STRUCTURAL RELATIONSHIPS AND GEOCHEMICAL INVESTIGATION

OF THE LYNN VOLCANIC COMPLEX, PINE HILL,

BOSTON NORTH QUADRANGLE, MASSACHUSETTS

By

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Field relationships at Pine Hill in the Middlesex Fells Reservation north of Boston, Massachusetts, demonstrate that felsic rocks assigned to the Lynn Volcanics are intruded by the late Precambrian Dedham Granodiorite. This indicates that at least part of the Lynn Volcanics are Precambrian in age, and not Siluro-Devonian as suggested by correlation with the Newbury Volcanics in northeasternmost Massachusetts. It is not yet known if all rocks presently assigned to the Lynn Volcanics are Precambrian, or if this correlation applies to other felsic volcanics (e.g. Mattapan Volcanics) in the Boston area. Near the contact at Pine Hill the Dedham contains xenoliths of the Lynn Volcanics. The granodiorite is structurally above the volcanics and the contact cuts sharply across the strike of bedding mapped within the volcanics. The felsite can be divided into three major members based on ground mass textures and the size and abundance of phenocrysts and xenoliths. Flow units were deposited prior to the tuffs which are structurally higher than, and contain fragments of the flows and older quartzite formations.
Mapped units at Pine Hill have distinctive major and trace element, including rare earth element (REE), compositions. In particular, two felsic units studied in detail,

the Mud Road and Pine Flow, are related along a liquid line of descent, indicating an important role for fractional crystallization. A volcanic xenolith in the Dedham Granodiorite has the major and trace element characteristics of the Pine Flow Unit. REE abundances are consistant with the Dedham Granodiorite as a "parental" source, from which the rhyolite rocks were fractionated; however, more geochemical study is required to evaluate the possible genetic relationship of the Dedham Granodiorite to the Lynn Volcanics. Reconnaissance geochemical analysis of the Mattapan, Newbury and Middlesex Fells Volcanic Complexes indicate that the Middlesex Fells and Newbury are unrelated, and that the Mattapan is very similar based on the geochemistry of the collected specimens.

Thesis Supervisor: Frederick A. Frey, Associate Professor, Geochemistry

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# CHAPTER I

## INTRODUCTION

This research involves a careful study of the field relationships, petrography and geochemistry of the Lynn Volcanic Complex at Pine Hill, Middlesex Fells Reservation, North of Boston. Pine Hill is located just north of the North Boundary Fault (Figure 1-1). This site was selected for study because contact relationships of the Lynn with the Dedham Granodiorite make it an ideal place to study the relative age of emplacement of the units and establish a Pre or Post Dedham age for the Lynn. My field observations of the Lynn at Pine Hill· indicate that this rhyolitic-rhyodacitic unit is older than the late Precambrian Dedham Granodiorite, hence the Lynn must be no younger than late Precambrian.

Two of the other Boston area felsites sampled, the Newbury Volcanic Complex and the Mattapan Volcanic Complex are considered possible correlates to the Lynn Volcanic Complex (LaForge, 1932; Shride, 1976). On the basis of geochemical and petrographic studies, the Lynn Volcanics at Pine Hill most closely resemble the Mattapan Volcanics, which may also be Precambrian, as they have been zircon dated at 570 m.y. by R.E. Zartman of the U.S. Geological Survey (personal communication).

Fig. 1-1

# GENERALIZED GEOLOGIC MAP
# OF SOUTHEASTERN NEW ENGLAND



Western Low Grade Belt

Central High Grade Belt

study area

BOSTON BASIN

Eastern Low Grade

P

P
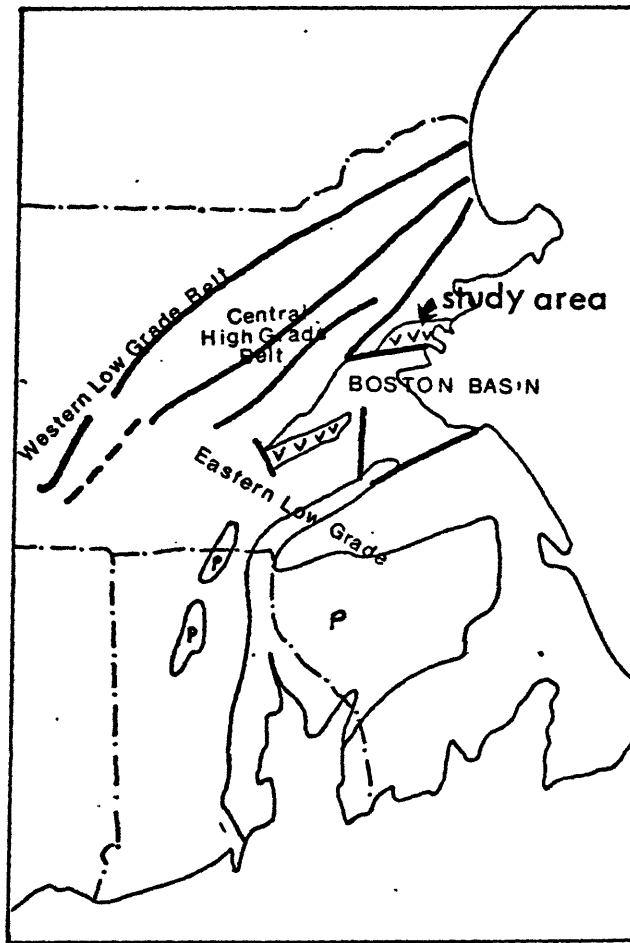
after Cameron and Naylor, 1976

LEGEND

——— Fault

P    Pennsylvanian Basin

V V    Volcanics

N

0      15 MILES
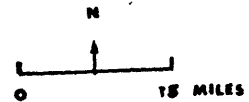
Fig. 1-2

# VOLCANIC COMPLEXES:
# SOUTHEAST NEW ENGLAND
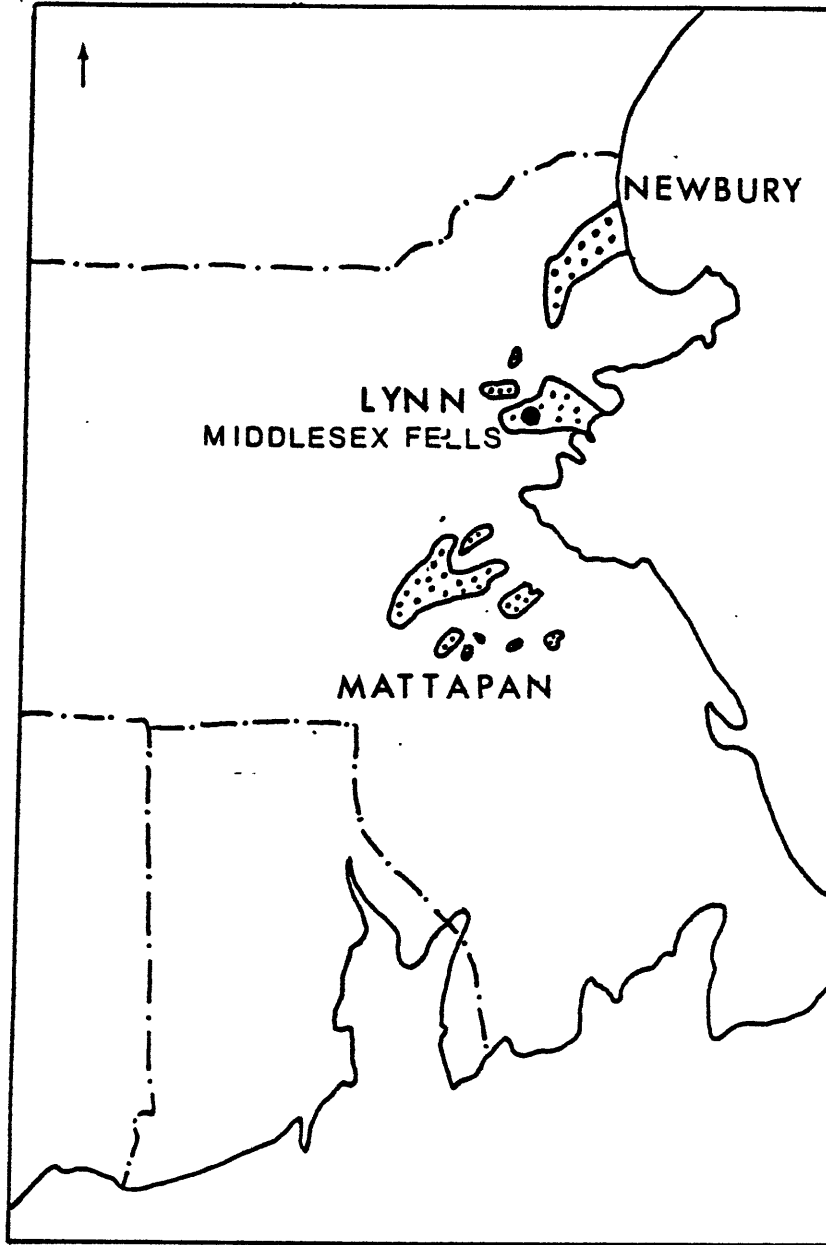
The Mattapan Volcanics underlie the Boston Basin, and it is their age which is the key in determining the lower boundary for the age of the basin. According to the regional synthesis in the early part of the century, the most plausible age for the Boston Basin was Carboniferous based on: association with the Narragansett Basin (Emerson, 1917) known Carboniferous age; the 1900 discovery of two poorly preserved tree trunk fossils of the same age (Burr and Burke, 1900) ; and an Upper Devonian age assumed for the Dedham Granodiorite (Emerson, 1917) which is the basement rock of the Boston Basin. However, in light of recent studies, there is little positive evidence for this correlation. The tree trunks have been declared sandstone dikes (Bailey and Newman, 1978) and no other fossils have been discovered. Billings (1929, pp. 99-112) deduced a Precambrian age for the Dedham based on field relationships with the fossiliferous Hoppin Hill Formation of Cambrian origin. This assignment was not widely accepted until the rocks were radiometrically dated. Fairbairn et al., (1967) reported Rb-Sr dates of lower Cambrian for the Dedham Granodiorite at Hoppin Hill. Although this first date appears somewhat young, it definitely removes the upper Devonian assignment for the Dedham. Subsequent isotopic dating by U-Th-Pb on zircons by Zartman and Naylor (1971); and Rb-Sr on a hornblende (Zartman, personal communication) provide ages of 600 m.y. Southeastern New England has proved extremely difficult

to date radiometrically, producing low dates on units whose age is known by other means (e.g. fossil control) (Olszewski, 1977). This is particularly true of fine grained volcanic rocks, such as the Newbury, where Rb-Sr whole rock dates (Fairbairn, 1967) produced an early Carboniferous age, but fossil evidence collected by Ulrich (in Emerson, 1917, p. 163) indicated a Siluro-Devonian age for these rocks. This fossil control has been confirmed by Cuppels (1967).

Because of the late Precambrian age for the Dedham Granodiorite, the Boston Basin strata cannot be correlated with the Narragansett Basin of Carboniferous age. Therefore in light of the Precambrian Dedham, a lack of fossil control, and a lack of convincing correlation to the Narragansett strata, there is little positive evidence for retaining a Carboniferous age for the Boston Basin.

The objectives of this study were to use field relationships and chemical data to determine internal relationships of the felsites at Pine Hill, and examine their relationship with the Dedham Granodiorite. Another objective was to perform reconnaissance geochemistry on the possible correlatives to the Lynn Volcanics, and examine the likelihood of these relationships. The chemical data were collected by X-ray fluorescence (XRF) and Instrumental Neutron Activation Analysis (INAA).

CHAPTER II

THE BOSTON BASIN AGE PROBLEM


In 1976 (Naylor and Sayer, p. 139) questioned the age of
the Mattapn Volcanic Complex, which is the floor of the Boston
Basin, and suggested that there was "no compelling reason to
assign an age younger than Late Silurian or Early Devonian to
the Mattapan  Volcanics." Although the Carboniferous age
assignment (Billings, 1929) was known to be based on minimal
evidence, the age of the Mattapan, and therefore the Basin,
was not seriously questioned until 1976 (Naylor and Sayer).
The extreme complexity of the Basin and the surrounding terrain
has left the geologic framework of this area relatively un-
known and poorly understood. At the present time, there is
no single theory which is generally accepted as the explana-
tion of when the Boston Basin was formed, and how it relates
to other Southeastern New England geologic units. An histori-
cal overview of the Boston Basin problem is the best means to
explore the past and present theories relating to the synthesis
of Boston Basin geology as we understand it today.

Much of Southeast New England is dominated by topographic,
structural and sediment filled basins (Figure 2-1). Five of
these, the Narragansett, Norfolk, Woonsocket, North Scituate
and Worcester Ccal Basins, are of Pennsylvanian, or supposed
Pennsylvanian Age (Lyons et al., 1976). According to Billings

Fig. 2-1

# BASINS OF NEW ENGLAND
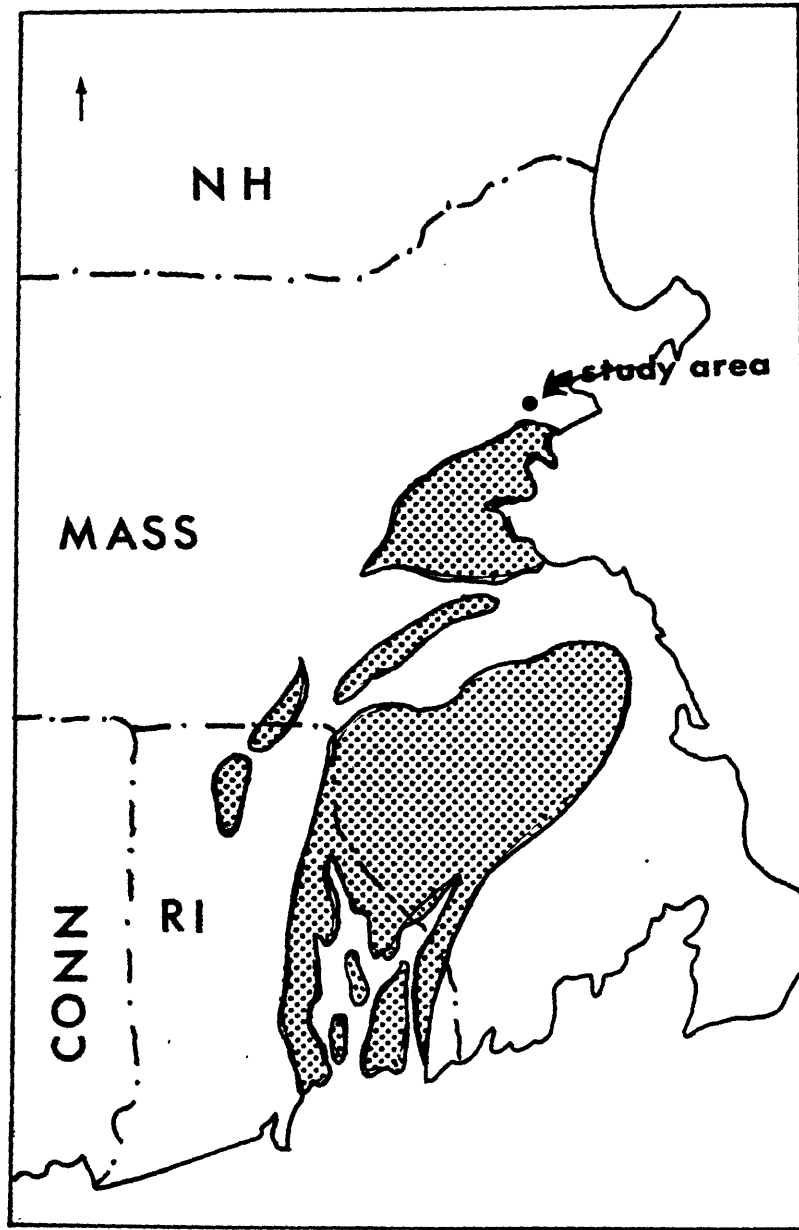
(1976) the Boston Basin is also a structural, sedimentary and topographic Basin. The Northern border is defined by an escarpment along the North boundary Thrust Fault, and the southern border is identified by en echelon thrust faults and locally by escarpment. The western boundary is not very clearly defined, and the eastern boundary is covered by the Atlantic Ocean and Boston Harbor (Figure 1-1). According to LaForge (1932) and Crosby (1880), during the mid-19th century, the Boston Basin was believed to be Cambrian in age. This concept was altered to late Paleozoic when, in 1900 Burr and Burke reported the find of two poorly preserved molds of tree trunk fossils in the Roxbury conglomerate. This allowed for the correlation of the Boston Basin to the basins of known Carboniferous age, most notably the Narragansett with its fossiliferous, Pennsylvanian coal seams. This correlation was backed up by "supposed" lithologic parallels between the two basins.

The synthesis of the Boston Basin in the early 1900's (Figure 2-2) was based on Emerson's 1917 Geologic Map of Massachusetts and many of his correlations are now being questioned. Bell (1948) and Naylor and Sayer (1976) do not find the stratigraphy in the Pennsylvanian basins convincingly similar to that of the Boston Basin. The tree trunk molds have been questioned, and are now considered to resemble

Figure 2-2.  Early 1900's Synthesis of Boston Basin Strati-
            graphy based on Emerson's (1917) geologic map
            of Massachusetts.

N

North Boundary Fault

Boston Basin

Roxbury Conglomerate

Carboniferous

Lynn Volcanics

Mattapan Volcanics

Dedham Granodiorite

Devonian

Newbury Volcanics

Dedham Granodiorite

14
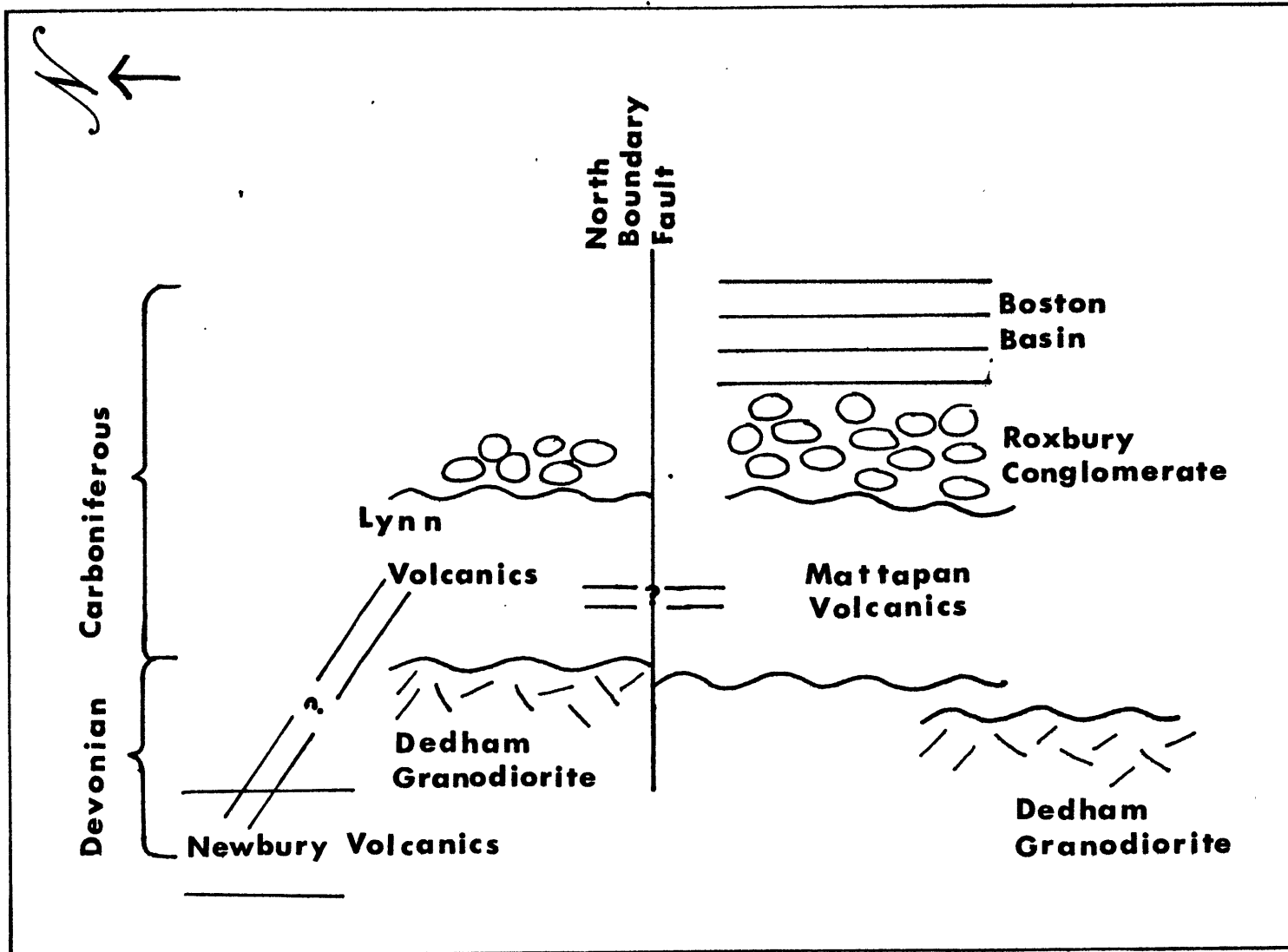
sandstone dikes (Bailey and Newman, 1978).

Perhaps the most important piece of evidence that has initiated this rethinking of Boston Basin geology is the defining of the age of the basement rock, the Dedham Granodiorite. The Dedham is the basement rock, and is overlain or interfingered with the Mattapan Volcanics, which are the pre-sedimentary floor of the Basin. This is indicated by clasts of these rocks in the Roxbury Conglomerate, where an unconformity is obvious. According to Emerson (1917, p. 172-176) the Dedham was assigned an Upper Devonian Age, based on LaForge's mapping. LaForge, (1932), suggested the correlation of the Mattapan Volcanics to two other volcanic complexes North of the Basin and the North Boundary Fault. All these units are grossly similar in lithology, ranging from basaltic to felsic members, and broadly covering the range of a "typical" volcanic pile. These units are the Lynn volcanics, which were the focus of this study, located north of the North Boundary Fault, and south of the Mystic Fault. Their age of these rocks were unknown by direct means, but rather were considered Siluro-Devonian by correlation with the fossiliferous Newbury Volcanics (LaForge, 1932). The proposed Newbury-Lynn-Mattapan correlation (LaForge, 1932) was facilitated by the Upper Devonian age of the Dedham (Figure 2-1). The fossils in the Newbury have been called Devonian at times, therefore the

problem of having Devonian volcanics unconformably upon Upper

Devonian granodiorite did not seem critical. These incon-

sistencies were ignored while major contact relationships

were being established and recognized. In 1929, however,

Billings concluded that the Hoppin Hill Formation rested

unconformably on granite, indicating a Precambrian age for

the granite. From this he deduced that the Dedham Grano-

diorite and other related granites were also Precambrian.

This was not widely accepted until 1967 when H.W. Fairbairn

reported a Rb-Sr whole rock age date of 514±17 m.y. for Hoppin

Hill and 591±28 m.y. for the Dedham Granodiorite. Although

these dates are a bit low, as more refined measurements were

made (R.E. Zartman, personal communication) and dates of 600

m.y., Rb-Sr on hornblende, were obtained, the age of the

Dedham was dropped into the Precambrian, confirming Billings's

1929 observations. This evidence precludes correlation of

the Boston Basin Mattapan, which may be the same age as the

Dedham Granodiorite, with the Newbury Volcanic Complex of

known Siluro-Devonian age. The age of the Lynn, however,

remained unresolved. Therefore, it was our hope that by

establishing the field relationships of the Lynn Volcanics

with the Dedham, an age for the Lynn could be established.

Another objective was to try and define lithologic, petro-

graphic and geochemical similarities between the Mattapan

and Lynn, and perhaps infer a lower limit for the age of the Boston Basin.

CHAPTER III

ROCK UNITS RELATED TO THE BOSTON BASIN PROBLEM


1.   DEDHAM GRANODIORITE


Nomenclature:

Crosby (1880) first mentioned a Dedham granite when dis-
cussing granitic rocks of eastern Massachusetts.  Loughlin
and Hechinger (1914, p. 49) first use the name of Dedham
granite, and describe the rocks as a complete gradation from
alaskite to granite to gabbro.  Emerson (1917, pp. 175-177)
first used the term granodiorite to describe the Dedham.  The
Dedham Granodiorite is named for typical exposures in Dedham,
Massachusetts.


Lithology:

Bell (1948, pp. 80-84) has described nine varieties of
the Dedham Granodiorite.  The variety which covers the unit
in the study region is known as the "normal" variety.  This
unit is characterized by diversity in color (greenish→whitish→
pinkish) with a coarse grained, subhedral granitic texture.
The normal variety ranges from slightly gneissic to porphyri-
tic but is generally equigranular.  Differential weathering
has caused a "hob-nailed boot texture" on most outcrops.

The prevalent mineral phases are calcic andesine, quartz, K-feldspar, and a mafic mineral. The accesories are magnetite and apatite. The andesine crystals are large and commonly euhedral and fractured with strained lamellae. Zone plagioclase is not common in the Dedham Granodiorite. The K-feldspar, in order of abundance occurs as microcine, orthoclase, and microcline-microperthite. The mafics are usually altered to green chlorite, with remnant biotite or hornblende structures present. All specimens examined by Bell (1948) contained calcite, (mafic and calcite $\leq$ 10% of rock), Plag $\tilde{} $ 50%, quartz 25%, K-feldspar $\tilde{} $ 10%, secondary minerals 5%.

## Contact Relationships:

The Dedham Granodiorite represents the oldest plutonic intrusive in southeastern New England. It is known to intrude an unnamed, metasedimentary stratified rock which occurs only as roof pendents and xenoliths in the Dedham, the Westboro Formation and the Middlesex Fells Volcanic Complex, where good contact evidence is observed (Bell and Alvord, 1976, pp. 196-201). The Dedham is also observed to have an intrusive contact with the Lynn Volcanic Complex at Pine Hill in the Middlesex Fells Reservation, North Boston quadrangle, Massachusetts (see Chapter IV).

## Age of the Dedham Granodiorite:

Emerson (1917, pp. 175-177) and LaForge (1932, p. 22)
assigned the Dedham to the Devonian (?) and pre-Devonian,
probably Ordivician, respectively. In 1929, however, Billings
concluded that the Hoppin Hill Formation, which as fossili-
ferous rocks of Cambrian age (Rb-Sr radiometric dates 514±17,
Fairbairn, 1967) were unconformably above the Dedham. From
this, Billings (1929, pp. 99-112) assigned a Precambrian date
to the Dedham Granodiorite. Until radiometric age dating
was employed, this idea was not well accepted. Foye and Lane
(1934, p. 137) concluded that the Dedham was Devonian. Fair-
bairn et al., (1967) obtained a Rb-Sr whole rock age date of
591±28 m.y. for the Dedham Graodiorite, and R.E. Zartman re-
ports a 620 m.y. zircon age date, and a Rb-Sr hornblende
age date (personal communication) of 600 m.y. on the Dedham
Granodiorite. Kovach (1977), reports a 608 m.y. (Rb-Sr) age
date for the Dedham. Thus, a Precambrian age for the Grano-
diorite is fairly well established.


## 2. MATTAPAN VOLCANIC COMPLEX

### Nomenclature:

Emerson ( 1917, p. 200-201) applied the term Mattapan
Volcanic Complex to the volcanic rocks in the Boston area,
which were named for exposures in Mattapan, Boston. Billings

(1929) applied the term Mattapan to the volcanics which under-
lie the Roxbury conglomerate, and rest upon an erosional sur-
face of the Dedham Granodiorite. The oldest of all the fel-
sites are tuffs, felsites, and breccias, which are intruded
by the Dedham Granodiorite, and are considered Precambrian in
age (Billings 1929, pp. 100-134).

### Lithology:

Several varieties of rock make up the Mattapan Volcanic
Complex. The earlier flows appear most felsic, while later
flows are more basic and dark colored. These flows are inter-
bedded, rather than a gradational change between rock types.
Compositional and textural variations are common (Bell, 1948).

Hiatus in activity of the complex is marked by the
accumulation of conglomeratic, lenticular deposits. They
are localized and display poorly rounded and ungraded sedi-
mentary material.

The light colored member shows very well developed flow
banding,with small to large amounts of angular fragments of
felsite incorporated in a fine grained matrix. The rock is
porphyritic, with phenocrysts subordinate (10-20%) over matrix,
which is generally aphanitic to cryptocrystalline. The
phases forming phenocrysts are oligoclase, orthoclase, and
quartz. They seem to be slightly rounded by resorption into

the magma (Bell, 1948). The mafic mineral constituents are
minor, and with the exception of magnetite grains are all
altered to chlorite and epidote. This and other alteration
minerals make up at least 5% of the rock volume. Calcite is
the most abundant replacement mineral.

The more basic flows appear rather abruptly. They are
both amygdaloidal and porphyritic. Many specimens have a
felty texture. Phenocrysts of plagioclase are slightly zoned,
and suffer from extreme alteration. The original mafic minerals
have been completely altered as well. Veins are filled with
calcite, chlorite, and epidote. These rocks are andesites
(Bell, 1948, p. 237).

### Contact Relationships:

The structural relationship of the Dedham and the Matta-
pan have been a question for some time. Outcrops portraying
intrusive contacts of the Dedham into the Mattapan, and visa
versa have been well demonstrated. Basalt dikes which seem
in some cases to originate from the Mattapan intrude into the
overlying Roxbury Conglomerate. The relationships need to be
clarified.

### Age and Correlations:

The age of the Mattapan is uncertain. Billings (1929,
1976, p. 8) assigns a Carboniferous age based on inconclusive

fossil evidence(Pollard, 1965), and because they underlie the
Roxbury Conglomerate (correlated to the fossiliferous Pond-
ville Conglomerate of known Pennsylvanian age, Shaler et al.,
1899). However, Billings (1976, p. 8) also assigns a possible
Siluro-Devonian age to the Mattapan, by correlation to the
Newbury Volcanics, as does Bell (1948, p. 242) and LaForge
(1932). Kaye (Barosh, et al., 1977, p.38) suggest that the
Mattapan may be Cambrian, Cambrian to Silurian, or even
through Carboniferous. A zircon date of 570 m.y. has been
reported by R.E. Zartman (oral communication) of the U.S.
Geological Survey. This late Pre-cambrian age may help to
correlate the Mattapan to the late Pre-cambrian at Pine Hill.


3.   ROXBURY CONGLOMERATE


Nomenclature:

This formation was named by Hitchcock (1861), and is
exposed in the Newton and South Boston Quadrangle (Barosh,
1977).


Lithology:

The Roxbury Conglomerate is thick, interbedded with mud-
flow, sanstone, arkose, argillite and tuffaceous beds. Color
ranges from red to grey (Barosh, 1977).

Contact Relationships:

The Roxbury Conglomerate interfingers with Boston Basin sediments. It lies unconformably above the Mattapan Volcanics and Dedham Granodiorite, of which it contains basal clasts, (LaForge, 1932). The Conglomerate is cut by dikes, which may be part of the Mattapan Volcanics.

Age:

The age of the Roxbury conglomerate is generally given as Devonian or Carboniferous, because of two poorly preserved tree trunk fossils found by Burr and Burke (1900). Bailey and Newman (1978) however, have concluded that these "fossils" are actually sandstone dikes, and cannot be used to date the Roxbury Conglomerate. Recent work by Kaye (personal communication to Barosh et al., 1977) indicate the possibility of an older age for the Roxbury.

4. MIDDLESEX FELLS VOLCANIC COMPLEX

Nomenclature:

This unit was previously included in the Marlboro Formation of Emerson (1917) and LaForge (1932). Field observations indicate that these metavolcanic rocks are older than the outcrop of type section Marlboro, and are separated from it

by stratified rocks.   The present nomenclature was devised
by Bell and Alvard (1976, p. 199).

Lithology:

The Middlesex Fells Volcanic Complex is a "typical" vol-
canic pile.   It consists of coarse pyroclastic deposits,
fine grained tuffs, and lentils of metamorphosed flow rocks
(Bell and Alvord, 1976, p. 200).   Many of the units are dis-
continuous, and cannot be traced from outcrop to outcrop.

Most of the rocks of the Middlesex Fells Volcanic Com-
plex are fine grained, dark grey to black, and have a secon-
dary metamorphic foliation which runs parallel to the layering
with epidotization and chloritization due to hydrothermal retro-
gressive alteration of pyroxenes, amphiboles, and biotite.
Most of the rocks consist of major hornblende and plagioclase
(oligoclase followed by andesine in abundance).   Pods and veins
of epidote are not uncommon.

Lentils of metamorphosed flow rock make up about 20% of the
Complex, but are most abundant in the lower half, with the
lower 300 m exhibiting well preserved pillow structures.
Fine grained tuffs appear to have the greatest continuity,
constituting 60% of the Complex, but lack distinctive features.
Discontinuous pods of metamorphic pyroclastic detritus are
also common   (Bell and Alvord, 1976, p. 199-201).

The tuff lentils are now thinly laminated amphibolite pods. Some are noticeably pinstriped, while others are seemingly massive, or vaguely laminated.

In the flows and pyrocalstic sediment deposits, fragmental deritus, pillows, arygdules and flow banding can be detected, except where intense retrogressive alteration has occured.

There are pods of light grey or reddish grey dacite in the upper part of the formation. All are less than 5 m thick.

Contact Relationships:

According to Bell and Alvord (1976, p. 199) the Middlesex Fells Complex conformably overlies the Westboro Formation.

Age and Correlation:

The Middlesex Fells Volcanic Complex is correlated to the Blackstone Series of Rhode Island, as described by Woodworth (in Bell and Alvord, 1976, p. 199).

