econ Geol 71, 772-794.


------------- (1974) Middle Keweenawan rocks of the Batchewana-Mamainse Point area, field guide. 20th Ann Inst Lake


Hamblin W K (1961) Paleogeographic evolution of the Lake Superior region from Late Keweenawan to Late Cambrian time. Geol Soc Amer, Bull 72, 1-18.


Herrmann A G (1970) Yttrium and lanthanides. in Wedepohl K H "Handbook of geochemistry", vol II/5, Springer-Verlag,
Berlin.
Irving R D (1883) The copper-bearing rocks of Lake Superior. U S Geol Surv, Mono 5.


Jolly W T (1972) Degradation (hydration)-aggradation (dehydration) and low rank metamorphism of mafic volcanic sequences. Inter Geol Cong 24th, Trans 2, 11-18.


Leeman, W P (1977a) Pb and Sr isotopic study of Keweenawan lavas and inferred ~4 BY old lithosphere beneath part of Minnesota. Geol Soc Amer, Abstr with Prog 9, 1068.

---------- (1977b) Comparison of Rb/Sr, U/Pb and rare earth characteristics of sub-continental and sub-oceanic mantle regions. in Dick, H J B (ed) "Magma genesis", Oregon Dept Geol and Min Ind, Bull 96, 149-168.


Liou, J G (1971a) P-T stabilities of laumontite, wairakite, lawsonite and related minerals in the system CaAlSi_2O_8-SiO_2-H_2O. J Petrol 12, 379-411.

----------- (1971c) Synthesis and stability relations of prehnite, $\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$. Amer Mineral 56, 507-531.

----------- (1973) Synthesis and stability relations of epidote, $\text{Ca}_2\text{Al}_2\text{FeSi}_3\text{O}_{12}(\text{OH})$. J Petrol 14, 381-413.


Logan, Sir William (1863) Geology of Canada. Geol Surv Canada, Rept Progress from its commencement to 1863.


Marchand M (1973) Determination of Rb, Sr and Rb/Sr by XRF, McMaster Univ, Dept Geol Tech Memo 73-2.


Mattey D P, Gibson I L, Marriner G F, and Thompson R N (1977) The diagnostic geochemistry, relative abundance, and


Neumann E-R and Ramberg I B (1978) 'Paleorifts -- concluding remarks.' In Ramberg I B and Neumann E-R (eds) "Tectonics


---------- (1973) Tectonic setting of basic volcanic rocks determined using trace element analyses. Earth Planet Sci Letts 19, 290-300.


Routti J T (1969) SAMPO, a FORTRAN IV program for computer analysis of gamma-ray spectra from Ge(Li) detectors, and for other spectra with peaks. Lawrence Radiation Lab Rept UCRL 19452.

Res 83, 1289-1304.


-------- (1976b) Widespread continental rifting: some considerations of timing and mechanism. Geology 4, 427-430.


177-190.


Stosch H G, Jagoutz E, Carlson R W and Lugmair G W (1979) Mantle differentiation as recorded by ultramafic nodules: oceanic mantle beneath continental crust. EOS 60, 971.


Tarney J, Saunders A D, Weaver S D, Donellan N C B and Hendry G L (1978) Minor-element geochemistry of basalts from Leg 49, North Atlantic Ocean. in Luyendyk B P,
Cann J R, et al., Init Rept DSDP 49, 657-691.

Thompson A B (1971) $\text{PCO}_2$ in low grade metamorphism: zeolite, carbonate; clay mineral, prehnite relations in the system $\text{CaO-Al}_2\text{O}_3-\text{SiO}_2-\text{CO}_2-\text{H}_2\text{O}$. Contrib Mineral Petrol 33, 145-161.


White W S (1966) Tectonics of the Keweenawan basin, western Lake Superior region. U S Geol Surv, Prof Paper 524-E.


"In Nature's infinite book of secrecy
A little I can read"

Anthony and Cleopatra (Act I, scene 2),