The Middlesex Fells Volcanic Complex is considered to be Precambrian, due to the intrusive nature of the radiometrically dated, late Precambrian Dedham Granodiorite into these stratified rocks (see Dedham Granodiorite, this chapter).

## 5.   NEWBURY VOLCANIC COMPLEX:

### Nomenclature:

McDaniel, (1884, p. 165, in Wilmarth, 1936) applied the term Newbury felsite to the rocks between the granite and diorite in that area.   Emerson (1917) named the fesites the Newbury Volcanic Complex, and LaForge (1932, p. 161-164) described it as rhyolitic through basaltic flows, breccias, tuffs, and shale, and occupying the Newbury and Parker River basins in Essex County, Massachusetts.   Shride, (1976) divided the Newbury Volcanic Complex in eleven different lithologic units.

### Lithology:

The first member is a rhyolite tuff which consists of a sheared, poorly welded vitroclastic tuff along the Parker River Fault.   A fine grained andesite (?) lies stratigraphically above the tuff.   This rock has been hydrothermally altered to such an extent that primary textures and structures are almost totally obliterated.   Relatively thick basalt flows (> 30 m) outcrop as topographic ridges, with interbedded depressions that reflect coria borders and thin fossiliferous zones.   The fourth, or Vitric Rhyolitic Lapilli Tuff member, is greenish grey, is friable and exhibits hackly fracturing.

Although devitrified, the outlines of shards are still clear in thin section. The fifth member is a dense, tough, dark grey, structureless rock, presumed to be a basalt by vague outlines of plagioclase laths in a cryptocrystalline matrix. It occurs in a few massive outcrops.

The Flow Banded Rhyolite Vitrophyre is 580 to 670 m thick, and is a dense, flow banded rhyolite vitropyre, and forms prominant outcrops. It is this unit which was geo-chemically analyzed, as most closely related to the Lynn Volcanic Complex. This unit displays a basal tuff, of greyish yellow green to pale red. The tuff contains a large variety of clasts that are platy chips (angular) or lensoidal in nature.

The flow banding in the dense bulk of the rock is its distinguishing characteristic. The laminae are usually 0.25 to 2 mm thick and are differentiated by variable amounts of hematite dust. They are often contorted or brecciated in a way which suggests slumping. Certain stratigraphic intervals have a profusion of spherulites. These zones are from 1-10 m thick. Plagioclase and perhaps anorthoclase occur as blocky phenocrysts (1 to 2 mm), but in many areas the phenocrysts are absent, or miniscule. Since no other flow banded rhyolite is observed in the Newbury, pebbles of such a rock in the overlying andesite are probably relicts from the sur-face.

Member seven, a porphyritic andesite is completely truncated by faults. It is the thickest member in the Newbury, probably 1,650 m, as well as the most diverse. It ranges from a highly propylitized greyish green to dark grey andesite, typified by plagioclase phenocrysts , to tuffs and breccias.

Above this unit are three sedimentary units, a siliceous siltstone, a red mudstone and a calcareous mudstone.

The whole unit is intruded by podlike bodies of micrographic rhyolite, and are aphanitic to sugary in texture. They have spherulitic intergrowths.

The total thickness of this set of volcanics is greater than 4,400 m.

Contact Relationships:

The Newbury Volcanic Complex is compeltely fault bounded, and cannot be observed in contact with any of the adjacent formations.

Age and Correlations:

This fossiliferous unit was first dated by Ulrich (in Emerson, 1917, p. 163) paleontologically as early Silurian-late Devonian. This was confirmed by Toulmin (1964).

Based on lithologic similarity, the Newbury Volcanic Complex has at times been correlated in time with the Lynn Volcanic Complex and the Mattapan Volcanic Complex (Emerson,

1917, p. 200 and Bell, 1948, p. 242). This correlation is not tested.

However, according to Shride (1976, p. 173) the Newbury Volcanic Complex may be the southernmost dated remnant of several Siluro-Devonian volcanic complexes which occur sporadically in a belt through Maine and into New Brunswick.

## 6.    LYNN VOLCANIC COMPLEX

### Nomenclature:

Clapp (1910) and Emerson (1917, p. 200) first use the term Lynn volcanics, however,  it is used to describe the older, more felsic part of the Mattapan Volcanic Complex as described by LaForge (personal communication to Emerson).  In 1921, Clapp (p. 30-31) revised Lynn volcanics to be applied to the felsites north of the Boston Basin.  LaForge (1932, p. 30) first used the term Lynn Volcanic Complex.

### Lithology:

The Lynn represents part of a volcanic pile, with the major component being rhyolitic to rhyodacitic in nature. For the most part, the Lynn has an aphanitic matrix with phenocrysts of two feldspars and quartz.  The mafic content in the felsic member is quite low (less than 1% in most cases).

The rock is extremely brittle, and has responded to deformation mainly by extensive fracturing (Bell, 1948) so the rocks easily break apart into cubic chunks.

Fragments of exotic volcanic material are abundant in the Lynn. They generally appear to be the same composition of the host rock. They tend to be small and angular and were probably an early formed surface which became incorporated in following flows.

Microscope work (Bell, 1948; Zarrow, this paper) shows that the groundmass in many cases is too fine for positive identification of the constituents. However, they appear to contain quartz, feldspar, magnetite, apatite, and mafics altered to chlorite and epidote. The feldspar phenocrysts are cloudy due to sericitization and sausserization, although the quartz is relatively unaffected. The mafics are completely altered to chlorite and epidotes. Veinlets of calcite and quartz and epidote are rather abundant.

Flow banding which is well developed in all the rocks in then section, is not evident in all units on the megascopic scale.

A more detailed look at these rocks, is pursued in Chapter IV and V dealing with field evidence for the age of the Lynn at Pine Hill, and the petrographic characteristic of the Lynn.

Contact Relationships:

The Lynn Volcanic Complex is believed to rest unconformably upon an erosional surface of Precambrian Dedham Granodiorite and metavolcanic rock (Bell, 1976). This relationship is shown to not be consistent with the field relationships observed at Pine Hill, Middlesex Fells Reservation (Chapter IV).

Age and Correlation:

The Lynn Volcanic Complex has been tentatively correlated to the Newbury Volcanic Complex by Emerson (1917) and LaForge (1932). Shride (1976, p. 174) concedes that even though the rocks are lithologically similar this relationship is of yet unsubstantiated. New field evidence at Pine Hill (Chapter IV), indicates a Precambrian age for the Lynn, and hence, these rocks cannot be correlated to the Siluro-Devonian (Shride, 1976) Newbury Volcanics. The Lynn are also tentatively correlated to the Mattapan Volcanics (Emerson, 1917) this relationship is yet to be proved.

CHAPTER IV

FIELD RELATIONSHIPS AT PINE HILL

1.   LITHOLOGIC DESCRIPTIONS

With intensive mapping (Figure 4-1) of the felsic units
at Pine Hill, it was possible to determine an internal strati-
graphy based on phenocryst size and abundance, matrix color
and texture, and xenolith content of the rocks.  Determining
an internal stratigraphy was one of the keys to defining
field relationships with the Dedham Granodiorite.

Pine Flow Unit:

The Pine Flow Unit is the best defined lithologic group
in the field, as well as petrographically and geochemically.
It is a uniform metavolcanic felsite with an aphanitic matrix
and a porphyritic texture.  The phenocrysts consist of quartz,
K-feldspar and plagioclase of $An_{29.4-30.5}$.  This composition
places the rocks on the rhyolite-rhyodacite boundary.  The
phenocrysts of quartz display graphic intergrowth with ortho-
clase, in some instances.  The matrix often displays a fea-
thery texture under the microscope, due to the formation of
feldspar and quartz during devitrification.  Flow banding
is visible in thin section, but unobserved on the macroscopic

Figure 4-1A. Location of study area, Boston North Quadrangle,
Massachusetts.

MASS.

QUADRANGLE LOCATION

Boston North, Mass.
Quadrangle

EX FELLS

VATION

Wrigh

Pine Hill
Lookout Tower

Bellevue
Pond

ROAD

Fulton
Sch

INTERCHANGE

1   Kilometer
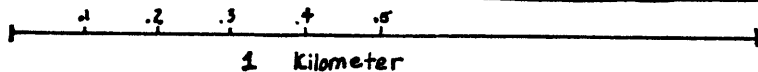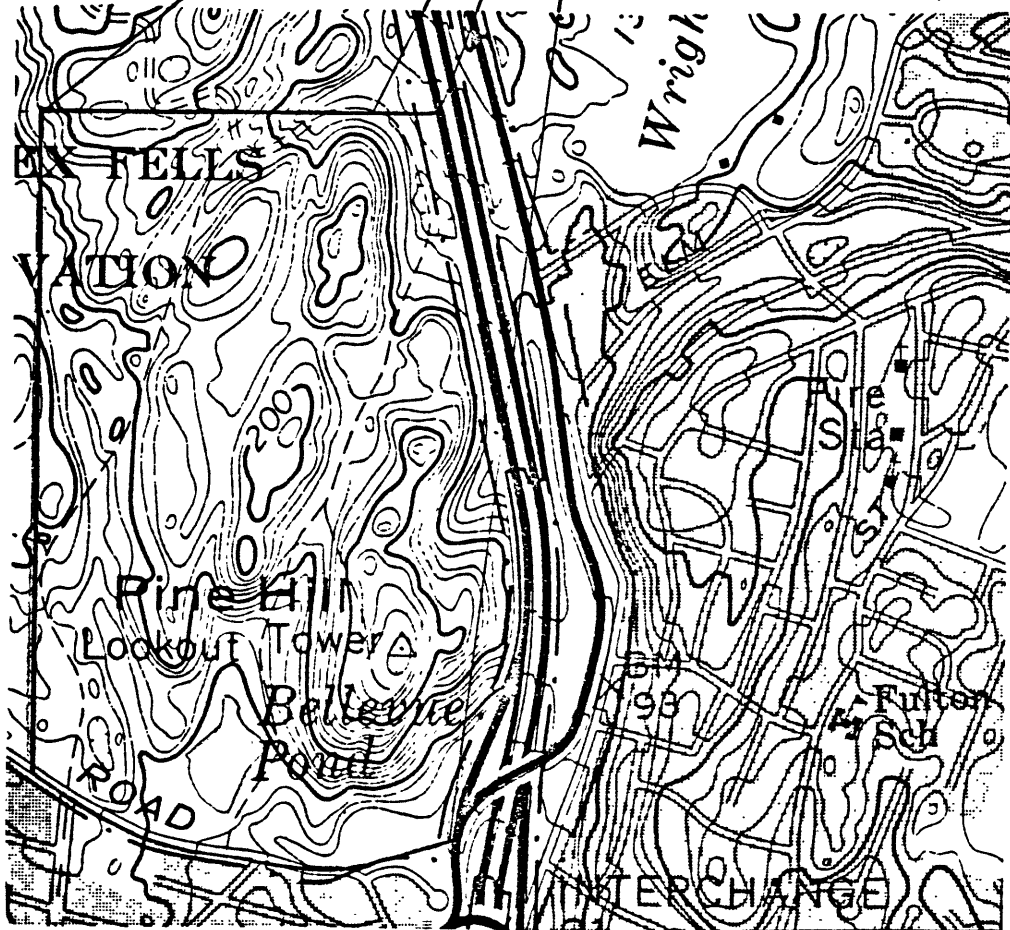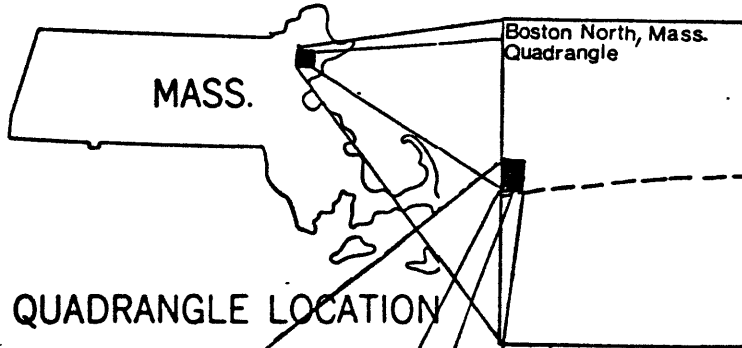
Figure 4-1B. Geologic map of Pine Hill, Boston North Quadran-
gle, Massachusetts.

# GENERALIZED
# GEOLOGIC MAP OF
# PINE HILL



KILOMETERS

## LEGEND

Pine Flow Unit

Mud Road Unit

Tower Unit

Dedham
Granodiorite

Granitic Dike

Medford Dike

MASS.

Quadrangle
Location

N
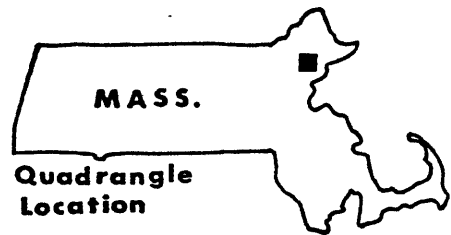
level.  Phenocryst content ranges from 10-20%.

The fine grained matrix is red→reddish grey to grey green
on fresh surfaces, weathering with a white rind typical of
feldspar rich rocks.  The red color of the unit is due to
hematite dust.  Mafic minerals are visually conscpiuous, and
constitute about 2% of the rock.  The minerals are mostly
alteration products such as chlorite and epidote, replacing
biotite and hornblende.  Remnant biotite and amphibole struc-
ture is observed.

The Pine Flow unit is highly fractured in  a blockly
fashion, and tends to be exceedingly brittle.  Specimens
from this unit fracture  conchoidally.

Xenoliths of foreign material are completely lacking,
though there are occasionally, what appear to be pieces of
the same unit (> 2 cm) in the matrix.  These fragments
were probably incorporated into the flow as the flow broke
off fresh, sharp surfaces that formed as a skin while cooling
occured.  These are rare and almost imperceptible.

The Pine Flow Unit has a visible, and at one location,
an almost vertical contact with the Tower Unit, which it
underlies.  It also is in contact with the Dedham Granodio-
rite.  It is cut by swarms of cross cutting dikes of unknown
age, plus the Triassic Medford dike of diorite composition.
(See Dike Geology, Chapter IV).  The best exposure of this

unit is located on the southbound side of Route 93 right near
Pine Hill.  Dikes of believed Triassic age cut the Pine Flow
at many locations, and are well exposed on this roadcut (see
Skehan, 1975).

### The Tower Unit:

The Tower Unit appears to be a crystal-lithic tuff.  The
matrix is aphanitic and felsophyric in nature.  The matrix
is dark grey on a fresh surface; and weathers with a white
rind.  It contains fragments of volcanic units which appear
to have local, and non-local origins, plus small xenoliths
of a pure orthoquartzite.  The unrelated volcanics have a
·black matrix, with prominent, but small ($\leq$ 2 cm) unoriented,
lathlike feldspar phenocrysts.  The matrix of this porphyritic
tower unit contains phenocrysts, and presumably xenocrysts
of feldspar and quartz.  The feldspar is plagioclase An $\sim$ 30,
and the K-feldspar is probably sanidine.  The weathered sur-
face is light grey to white in color.  The darker weathering,
and more resistant character of the xenoliths allows for easy
visibility on the outcrop.  The matrix of the unit exhibits
flow banding around the xenoliths, which do not appear to
have resorbed a significant amount.

These rocks have observable contacts with the Pine Flow
unit and the Medford Dike.  It appears to be structurally
above the Pine Flow, and is primarily distinguished by the

presence of quartzite and unrelated felsite xenoliths. This
characteristic was chosen for identification in the field
due to its pronounced appearance, and consistent nature.

The Tower Unit occupies the topographically highest posi-
tion in the field region. It appears to have been in place
pre-Dedham, due to a distinct lack of any granitic or granite-
like fragments or xenoliths, despite intensive investigation.

The best exposure of these rocks is directly beside,
and surrounding the tower, especially on the outcrop to the
left of the tower, on the path as you face SEE.

This unit is fractured in the same cubic fashion as the
Pine Flow rhyolite, and is cut by small dikes of unknown age
as well.


Mud Road Unit:

This cryptocrystalline, porphyritic rock contains pheno-
crysts of plagioclase (An ≅ 28-30.5), K-feldspar, and quartz.
The fine grained matrix is a dark grey to grey brown devitri-
fied glass, on a fresh surface. It weathers with the same
white rind typical of feldspar-rich rocks.

The unit is highly fractured and brittle. It occasionally
weathers with a peculiar chipping or flaking, which at times
renders it very granitic-like in appearance, and care must
be taken during rock identification.

This is the least well defined, or rather, the most variable of all the rocks mapped in this region. In certain areas, the crystallinity changes from cryptocrystalline to very fine grained within meters. Therefore, chemically it may prove to be inhomogeneous. This is apparent from thin section work, where the matrix texture varies markedly in all three samples (Chapter V). The specimen closest to the Dedham Granodiorite contact appears cataclastic in nature. This cataclasis is assumed to be related to an intrusive event sometime after the implacement of the Mud Road unit. Another unusual feature of this specimen is graphic intergrowth of quartz and orthoclase, similar to those in the Pine Flow specimens.

A specimen further from the Dedham Granodiorite contact, shows a similar, but less drastic cataclastic effect, while the most distant sample remains totally uneffected and displays relict perlitic textures in the devitrified glass. The An content for all these rocks is fairly consistent, ranging from An 28.1 to An 30.5.

In the field, the unit is occasionally layered in dark and light components, ranging from mm's to cm's in thickness. In many cases, this layering is interpreted as flow banding which has a consistent strike and dip, and plays a key role in determining field relationships between the Dedham and

the Lynn in this area.

In other areas, the felsite appears to exhibit a thin layer of granitic like material above it, indicating the bottom portion of an intrusive unit.

The xenoliths found in nearby Dedham seem to have the Mud Road unit as a likely candidate for source area. The xenolith exhibits the same flow banding and macroscopic characteristics as the Mud Road. However, chemical data appears to confirm a relationship between the Pine Flow unit and the xenolith (Chapters VI and VII).

## Dike Geology

Although studying the dikes which cross cut all of the units at Pine Hill was not part of my research, Koch (1978) an undergraduate at Harvard, mapped and classified the dikes with the purpose of creating a magnetic survey map of these rocks. Due to his generosity I have included a description of these units based on P. Koch's interpretation.

### Geometry and Petrography of Dike Groups

1. Older Dikes

--Original mineralogy entirely absent (i.e. meta-morhism of mafics)

--Can distinguish two events; the presence of medium and low grade metamorphic characteristics

--Age relationships determined using cross-cutting
relationships, when observed in the field, and
the degree of metamorphism

TABLE 4-1

| I.D. (Koch) | (Billings) | Number of Dikes | Trend | Rock Type | Distinguishing Characteristics |
|---|---|---|---|---|---|
| A | I | 1 | N25W | Epidosite; medium grade $m^m$ | quartz and epidote only. May only be in Dedham. |
| B | — | 1 | N35W | medium grade amphibolite | brown amphibole and plagioclase, trace biotite, quartz, no chlorite and epidote. |
| C | V | 3 | N75W | low grade amphibolite | brown amphibole, plagioclase, chlorite and epidote. |
| D | IV | 3 2 | N50W N75W | low grade amphiboltie (porphyritic) | irregular contacts, often pitted in the field. Brown amphibole, plagioclase, biotite, epidote, and calcite rimmed with chlorite. |
| E | III | 2 | E-W | low grade amphibolite | brown amphibolite with plagioclase, quartz and epidote. |

2.  Younger Dikes

--Display original mafic mineralogy, augite still

present          ,

--All dikes have undergone partial alteration to

chlorite, but some grains do not display altera-

tion

--Relative ages fairly well established due to

abundant cross-cutting field relationships

TABLE 4-2

| I.D. (Koch) | (Billings) | Number of Dikes | Trend | Rock Type | Distinguishing Characteristics |
|---|---|---|---|---|---|
| F | III | 2 | N85W | chlorite-amphibole diabase | chlorite and amphibole |
| G | — | 4 | N10W | chloritized diabase | variety of widths |
| H | VII | 6 | N35W | chloritized diabase | moderate thickness, occasional kinks |
| I | VI | 7 | EW | chloritized diabase | great widths with frequent feeders |
| J | VII | 1 | N15E | chloritized Medford dike | great width, coarse texture, spheroidal weathering |
| K | — | 3 | N75W | chloritized weathering | relatively thin attenuating contacts |

All these dikes are presently of unknown age, except for group
I, the Medford dike which is considered to be Triassic in
age (Skehan, 1975) which cuts all the existing dikes in its
path. Hence, the other dikes are pre-Medford dike, and post
Dedham Granodiorite. To this date, a more restructive time
for the emplacement episodes is not defined.


2. FIELD RELATIONSHIPS CRUCIAL FOR DETERMINING A
   PRECAMBRIAN AGE FOR THE LYNN VOLCANICS AT PINE HILL


Establishment of a Precambrian age for the Lynn Volcanics
at Pine Hill was accomplished by synthesizing many field
observations, which conclusively demonstrate that the Lynn
was intruded by the Dedham Granodiorite, in this region.

Pine Hill is separated from the Boston Basin by the
North Boundary Fault. The Lynn Volcanics are overlain by
patches of a conglomerate similar to the Roxbury Conglomerate
within the Boston Basin (Naylor, oral communication). This
area was selected for detailed study because of a relatively
well defined contact, (however, prior to this there was no
known observable contact, to the best of my knowledge), be-
tween Lynn and Dedham, which was previously described as the
Lynn unconformably above the Dedham. My work shows that the
reverse is true. The Lynn at Pine Hill is intruded by the
Dedham, and therefore Precambrian.

The evidence which brought me to this conclusion is:

1.   The contact between the Dedham and the Lynn is sharp, with the Dedham structurally on top.

2.   Although separation of felsite flows is difficult, with extensive investigation, they can be subdivided.  I have been able to define an internal stratigraphy within the Lynn (Chapter IV).  The contact between these units strike into the granite and are sharply truncated.

3.   Location of several felsic xenoliths in the Dedham, which resemble the adjacent Lynn petrographically, chemically, and megascopically has been established.

Only one "dubious clast" of granitic material has been found in the Lynn.

4.   Finally, there is a possible dike of fine grained Dedham intruded into the Lynn.

The Dedham, located north and west of the contact with the felsite (Figure 4-1) is an equagranular to slightly porphyritic granodiorite with approximately 45% plagioclase, 33% quartz, 10% K-feldspar, 9% mafics (chlorite, and epidote as alteration products) and the remaining 3% scattered between opaques, ankerite and accessory minerals.  It weathers with a hobb-nail texture caused by the resistance of quartz, and displays the typical pink color of the Dedham.  Its weathering is speroidal and displays few of the joints or

fractures noted in the surrounding felsite. This unit is
also cross-cut by the dikes that dominate the geology of
Pine Hill. No work was done to try and develop the internal
stratigraphy of the Dedham Granodiorite.

At Pine Hill, the Dedham and the Lynn both occupy the
hilltops and have good exposure. The Lynn are resistant to
weathering compared to the Triassic Medord Diabase (which
forms a valley and has been glacially smoothed in many
instances).

The contact between the Dedham granodiorite and the Mud
Road Unit is directly exposed. It shows that the Mud Road
is directly cut by the Dedham, and places the granodiorite
structurally above the felsite. The contact strikes N41E,
dipping 70° W. There is a slight decrease in grain size of
the granite as one approaches the contact, but this may not
be statistically real. There are no pieces or fragments of
the felsic unit in the Dedham that would indicate an uncon-
formable erosional contact as previously suggested. It is
important to note that the granite does not appear more wea-
thered closer to the contact, which would be another indicator
of an erosional surface, or an unconformable contact with
the felsic volcanics.

Xenoliths of the Lynn are observed in the granodiorite.
They are most abundant near the contact between the two units

(Figure 4-1). These xenoliths range from two feet to ten feet across. Lithologically they resemble the felsites of the Mud Road group. Color, weathering, and flow banding of these xenoliths are not different from nearby felsic units. The strike of the flow banding in the xenoliths is subparallel to the flow banding in the Mud Road. The strike of the flow banded Mud Road Unit is approximately N6E, and dip steeply at 85 - 90° W. Extrapolation of the banding is sharply truncated by the intrusive granite. The xenoliths are suggestive of small roof pendents in a magma. Near the contact with the Dedham, thin sections of the Mud Road exhibits a cataclastic texture (Chapter V). This texture is probably indicative of the disruption that occured upon intrusion of the felsite, and provides a mechanism for getting the xenoliths into the Dedham.

The contact of the Pine Flow Rhyolite and the Mud Road Unit is truncated by the Dedham in much the same way as the flow banding is truncated. The contact is obscured by the Medford Dike in several places. There are no flow banding or other linear features in the Pine Flow to indicate orientation of this unit. However, the Pine Flow has a clear, and almost vertical contact with the Tower unit, a crystal lithic tuff, which it underlies. The Tower Tuff is completely surrounded by the Pine Flow Rhyolite, and is never in contact with the Dedham. The tuff contains small xenoliths of identifiable felsite flow (volcanic units which are unknown at

Pine Hill) and an orthoquartzite member. They contain no
fragments of a granitic rock, as would be anticipated if the
granite had indeed been in place prior to eruption.

A thin rind of porphyritic granitic material is observed
weathering off of outcrops of Mud Road felsite. This rind may
represent the remnants of an intrusion of granitic rock into
the volcanic pile.

Finally, in a region largely obscured by swamps (Figure
4-1), there is an intrusion into the felsite of a finer grained
granitic-like rock in the form of a "dike". The dike seems
to extend back into the Dedham, however, actual checking has
been difficult due to the topographic conditions.


## 3. DISCUSSION


At this point I would like to re-emphasize that the Ded-
ham Granodiorite block at Pine Hill has been dated at 600 m.y.
(Rb-Sr on a hornblende) by R.E. Zartman of the U.S. Geological
Survey. Therefore the Lynn at Pine Hill must be, by associa-
tion, at least late Precambrian or older due to the intrusional
nature of the contact.

The relationships described here cannot indicate whether
the Dedham Granodiorite and the Lynn Volcanics at Pine Hill
are in fact comagmatic, or if they evolved during two totally
independent igneous events. Moreover, a minimum age of 600

m.y. on the Lynn does not clarify the relationship with the
Mattapan, on the opposite side of the North Boundary Fault,
which was one of the objectives of this study.  The Mattapan
was also zircon dated by R. Zartman at 570 m.y. (personal
communication).  Based on lithology and limited petrography,
the Lynn and Mattapan are difficult to distinguish.  If
they should prove to be cogenetic, then the age of the Boston
Basin may be dropped into the Precambrian.

CHAPTER V

SAMPLE LOCATION, PETROGRAPHIC DESCRIPTIONS,

AND SAMPLE PREPARATION


## Sample Location

Sample locations at Pine Hill (Pine Flow and Mud Road units of felsite, and the Dedham Granodiorite) are specified in Figure 5-1 . Coordinates were determined as a permanent reference, and are listed in Table 5-1.


TABLE 5-1

LONGITUDE AND LATITUDE OF PINE HILL SAMPLES

| Sample | Longitude | Latitude |
|---|---|---|
| Pine Flow | | |
| PF 1 | 71°06'13" | 42°25'58" |
| PF 2 | 71°06'12" | 42°26'01" |
| PF 3 | 71°06'14" | 42°26'08" |
| Mud Road | | |
| MR 1 | 71°06'32" | 42°25'59" |
| MR 2 | 71°06'32" | 42°26'01" |
| MR 3 | 71°06'31" | 42°26'08" |
| Felsite Xenolith | | |
| X 5 | 71°06'34" | 42°26'14" |

TABLE 5-1

LONGITUDE AND LATITUDE OF PINE HILL SAMPLES
(Continued)

| Sample | Longitude | Latitude |
|---|---|---|
| Dedham Granodiorites | | |
| DG 1 | 71°06'23" | 42°26'15" |
| DG 2 | 71°06'40" | 42°26'05" |

The Mattapan Volcanics specimen was collected in the abandoned Sally Rock Quarry (Figure 5-2, after Skehan, 1975).

The Newbury Volcanic Complex was collected from the flow banded rhyolite vitrophyre member (after Shride, 1976). The outcrop is a high roadcut, approximately 700 meters south of the Parker River Bridge on U.S. 1, in the southeast corner of the Newburyport West Quadrangle (Figure 5-3).

The Middlesex Fells Volcanic Complex specimen was collected by W. Olszewski. The locality is in the Boston North Quadrangle, at the Stoneham Jr. High School. The outcrop is just east of the tennis courts which are 200 meters northeast of the school (Figure 5-4).

Figure 5-1.  Location of specimens used in petrographic and geochemical analysis of Pine Hill units.

# SAMPLE LOCATION MAP OF PINE HILL



0    0.5 Kilometers
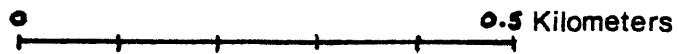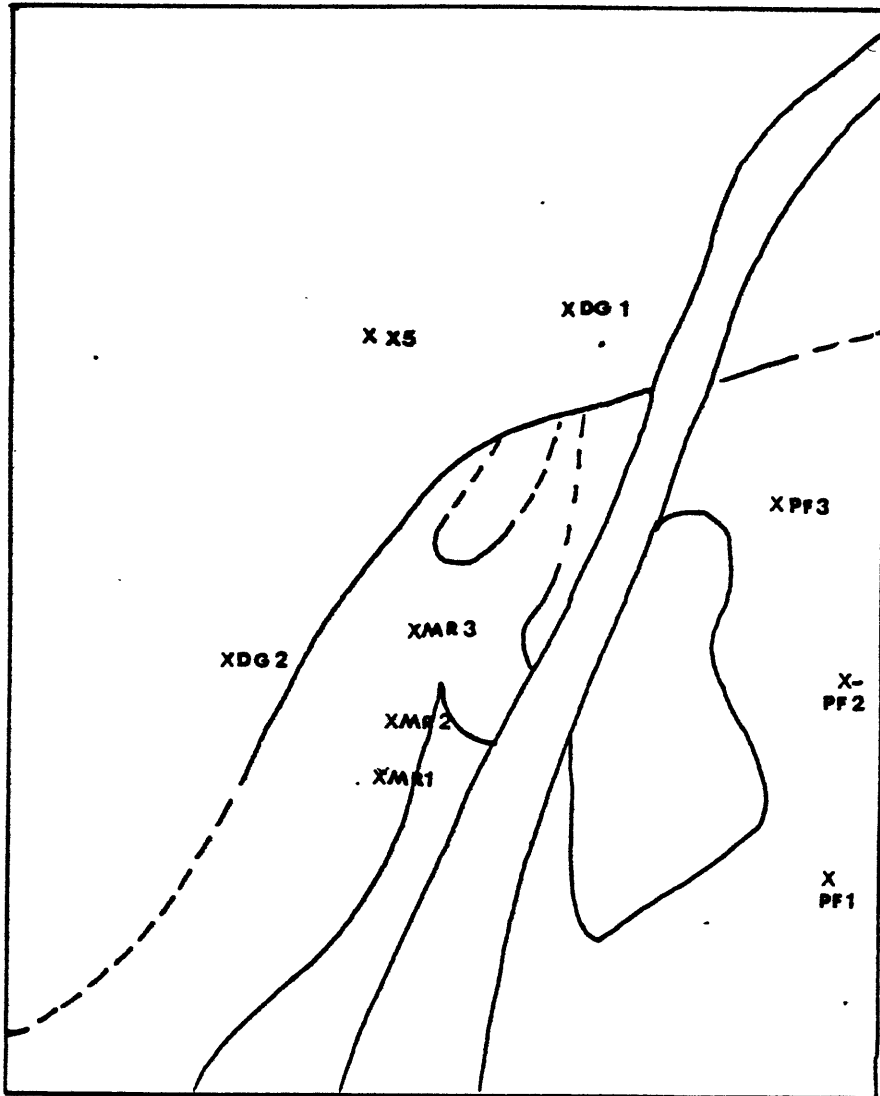
PF = Pine Flow Unit
MR = Mud Road Unit
DG = Dedham Granodiorite
X = Xenolith

Figure 5-2.   Location map for Mattapan Volcanic Complex sample,

MV 1, (after Skehan, 1975).

Figure 5-3.   Location map for Newbury Volcanic Complex sample,

NV 1, (after Skehan, 1976).
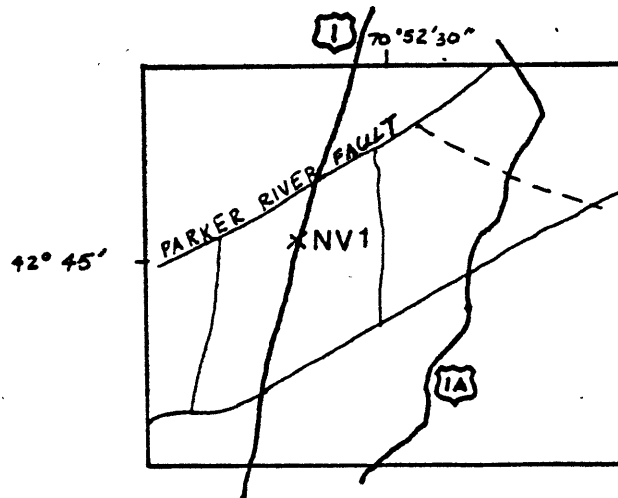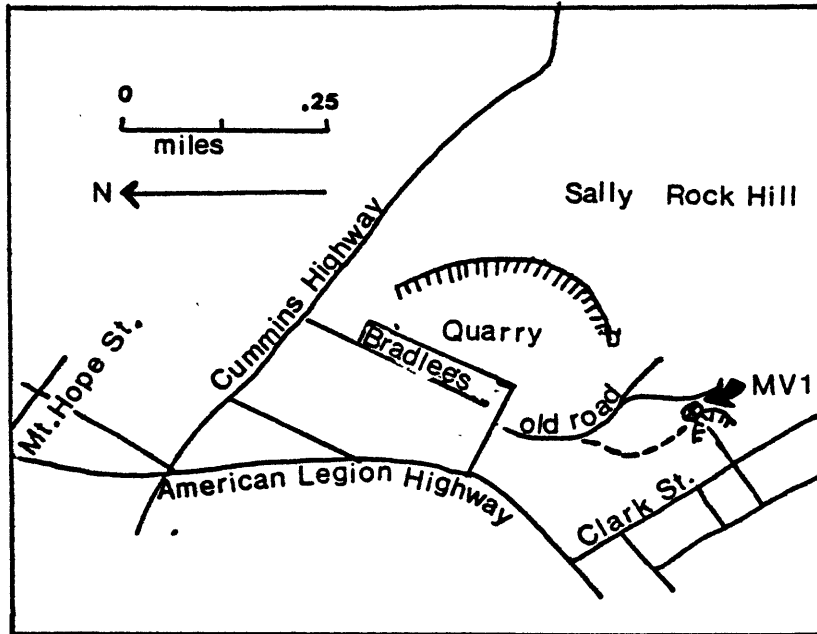
Figure 5-4.   Location map for the Middlesex Fells Volcanic

Complex sample, MF 34 (after W. Olszewski, map

after Bell and Alvord, 1976).

Boston North Quad.

•MF 34

- - - Faults
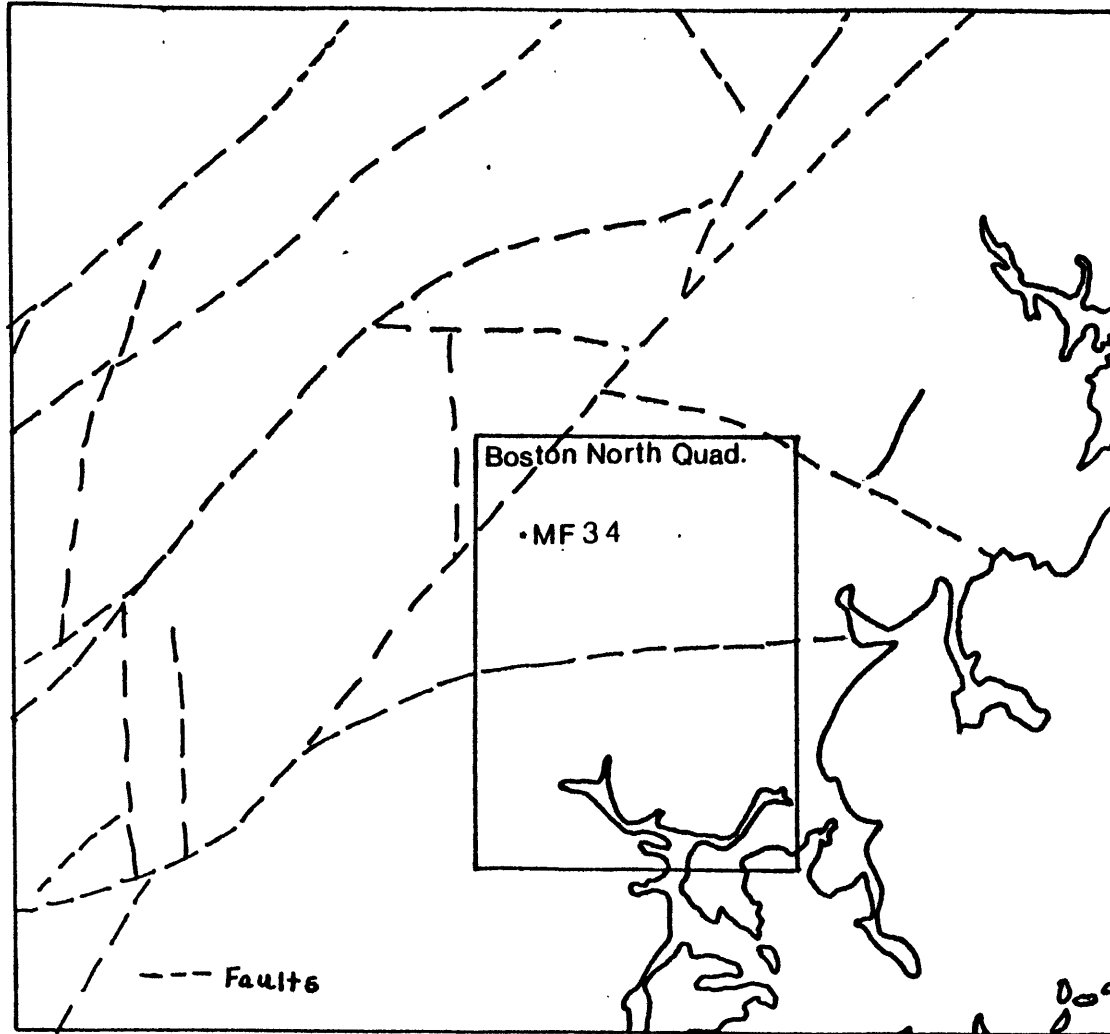
## Petrographic Descriptions

Procedures: Point counts (1000 counts), to establish modal proportions of phases were performed on the coarse grained granites, thin section and stained slabs. Thin section estimates of phenocryst phases were made on volcanic rocks. Plagioclase An contents were determined using the basal cleavage U-stage method of analysis, (Slemmons, 1962).

Results: U-stage. Based on plagioclase An content (28.1-30.3) the felsic rocks at Pine Hill are rhyolites and rhyodacites. According to Carmichael, Turner and Verhoogen (1974) rhyolites are acid volcanic rocks which occur with quartz, oligoclase, sanidine and minor ferromagnesian minerals, whereas rhyodacites contain andesine in lieu of oligoclase. Based on An = 30 as the dividing line between oligoclase and andesine, MR 1 and 2, plus PF 2 are rhyolites, and MR 3, PF 1,3, and X 5 are rhyodacites.

An CONTENT OF PLAGIOCLASE PHENOCRYST COMPONENTS

(Precision to within ±3%)

| | |
|---|---|
| PF 1 | An = 30.5 |
| PF 2 | 29.4 |
| PF 3 | 30.0 |
| MR 1 | 29.2 |
| MR 2 | 28.1 |
| MR 3 | 30.2 |
| X 5 | 30.3 |
| DG 1 | 28.9 |
| DG 2 | 29.5 |
| MV 1 | 28.3 |
| NV 1 | -- |
| MF 34 | 32.2 |

The most important observation is the extremely restricted range of An values for the plagioclase phenocrysts at Pine Hill, and the Dedham Granodiorite.

### Pine Hill - Mud Road

#### MR 1

This porphyritic rock displays a remnant perlitic texture in which the glass has crystallized into a matrix of mostly quartz and small amounts of plagioclase. Minor opaques are probably magnetite. The matrix is highly altered with sericite, epidote and minor chlorite matrix components ranging in size from 0.2 mm to cryptocrystalline. Matrix grain boundaries are sharp and jagged. The rock displays flow banding in the matrix, and prominant perlitic textures, indicating the now devitrified remnant glassy component (Figures 5-5, 5-6).

The lathlike phenocrysts of feldspar are 10-20% of the rock. They range from 0.5-2 mm in size, and are highly altered with sericite scattered throughout the feldspars. Many pheno-crysts show a "patchwork" like extinction. Twinning appears to be mostly carlsbad with minor albite in the phenocrysts, however, this is not the case in the matrix, which displays major albite twinning and carlsbad twinning (An = 29.2).

## MR 2

This porphyritic rock has an aphanitic-cryptocrystalline matrix of quartz and feldspar with common opaques (probably magnetite). The groundmass appears to be a devitrified glass. It is highly altered, with alteration products consisting of sericite, epidote, and chlorite. Veins are filled with calcite, quartz, and epidote. Mafic minerals appear to be pennine, a member of the chlorite group which displays the anomalous berlin blue, and other members of the epidote group with anamolous and high birefringence. These mafic minerals are associated with magnetite, and have wavy extinction. The chlorite is green (olive) and slightly pleochroic. Chlorite is observed as aggregates of crystals or columnar in habit, possibly with relict biotite structure.

The major phenocrysts are feldspars which are highly altered to sercite (intercrystalline) and often exhibiting no, carlsbad, or albite twins. Some have patchwork extinction. Quartz phenocrysts were not observed. Feldspar phenocrysts are $\sim$ 1.7 mm - 0.5 mm and comprise 10-20% of the rock (An = 28.1). Some phenocrysts show flow banding around them but the phenocrysts are not oriented.

## MR 3

This rock has several striking features. First it exhibits a cataclastic texture, which is not seen in any other

specimen. The rock has been shattered, and consists of broken lithic prices and phenocrysts in a matrix of crushed rock in an apanitic-cryptocrystalline background, which is highly altered (Figure 5-7A, 5-7B). Rock cracks are filled with chlorite (pennine) with the anomalous blue color and aggregate crystals (radiating). There are opaque minerals (probably magnetite), plus various accesory minerals (sericite, zircon). Major components of this rock are quartz, feldspar with a matrix of crushed rock fragments and devitrified glass.

The second unusual feature is that there is an abundant graphic intergrowth of quartz and orthoclase. This inter-growth is often cuniform..

The feldspars exhibit predominantly albite (An = 30.2) as well as carlsbad twins. Some exhibit patchwork extinction. Another feature not observed in the other MR rocks, is a few cases of zoning in the feldspars. Phenocryst content is impossible to estimate.

## Pine Hill - Pine Flow

### PF 1

PF 1 has an aphanitic matrix of recrystallized felspar and quartz plus mafics of undetermined proportions. The plagioclase phenocrysts, An = 30.5, range in size from approximately 1.0 mm to microphenocryst size. There are pheno-crysts of quartz and K-feldspar as well, with phenocrysts

comprising approximately 15% of the rock. PF 1 is the only Pine Hill rock with identifiable unaltered hypersthene which is associated with apatite (Figure 5-8).

## PF 2

In this porphyritic rock, all the large phenocrysts (10-20% volume) which are 1.1 - 6 mm in size, are highly altered feldspars, (An = 29.3) with the secondary mineral being sericite. Twins of albite and carlsbad nature are common. A few phenocrysts have patchwork extinction. There is no apparent zonation. Most of the crystals have straight edges, however, some irregular (lobate) edges and boundaries are present.

A group of phenocrysts which are smaller in size ($\sim$0.2 - 0.9 mm) consist primarily of quartz, and feldspars, with the same characteristics previously mentioned, with the exception that the feldspars are less altered. Quartz crystals display embayed grain boundaries with a cuniform shape, and quartz occasionally appears as micrographic intergrowth with orthoclase.

The opaques appear to be magnetite, and are scattered throughout the matrix, and, are associated with the chlorite.

The matrix consists of embayed crystals of feldspar and quartz, apparently formed upon devitrification of the glass. The texture of these crystals is often feathery.

Chlorite fills veins, and replaces biotite in a fairly large percent, (~2%) of the rock.

## PF 3

This porphyritic rhyolite has an aphanitic to cryptocrystalline matrix of quartz and feldspars. These constituents commonly exhibit a "feathery" texture, which is typical of devitrified glass. The matrix is primarily quartz, with much of the feldspar being replaced by epidote. The feldspars present have patchwork extinction, and are riddled with sericite, zircon, and apatite as minor inclusions.

The phenocrysts consist of graphic intergrowths of quartz and orthoclase (Figures 5-9, 5-10). Many of the quartz pehnocrysts show wavy extinction, although they appear relatively fresh and unaltered. Feldspars exhibit no, carlsbad,albite and periclene twinning as well as patchwork extinction. In some instances there are clumps of similar phenocrysts. The plagioclase is An = 30. Much of the rock is chloritized.

Mafic minerals present in small amounts are conspicuous. They are hypersthene, chlorite, epidote, and anthopylite (probably replacing biotite). Muscovite is present in crystals (tabular) of about 0.2 mm (probably secondary). Magnetite is associated with all the mafics. This rock is phenocryst-rich,

with ~ 25% of the rock as phenocrysts.  This rock also exhi-
bits flow banding on the microscopic scale.


## Pine Hill-Xenolith in Dedham Granodiorite

### X 5

This xenolith is a porphyritic rock with phenocrysts
comprising about 10% of the rock.  80% of the phenocrysts are
K-feldspar, with the rest plagioclase An = 30.3, and minor
quartz phenocrysts.  The feldspars are altered to sericite
and epidote to an extent.  The grain boundaries are straight
and well formed.  The average phenocryst size is approximately
1.7 mm.

The  groundmass is almost all quartz and alteration pro-
ducts.  It is aphanitic to cryptocrystalline.  There are mafic
flecks which have been largely altered to chlorite.  Veins in
the rock are primarily filled by epidote.


## Pine Hill - Dedham Granodiorite

### DG 1  (See Table 5-2)

This coarse grained granodiorite has very altered
plagioclase feldspars which  exhibits polysynthetic
twinning.     There is no observable carlsbad or pericline
twinning, although twinning  may have been decimated by
alteration.  There appears to be a slight amount of zonation
of the plagioclase (An = 28.9) which have straight grain

boundaries. The feldspar grains are generally sericitized with some chlorite as inclusions and epidote is also replacing feldspar. Other inclusions in feldspar are opaques (magnetite) and some quartz. Feldspar have patchwork extinction.

The alkali feldspar present in this rock is microcline. It is farily clear and unaltered compared to the plagioclase, although it is slightly sericitized. These feldspars contain some fairly high birefringent accesory minerals.

The quartz is clear and almost unaltered. It is cracked and fractured, which is typical for the Dedham. The extinction is wavy. Their grain boundaries are curved, straight and lobate, and the grains are approximately 1 cm in size.

Chlorite is replacing mafic minerals. It is green, pleochroic associated with magnetite and they have possible relict biotite shapes (Figure 5-11).

Ankerite appears brown, tabular with excellent cleavage (3 directions) and extreme birefringence.

DG 2 (See Table 5-2)

The plagioclase is very altered to sericite and epidote. In most cases albite twinning is discernable, although grains usable for U-stage analyses are not common. Chlorite has replaced all the original mafic minerals The quartz grains have undulatory extinction, and

TABLE 5-2

MODAL ANALYSIS OF DG 1 AND DG 2

| Mineral | DG 1 | DG 2 |
|---|---|---|
| Plagioclase | 45% | 46% |
| Quartz | 32% | 35% |
| K-feldspar | 11% | 7% |
| Chlorite | 7% | 7% |
| Epidote | 1% | 4% |
| Ankerite | 0.8% | 0.3% |
| Apatite | 0.3% | 0.2% |
| Zircon | -- | 0.1% |
| Opaques | 0.6% | 1% |

are highly fractured.  The grain boundaries are fairly

straight.


## Mattapan

### MV 1

The matrix of this porphyritic rock is exceedingly

fine grained to cryptocrystalline which has been altered to

sericite and epidote.  The main groundmass constituents are

feathery quartz and some feldspar with very little mafic

material.  The matrix shows laminations of interlayered

very fine grained material and cryptocrystalline material.

They both contain microphenocrysts of $\sim$ 60% quartz and $\sim$ 40%

feldspars (approximately 0.07 - 0.18 mm size) which are rela-

tively unaltered.  These occur mostly as stubby laths.

The phenocrysts ($\sim$ -.56 - 1.9 mm) are fairly unaltered

feldspar (An plagioclase = 28.3).  Many exhibit a strange

mottled extinction.  Some are partially replaced by mafics.

The grain boundaries are mostly straight, with some jagged

edges.

Veins are filled with slightly chloritized quartz.


## Newbury

### NV 1

This cryptocrystalline to aphanitic rock appears to

be devitrified glass that has recrystallized as feldspar and

quartz. The feldspar is commonly present as spherulites
(Figure 5-12) and is altered to sericite. The very fine
grained matrix appears to be flow banded with alternating
layers of cryptocrystalline and aphanitic material. Magne-
tite and mafic minerals, which have been totally altered to
chlorite, are sprinkled throughout the matrix. The layers
are easily distinguished by variable amounts of hematite
dust.

Modal analysis was impossible due to the extreme fine
grained texture, but chemical data indicate the rhyolitic
composition of this rock. No satisfactory grains were found
on which to determine an An content for the plagioclase.

Veins are common and filled with calcite and quartz.


## Middlesex Fells

### MF 34   (Specimen courtesy of W. Olszewski)

This apanitic, porphyritic rock has large pheno-
crysts of plagiocalse (An = 32.2), which are about 1 - 2 mm
in size. Biotite flakes which range from 0.5 - 1 mm, are
now largely converted to chlorite and magnetite. These two
minerals make up about 20% of the rock. The groundmass is
made up of feldspar and quartz (10 - 15%).

Magnetite is peppered throughout the matrix. The pheno-
crysts are largely altered to sericite and epidote. They
are not extensively twinned, and the grain boundaries are

Figure 5-5.  MR 1 - Perlitic texture in recrystallized glass
matrix, under crossed nicols.

Figure 5-6.  MR 1 - Perlitic texture without crossed nicols.
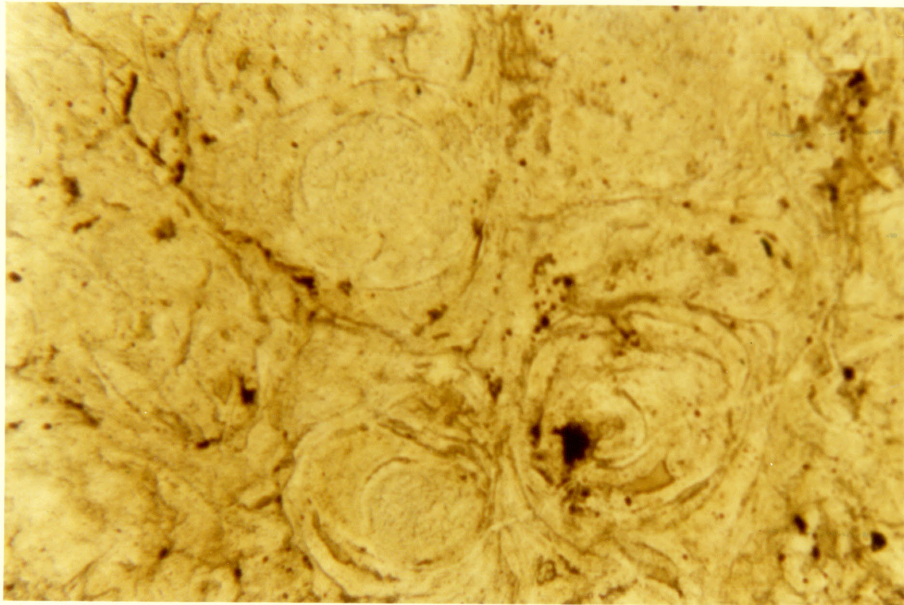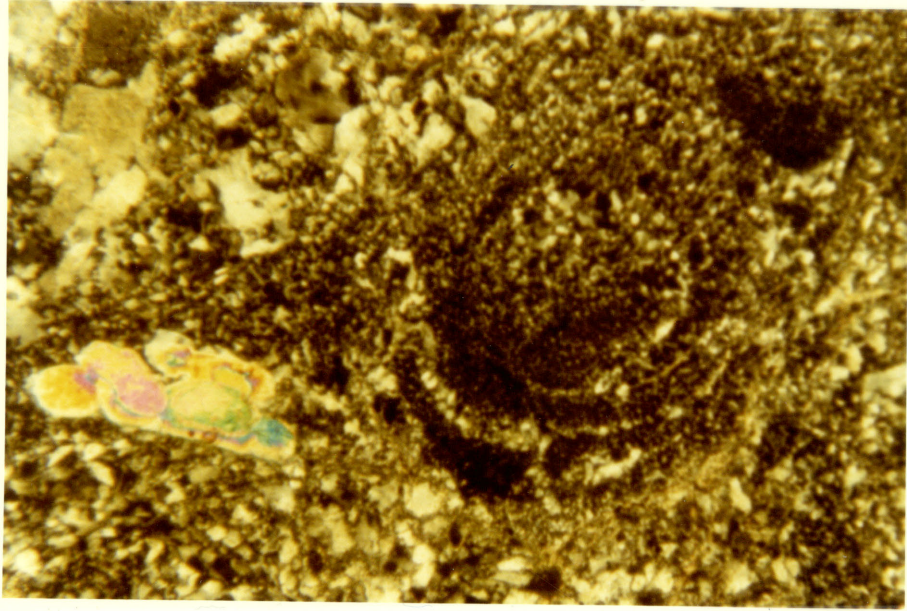
Figure 5-7A. MR 3 - Cataclastic texture demonstrated under
crossed nicols.

Figure 5-7B. MR 3 - Cataclastic texture without crossed
nicols.
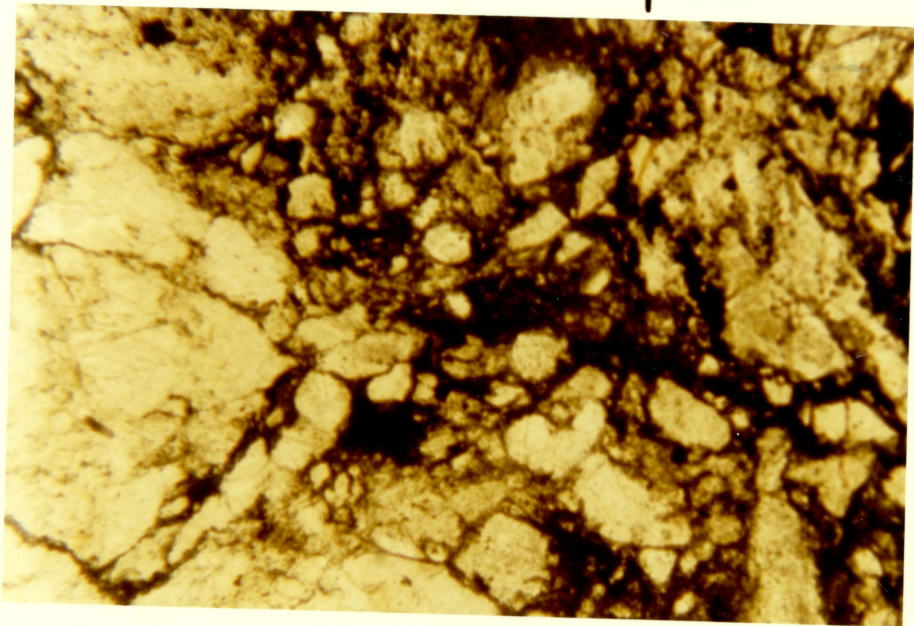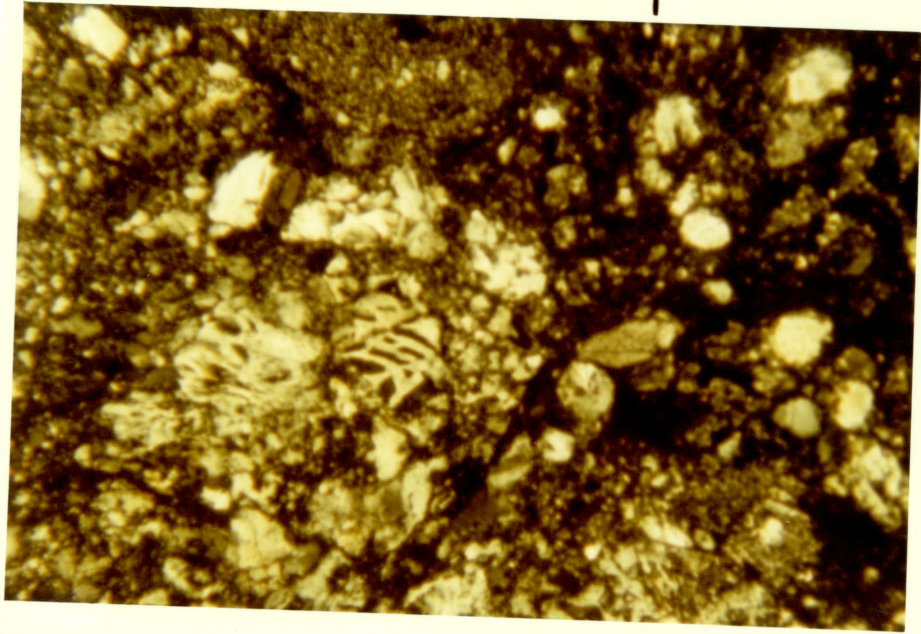
Figure 5-8.  PF 1 - Large hypersthene crystal in association
with apatite and the recrystallized glass matrix.

Figure 5-9.  PF 3 - Graphic intergrowths of quartz and feld-
spar.
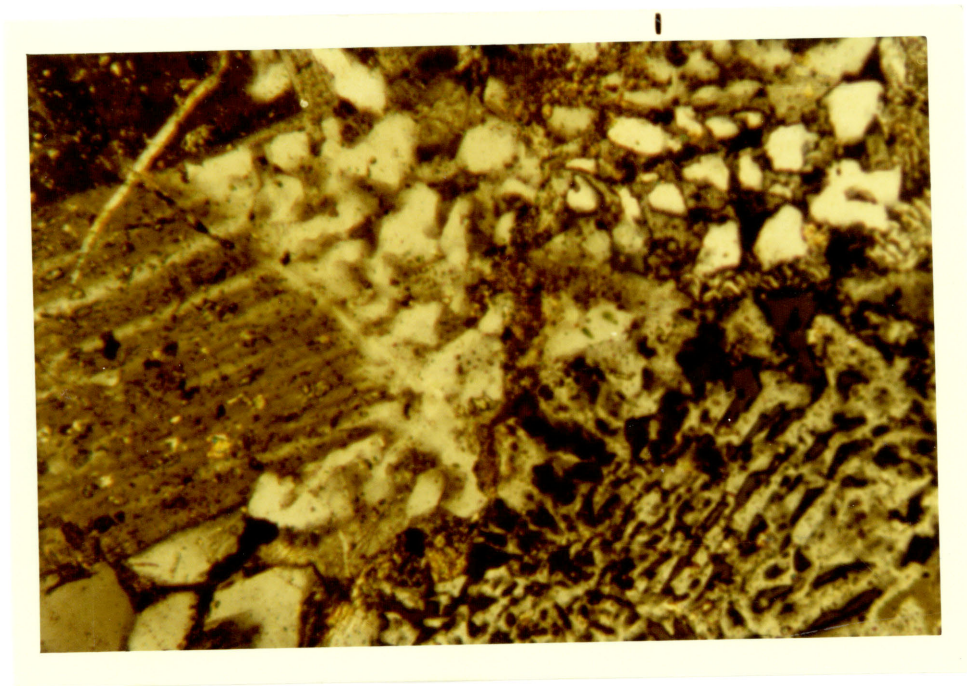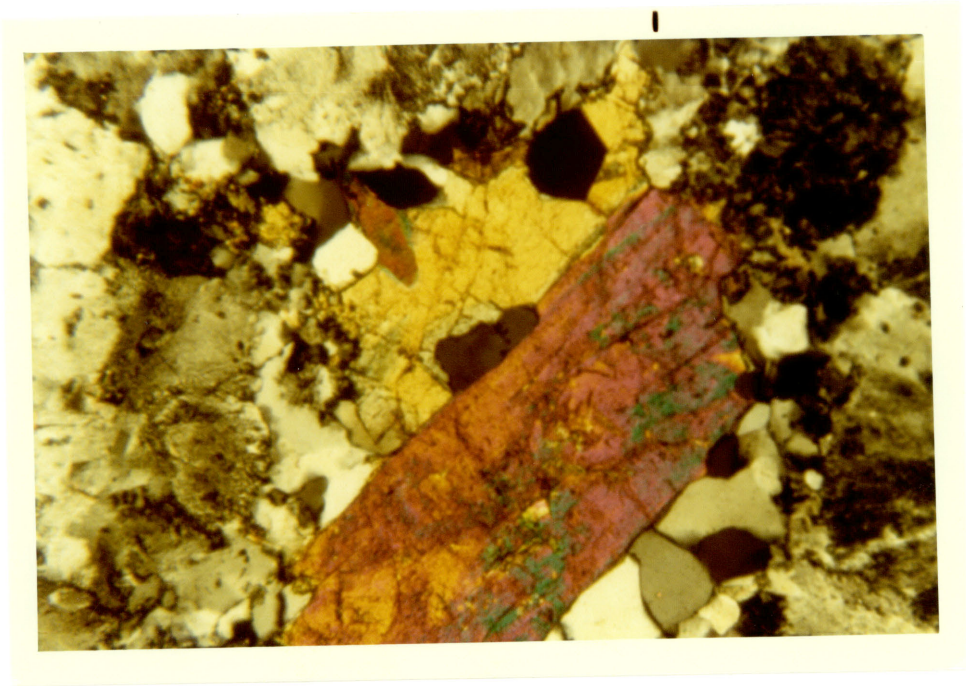
Figure 5-10. PF 3 - Graphic intergrowth of quartz and feld-
spar.

Figure 5-11. DG 1 - Chlorite and epidote are seen replacing
mafic minerals in the granodiorite.
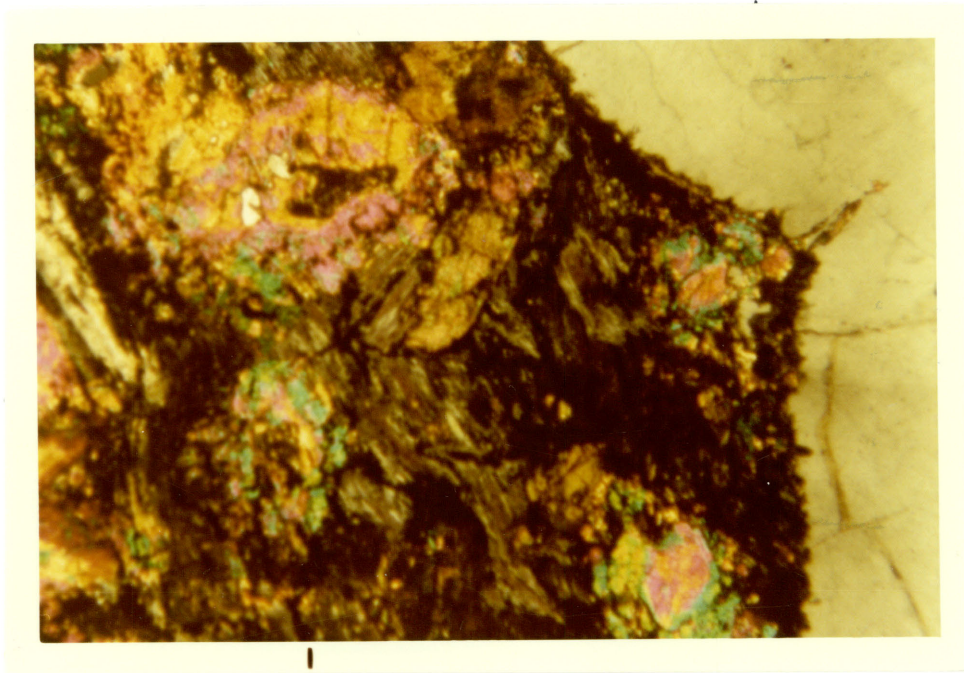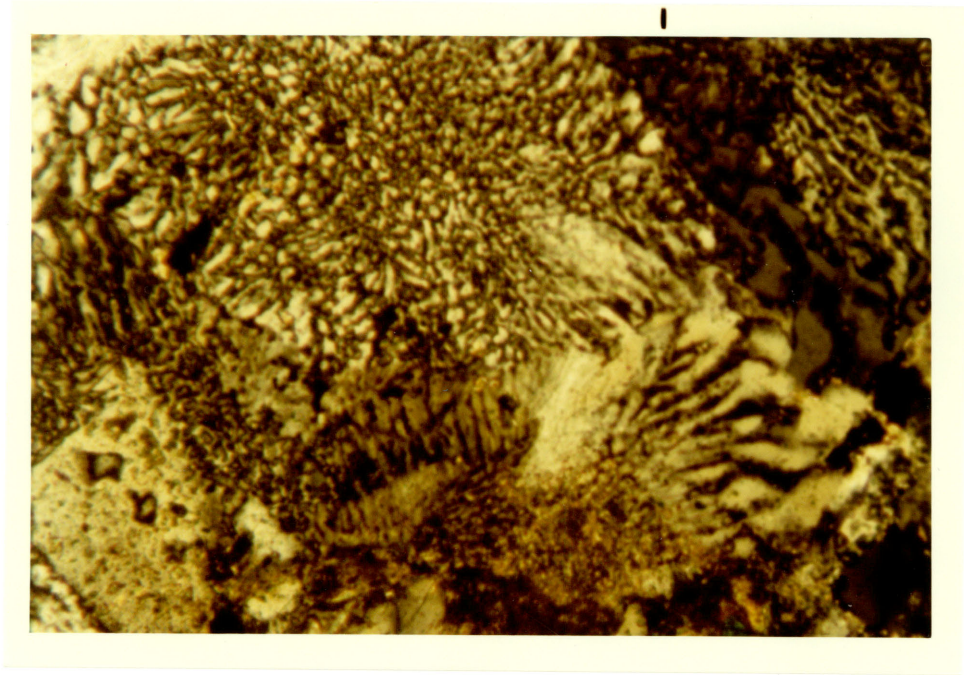
Figure 5-12. NV 1 - Spherulites of feldspar crystals.

Figure 5-13. MF 34 - Biotite flake altering to chlorite.
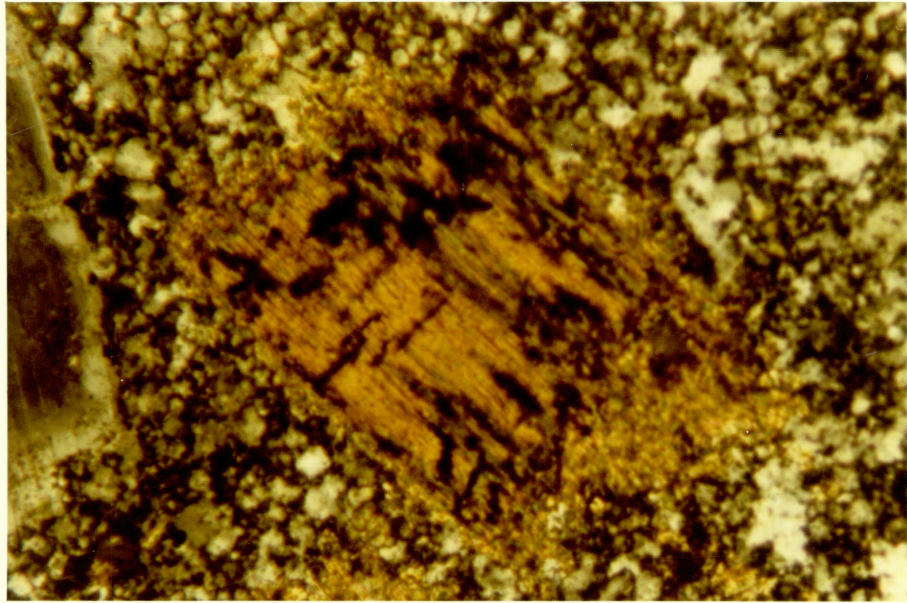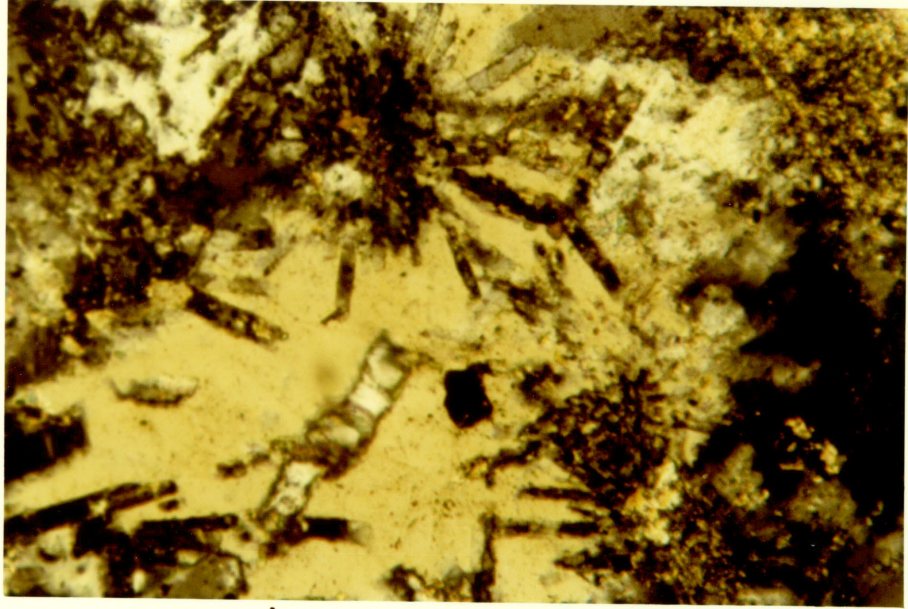
are embayed and eroded. Recrystallization of the matrix into larger grains is commonly observed. (Figure 5-13)


### Sample Preparation

Sample Selection. Of the three felsite units at Pine Hill, only two flow units (Pine Flow and Mud Road) were sampled, for chemical analysis. These units were selected because of their relative homogenous matrix, constant phenocryst size and abundance, and an apparent lack of xenoliths of other felsite and quartzite units, which characterize the tuffaceous lithologies. Relatively fresh specimens of the Mud Road and Pine Flow Units were easily obtained. At least 1000 grams of the volcanic rock units were collected. 2000 grams of coarse grained Dedham Granodiorite were collected for chemical analysis and thin section work. The two freshest samples were selected. The same criteria for sample selection applies to the Mattapan and Newbury Volcanic Complex. The Middlesex Fells Volcanic Complex sample was supplied by W. Olszewski.

Preparation. Weathered surfaces were removed from PF 1, 3, and MR 1 by the use of a slab saw. The rest of the specimens had the weathering rinds removed in the field. These samples were sequentially placed in two jaw crushers of large and fine crushing capacity. After the first large pieces

were borken up, the fragments with weathering along cracks were discarded.  The remaining fragments were crushed again, with care not to lose any fine grained material.

This fraction was split in half, and one half was pulverized to 1 mm with a percussion iron morter and pestle. This coarse powder was then ground to a fine powder using the Pica Ball Mill Blender, with tungston-carbide containers. The resulting powder was used for INAA, XRF and C-H-N analytical techniques.

CHAPTER VI

MAJOR ELEMENT GEOCHEMISTRY

Major element compositions are important in the classi-
fication of rocks and interpreting the evolution of rock
suites. An objective of this study was to use major elements
to determine general chemical relationships, and possible
fractionation trends among the Lynn, Middlesex Fells Volca-
nics, Newbury, Mattapan, and the Dedham Granodiorite.


1. ANALYTICAL METHODS


Major element abundances were determined by X-ray fluo-
rescence (XRF) techniques, on the Woods Hole Oceanographic
Institute's XRF machine, by Dr. Geoffrey Thompson and techni-
cian Brian Schroeder. U.S. Geological Survey standard BCR-1
was used as a drift monitor. The precision (counting statis-
tic error at ± 1 sigma, hence the least possible error) is
less than 0.5% for Si, Al, K, Fe, Ti, and Cu. The precision
on Mg, Na, and P is poor in some samples, ranging from 1 -
10% in Mg, 2 - 8% in Na, and 1 - 18% (at very low abundances)
for P. The samples were fused into glass beads and prepared
according to the WHOI procedure, with spectroflux 105, (after
Hendry and Bancroft, 1973).

## 2. RESULTS

Major element data and C.I.P.W. norms are in Table 6-1.

All specimens studied have high $SiO_2$ content, ranging from 70.61% to 77.94% (normalized to 100%), except for MR 3 with an anomously low 66% $SiO_2$. This low $SiO_2$ in MR 3 may be the result of extensive $SiO_2$ leaching, which is enchanced due to its highly cataclastic texture (see Chapter V). For this reason MR 3 does not appear to fall on the liquid line of descent which is established by the other felsites at Pine Hill. As an exercise I decided to test the hypothesis that the reason MR 3 did not fall on the line in the variation diagrams was due to $SiO_2$ leaching. I assumed this was the only factor involved in the lack of continuity in the major element data. If one assumes that the original $SiO_2$ value = 77.5%(mean between MR 1 and MR 2), and normalizes the rest of the elements to 100%, the values obtained are:

| | |
|---|---|
| $SiO_2$ | 77.5 |
| $Al_2O_3$ | 11.47 |
| $\Sigma FeO + Fe_2O_3$ | 2.16 |
| $MgO$ | 0.56 |
| $CaO$ | 1.54 |
| $Na_2O$ | 3.67 |
| $K_2O$ | 2.10 |

| | |
|---|---|
| $TiO_2$ | 0.44 |
| $P_2O_5$ | 0.11 |
| $H_2O$ | 0.47 |

When these values are plotted on the variation diagrams, $TiO_2$ $P_2O_5$, $\Sigma FeO + Fe_2O_3$, MgO, and CaO are enriched relative to the predetermined trend. $Na_2O$ is fairly well fit into the trend, and $K_2O$ is substantially depleted. This suggests that not only $SiO_2$, but $K_2O$ and some $Na_2O$ were leached as well. This is anticipated due to the fact that $K^+$ and $Na^+$ will form salts and be lost in solution fairly rapidly. CaO was increased by calcite replacing minerals and filling veins. The other elements are less mobile with alteration and extensive weathering, which was enhanced by the extensive cataclasis. This explains why major and some TE abundances are aberrant in the variation diagrams.

All the rocks except the Middlesex Fells sample, MF34, are prealuminous. That is, the molecular proportion of $Al_2O_3$ exceeds (CaO + $Na_2O$ + $K_2O$), and corundum appears in the norm. This,in conjunction with the other chemical data, casts doubt on the hypothesis that the Middlesex Fells Volcanic Complex is part of the same volcanic pile as the Lynn at Pine Hill, as a peraluminous character is distinctive of source origin.

The variation diagrams of various oxides versus $SiO_2$ ($SiO_2$ was selected due to the very low MgO content, which is

# TABLE 6-1

## MAJOR ELEMENT ABUNDANCES* AND C.I.P.W. NORMS

| | PF 1 | PF 2 | PF 3 | MR 1 | MR 2 | MR 3 | X 5 | DG 1 | DG 2 | MV 1 | NV 1 | MF 34 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$** | 75.14 | 75.93 | 76.13 | 77.94 | 77.08 | 66.12 | 75.56 | 70.61 | 72.03 | 75.66 | 77.63 | 71.31 |
| $Al_2O_3$ | 13.24 | 12.47 | 12.48 | 12.34 | 12.88 | 17.27 | 13.10 | 14.40 | 13.92 | 13.41 | 11.96 | 10.63 |
| $Fe_2O_3$ as $\Sigma Fe$ | 1.73 | 1.51 | 1.69 | 1.05 | 0.24 | 3.26 | 1.48 | 4.10 | 3.13 | 0.80 | 1.42 | 4.20 |
| MgO | 0.45 | 0.38 | 0.29 | 0.19 | 0.19 | 0.85 | 0.31 | 0.90 | 0.66 | 0.10 | 0.07 | 2.77 |
| CaO | 0.59 | 1.24 | 0.80 | 0.12 | 0.38 | 2.32 | 1.42 | 2.84 | 3.25 | 0.10 | 0.84 | 7.10 |
| $Na_2O$ | 4.10 | 3.81 | 4.11 | 3.13 | 3.32 | 5.52 | 3.91 | 3.17 | 3.18 | 3.98 | 2.96 | 1.90 |
| $K_2O$ | 3.82 | 3.58 | 3.75 | 4.60 | 4.27 | 3.16 | 3.45 | 2.46 | 2.14 | 5.47 | 4.44 | 1.12 |
| $TiO_2$ | 0.41 | 0.44 | 0.39 | 0.24 | 0.24 | 0.66 | 0.33 | 0.65 | 0.53 | 0.25 | 0.23 | 0.27 |
| $P_2O_5$ | 0.06 | 0.06 | 0.03 | 0.01 | 0.01 | 0.17 | 0.01 | 0.15 | 0.12 | 0.01 | 0.01 | 0.06 |
| $H_2O$ | 0.52 | 0.62 | 0.38 | 0.43 | 0.43 | 0.71 | 0.48 | 0.76 | 1.07 | 0.36 | 0.48 | 0.67 |
| $(Na_2O+K_2O+CaO)/$ $Al_2O_3$ (molecular proportions) | 0.90 | 0.99 | 0.98 | 0.84 | 0.84 | 0.97 | 0.97 | 0.91 | 0.95 | 0.93 | 0.94 | 1.62 |
| $MgO/(MgO+\Sigma Fe)$ | 0.21 | 0.20 | 0.15 | 0.15 | 0.13 | 0.21 | 0.17 | 0.18 | 0.17 | 0.11 | 0.40 | 0.05 |
| Quartz | 34.99 | 37.06 | 35.88 | 41.63 | 40.37 | 16.23 | 36.22 | 35.77 | 37.77 | 31.45 | 41.56 | 40.65 |
| Corundum | 1.46 | 0.23 | 0.30 | 2.00 | 2.11 | 0.97 | 0.40 | 1.72 | 0.76 | 0.93 | 0.77 | -- |

TABLE 6-1 (Continued)

| | PF 1 | PF 2 | PF 3 | MR 1 | MR 2 | MR 3 | X 5 | DG 1 | DG 2 | MV 1 | NV 1 | MF 34 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Orthoclase | 22.55 | 21.11 | 22.11 | 27.18 | 25.23 | 18.64 | 20.34 | 14.53 | 12.63 | 32.30 | 26.21 | 6.58 |
| Albite | 34.62 | 32.23 | 34.76 | 26.44 | 28.06 | 46.65 | 33.03 | 26.82 | 26.89 | 33.64 | 25.02 | 16.07 |
| Anorthite | 2.50 | 5.75 | 3.74 | 0.58 | 1.88 | 10.40 | 6.96 | 13.09 | 15.33 | 0.05 | 4.16 | 17.19 |
| En-Hy | 1.11 | 0.94 | 0.72 | 0.46 | 0.46 | 2.11 | 0.76 | 2.24 | 1.63 | 0.24 | 0.17 | 6.88 |
| Ferrosilicate | 2.50 | 2.04 | 2.45 | 1.54 | 1.88 | 4.89 | 2.17 | 6.47 | 4.88 | 1.07 | 2.23 | 7.26 |
| Rutile | 0.41 | 0.44 | 0.37 | 0.23 | 0.23 | 0.66 | 0.33 | 0.64 | 0.53 | 0.24 | 0.23 | -- |
| Apatite | 0.14 | 0.14 | 0.07 | -- | -- | 0.40 | 0.24 | 0.35 | 0.28 | -- | -- | 0.14 |
| Hematite | 1.73 | 1.50 | 1.68 | 1.05 | 1.24 | 3.25 | 1.48 | 4.10 | 3.13 | 0.80 | 1.42 | 4.20 |
| Wollastonite | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | 6.98 |
| Titanite | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | 0.66 |

No duplicate analyses.

*Normalized to 100%

**$SiO_2$ values above 77% (normalized) are out of the range of standards on the (WHOI) XRF. These values may be a few % high due to the non-linear calibration curve.

***$H_2O$ numbers determined on C-H-N analyzer at WHOI. Accuracy is probably greater than 15%; precision is comparable.

KEY FOR FIGURES 6-1 TO 6-8 and 7-1 TO 7-13

★ Mud Road Unit

● Pine Flow Unit

▲ Xenolith

✪ Dedham Granodiorite

○ Mattapan Volcanic Complex

□ Newbury Volcanic Complex

☆ Middlesex Fells Volcanic Complex

Figure 6-1.  Variation diagram of % total Fe vs. % SiO$_2$.

Figure 6-2.  Variation diagram of % MgO vs. % SiO$_2$.
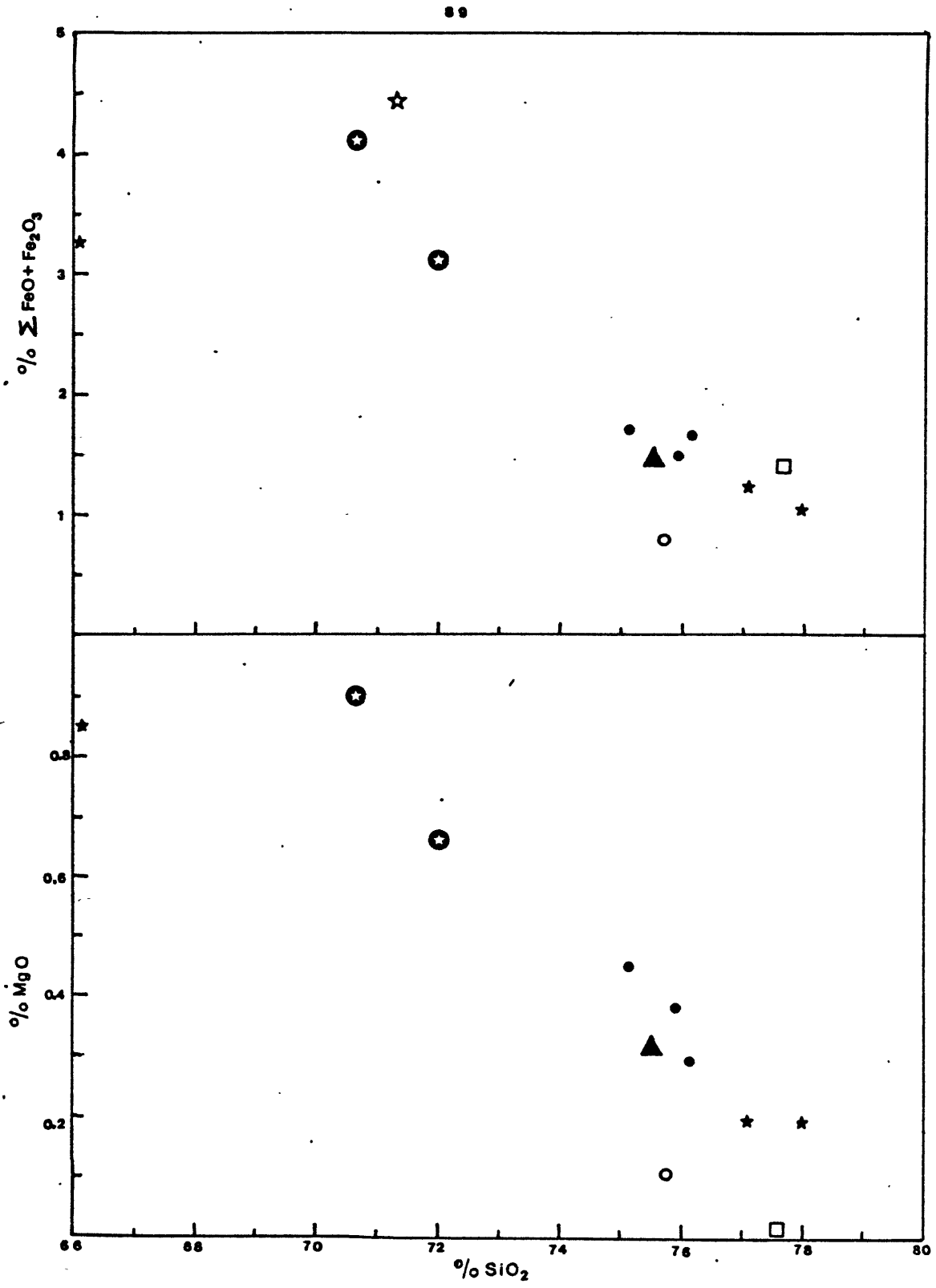
Figure 6-3.  Variation diagram of % $Na_2O$ vs. % $SiO_2$.

Figure 6-4.  Variation diagram of % $K_2O$ vs. % $SiO_2$.
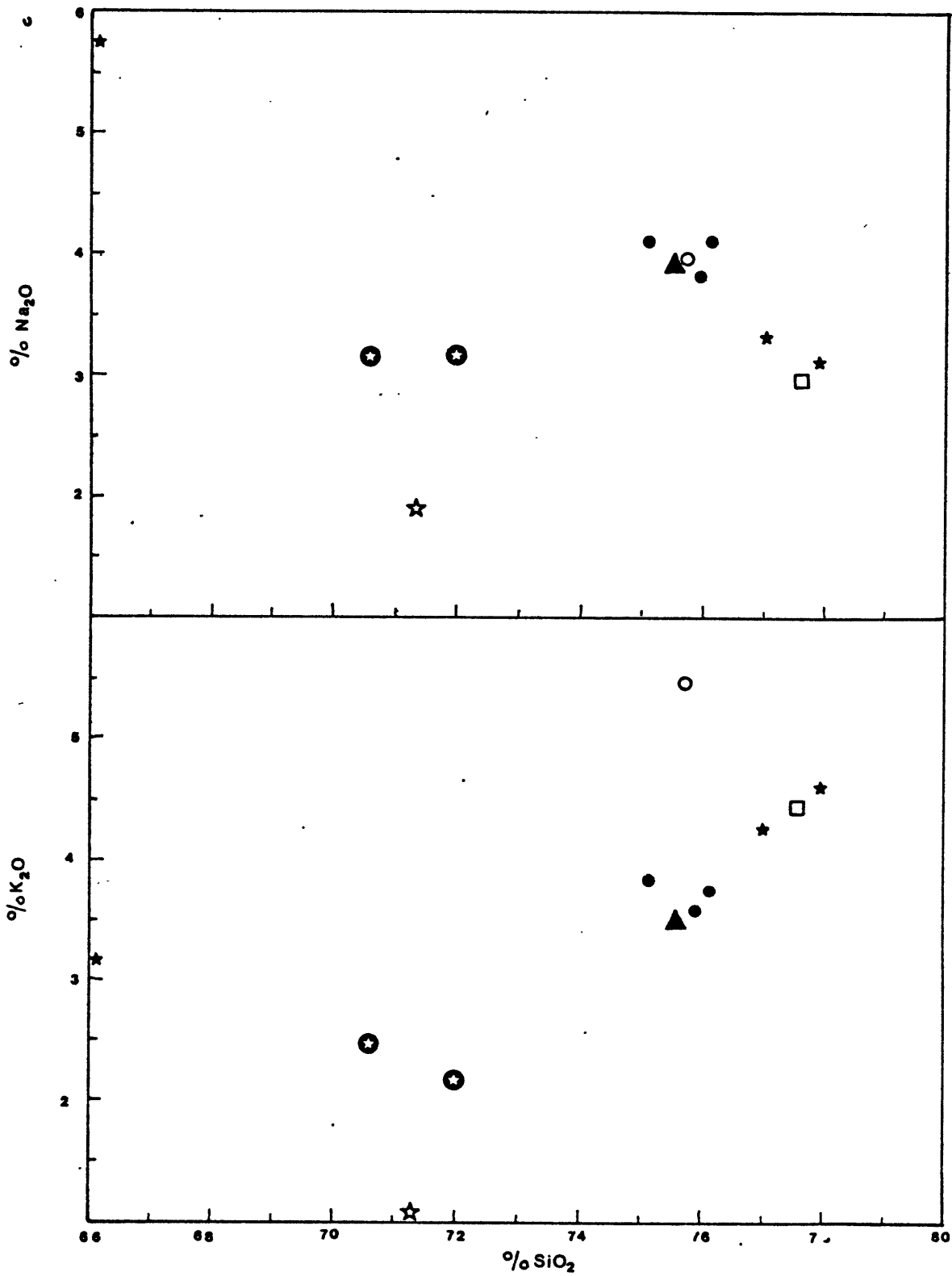
Figure 6-5.   Variation diagram of % $TiO_2$ vs. % $SiO_2$.

Figure 6-6.   Variation diagram % $P_2O_5$ vs. % $SiO_2$.
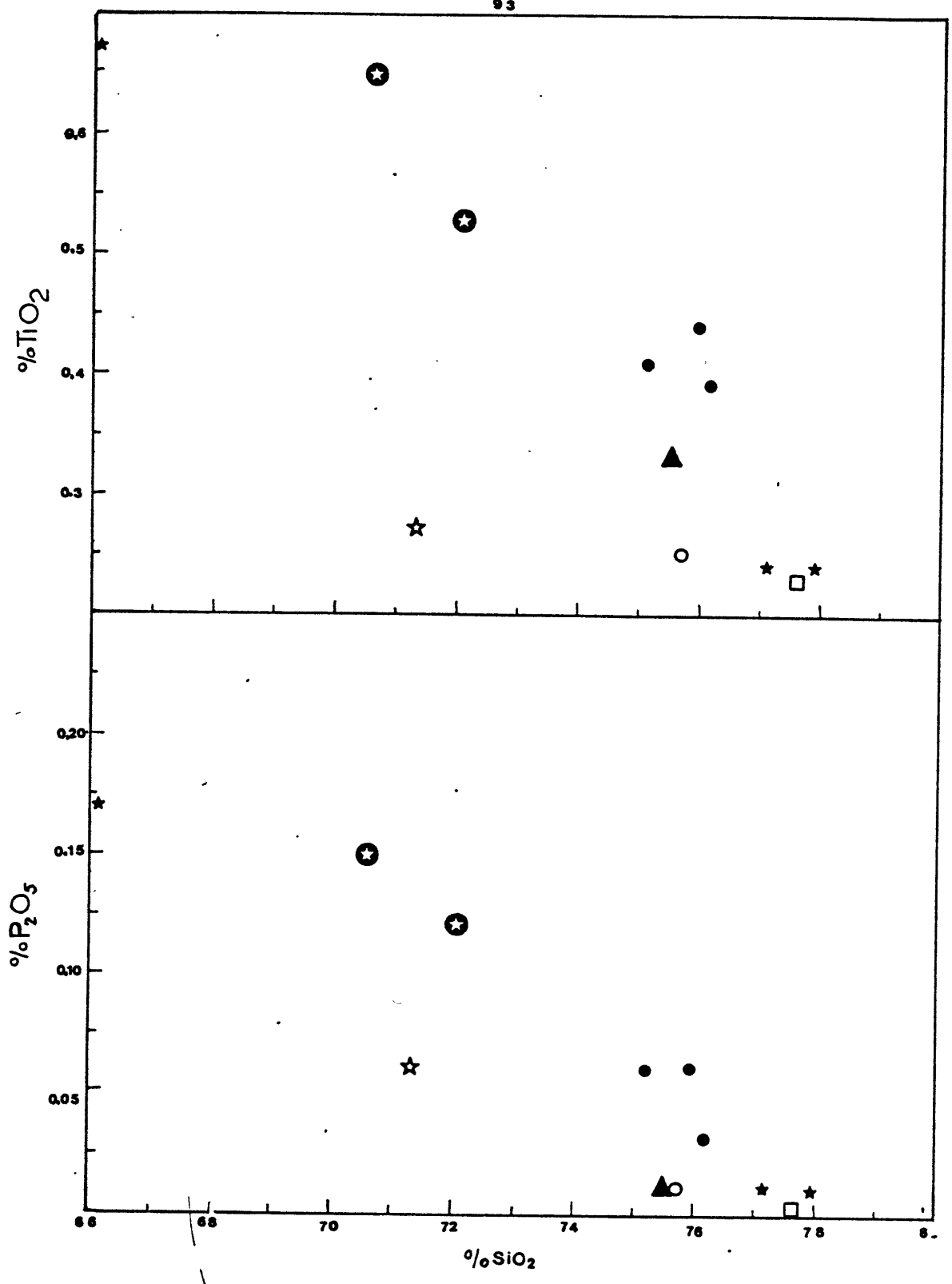
Figure 6-7.   Variation diagram of % CaO vs. % SiO$_2$.

% CaO
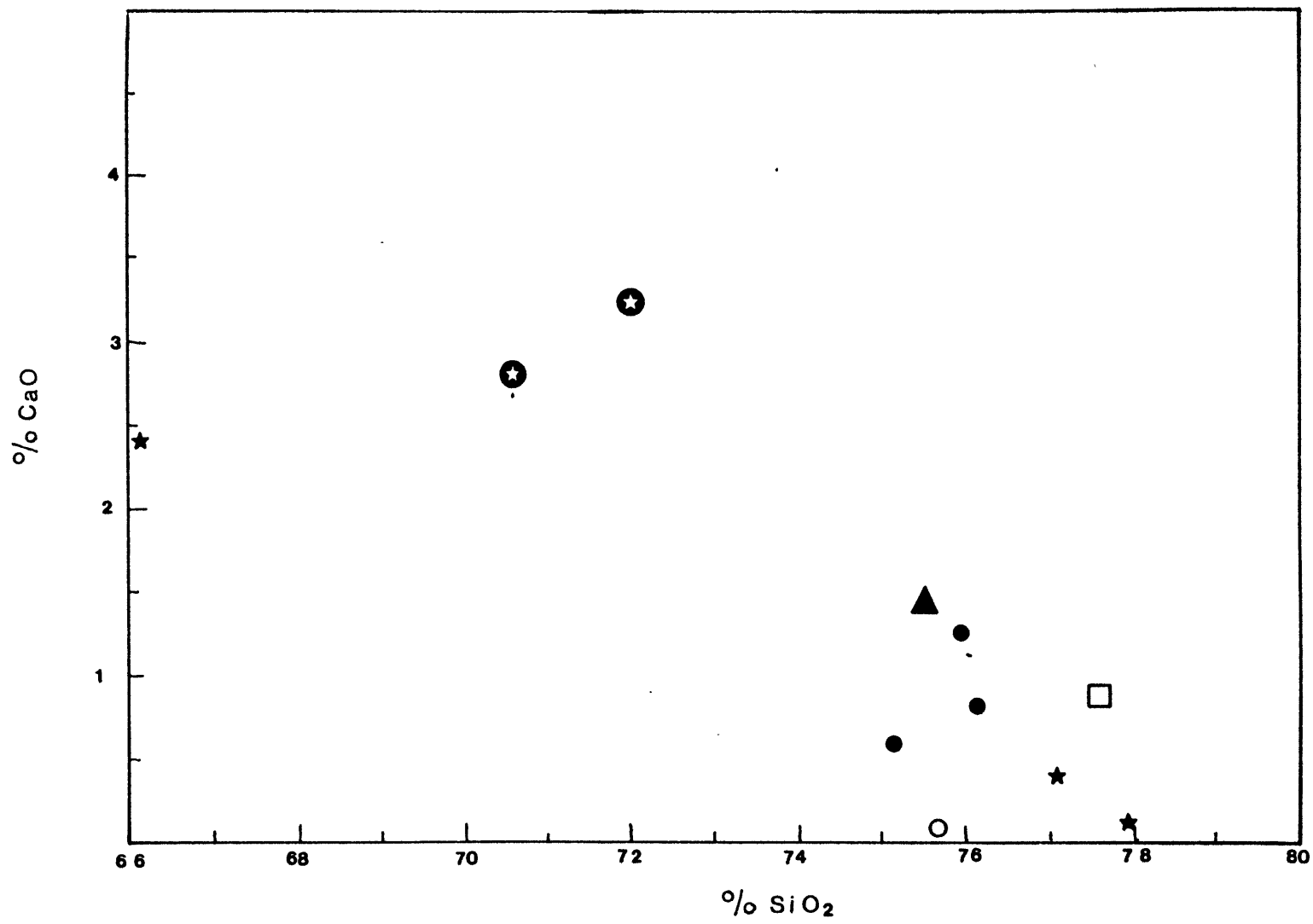
% SiO₂

normally a better indicator of fractionation) are in Figures 6-1 to 6-7. Based on $SiO_2$ content, the hypothesis can be put forward that MR 1 is the most fractionated felsite at Pine Hill (78%), and that PF 1 is the least fractionated (76% $SiO_2$). The variation diagrams can be used to support the lithologic groups identifed in the field. The MR are generally more fractionated, PF are less, and the DG's have still lower $SiO_2$ contents (possibly most "primitive").

Total Fe, MgO, $TiO_2$, $P_2O_5$, and CaO have negative correlations with $SiO_2$ content, ranging from DG 1 with high total Fe, MgO, $TiO_2$, and $P_2O_5$ to the intermediate Pine Flow Unit and the xenolith to the highly fractionated Mud Road samples MR 1 and MR 2.

The general trends of decreasing FeO and MgO may be related to the early crystallization of mafic minerals (i.e. pyroxenes, clinopyroxenes, olivine, amphiboles), which incorporate and fractionate Fe and Mg out of the melt. Similarly decreasing $TiO_2$ and $P_2O_5$ contents with increasing fractionation and increasing $SiO_2$ content could result from removal of apatite, sphene and ilmenite. Also, CaO and $Na_2O$ contents should decrease and $K_2O$ content increase as plagioclase crystallizes and fractionates out at an increasingly rapid rate, until a rhyolitic composition is reached. The variation diagrams for the Pine Hill rocks nicely follow the expected fractionation trends and the data suggest a cogenetic sequence.

The Mattapan and Newbury Volcanic samples manage to fit inconspicuously into the trends delineated by the Pine Hill rocks in $TiO_2$, $P_2O_5$, $Na_2O$ and not in the others. The Middlesex Fells Volcanic Complex sample fall below the trend in $P_2O_5$, $TiO_2$, $Na_2O$, and $K_2O$, and above the trends in CaO, MgO, and total Fe. This would indicate a situation where MF 34 might be a cumulate rock. High amounts in ferromagnesium minerals, and early Ca-rich plagioclase, and low in apatite, sphene and late feldspars might produce this type of trend. It is, none the less, a more dacitic, or unfractionated magma. It is obvious, however, that this rock does not fall along the same fractionation trend as the Pine Flow rocks and it may be totally unrelated to the Pine Hill rocks.

An important point to keep in mind when examining the variation diagrams is that the Dedham granodiorite, is a coarse grained rock, and hence may not truely represent a liquid line of descent. It may be coincidence that they fall on the same trend as the Lynn Volcanics at Pine Hill, although this in unlikely. Another assumption is that the felsites all represent the original liquid, and have not been contaminated by xenocrysts, xenoliths, or mixing of magma.

3.  AFM DIAGRAM DISCUSSION

The AFM diagram is often used to evaluate fractional crystallization as a mechanism in magma generation. The graphic representation of the Pine Hill rhyolites and the Dedham Granodiorite (Figure 6-8), are consistent with a fractional crystallization model relating the rhyolites and granite. However, due to the low density of points in the higher iron range, the designation of the most "primitive" melt capable of producing the rhyolites at Pine Hill is not clear cut. It should be noted that the granites are coarse grained plutonic rocks, and therefore they may not represent an initial liquid, but rather a cumulative rock.

If the rhyolites are considered separately, the liquid line of descent is PF 1 - PF 2 - X 5 - PF 3 - MR 2 - MR 1. This confirms the identity of the units as grouped in the field, and indicates that the PF's and X 5 are less fractionated than Mud Road. The $MgO/MgO + \Sigma FeO + Fe_2O_3$ ratio decreases as the exception of MR 2 and MR 1 being reversed. This trend corroborates other evidence (Chapter VII) in support of fractional crystallization.

When DG 2 is considered, it plots on the linear trend defined by the rhyolites. The trouble develops with the $MgO/MgO + \Sigma FeO + Fe_2O_3$ ratio. DG 1 and DG 2 both display

Figure 6-8.  AFM diagram for all analyzed specimens.  Possible

liquid line of descent drawn through Pine Hill

rocks.
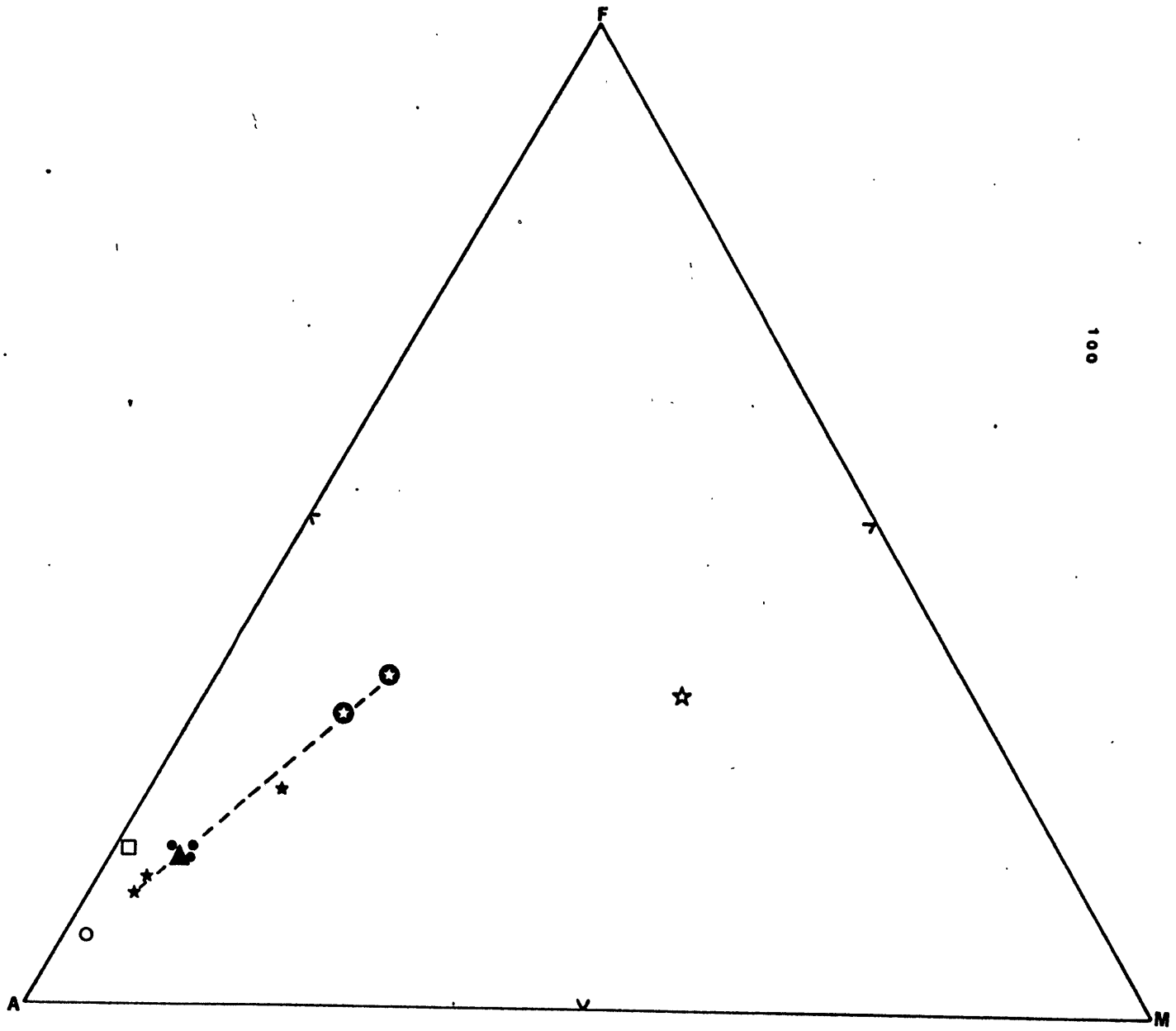
ratios that are anomalously low for the trend to be related by fractional crystallization. The explanation may be that the granite is enriched in total Fe relative to the rhyolite rocks, which would reflect the tendency for accumulation of the early mafic phases in the granitic liquids. The other explanation is that the two rock types are completely unrelated, and the trends, a matter of coincidence.

Therefore, the AFM diagram is useful in this case for it verifies that the rhyolites are related by fractional crystallization, and suggests that the Dedham might be a more "primitive" and related magma.

## 4.    Ab-An-Or-Qtz TETRAHEDRON

The composition of granitic magmas fluctuate with changes in water pressure, temperature, $P_{total}$, and volatile content. The Ab-An-Or-Qtz tetrahedron at various $P_{(H_2O)}$ conditions has been used by geologists to model naturally occurring rock suites. Most experimental work for determining cotectics as a function of water pressure, has been conducted on the Ab-Or-Qtz face of the tetrahedron, and projected onto the Ab-Or-An face. A good indicator of changing $P(H_2O)$ is the Ab/Or ratio which increases with increasing $P(H_2O)$.

Data for PF 1, 2, 3, MR 1, 2, 3, X 5 and DG 1 and DG 2 were plotted on the tetrahedron (Figure 6-9). The points are

Figure 6-9.  Quartz-Albite-Anorthite-Orthoclase-Water Tetra-
hedron (Q-Ab-An-Or-$H_2O$) projected onto a single
plane.

## KEY

### Cotectics

■⦚⦚⦚⦚⦚ = effect of $H_2O$ undersaturation at P = 4Kb (after Steiner
et al., 1975).

□ = P($H_2O$) = 1 Kb (after James and Hamilton, 1969).

○ = P($H_2O$) = 2 Kb (after von Platen, 1965).

★ = P($H_2O$) = 7 Kb (after Winkler et al., 1975).

● = P($H_2O$) = 5 Kb (after Winklet et al., 1975).

### Samples

| | | | |
|---|---|---|---|
| A = PF 1 | D = MR 1 | G = X 5 | J = MV 1 |
| B = PF 2 | E = MR 2 | H = DG 1 | K = NV 1 |
| C = PF 3 | F = MR 3 | I = DG 2 | L = MF 34 |
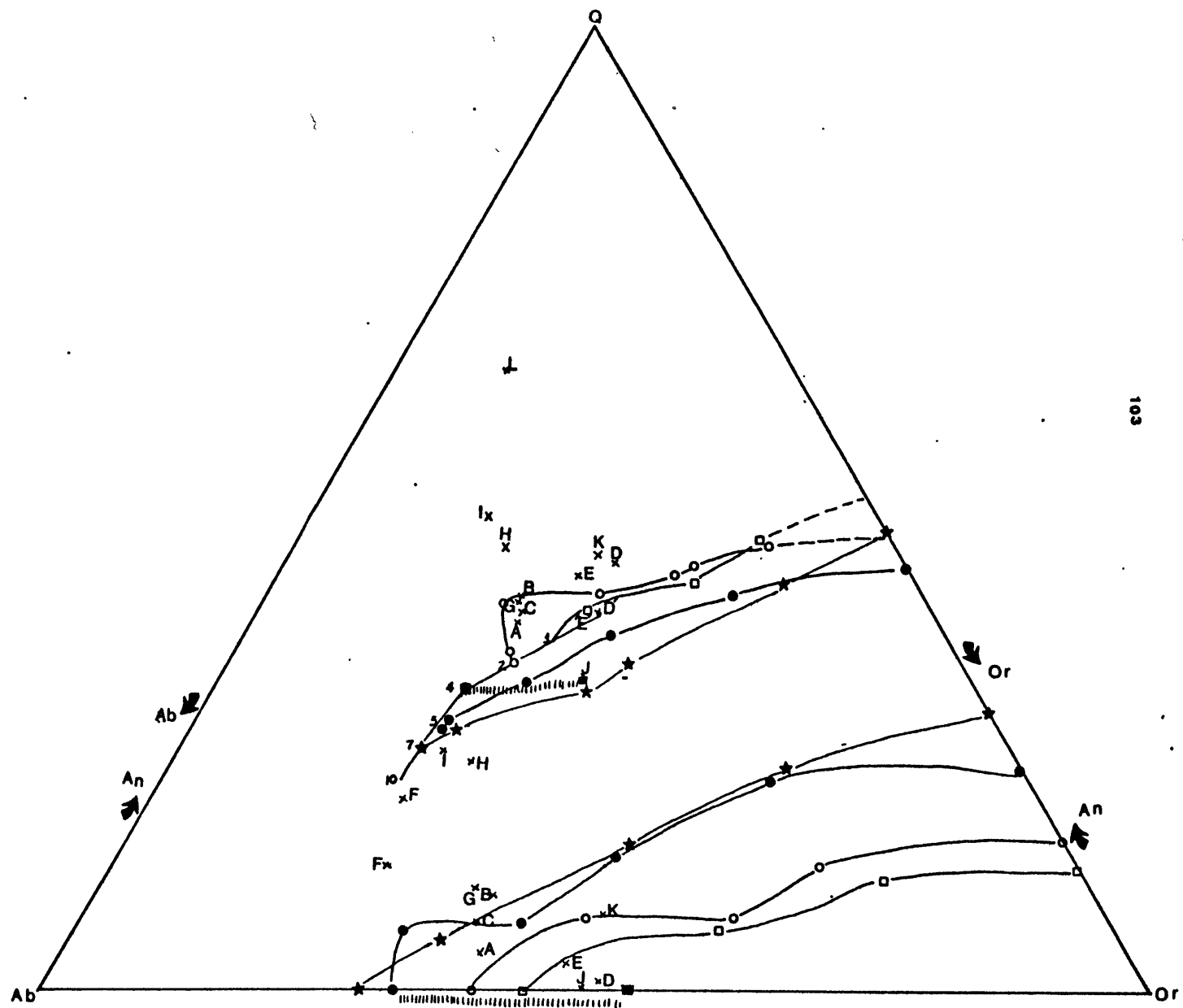
based on normalized C.I.P.W. values. On both faces of the

tetrahedron, MR 3 and the granites do not plot in the experi-

mentally determined ranges for the given $P(H_2O)$. Therefore,

DG 1 and DG 2 probably do not represent true liquids, but

have some cumulate characteristics which situate them well

off the cotectics. As previously discussed, the MR 3 com-

position was strongly affected by leaching and alteration.

These three samples will not be interpreted in the context

of this diagram.

When considering the Ab-An-Or face, all of the felsites

lie below a "smoothed" 5 Kb = $P(H_2O)$ cotectic determined by

Winkler et al. (1975). The specimens trend towards decreas-

ing $P(H_2O)$. For example, B and G lie along a 5 Kb, and sample

E lies near the 1 Kb cotectic. A model to explain this trend

is decreasing $P(H_2O)$ in a magma chamber. Decreasing pressure

will force the melt off the cotectic and precipitation of

plagioclase will continue alone as the melt works its way to-

ward a new, lower $P(H_2O)$ cotectic where Or is once again

crystallizing. This pattern appears to be dominant for the

felsites at Pine Hill, from the Pine Flow unit and the xenolith

to the Mud Road. The required change in pressure is fairly

great, going from at least 5 Kb ($H_2O$) to less than 1 Kb ($H_2O$)

prior to the time of erruption. This drop in pressure cor-

responds to the dropping Ab/Or (Table 6-2) ratio very well,

TABLE 6-2

Ab/Or RATIO


| PF 1 | 1.536 |
|------|-------|
| PF 2 | 1.527 |
| PF 3 | 1.572 |
| MR 1 | 0.973 |
| MR 2 | 1.112 |
| MR 3 | 2.502 |
| X 5  | 1.642 |
| DG 1 | 1.846 |
| DG 2 | 2.128 |
| MV 1 | 1.041 |
| NV 1 | 0.955 |
| MF 34 | 2.442 |

except for PF 2, which display a lower value than anticipated.

The Qtz-Ab-Or diagram is very similar for these rocks, except for MR 1 and MR 2. These plot out of the field of cotectics, toward high $SiO_2$. When original XRF data are examined, it becomes evident that the totals are too high (101%). The $SiO_2$ is 80% and above for these rocks, which is out of the range of the Woods Hole XRF standards. The calibration curve is not linear, and a higher value of $SiO_2$ than actually is present in these samples may be recorded.

If it is assumed that $SiO_2$ is lowered by 4% for both samples, they plot between the 1 Kb ($H_2O$) and 0.5 Kb ($H_2O$) cotectics. If it is assumed that this represents the liquid at the time of crystallization, then the same cotectic crystallization with sudden shifts (decreases) in $P(H_2O)$ as seen in the feldspar ternary diagram, can be identified on this face of the tetrahedron as well. In this case, however, the pressure for these rocks coincides with a very low pressure range, from 2 - 0.5 Kb ($H_2O$), as compared to greater than 4 Kb ($H_2O$) on the feldspar ternary. The trend in specimens is similar, with the Pine Flow fractionating along the cotectic with changes in $P(H_2O)$, toward the most fractionated Mud Road group.

Therefore the important observations to be made from this diagram, pertaining to the Pine Hill rocks:

1. The Dedham probably does not represent the original liquid, and suffers from some cumulate characteristics, or, it is totally unrelated to the felsites at Pine Hill.

2. As previously concluded, MR 3's chemistry is either, disturbed by cataclasis, or fractionated at very high $P(H_2O)$.

3. The Pine Flow units are definitely related to the Mud Road along a liquid line of descent, with equilbrium upset by changes in $P(H_2O)$.

These $P(H_2O)$ changes are easily modelled by assuming an explosive volcanic environment. Erruption from the main chamber, and emplacement as a sill at a lesser depth, where fractional crystallization can continue at less $P(H_2O)$ is but one of many mechanisms that are capable or producing the major element trends seen in these rocks.

Normative proportions for other specimens are also interesting. The Mattapan Volcanics plot directly on the $H_2O$ undersaturated contectic at $P(T) = 4$ Kb. The estimated temperature is high compared to the other rhyolites, at approximately 900° C. This indicates that the chemical composition should not have been affected by a vapor phase, as all the water present will be incorporated into hydrated minerals.

The Newbury volcanics plot directly on the $P(H_2O) = 2$ Kb cotectic in the Or-Ab-An ternary diagram. However, in the

Q-Or-Ab diagram, it plots high on the $SiO_2$ side and out of the area of experimental determinations for this system.

The Middlesex Fells member plots way up towards the Quartz and An end respectively, and this is due to a very low amount of orthoclase (low $K_2O$ in the rock), and a lesser degree of fractionation than the other samples. It is again evident that this rock is chemically dissimilar to the Pine Flow rhyolites and rhyodacites. The Ab/Or ratio indicates a less fractionated magma, and crystallization at a very high $P(H_2O)$.

## 5. CONCLUSIONS BASED ON MAJOR ELEMENT DATA

The major element data clearly indicate that the Pine Flow and Mud Road rhyolites lie along a liquid line of descent caused by fractional crystallization. Variation diagrams of oxide versus $SiO_2$ content consistently indicate increasing fractionation of the rhyolites from the Pine Flow units to the Mud Road. DG 2 may be the "primitive" source magma, however, this relationship is not clear cut.

The Qtz-Or-Ab-An-$H_2O$ tetrahedron implies cotectic crystallization at descending $P(H_2O)$, with 2-5 Kb the upper limit, down to 0.5 Kb (from the PF to MR units). The temperatures for the rhyolites probably range from 700-800°C based on calculations ofa typical rhyolite, compositionally similar to the Pine Hill rocks, by Kern and Weisbrod (1967) using

Barth's geothermometer. This could not be performed on the
Pine Hill samples because no microprobe analysis of the pla-
groclase - K feldspar solid solution are available.

## CHAPTER VII

## TRACE ELEMENT GEOCHEMISTRY

Trace element abundances are a more sensitive indication of igneous rock petrogenesis than major elements. This is especially important in acidic rocks, where the bulk major composition of the fractionating crystals is often very similar to the source magma. For this reason Instrumental Neutron Activation Analysis, (INAA) was used to determine the trace elements (TE), including rare earth elements (REE), in the twelve specimens studied.

## 1. ANALYTICAL METHODS

Trace element abudnaces were determined by X-ray fluorescence (Norrish and Hutton, 1969) and Instrumental Neutron Activation Analysis (INAA) (Gordon et al., 1968). The samples, and a prepared standard solution (prepared by S. Roy and M. Loiselle) were irradiated at the MIT Nuclear Reactor for eight hours, at a flux = $1 \times 10^{13}$ neutrons $cm^{-2}$ $sec^{-1}$. Each of the twelve samples contained approximately 0.5 grams of rock powder (see sample preparation; Chapter V), and were allowed to cool down for five days. Counts on the Low Energy Photon Scintillator (LEPS) and the Ortec Ge(Li) detectors

## TABLE 7-1

### TRACE ELEMENT ABUNDANCES (ppm)

| | PF 1 | PF 2 | PF 3 | MR 1 | MR 2 | MR 3 | X 5 | DG 1 | DG 2 | MV 1 | NV 1 | MF 34 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Rb | 91.0 | 120.4 | 75.5 | 123.1 | 139.6 | 81.8 | 100.8 | 64.9 | 83.3 | 174.9 | 149.3 | 20.3 |
| Sr | 134.9 | 292.6 | 169.1 | 121.1 | 163.3 | 462.0 | 227.7 | 370.3 | 315.2 | 32.4 | 133.3 | 71.6 |
| Zr | 236.5 | 220.9 | 198.1 | 171.9 | 179.1 | 310.8 | 234.7 | 246.6 | 286.3 | 252.6 | 198.7 | 117.2 |
| Hf | 4.62 | 4.25 | 4.30 | 3.40 | 3.55 | 6.05 | 4.51 | 4.42 | 5.42 | 4.98 | 4.27 | 1.98 |
| Ta | 3.60 | 8.04 | 4.01 | 4.03 | 4.46 | 2.74 | 3.47 | 5.80 | 7.18 | 5.24 | 3.67 | 2.09 |
| Cs | 0.96 | 1.46 | 1.00 | 0.59 | 1.38 | 1.02 | 0.94 | 0.73 | 0.70 | 2.12 | 2.49 | 0.66 |
| U | 2.79 | 4.95 | 4.24 | 3.63 | 6.34 | 2.99 | 3.12 | 0.64 | 3.55 | 4.64 | 5.79 | 1.36 |
| Th | 10.67 | 10.53 | 9.94 | 10.50 | 11.19 | 9.36 | 8.78 | 4.81 | 4.56 | 12.34 | 23.71 | 1.74 |
| Y | 23.6 | 26.7 | 24.6 | 34.1 | 25.2 | 32.9 | 34.7 | 36.1 | 51.2 | 24.1 | 43.0 | 38.7 |
| Sc | 4.53 | 4.82 | 4.39 | 2.52 | 2.56 | 7.99 | 5.11 | 8.58 | 14.57 | 4.81 | 3.04 | 17.02 |
| Cr | 3.21 | 2.06 | 1.86 | 3.48 | 2.18 | 2.14 | 2.46 | 6.12 | 5. 75 | 4.87 | 1.95 | 3.32 |
| La | 111.83 | 126.24 | 112.21 | 290.86 | 124.22 | 145.28 | 117.48 | 84.42 | 64.27 | 131.07 | 116.56 | 24.35 |
| Ce | 98.52 | 101.42 | 87.80 | 123.06 | 96.24 | 119.88 | 95.73 | 62.49* | 47.93 | 87.22 | 91.87 | 24.74 |
| Nd | 46.26 | 51.99 | 44.90 | 96.06 | 46.04 | 62.18 | 51.92 | 37.74* | 40.39 | 52.22 | 42.74 | 18.51 |
| Sm | 31.42 | 35.62 | 32.77 | 59.38 | 30.02 | 47.54 | 34.60 | 35.55 | 43.54 | 35.03 | 32.52 | 22.28 |
| Eu | 16.88 | 17.39 | 16.09 | 32.35 | 16.22 | 30.59 | 26.84 | 26.36 | 27.33 | 14.62 | 9.99 | 16.81 |

-111-

TABLE 7-1 (Continued)

| | PF 1 | PF 2 | PF 3 | MR 1 | MR 2 | MR 3 | X 5 | DG 1 | DG 2 | MV 1 | NV 1 | MF 34 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ho | 14.31 | 13.76 | 12.79 | 18.91 | 12.51 | 15.59 | 15.63 | 13.06 | 20.63 | 11.46 | 18.87 | 18.61 |
| Yb | 12.64 | 12.90 | 10.09 | 10.77 | 11.14 | 16.72 | 16.05 | 12.39* | 26.84 | 12.63 | 20.10 | 20.07 |
| Lu* | 12.26 | 13.71 | 12.15 | 9.50 | 10.32 | 13.68 | 14.06 | 7.45* | 24.26 | 12.38 | 21.24 | 18.56 |
| $(La/Sm)_N$ | 3.56 | 3.54 | 3.42 | 4.89 | 4.14 | 3.06 | 3.39 | 2.37 | 1.48 | 3.74 | 3.58 | 1.09 |
| $(La/Yb)_N$ | 8.85 | 9.79 | 11.12 | 27.00 | 11.15 | 8.93 | 7.32 | 6.81* | 2.39 | 10.38 | 5.80 | 1.21 |
| $(Sm/Yb)_N$ | 2.49 | 2.76 | 3.25 | 5.51 | 2.69 | 2.92 | 2.16 | 2.87* | 1.62 | 2.77 | 1.62 | 1.11 |
| $(Eu/Eu*)_N$ | 0.63 | 0.59 | 0.60 | 0.69 | 0.64 | 0.82 | 0.91 | 0.90 | 0.73 | 0.52 | 0.34 | 0.79 |

No duplicate analyses

*These values for DG 1 were all calculated on the 15 day count using INAA. Apparently, the detector shut off before the full 20,000 second count was completed, and gave anomalously low values, when compared with the abundances of other elements determined using 5, 8, or 30 day data, as well as 15 day data, also for DG 1, such as Yb and Lu. The ratio of Lu(8 day)/Lu(15 day) counts was used as a correction factor for the 15 day elements without peaks on alternate days, and these values are designated with (*). They should not be used for calculations. Correction factor = 2.478/0.538 = 4.25.

(Eu/Eu*): Eu* is value of Eu determined by interpolation between Sm and Ho abundances of individual rocks.

Lu* = corrected conc. Lu = initial concentration Lu (ppm in sample) x $\dfrac{1-.02 \text{ x (Yb ppm/Lu ppm)samp}}{1-.02 \text{ x (Yb ppm/Lu ppm)STD}}$

(2% of Yb in sample changes to $Lu^{177}$).

(efficiency is approximately = 10%), were measured at 5, 8, 15, and 30 day intervals after irradiation. The data were reduced manually on a pocket calculator. The rare earth elements (REE; La, Ce, Nd, Sm, Eu, Ho, Yb, Lu), Cs, Sc, U, Th, Cr, Zr, Hf, and Ta were determined using INAA (Table 7-1). Sr, Rb, Zr, and Y were determined by XRF as well (Table 7-1). INAA precision is believed to be better than ±5% for all the elements except Y(11%), Ho and U (10-15%). The accuracy is considered comparable to precision (Frey et al., 1971).

## 2. RESULTS

### Rubidium:

The only major element that Rb can substitute for is K. The electronegativities and ionization potentials are very similar, but the size difference is significant. The ionic radius of $K^+$ = 1.33, and $Rb^+$ = 1.47 (Table 7-2). Rubidium forms no major phases of its own, but is incorporated into biotite and K-feldspar in igneous rocks. However, the mineral/liquid partition coefficient of $Rb^+$ for these minerals is less than that of $Ba^{2+}$ for biotite, and an order of magnitude less than that of Sr and Ba in K-feldspar. The differences are probably due to the greater ionic radius ($Sr^{2+}$ = 1.18 Å, $Ba^{2+}$ = $1.34^{2+}$) of $Rb^{2+}$ (P.C. from Arth, 1976). Therefore Rb will increase in the melt as fractionation progresses.

TABLE 7-2

TABLE OF ELECTRONEGATIVIES AND IONIC RADII

| | r | Cn | e |
|---|---|---|---|
| $Mg^{2+}$ | 0.66 | IV | 1.2 |
| $Fe^{2+}$ | 0.71 | IVH | 1.7 |
| $K^{+}$ | 1.46 | VI | 0.80 |
| $Al^{3+}$ | 0.47 | IV | 1.50 |
| $P^{5+}$ | 0.25 | IV | |
| $Ca^{2+}$ | 1.08 | VI | 1.00 |
| $Sc^{3+}$ | 0.83 | VI | 1.3 |
| $Ti^{4+}$ | 0.61 | V | 1.6 |
| $Cr^{3+}$ | 0.70 | VI | 1.6 |
| $Rb^{+}$ | 1.57 | VI | 0.8 |
| $Sr^{2+}$ | 1.21 | VI | 1.00 |
| $Y^{3+}$ | 0.98 | VI | 1.2 |
| $Zr^{4+}$ | 0.80 | VI | 1.5 |
| $Hf^{4+}$ | 0.79 | VI | 1.4 |
| $Cs^{+}$ | 1.78 | VI | 0.75 |
| $Ta^{5+}$ | 0.72 | VI | 1.7 |
| $Th^{4+}$ | 1.08 | VI | 1.4 |
| $U^{4+}$ | 1.06 | VII | 1.4 |
| $La^{3+}$ | 1.13 | VI | 1.1 |

TABLE 7-2

TABLE OF ELECTRONEGATIVITIES AND IONIC RADII

(Continued)

| | $\underline{r}$ | $\underline{Cn}$ | $\underline{e}$ |
|---|---|---|---|
| $Ce^{3+}$ | 1.09 | VI | 1.1 |
| $Nd^{3+}$ | 1.06 | VI | ~1.2 |
| $Sm^{3+}$ | 1.04 | VI | ~1.2 |
| $Eu^{2+}$ | 1.25 | VI | ~1.1 |
| $Ho^{3+}$ | 0.98 | VI | ~1.2 |
| $Yb^{3+}$ | 0.95 | VI | ~1.1 |
| $Lu^{3+}$ | 0.94 | VI | ~1.2 |

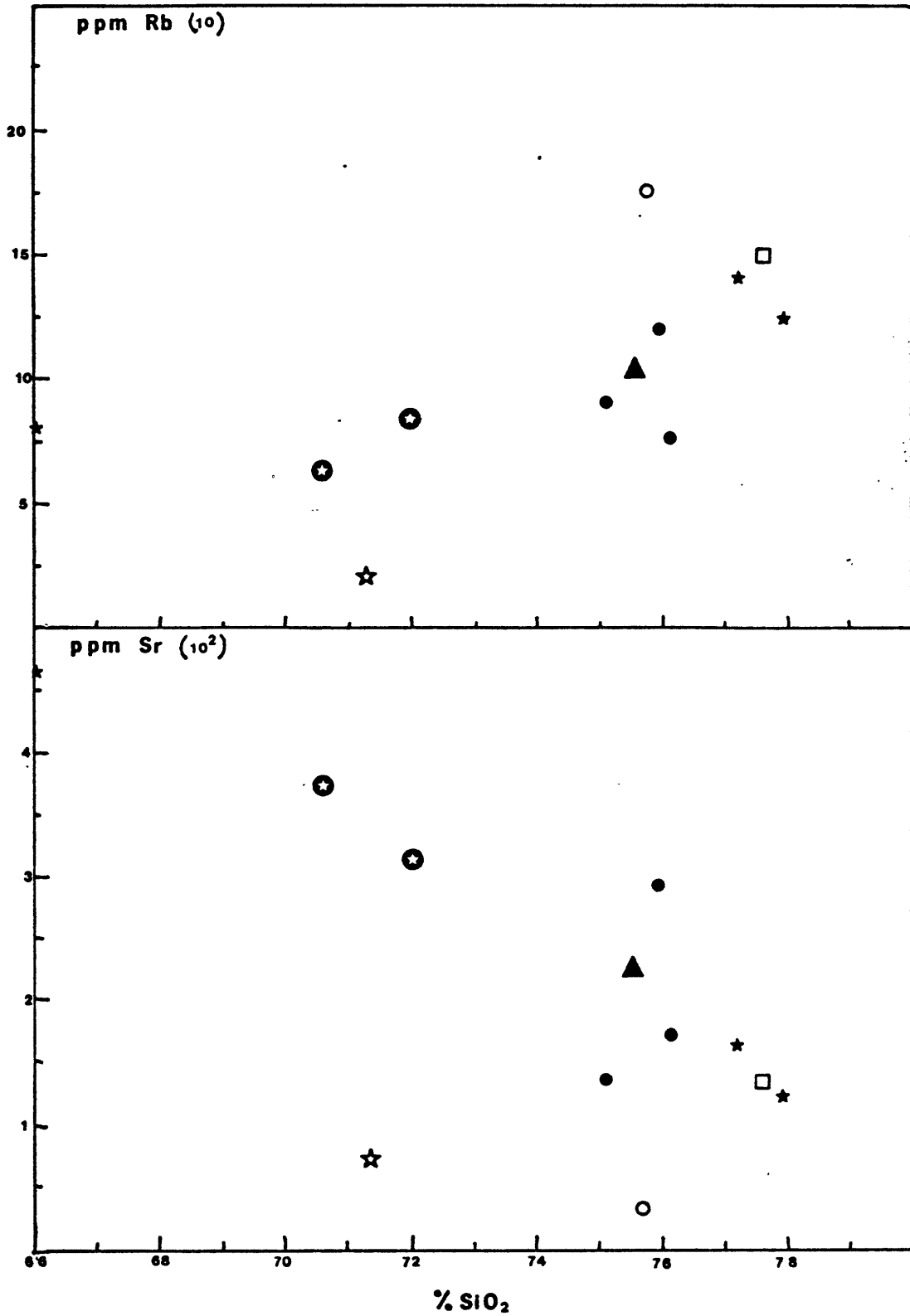r = Ionic radius
Cn = Coordination number
e = Electronegativity

a.   Ionic radii from Shannon and Prewitt, 1969.

b.   Electronegativities from S.R. Taylor, 1965.

Figure 7-1.  Variation diagram of ppm Rb vs. % $SiO_2$.

Figure 7-2.  Variation diagram of ppm Sr vs. % $SiO_2$.

This pattern is well demonstrated in the variation diagram (Figure 7-1) of Rb versus $SiO_2$ content (i.e. degree of fractionation). A positive correlation indicates that Rb is enriched in the liquid that is most fractionated.

The Newbury sample is comparable to the Pine Hill rhyolites. The Mud Road samples appear to be the most highly fractionated, with the Pine Flow samples intermediate, and the Dedham Granodiorite the least fractionated. The Rb/K ratio, which increases with increasing differentiation, roughly correlates to this pattern, although it is not convincing if viewed alone. MR 3 is an aberrant point for the Pine Hill rocks. Careful examination indicates that this is the case for most of the trace element diagrams, and as previously discussed in the Major Element Chapter, I will not consider this sample because of its altered nature.

### Strontium:

The size of $Sr^{2+}$ ion (r = 1.18 Å) infers that it can substitute for $Ca^{2+}$ (r = 0.99) by admission or potassium$^+$ (r = 1.33) by capture due to its higher charge, ($Sr^{2+}$ = 1.0, $K^+$ = 0.80). Although $Sr^{2+}$ is capable of substituting for K in K-feldspar, the partition coefficient for $Ba^{2+}$ into K-feldspar is 2-fold greater than that of $Sr^{2+}$, and hence should dominate in replacement of $K^+$ in this mineral.

Figure 7-3. Comparison of Rb abundances versus Sr abundances

in ppm.
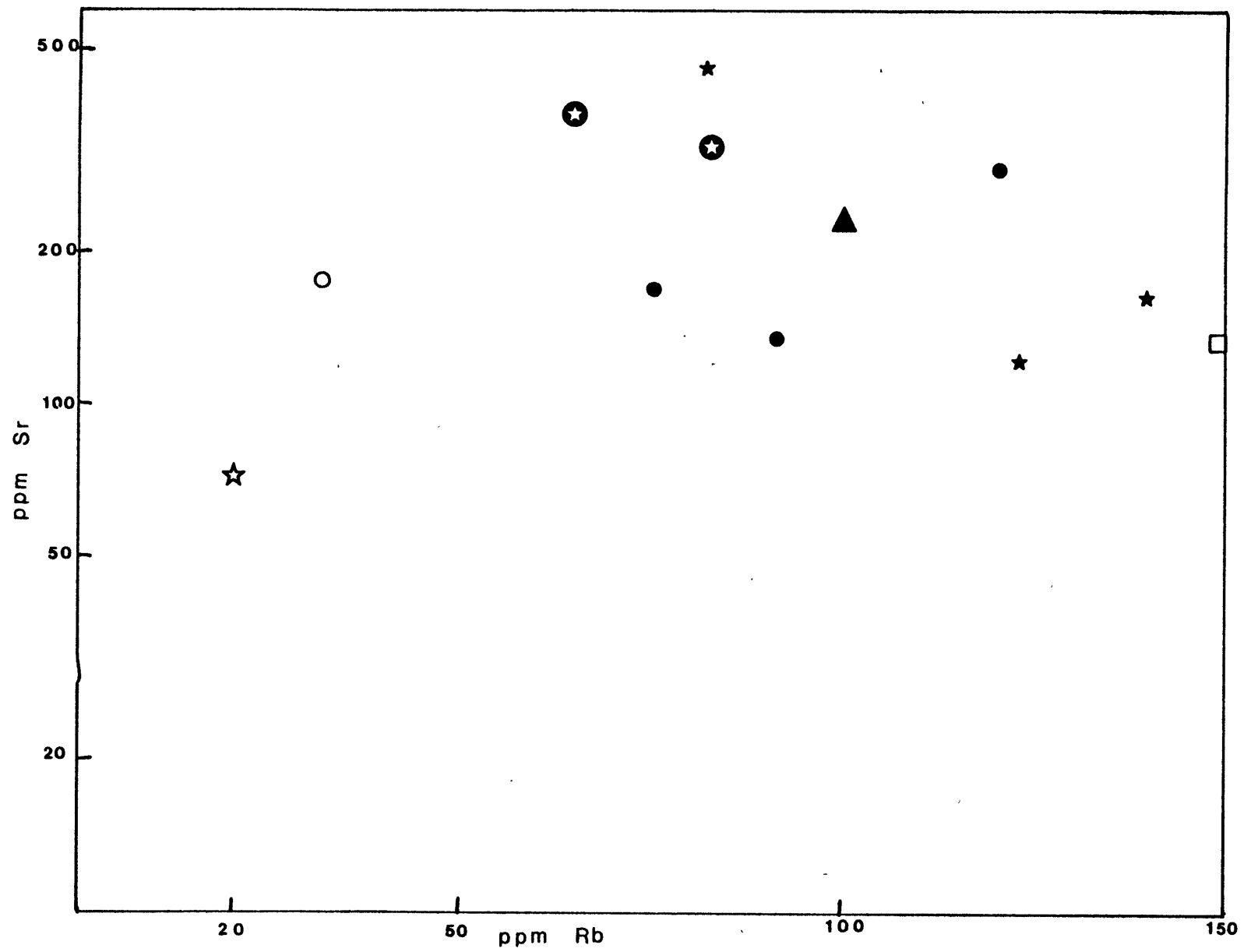
However, in replacing $Ca^{2+}$ in plagioclase the P.C. for $Sr^{2+}$ is at least an order of magnitude higher than any of the other trace elements of significant amount, and hence Sr is concentrated into plagioclase during fractionation. The admittance of $Sr^{2+}$ in place of $Ca^{2+}$ is not dominant in all minerals, such as augite, where it is present in insignificant amounts. In these felsic rocks, the removal of plagioclase causes a decrease of $Sr^{2+}$ in the melt, as fractionation continues (Figure 7-2). The variation diagram reflects this principle and decreases from the Dedham→Pine Flow→Mud Road. The Pine Flow rhyolites vary widely on Sr, and PF 2 deviates from the trend. MV 1 and MF 34 are lower than the Pine Hill trend, while NV 1 is correlative.

A graph (Figure 7-3) of Sr vs. Rb has a negative slope indicating Rb enrichment and Sr depletion in the late stage fractionates at Pine Hill.

## Zirconium and Hafnium:

Zirconium and Hafnium are chemically very similar, with ionic radii = 0.79 Å for $Zr^{4+}$ and 0.78 Å for $Hf^{4+}$, and electronegativity = 1.5 and 1.4 respectively. This combination sets $Zr^{4+}$ and $Hf^{4+}$ apart from the major igneous rock forming elements. For this reason, $Zr^{4+}$ is forced into a separate mineral, zircon ($ZrSiO_4$), and $Hf^{4+}$ occurs as a camouflaged

Figure 7-4. Variation diagram of ppm Zr versus % $SiO_2$.

Figure 7-5. Variation diagram of ppm Hf versus % $SiO_2$.
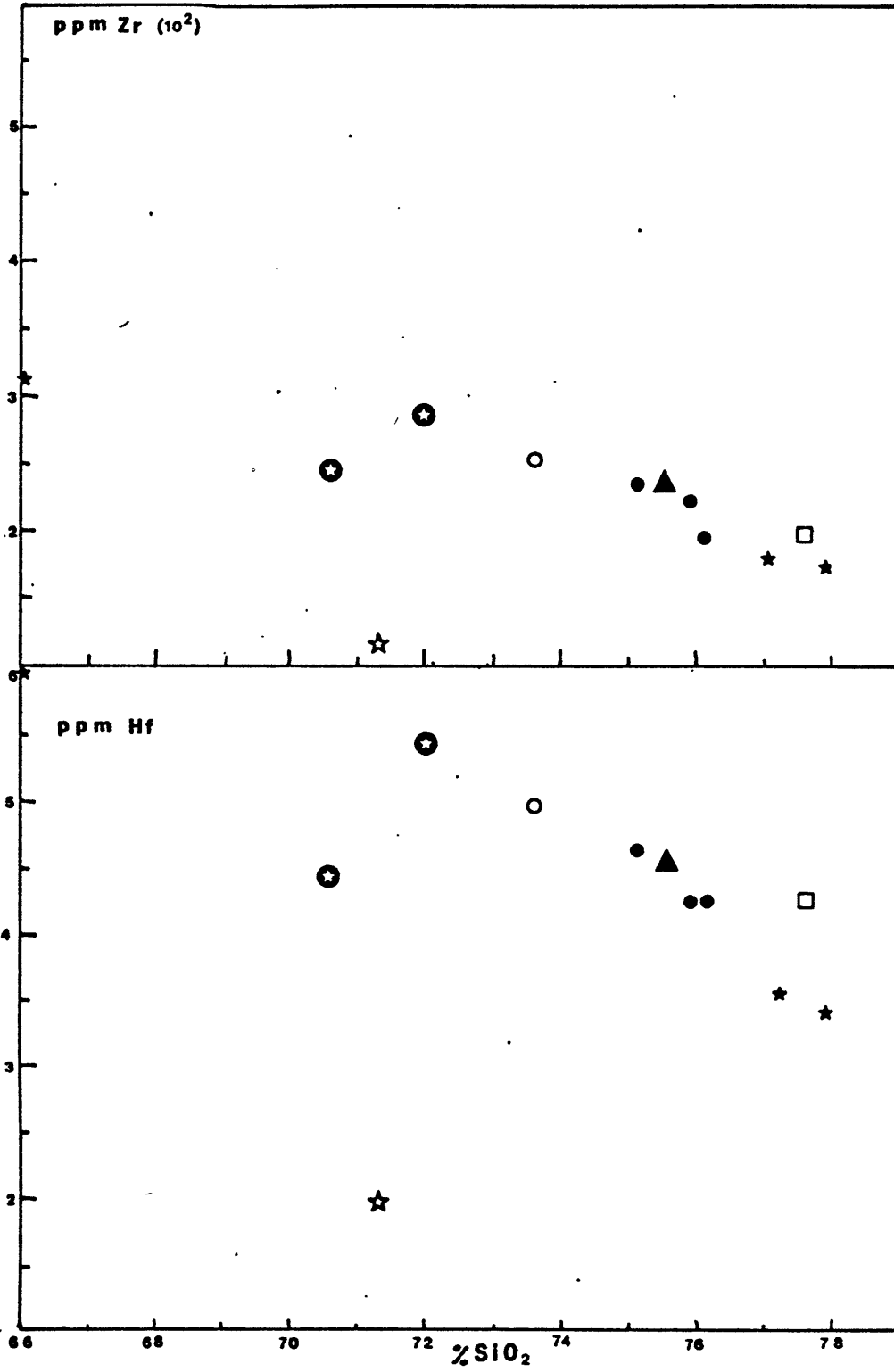
element in zircon. Zircon is relatively abundant in the later

fractionated liquids, because zirconium activity in early

magmas is not sufficient for the formation of zircon. $Zr^{4+}$

and $Hf^{4+}$ can substitute in pyroxenes and late apatites

(Taylor, 1965) to some extent.

According to theory, the Zr: Hf ratio should remain

constant throughout fractionation processes due to the similari-

ty of their chemical nature. The Pine Hill rocks however,

show a decreasing ratio (Table 7-3) with increased fractiona-

tion. Zr is being depleted relative to Hf, during the frac-

tionation process. It is important to note that in these

rocks, Zr and Hf both decrease with fractionation, indicating

that Zr content in the magma is being lowered by removal of

a Zr-rich phase, possibly zircon (Figure 7-4 and 7-5). In

order to explain the decreasing Zr/Hf ratio, Zr, is preferen-

tially entering another phase relative to Hf, or Hf is not

being admitted into zircon at comparable rates, and hence,

remaining in the melt, or more likely, a combination of

the two processes. It is interesting to note that $TiO_2$ is

also decreasing, so it is likely that a Ti-rich phase could

be aiding the lowering of Zr and Hf. Buma, (1970) suggests

that the Zr/Hf ratio does change during crystallization, with

Hf becoming enriched in late stage liquids.

## TABLE 7-3

## Zr/Hf RATIOS

| | |
|---|---|
| PF 1 | 51.18 |
| PF 2 | 51.95 |
| PF 3 | 46.11 |
| | |
| MR 1 | 50.53 |
| MR 2 | 50.69 |
| MR 3 | 51.41 |
| | |
| X 5 | 52.02 |
| | |
| DG 1 | 55.80 |
| DG 2 | 52.87 |
| | |
| M 1 | 50.69 |
| NV 1 | 46.58 |
| MF 34 | 59.07 |

## Tantalum:

Tantalum, which is supposed to be the "perfect" incompatible element, (Vlasov, 1964) is enriched in highly silicic rocks. These rocks are very enriched relative to the "normal" 3 ppm Ta in granodiorites (Flanagan, 1972), with values for the Dedham of 5.8 - 7.2 ppm, and decreasing abundance with increasing $SiO_2$ content, down to 3.5 ppm in the xenolith. The interesting observation is that Ta, (Figure 7-6) becomes depleted with fractionation. The concentration of $Ta^{5+}$ in zircon (based on ionic radii) for example (Vlasov, 1964) may account for the depletion of $Ta^{5+}$ during crystallization. The trend (Figure 7-6) is reasonably defined, and is in fact similar in slope to $Zr^{4+}$, indicating a direct relationship between Zr and Ta. The Zr/Ta ratio infers that with increased fractionation, Ta increases relative to Zr, and hence decreases the ratio. Ta is still a poorly understood element. However, this simple scheme for general enrichment, linked with relative depletion due to increased fractionation of zircon is justified.

## Cesium:

Cesium is a large cation, (r = 1.67 Å) and can substitute only for $K^+$ (r = 1.33 Å) among the major elements, but due to the great difference in size, it has difficulty substituting, and has very low S/ℓ parition coefficients. Thus, Cs

Figure 7-6. Variation diagram of ppm Ta vs. % SiO$_2$.

Figure 7-7. Variation diagram of ppm Cs vs. % SiO$_2$.
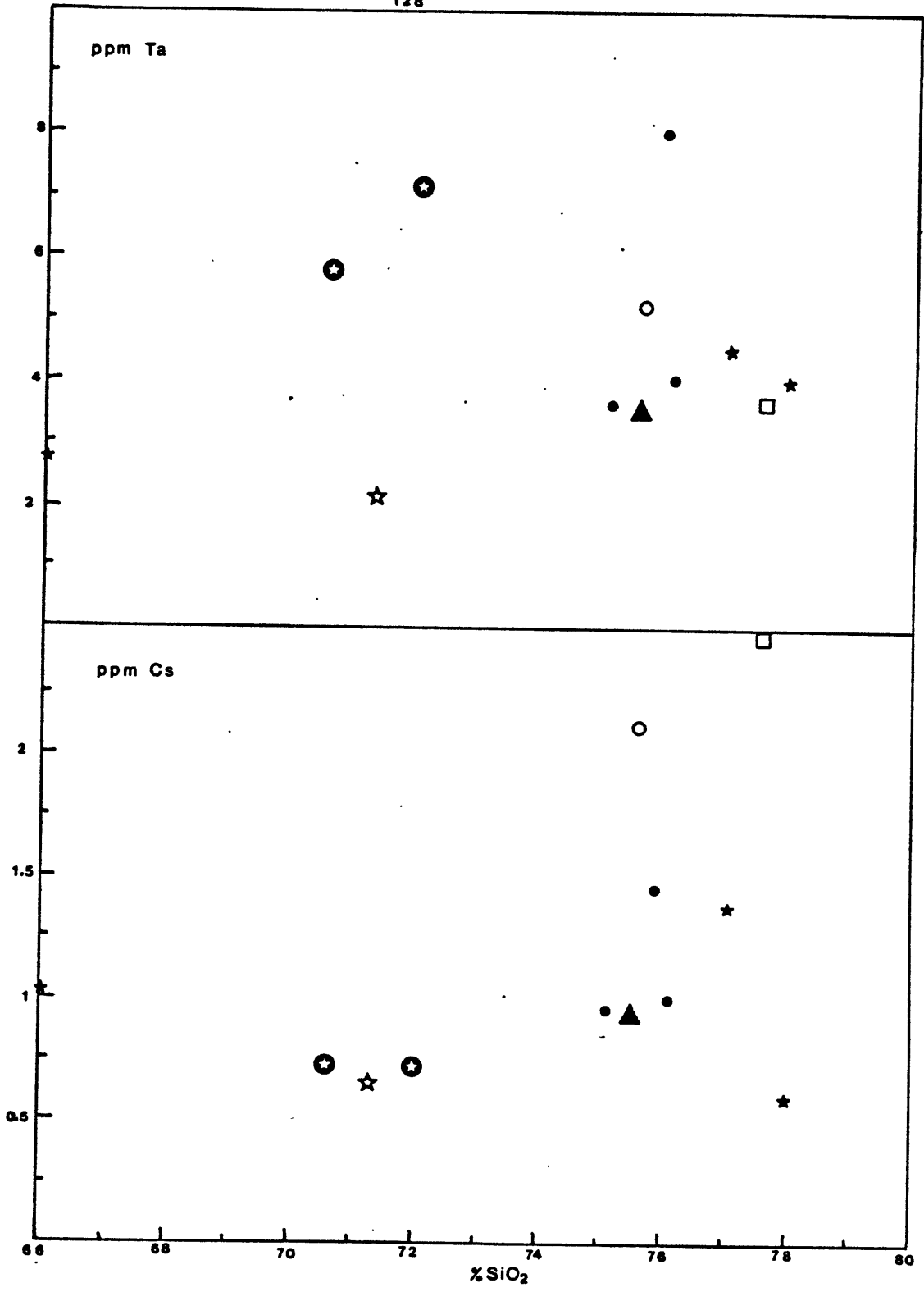
is an incompatible element, which is expected to be enriched
in residual liquids (Figure 7-7). The erratic enrichment of
Cs with increasing $SiO_2$ content is compatible with the pro-
posed fractional crystallization model of these rocks at
Pine Hill.

INAA was used to determine abundances of Cs. The nor-
mally used 604 peak was consistently high when compared with
the Cs 795 peak. Common interferences were investigated,
and antimony ($^{124}$Sb) was identified at its two characteris-
tic gamma ray energies, 602.5 KeV and 1691 KeV. The amount
of $^{124}$Sb in some rocks (e.g. MV 1, NV 1) is substantial,
and the asymmetrical nature of the Cs at the 604 KeV peak is
obvious, and the $^{124}$Sb 3382 KeV peak is very well defined.
Surprisingly, there is what appears to be a substantial
amount of Sb in the standards,NG 19 and 22. No calibration
was possible for any of the rocks, due to the unknown quanti-
ty in the standard, necessary for calculation. This would
be an interesting element to study in these rocks, which have
a well defined fractional crystallization pattern. Observa-
tions of systematic changes in abundances of Sb with the frac-
tional crystallization process would help our modeling of
rock petrogenesis.

Figure 7-9.  Variation diagram of ppm U vs. % SiO$_2$.

Figure 7-8.  Variation diagram of ppm Th  vs. % SiO$_2$.
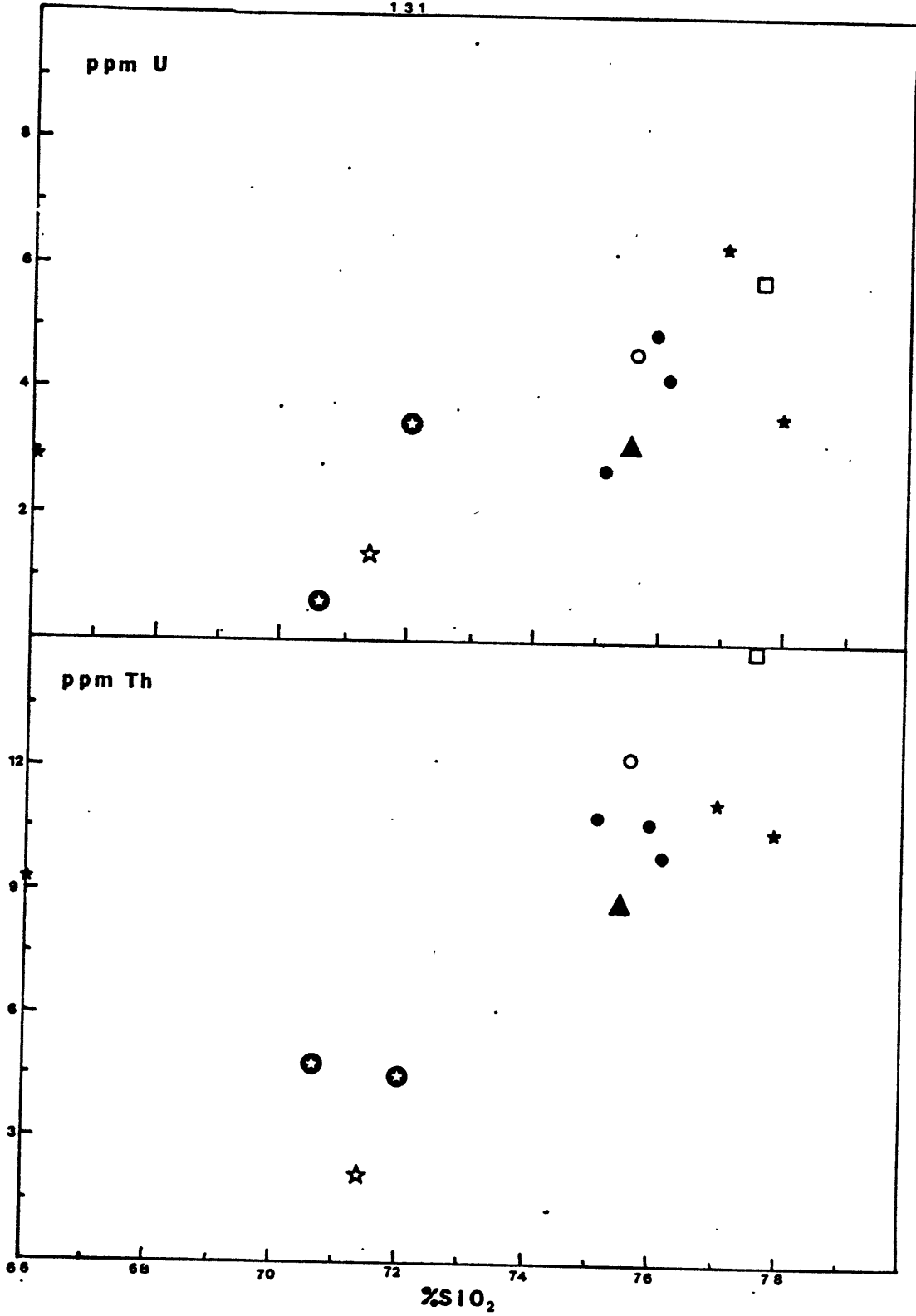
## Uranium and Thorium:

Uranium and Thorium are considered to be incompatible elements, and are generally enriched in residual liquids. According to Rogers and Adams (1969) in a large set of differentiation sequences studied, only one existed where the Th content decreased toward the more fractionated rocks. The general rule of enrichment in late stage liquids is observed in the Pine Hill series. Variation diagrams show considerable scatter however, indicating that $SiO_2$ content is more of a factor than actual abundances of Th and U (Figures 7-8 and 7-9). The slope of Th vs. $SiO_2$ is much steeper than the U variation diagram, with the liquid line of descent drawn between the Dedham values and the Pine Hill rhyolite data. However, if it is considered that Th tends to be incorporated into primary minerals in igneous rocks relative to U, then the Th/U ratio should decrease with increasing fractionation. This is not strictly the case as seen in Table 7-4. One problem may be the large error (> 15%) associated with Uranium abundance determination using INAA.


## Yttrium:

$Y^{3+}$ decreases with increasing fractionating (Figure 7-10) in the Pine Hill rocks. This is due to the fact that Y behaves like a HREE and is incorporated into early forming mafic minerals. This factor is enhanced by late stage fractionation,

TABLE 7-4

Th/U RATIOS

| PF 1 | 3.827 |
|------|-------|
| PF 2 | 2.127 |
| PF 3 | 2.347 |
| | |
| MR 1 | 2.897 |
| MR 2 | 1.765 |
| MR 3 | 3.133 |
| | |
| X 5 | 2.813 |
| | |
| DG 1 | 7.516 |
| DG 2 | 1.319 |
| | |
| MV 1 | 2.661 |
| NV 1 | 4.096 |
| MF 34 | 1.275 |

.Figure 7-10. Variation diagram of ppm Y vs. % SiO$_2$.

Figure 7-11. Comparison of ppm Y vs. ppm Yb.

135

%SiO₂

ppm Y

linear regression of
Pine Hill rocks yields

slope : 1.44
r = 0.8585
y intercept = 11.49

ppm Yb
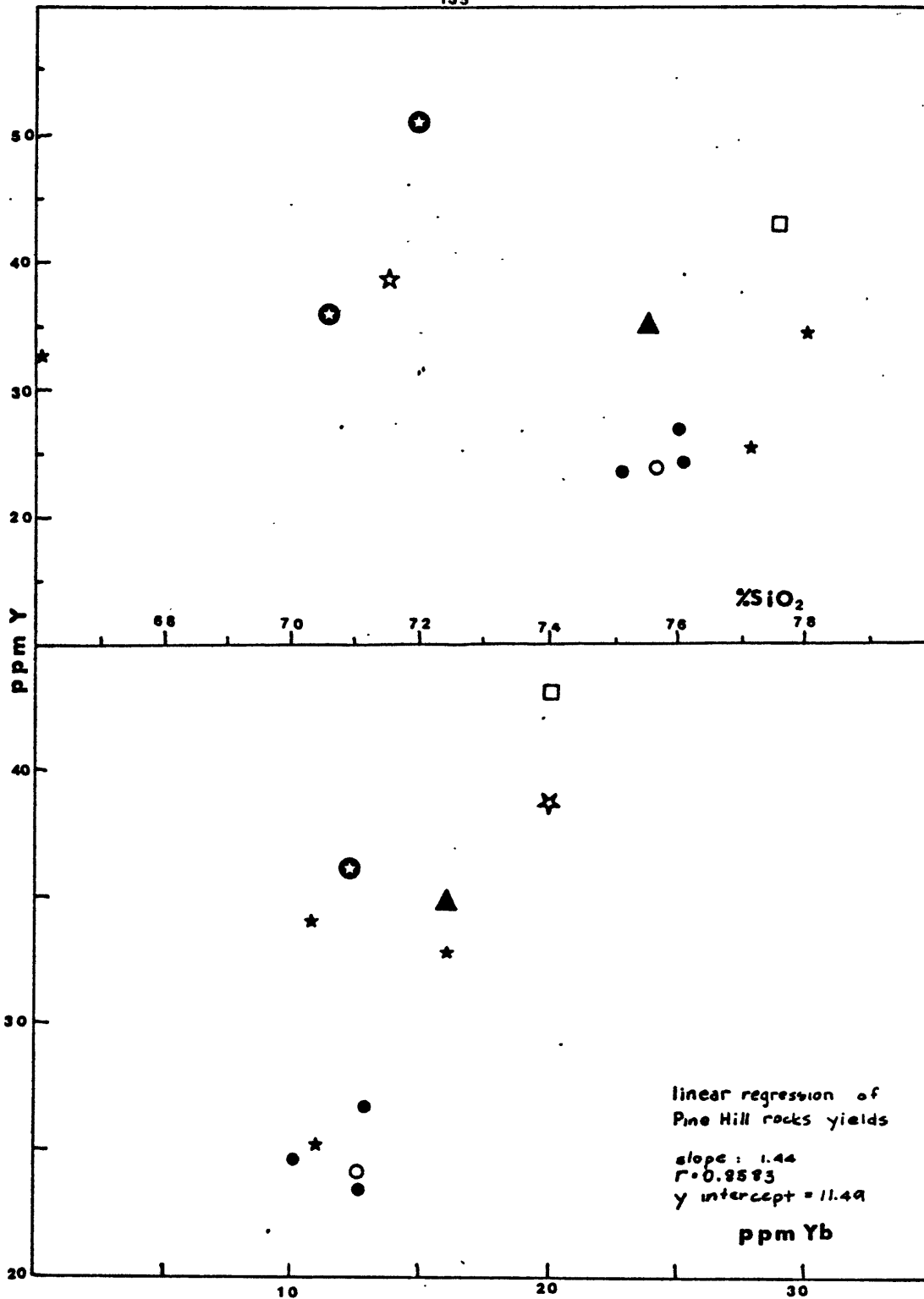
and concentration of Y in apatite and sphene, which occur in these rocks. Due to this behavior, one would expect to see a correlation between Y and Yb (Figure 7-11). This is indeed observed in the Pine Hill rocks, and the other specimens analyzed as well.

### Scandium:

Scandium is most closely associated with $Fe^{2+}$ among the major cations, by close size in ionic radii. $Sc^{3+}$ is concentrated in early forming pyroxenes (Norman and Haskin, 1968), amphiboles, and fractionated out of the magma, leaving the late stage melt severely depleted in Sc. The data for the Pine Hill rocks reflects this theory (Figure 7-12). The slope of Sc versus $SiO_2$ content is negative, steep and well defined between the various units. Therefore, early pyroxene or amphibole depletion of the rhyolites is likely, with the granodiorite abundances comparable to those of a "typical" granodiorite selected by Taylor (1965).

The major use of Sc is as a fractionation indicator for pyroxene, but in these rocks, if the $P(H_2O)$ of up to 5 Kb as determined by the Qtz-Ab-An-Or tetrahedron is correct, amphibole (Hornblende) is a much more likely recipient of Sc. There is no evidence to suggest post magmatic mobility of Sc during alteration in my rocks, as noted for some rocks

Figure 7-12. Variation diagram of ppm Cr vs. % $SiO_2$.

Figure 7-13. Variation diagram of ppm Sc vs. % $SiO_2$.
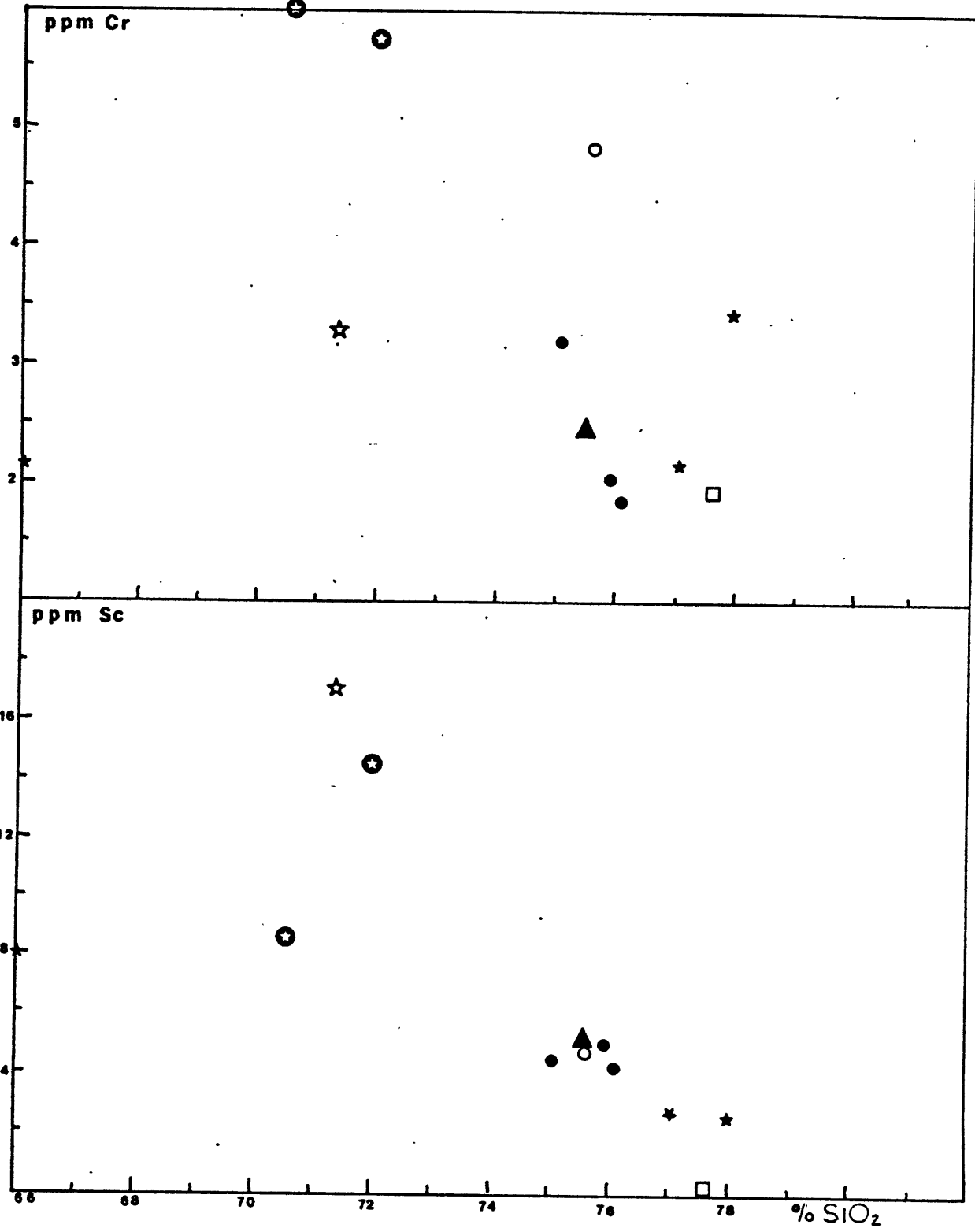
by Vlasov (1964), and suggested by Buma (1970) as an explanation for Sc depletion in the Quincy granite.

Chromium:

Chromium, ($Cr^{3+}$) is extremely close in size to $Fe^{3+}$, and preferentially substitutes into $Fe^{3+}$ positions causing a depletion at an early stage of fractional crystallization, with increasing depletions at later fractionation stages is less pronounced. This is seen in the Pine Hill rocks (Figure 7-13) with the drop from the granodiorites to the rhyolites very marked, but within the highly frationated rocks, the difference in chromium abundance is less distinct, and occurs as a blob on the variation diagram rather than a linear trend. $Cr^{3+}$ substitutes mostly in dripside, and in a lesser degree, enstitite. $Cr^{3+}$ is also difficult to get good values for using INAA at low abundance levels, which may account for some of the observed scatter.

3.   THE RARE EARTH ELEMENTS (REE):

The Rare Earth elements are very similar in their chemical characteristics, and they typically occur in rocks in very small (ppm) amounts. Because of their behavior, the trends of their relative abundances can be used to infer rock petrogenesis (Hanson, 1978).

## REE (Whole Rock) Results:

All of the samples analyzed display some "typical" granitic (Haskin et al., 1966) characteristics, that is, the REE are enriched relative to chondrites and the light rare earth elements (LREE) are enriched relative to the heavy rare earth elements (HREE).

In general, the variations in REE abundances (Table 7-1, Figures 7-14, 15, 16) correlate well with lithologic units based on field criteria and major element characteristics at Pine Hill. For example, a cursory look at the different normalized plots (Figures 7-14, 15) indicate that MR 2 of the Mud Road, and the Pine Flow samples are similar in REE content. Note that MR 3, which was poorly correlated by major element data to the other Mud Road felsites, is intermediate between MR 1 and MR 2 in REE content (Figure 7-15). Since REE are less affected by metamorphism and alteration (Frey, 1969; Cullers et al., 1974; Philpotts et al., 1969) than many other TE or major elements, they may be the most reliable in defining rock petrogenesis.

The other units sampled for reconnaisance geochemistry are noteworthy. The Mattapan Volcanic Complex specimen falls directly into the range determined by the Mud Road and Pine Flow Units (Figure 7-17). The Eu anomaly is greater than any of the Pine Hill rocks.

The Newbury Volcanic sample has the most extreme Eu depletion of all the specimens, and does not lie within the

Normalized R E E Abundances
Pine Flow Unit

▲ PF 1
☐ PF 2
● PF 3

whole rock/ave. chondrite

100

10

La Ce    Nd    Sm Eu        Ho        Yb Lu

Normalized REE Abundances
Mud Road Unit

□ MR 1
● MR 2
★ MR 3
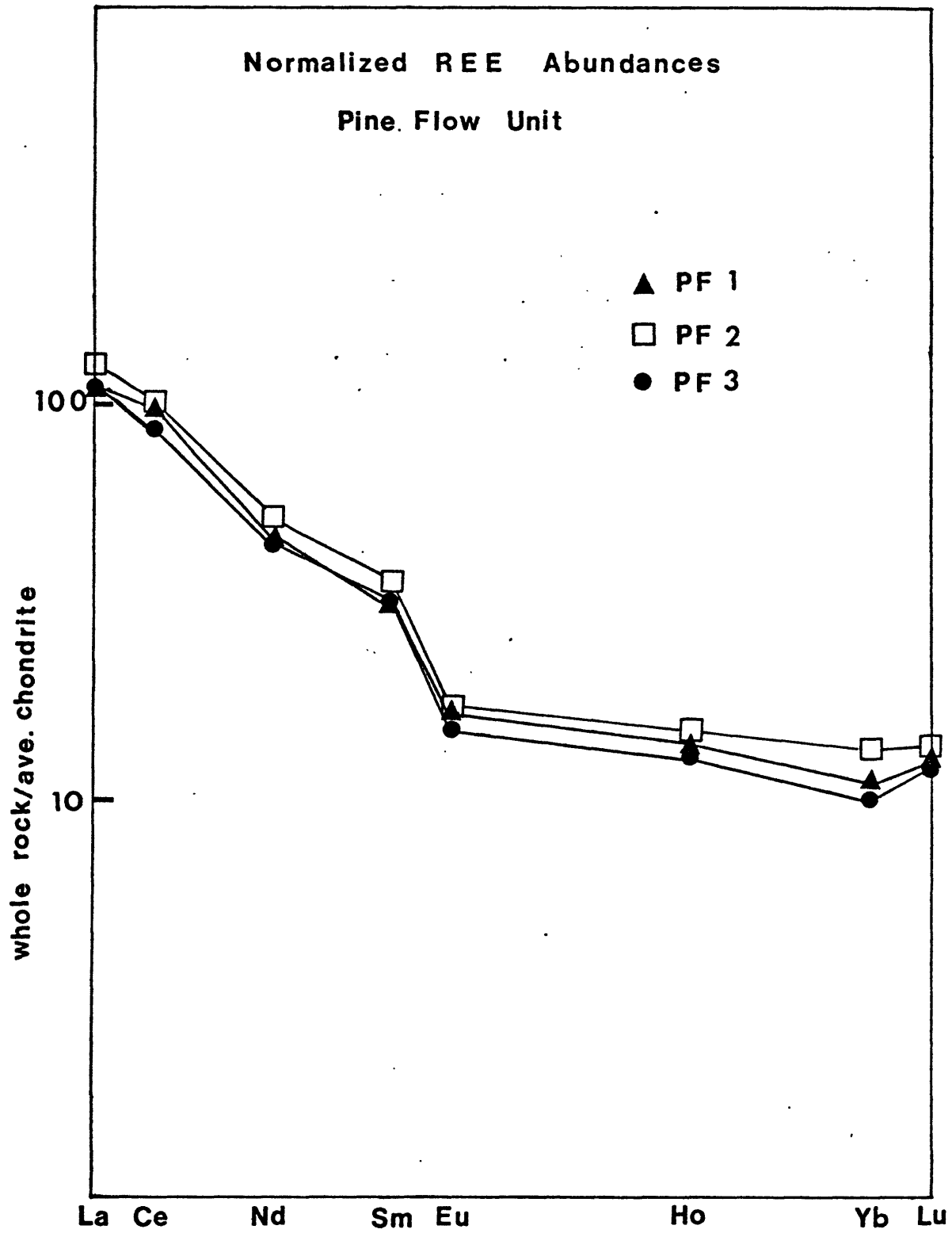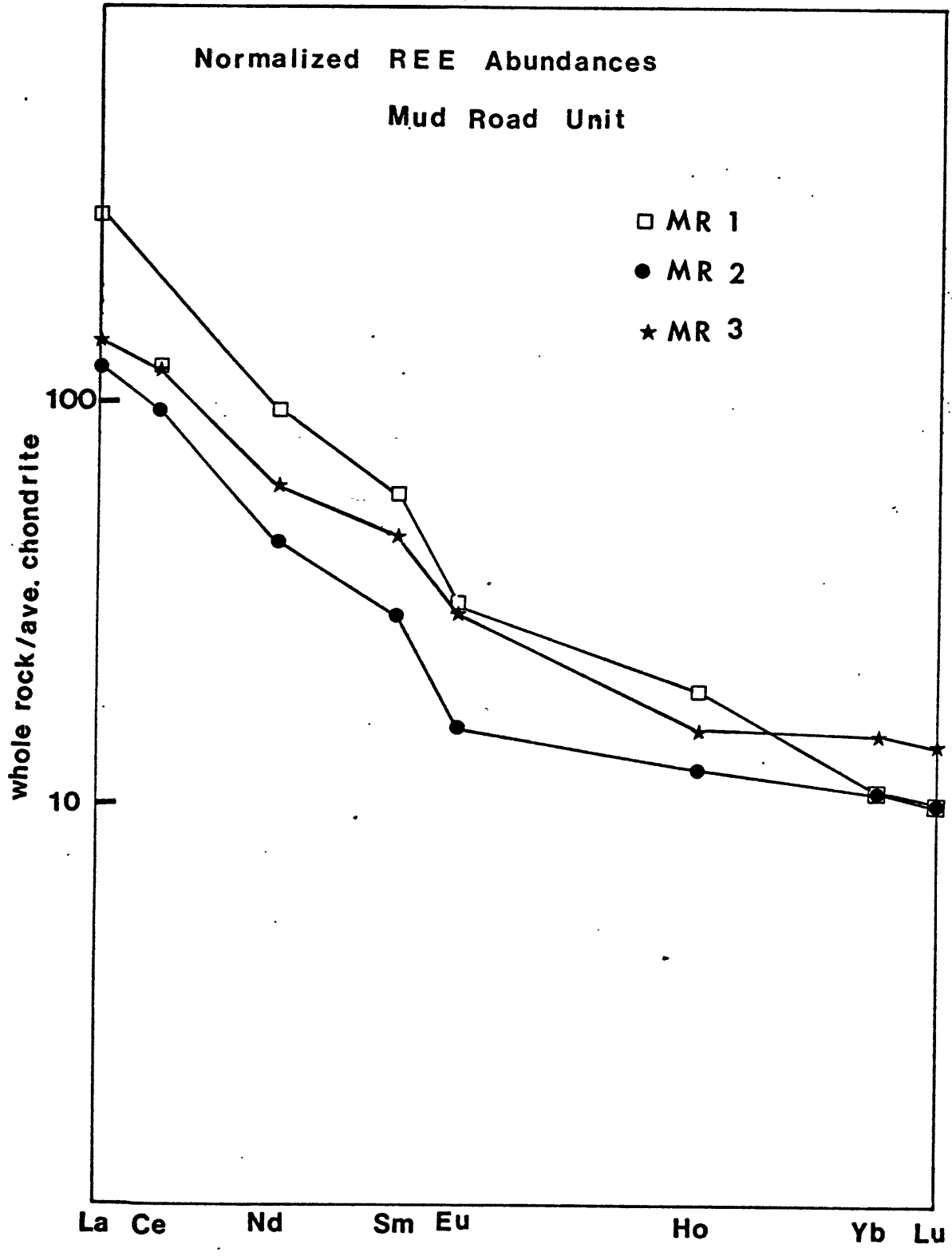
Figure 7-16. Comparison of normalized REE abundances for
the Dedham Granodiorite sample at Pine Hill.

144

Comparison of Normalized REE Abundances

● MV 1

Mattapan Volcanics

whole rock/ave. chondrite

100

10

Range

La Ce    Nd    Sm Eu         Ho         Yb Lu

**Comparison of Normalized R E E Abundances**

● **N V 1**
**Newbury Volcanics**

whole rock/ave. chondrites

100

10

Range

La   Ce      Nd       Sm  Eu            Ho          Yb  Lu

Comparison of Normalized REE Abundances

● MF34
(Middlesex Fells)

whole rock/ave. chondrite

100

10

Range

La  Ce      Nd      Sm  Eu          Ho        Yb  Lu
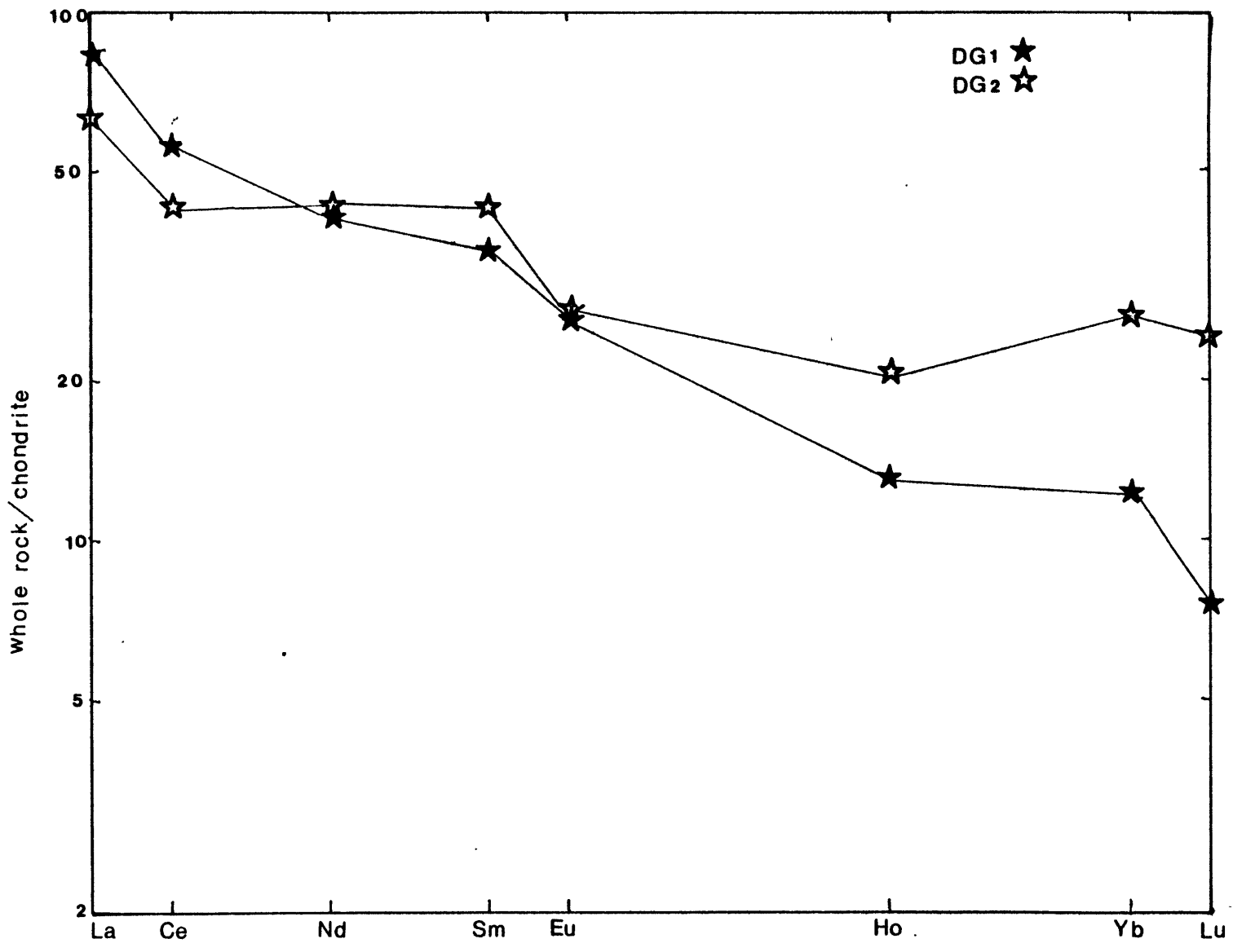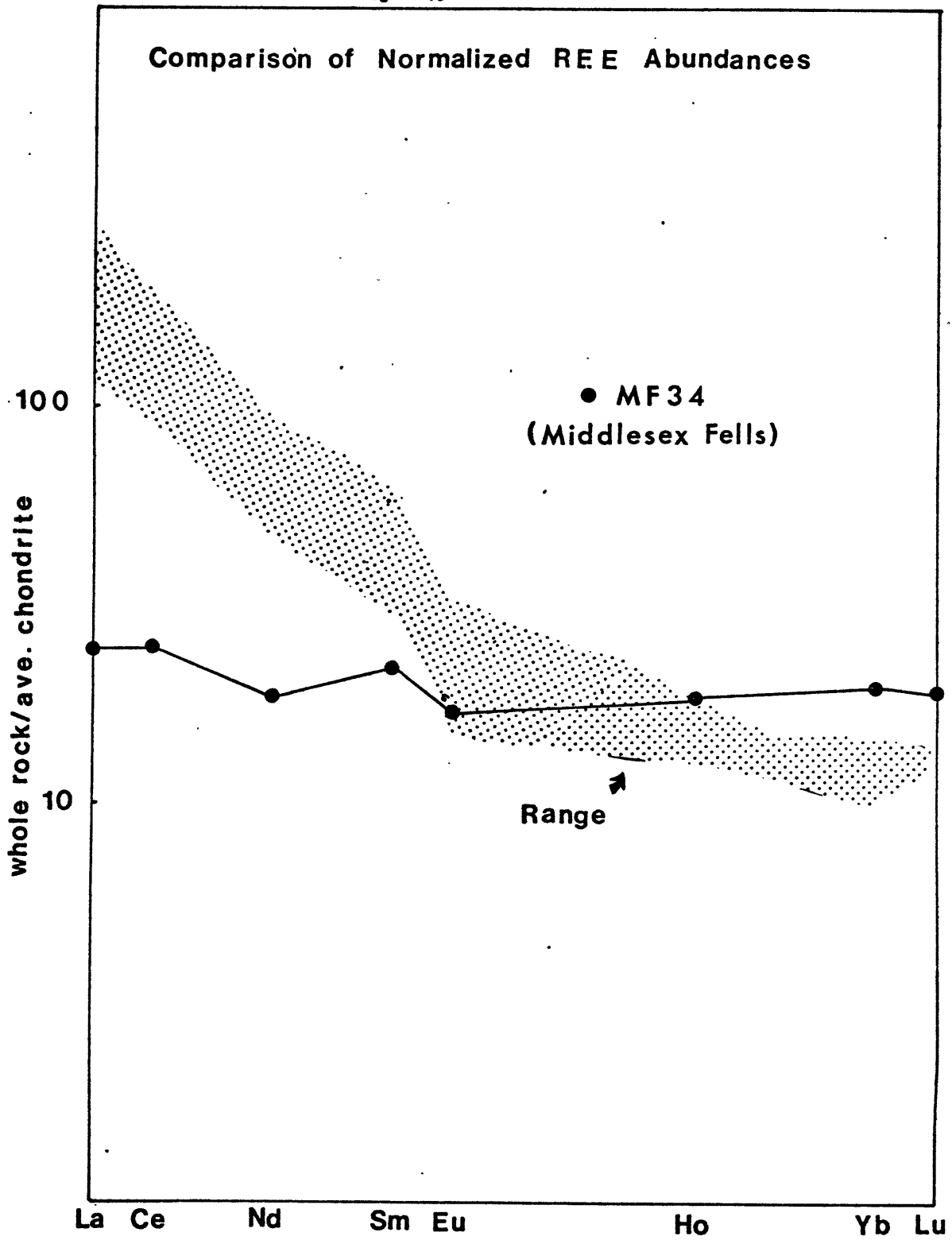
range within the Pine Hill range for HREE (Figure 7-18). Yb and Lu are significantly enriched in NV 1 compared to Pine Hill samples. The LREE are on the lower boundary of the range.

Finally, the Middlesex Fells Volcanic Complex sample displays an unusually flat pattern that indicates a much lesser degree of fractionation has occured in this unit (Figure 7-19). Both the LREE and HREE fall out of the established range. Thus, the REE data are very different, and so were the major element data.

## The Effect of Phenocryst Fractionation on REE Patterns

Crystallization of plagioclase or K-feldspar from a magma should result in relative enrichment of HREE over the LREE. But the S/$\ell$ partition coefficients of plagioclase and K-feldspar are very small (L > 1) (Arth, 1976),except for Eu, and thus the effect should be relatively small. Therefore, the REE (except Eu) act as incompatibles with respect to feldspar, and increase in the magma. The LREE·HREE ratio would also lower with increasing feldspar fractionation.
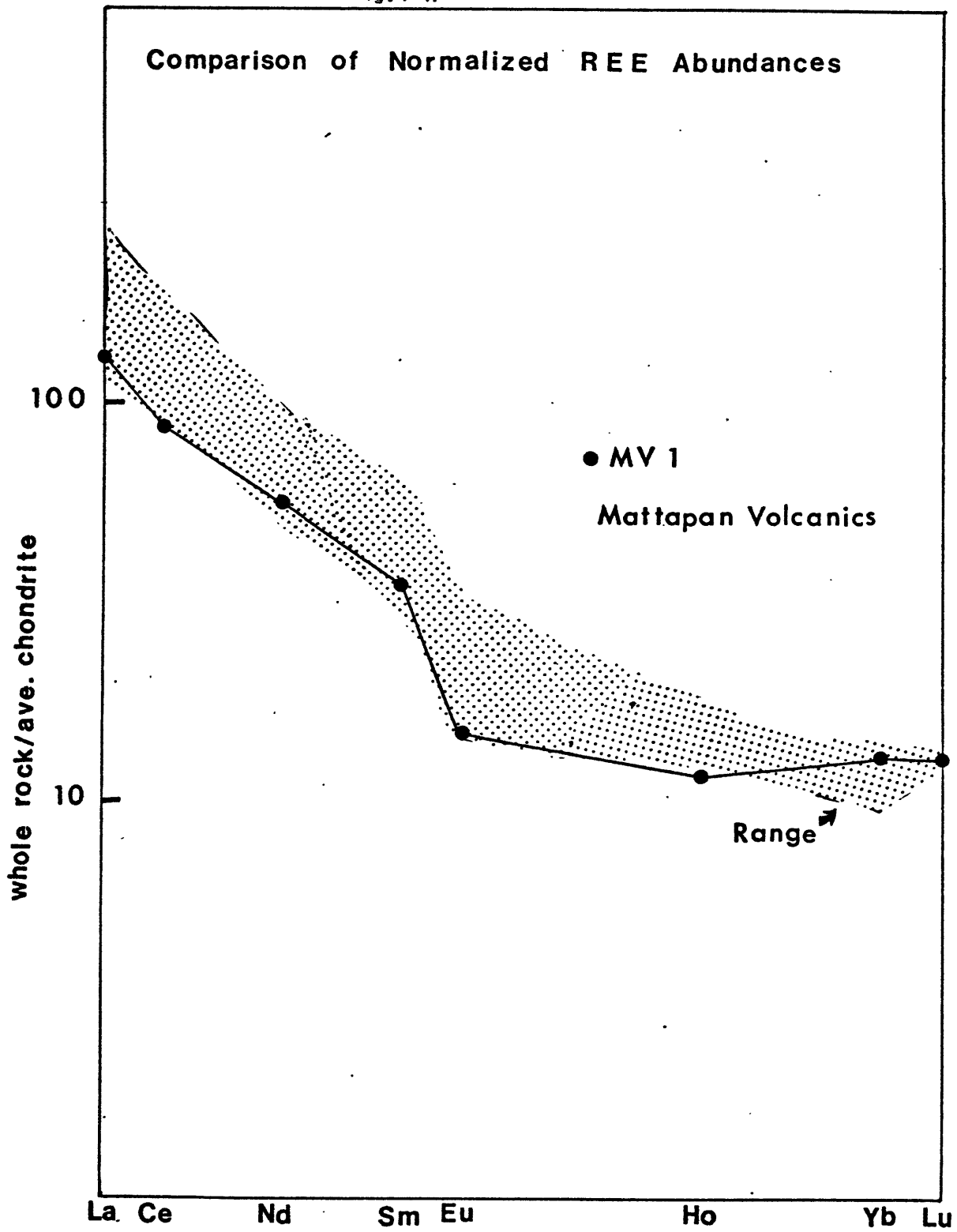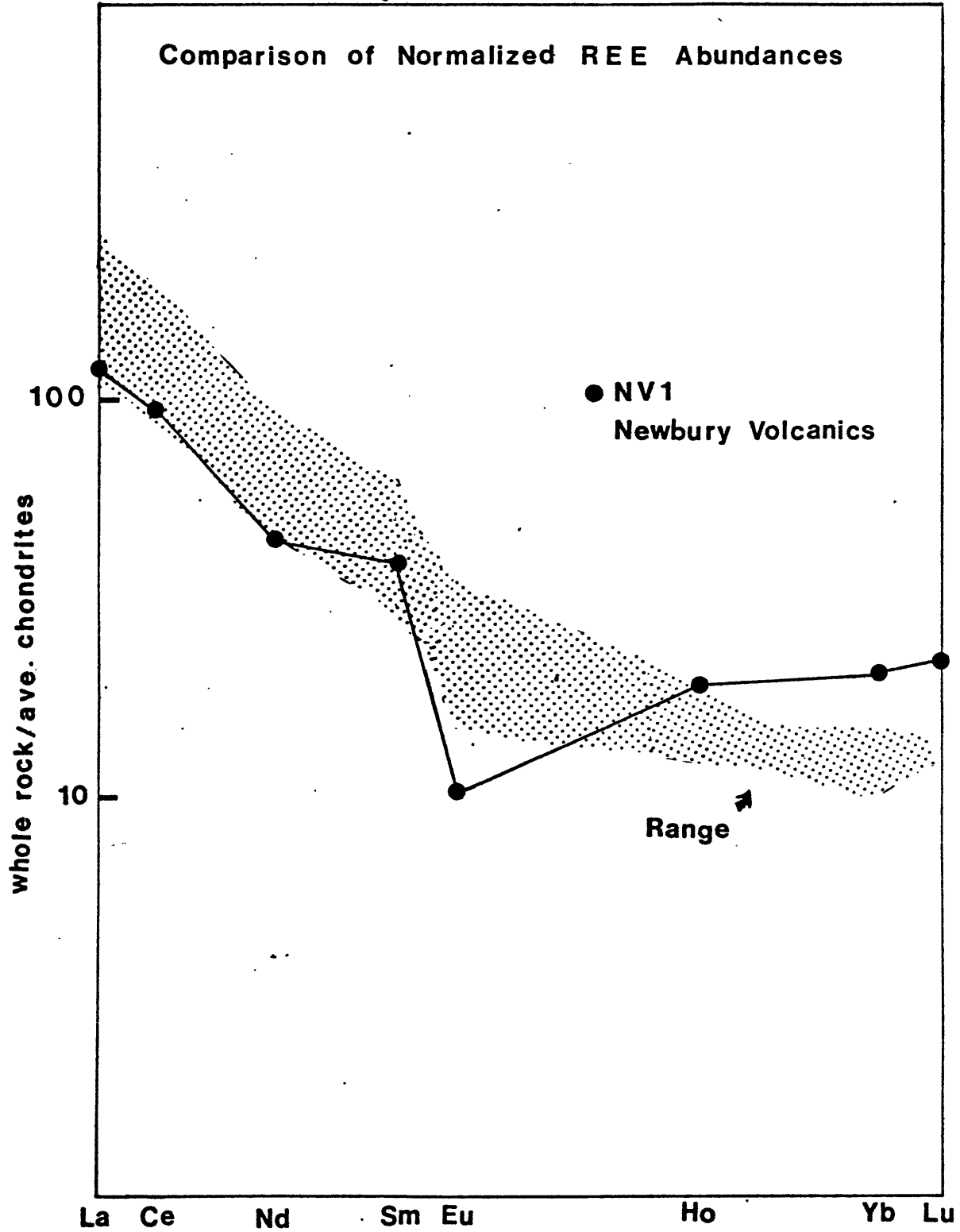
Zircons, on the other hand, have S/$\ell$ partition coefficients for the HREE which are exceedingly high; from 135 in Er, to 323 in Lu (Arth, 1976) in rhyolitic rocks. LREE are less strongly enriched in zircon, (e.g. S/$\ell$ partition coefficient is 2.64 for Ce (Arth, 1976). The precipitation of

zircon from a melt can considerably change its REE pattern due to the very large partition coefficient for the HREE, which rapidly become significantly depleted in comparison to the LREE.

Apatite has fairly high partition coefficients for all the REE, and upon crystallization, may significantly deplete all the REE, with some tendency to deplete the middle REE slightly more than the others (Nagasawa et al., 1971).

Mafic phases, such as hornblende, biotite, and hypersthene will deplete the middle and HREE, and enrich the LREE in the melt. Hornblende is unique, however, in that the P.C. > 1.

All the felsites at Pine Hill display La values between 111-146 ppm, with the exception of MR 1 whose La is 2-fold that of the other specimens at 290 ppm (Table 7-1). This is important when noted that MR 1 is the most enriched in the LREE, and most depleted in the HREE. This pattern is usually expected in the most fractionated liquid. In fact, the $(La/Yb)_N$ ratio is exceedingly high (27.00) when compared to the other samples (Table 7-1). The $(La/Sm)_N$ and $(Sm/Yb)_N$ ratios are also the highest for MR 1, indicating substantially more fractionation than the other specimens. However, $(Eu/Eu^*)_N$ values are not the lowest of the samples. These data are supported by the major elements, for MR 1 to be the most fractionated. However, MR 1 has less Th, U, Cs, Zr, Hf, and

Rb, but more Cr and similar Sc than MR 2.

If the Pine Flow, Mud Road and Dedham Granodiorite units are considered as individual groups, certain internal consistencies become apparent. The Mud Road specimens, (except MR 1) are characterized by a Lu/Yb ratio $<$ 1. These values have been corrected to account for Yb which shows up as Lu[177] after irradiation (footnote, Table 7-1). The $(La/Sm)_N$, $(La/Yb)_N$, and $(Sm/Yb)_N$ ratios are the highest for this group when compared to the other units (Table 7-1). This implies a higher degree of fradtionation. Within the Mud Road, the $(La/Sm)_N$ and $(La/Yb)_N$ ratios consistently increase from MR 3 to MR 1. The major element data (Table 6-1) are consistent with this relationship. The (Eu/Eu*) ratios are not considerably different from the other felsites, except for MR 3 which exhibits an anomoulously high ratio, indicating its differentiation was less than in the other Mud Road rocks.

Within the PF unit, Yb is slightly depleted and the Lu/Yb ratio is $>$ 1. The Eu/Eu* ratio (Table 7-1), indicates that Eu depletion is considerable, with the most depleted sample being PF 2. The most striking characteristic, however, is that these Pine Flow samples are probably identical for the REE, within the error limits.

According to the major element and trace element data, the Dedham Granodiorite (#2) is a candidate for the most

primitive magma, related to the rhyolites along a liquid line of descent. In DG 2, the $(La/Sm)_N$, $(La/Yb)_N$, and $(Sm/Yb)_N$ ratios are low and portray a flat, relatively unfractionated liquid (Table 7-1). The $(Eu/Eu*)_N$ value of 0.73 for DG 2 is low, but 0.90 for DG 1 may be more realistic for the "bulk" Dedham at Pine Hill. The $(La/Sm)$, $(La/Yb)_N$, and $(Sm/Yb)_N$ ratios for DG 1 are quite a bit higher than DG 2 (Table 7-1). Note that the data for DG 1 are estimated for Ce, Nd, Yb, and Lu (see footnote, Table 7-1). However, absolute abundances alone indicate the more fractionated nature of DG 1.

Based on the assumption that DG 2 is the most primitive composition, it would be anticipated that during the process of fractionation, the residual melts would become enriched in LREE, and depleted in the HREE because upon fractionation, pyroxene, zircon, hypersthene, biotite and hornblende will increase the LREE/HREE ratio in a coexisting rhyolitic liquid (Nagasawa and Schnetzler, 1971). Therefore, if all the samples are normalized to the "primitive" magma, they should exhibit preferential enrichment in the LREE relative to the HREE (due to relative exlcusion from structural sites during early crystallization of mafic minerals). The anticipated results are seen in all the rocks from Pine Hill (Figures 7-21, 22). There are, however, some puzzling results. Why is the Eu of MR 1 and MR 3 greater than 1? If these formed

**Comparison of Normalized REE Abundances**

whole rock/ave. chondrite

100 —

10 —

○   MR 3

▲   X 5
(xenolith)

Range of PF and MR
Units

La  Ce        Nd        Sm  Eu              Ho              Yb  Lu
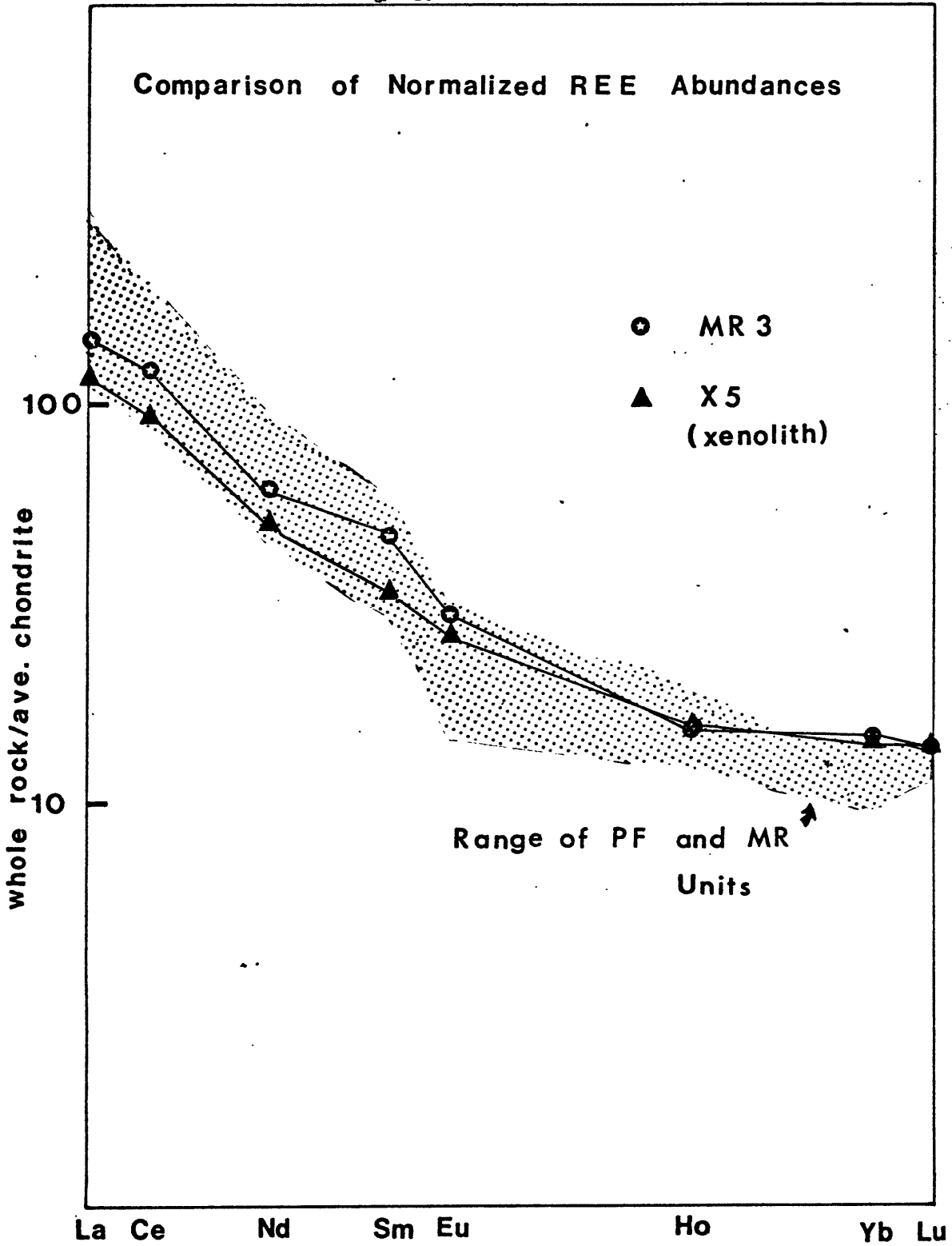
Figure 7-21. $(X\ 5)_N/(DG\ 2)_N$ and $(PF\ samples)_N/(DG\ 2)_N$ vs. atomic numbers of the REE.

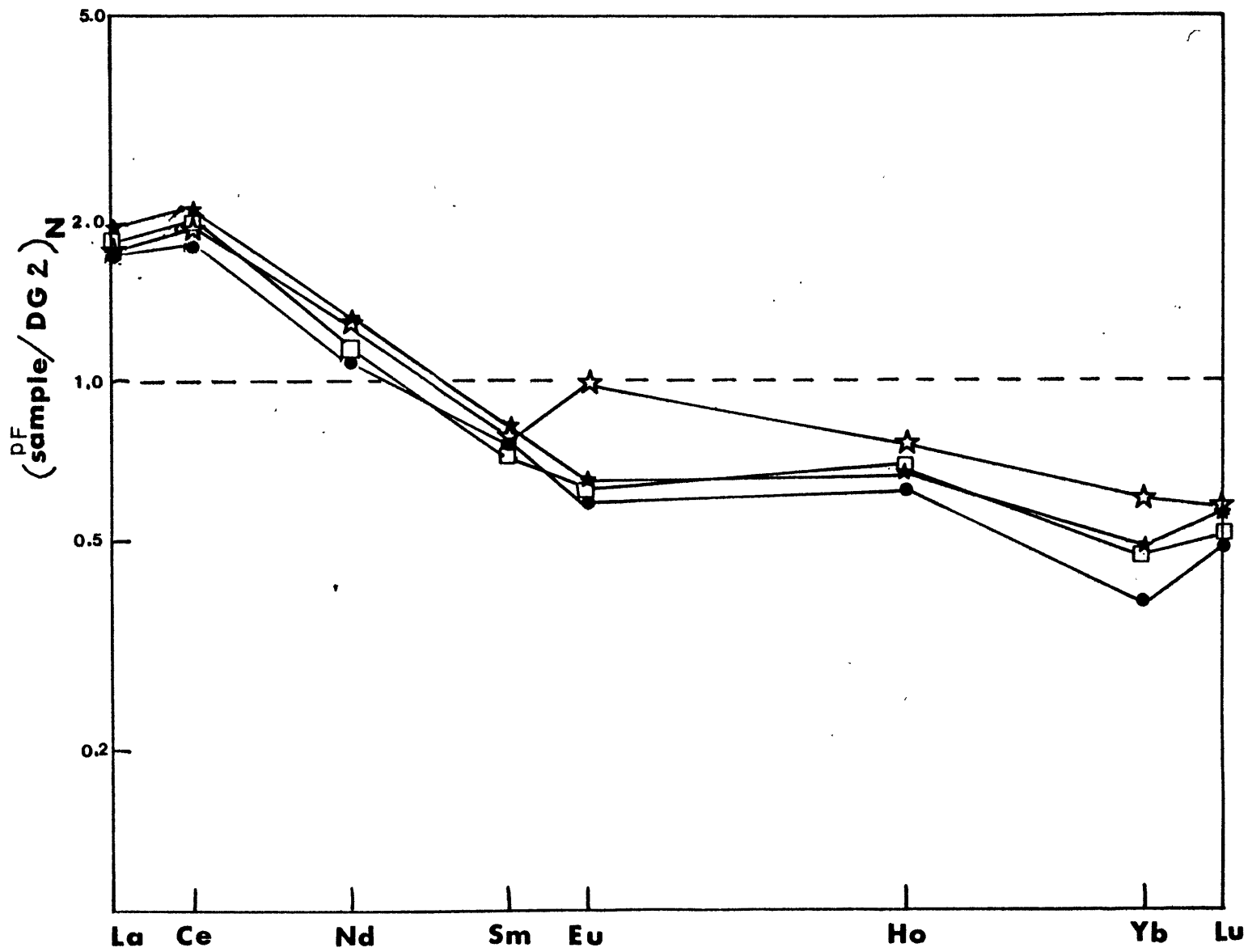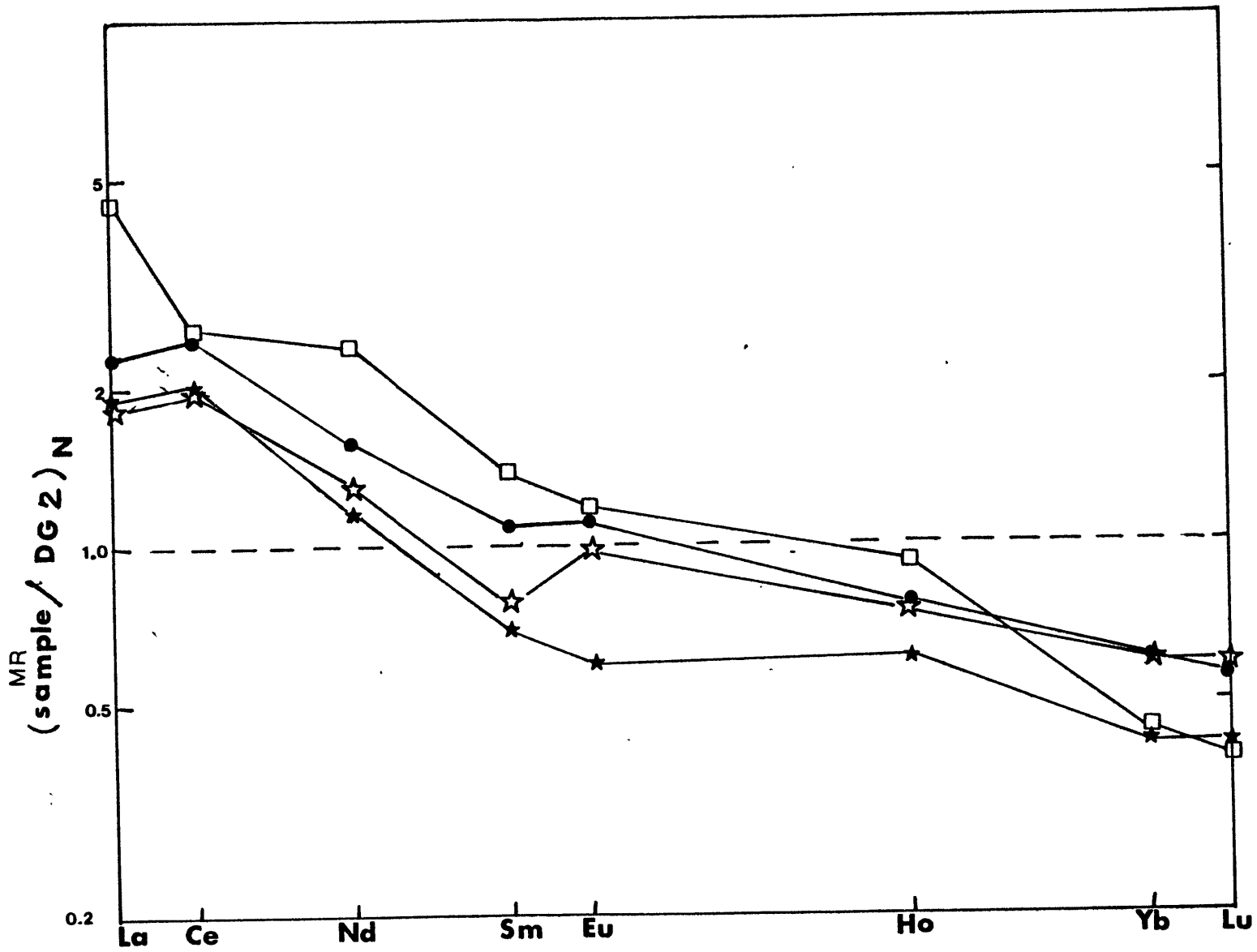Figure 7-22. $(X\ 5)_N/(DG\ 2)_N$ and $(MR\ samples)_N/(DG\ 2)_N$ vs. atomic numbers of the REE.

Figure 7-23. $(X\ 5)_N/(PF\ 2)_N$ and $(X\ 5)_N/(MR\ 3)_N$ vs.

atomic numbers of the REE.
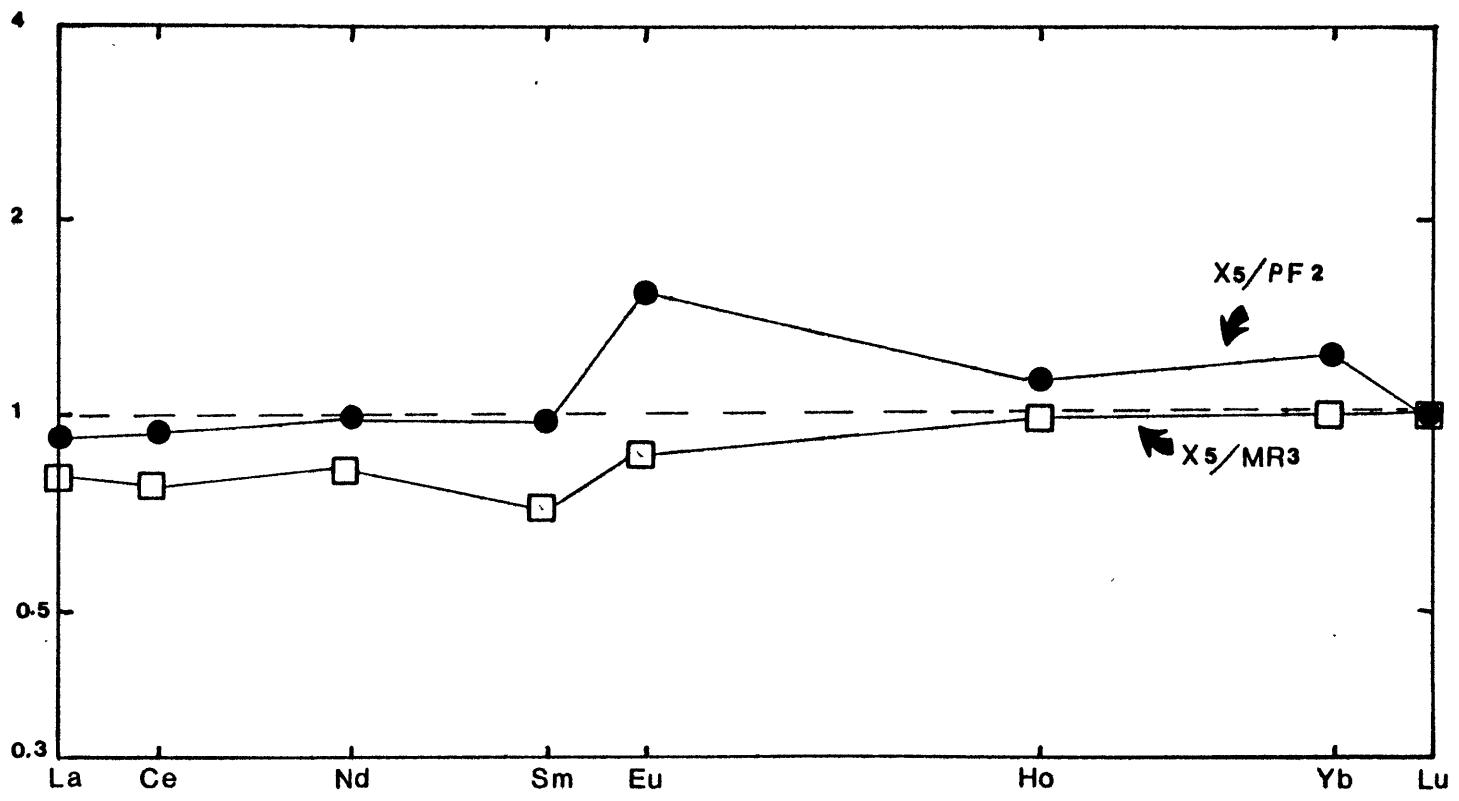
by fractional crystallization of DG 2, one could expect the $Eu^{2+}$ to become depleted by substitution for K in K-feldspar and $Ca^{2+}$ in plagioclase, unless the bulk $\overline{D}_{Eu}$ changes significantly between samples.

The REE data for X 5 is inconclusive as far as establishing the source unit for the xenolith. Absolute REE abundances/ chondrite place the pattern in the middle of the range delineated by the Mud Road and Pine Flow Units (Figure 7-20). The Lu/ Yb ratio is < 1 like the Mud Road rocks. However, the pattern is relatively flat (i.e. lower La/Yb) when compared to MR and PF units (Figure 7-20). The Eu depletion is very small (Table 7-1) $(Eu/Eu^*)_N$ = 0.91. The $(La/Sm)_N$, $(LA/Yb)_N$, and $(Sm/Yb)_N$ ratios are not distinctive (i.e. they fall within the range for the PF and MR units). Another interesting phenomenon to note is that the xenolith mimics the PF/DG 2 trends except for the Eu anomaly, which is positive (Figures 7-21, 22). Whereas the xenolith Lu/Yb ratio is less than 1, the PF Lu/YB ratio is greater than 1. The disturbing thing about this is that according to the major element data (Table 6-1), (Figures 6-1, 6-7), X 5 definitely belongs to the PF unit. Thus, the REE data does not support or reject this hypothesis. In terms of REE content, X 5 also falls in the range of the Mud Road felsite, and mimics MR 3 reasonably well (Figure 7-30). MR 3 is the most likely felsite to be caught up as a xenolith

because it is near the contact,with a cataclastic texture.
Plots of X 5/MR 3 and X 5/PF 2 are illustrated (Figure 7-23).
The match with PF 2 is convincing in the LREE, but much too
enriched in the HREE. The opposite is true for the MR 3
normalized pattern, HREE are convincing ($\sim 1$), but the LREE
are depleted. No unambiguous conclusion can be drawn.

From the major element data, there was a slight question
about the possibility of MR 3 being the primitive liquid.
Hence, samples were normalized to MR 3 and plotted on a graph.
All of the specimens at Pine Hill, except for DG 2 are depleted
in all REE relative to MR 3. DG 2 is depleted in LREE and
enriched in HREE. This suggests the MR 3 is one of the more
highly fractionated specimens collected, and that the major
element abundances have been altered by the cataclasis, and
events precepitated by the cataclasis, (i.e. easy leaching
of $SiO_2$, etc.).

Based on the REE data for Pine Hill samples, several
conclusions can be drawn.

(1)   DG 2 is the most primitive rock at Pine Hill, and
is possibly the original liquid from which the rhyolites frac-
tionated.

(2)   X 5 was detached from the Pine Flow unit or the
Mud Road unit. Based on REE data, no conclusion can be drawn.

(3)   The Pine Flow unit is chemically homogeneous over

the sampled area, while the Mud Road is much more variable in composition.


## 4.  FRACTIONAL CRYSTALLIZATION MODELLING


The model of petrogenesis which is applied to the rhyolites at Pine Hill has been fractional crystallization from DG 2. This can be quantified if one applies a modified Shaw (1970) equation.

$$\frac{C_{sample}}{C_{source}} = (1 - F)^{D-1}$$

where:  $C_{source}$ = Concentration of element in DG 2

$C_{sample}$ = Concentration  of element in rhyolite

F = Degree of crystallization

D = Bulk distribution coefficient for the element in question.

Some basic assumptions which are made when applying this model are:

(1)   DG 2 is the original liquid.

(2)   $D^{Bulk \ solid/liquid} = X_{\alpha}D_i^{\alpha/\ell} + X_{\beta}D_i^{\beta/\ell} + X_{\gamma}D_i^{\gamma/\ell}$ ,etc.

I am assuming that the $D^{Bulk}$ for Eu, is in fact D for Eu in

feldspar. This assumes that other phases (e.g. apatite) have not removed Eu from the liquid.

(3)   The rhyolites and granite all represent liquids which are pristine, and therefore are uncontaminated by xenocrysts, xenoliths, and other contaminants.

(4)   That the specimens are unaltered, or at least alteration has not changed T.E. abundances.

(5)   $D_{Eu}$ is affected by $FO_2$.

(6)   $C_{XTAL} = \lambda C_{\ell}$ (diffusion in solid is slow with respect to crystal growth rate).

Compatible elements such as Eu and Sr in feldspar, are sensitive to the proportions of fractionating minerals is a liquid. As a gross generalization, for the purpose of calculations, the only fractionating phases in the felsites were considered to be feldspar and quartz. Therefore $\bar{D}_{Bulk} = X_{Qz}D_{Qz} + X_{Spar}D_{Spar}$. The more quartz which fractionates, the lower $\bar{D}_{Bulk}$, due to the extremely small amount of trace elements quartz incorporates in its structure. Variations in phenocryst phase proportions will be reflected in $\bar{D}_{Bulk}$ for Eu and Sr. These variations may indicate

(1)   Differing degrees of fractionation, and hence different modal proportions of phenocrysts precipitation.

(2)   Changes in $P(H_2O)$ will force crystallization off the cotectic. More specifically, the decrease in $P(H_2O)$

experienced by the MR units (at less than 2Kb on the Qtz-Ab-An-Or Tetrahedron) would stop feldspar crystallization and in fact, the resorbtion of feldspar would occur, and quartz would precipitate while trying to reestablish equilibrium and return to the cotectic. For MR 1 and MR 2, the proportion of quartz/feldspar phenocrysts would become larger with decreasing $P(H_2O)$ (Figure 6-9). This would

A. Lower the $\bar{D}_{Eu}$ due to the increased percent of quartz phenocrysts and their very low $D_{Eu}$.

B. Resorb feldspar phenocrysts into the melt, and therefore, by both mechanisms increase the Eu in the liquid.

Incompatible elements like La, Ce, Nd, and Rb are less sensitive to fractionation of specific phases, and can be used to calculate the absolute amounts of crystallization that have occured within the different samples.

If we assume that $\bar{D}_{Bulk}$ for these elements is equal to zero, the minimum amount of crystallization of DG 2 "liquid" necessary to achieve the levels of incompatibles observed in the felsites can be determined. This is done in Table 7-5.

The values calculated for La and Ce are in good agreement, considering that $\bar{D} = 0$ is not the true distribution coefficient for these incompatible Nd and Rb on the other hand display widely different values. Nd may be more discrepant because it is more compatible than La and Ce. Rb is

TABLE 7-5

MINIMUM CRYSTALLIZATION FOR FELSITES

CALCULATED WITH D = 0 FOR VARIOUS ELEMENTS (%)

| I.D | La | Ce | Nd | Rb |
|------|-------|-------|-------|--------|
| PF 1 | 42.53 | 51.37 | 12.69 | 8.46 |
| PF 2 | 49.09 | 52.74 | 22.31 | 30.81 |
| PF 3 | 42.72 | 45.41 | 10.04 | -10.33 |
| | | | | |
| MR 1 | 77.90 | 61.05 | 57.95 | 32.33 |
| MR 2 | 48.26 | 50.20 | 12.27 | 40.33 |
| MR 3 | 55.76 | 60.02 | 35.04 | - 1.83 |
| | | | | |
| X 5 | 45.29 | 49.93 | 22.21 | 17.36 |

known to be very mobile during low grade, greenschist meta-morphism, (Cann, 1970) and hence low values of this incom-patible could be anticipated, based on chlorite grade meta-morphism exhibited by these rocks. MR 3 and PF 3, which are the closest in proximity to the intrusive contact, not sur-prisingly have the lowest Rb contents (Table 7-1).

If it is assumed that the values of F derived from La and Ce are accurate, and substitute this value (using La value) into

$$\frac{C_{Sample}}{C_{Source}} \text{ (DG 2)} = (1 - F)^{D-1}$$

for Eu and Sr, $\overline{D}_{Bulk}$ can be calculated for each specimen for Eu and Sr. Then the proportions of quartz and feldspar phenocrysts can be determined by

$$\overline{D}_{Bulk} = X_{Qz} D_{Qz} + X_{Spar} D_{Spar} .$$

$\overline{D}_{Bulk}$ is calculated, $D_{Qz}$ is assumed to equal 0.001, and $D_{Spar}^{Eu} = 2.15$, (Arth, 1976). $D_{Spar}^{Sr} = 4.4$, $X_{Qz} = 1 - X_{Feldspar}$, and hence the variable $X_{Feldspar}$ can be solved for. This was done, and the values reported, (Table 7-6).

The amounts of feldspar and quartz phenocrysts cal-culated by using $\overline{D}_{Eu}$, and $\overline{D}_{Sr}$ are different. The proportions

TABLE 7-6

| I.D. | % Fractional Crystallized | Calculated $\bar{D}_{Eu}$ | Calculated Phenocryst Phases | | Calculated $\bar{D}_{Sr}$ | Calculated Phenocryst Phases | | Recalculated* $\bar{D}_{Sr}$ |
|------|------|------|------|------|------|------|------|------|
| | | | Feldspar | Quartz | | Feldspar | Quartz | |
| PF 1 | 42.53 | 1.8727 | 0.8710 | 0.1290 | 2.5320 | 0.5754 | 0.4246 | 3.8315 |
| PF 2 | 49.09 | 1.6696 | 0.7765 | 0.2235 | 1.1102 | 0.2521 | 0.7479 | 3.4158 |
| PF 3 | 42.72 | 1.9508 | 0.9073 | 0.0927 | 2.1175 | 0.4811 | 0.5189 | 3.9912 |
| MR 1 | 77.90 | 0.8883 | 0.4129 | 0.5871 | 1.6337 | 0.3712 | 0.6288 | 1.8163 |
| MR 2 | 78.26 | 1.7927 | 0.8337 | 0.1663 | 1.9991 | 0.4542 | 0.5478 | 3.6674 |
| MR 3 | 55.76 | 0.8618 | 0.4006 | 0.5994 | 0.5312 | 0.1208 | 0.8992 | 1.7622 |
| X 5 | 45.29 | 1.0299 | 0.4788 | 0.5212 | 1.5391 | 0.3496 | 0.6504 | 2.1062 |

*Recalculated $\bar{D}_{Sr}$ = The $\bar{D}_{Sr}$ value required to produce the same fraction of phenocryst phases as $\bar{D}_{Eu}$ for same "liquid".

determined with Eu coincide with the modal proportion of phenocrysts actually in the samples better than Sr. Therefore, the most probable reason for the disparity, is that $\bar{D}_{Sr}$ is wrong. A value for $\bar{D}_{Sr}$, was recalculated, so that the proportion of phenocryst phases determined using Eu and Sr $\bar{D}_{Bulk}$ would agree. The recalculated $\bar{D}_{Sr}$ (Table 7-6) is reasonable, and so is the calculated $\bar{D}_{Eu}$. The Eu bulk $\bar{D}$ is centered in the middle of the curves defining upper and lower limits for An 30 as drived from the literature (Figure 7-24). The recalculated Sr values for $\bar{D}$ of the PF units practically fall on the line defined by the upper bound of the Schnetzler and Philpotts data (1970), (Figure 7-25). MR data fall on the lower bound.

The higher percent of feldspar phenocrysts observed in the PF units compared to the MR rocks are due to the lesser degree of fractionation, which is corroborated by all the chemical data. Thus, the more fractionated a liquid becomes, the higher the proportion of quartz/feldspar. This is observed in all the rocks, with MR 1 and 3 having values of $\bar{D}_{Eu} < 1$. This result may be explained by the fact that $P(H_2O)$ changed, causing the melt to resorb feldspar crystals as it continued to crystallize quartz. MR 2 appears more similar in phenocryst proportions to PF, and X 5 to the MR 1 and 3. The $\bar{D}_{Bulk}$ for Sr and Eu for MR 3 appear consistent

Figure 7-24. Eu partition coefficients vs. % An in plagioclase.

Figure 7-25. Sr partition coefficients vs. % An in plagioclase.

## KEY

O = Schnetzler and Philpotts (1970).

O = K-feldspar after Schnetzler and Philpotts (1970).

□ = Dudas (1971)

● = Data points calculated from study samples (Table 7-6).
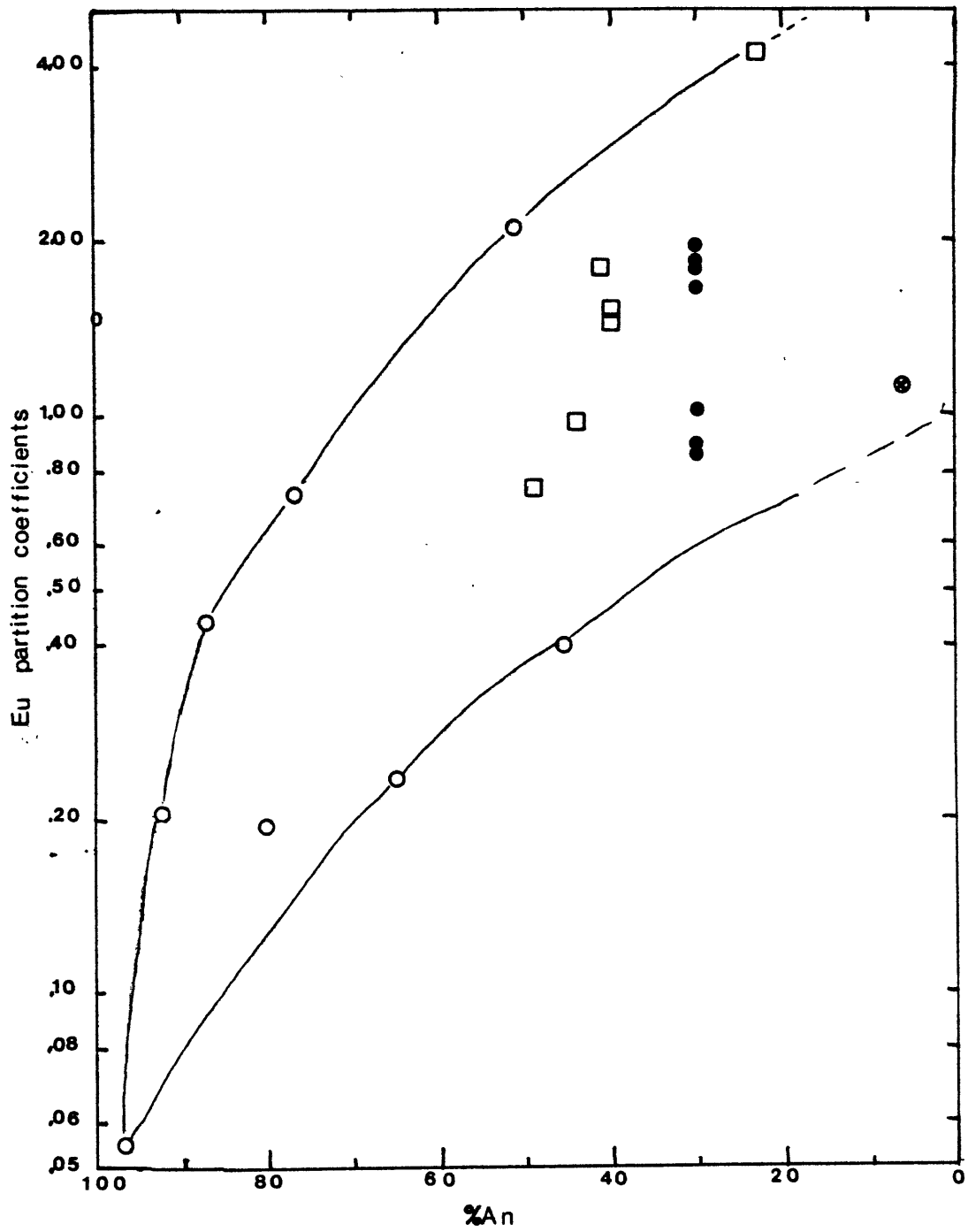
with the PF.  X 5 is actually closer to the mean of values for both units.
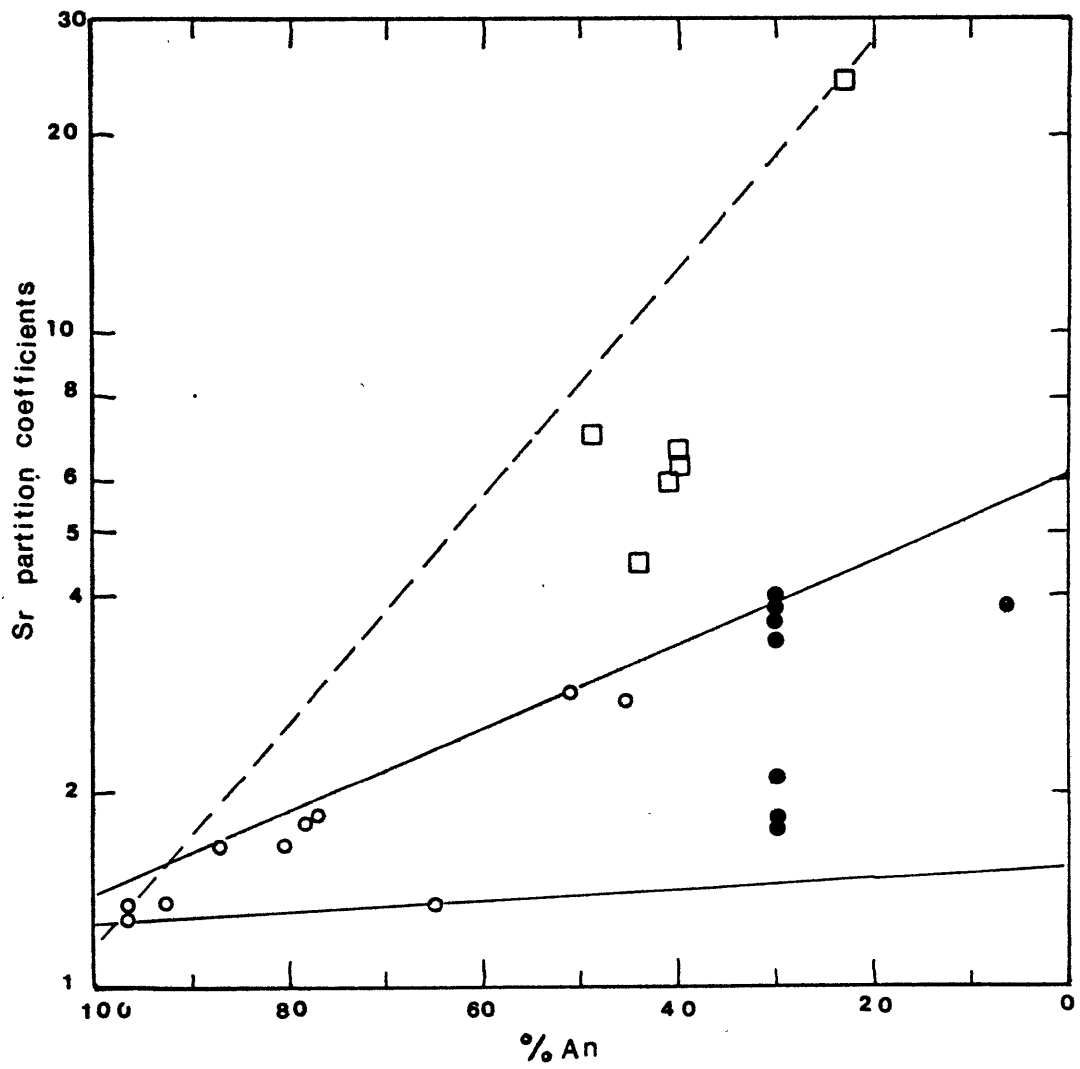
Because the distribution coefficients are reasonable, and the results obtained by applying this model to the collected specimens are consistent with the other major and trace element abundances, I conclude that DG 2 is a reasonable source magma for the rhyolites at Pine Hill.  This is not conclusive, since many more samples must be run, and detailed phenocryst matrix studies performed in order for this model to be definitive.

This comagmatic relationship, with the felsites being derived by fractional crystallization can be reckoned with the field observations, and will be discussed in the conclusion.

## 5.  THE EFFECT OF VOLITILES AND LOW GRADE METAMORPHISM

Since the water saturation point of a solid phase is reached much faster than that of another liquid, as crystals precipitate from a liquid, the $H_2O$ saturation point of the residual liquid is quickly attained, and a new phase, vapor, enters the system.

According to Kosterin (1959), fine grained, volatile rich rocks which seem to crystallize quickly and at shallow depths, may lose a considerable amount of HREE in the escaping volatile phase.  This is because the hypothesized greater

stability of HREE complexes when compared with LREE, gives the HREE greater mobility. Although they have not been analyzed, one would anticipate pegmatites at Pine Hill to be enriched in HREE. Complexes of Ta, such as $TaF_5$ may behave the same way as HREE, as do similar complexes of Zr and Hf. This might be an alternative explanation for the fact that Ta, Zr, and Hf seem to be behaving like compatible elements in the Pine Hill rhyolites, but perhaps their complexes are actually being removed in a volatile phase.

One of the anticipated problems in this study was geochemical incoherence due to the effects of low grade metamorphism on the rocks. The only systematic mobility noted was some Rb depletion, which was emphasized by the fractionation model. K, and to a lesser extent Sr are also known to be affected by metamorphism (Hart 1971), so that their abundances are to some extent controlled by the metamorphic history of the rock rather than igneous effects. All three elements are depleted during greenschist facies metamorphism, but Y, Zr, REE and Ti seem less effected by post volcanic conditions (Cann, 1970).

CHAPTER VIII

CONCLUSIONS

Field evidence indicates that the Dedham Granodiorite
has intruded the rhyolitic rocks at Pine Hill. Two Pine Hill
felsite groups (Mud Road and Pine Flow) have been studied
geochemically, and the interpretation of these results indi-
cate:

(1) The units as mapped are confirmed by distinct dif-
ferences in absolute abundances of major and trace elements.
Compared to the PF unit, the MR unit is the most fractionated,
and it is the most variable in terms of chemistry and petro-
graphy.

(2) Variation diagrams imply that the units are related
along a "liquid" line of descent. The assumptions are numer-
ous, however, $SiO_2$ content versus major and T.E.'s show con-
sistent, distinct trends.

(3) Fractional crystallization modelling for T.E. con-
firms that DG 2 is a likely candidate for the most primitive
"liquid" at Pine Hill, and, that it is possible to fractionate
the volcanic rocks from DG 2 if a variable $\overline{D}_{Bulk}$ for Eu and
Sr are assumed. Variations in $\overline{D}_{Bulk}$ are based on the pheno-
cryst phases present and their proportions, which in turn, are
controlled by the degree of fractionation, and whether

crystallization is on the cotectic (influenced by $P(H_2O)$).

It has been demonstrated that the Lynn volcanics at Pine Hill are older than, or comagmatic with the Dedham Granodiorite. The next question should be, what effect does this have on the interpretation of correlations to other units, particularly the Mattapn, in light of it's importance to the study of the Boston Basin. Geochemical correlation of the Pine Hill Rock to the Newbory is not conclusive based on the reconnaissance work performed in this study. They are obviously similar in many respects, however, the absolute . age date of Siluro-Dvonion as determined by fossil control, indicates a distinct time between the units. However, it should be noted that based on chemistry alone, this time gap could not be identified, for rhyolites occur throughout geologic time, and their chemical characteristics are similar to those at Pine Hill (Hon, 1967; Zielinski, et al., 1977).

Shride (oral communication) presented the possibility that the Lynn at Pine Hill may in fact have been mismapped, and belong to the Middlesex Fells Volcanic Complex. The Middlesex Fells is also of Precambrian age, and displays similar petrographic properties. However, based on chemistry, it is fair to say that the Middlesex Fells specimen analyzed does not appear to be related to these rocks along a fractionation trend of the type modelled

for Pine Hill. Mafic constituents make up a large portion of
this rock. The rock appears to be biotite-rich, by petrogra-
phic methods. This is probably the major mafic mineral, and
is confirmed by the fact that $\bar{D}_{REE}$ for dacitic rocks into
biotite is very low when compared to other mafic minerals
such as hornblende, which tends to concentrate the HREE (Arth,
1976), and the pattern for MF 34 appears relatively undepleted
in the REE. On the other hand, biotite incorporates a large
amount of Rb ($D_{Rb}$ = 3.26) in dacitic rocks (Arth, 1976), and
MF 34 has an anomoulously low Rb value of 20.3 compared to the
other specimens (Table 7-1). Therefore biotite fractionation
is likely. Comparisons of the REE patterns indicated that a
correlation between the Pine Hill and Middlesex Fells sample
is not likely.

The Mattapan Volcanics specimen is remarkably similar
to the Pine Hill felsites. Major and TE variation diagrams
place the Mattapan at the highly fractionated end of the
trend. REE diagrams are very similar, with the Mattapan
barely fitting in the Pine Hill Felsite Range.

The suggestions for future work go from the enormous,
lifetime tasks of developing a scheme for south eastern
New England Geology, to more workable projects, such as deter-
mining the amount of Sb in the rocks, and investigating to
see if it may be useful as an indicator of rock petrogenesis.

Future emphasis should be on detailed geochemical comparisons with other, possibly correlative felsite units in New England whose statigraphy and structure are reasonably well understood on a small scale. This may help us to unravel the age and structure of the Boston Basin and the surrounding terrains, which range determined by the MR and PF units. The one major difference is that the Mattapan seems to have formed in a water undersaturated environment, while the other rocks display variable amounts of $P(H_2O)$. Unfortunately, the lack of sufficient field and chemical data limits drastically the conclusions which can realistically be drawn concerning the relationships of the two felsite groups. However, due to the unresolved field relationships between the Dedham and the Mattapan, the possibility of a similar, comagmatic environment between these two units are in the long run important determining the origins and tectonic framework of southeastern New England.

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