Petrology and Geochemistry of Ignimbrites

from the Bears Brook Volcanic Group,

Arisaig, Antigonish County, Nova Scotia

by

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Time Estimates

- field work : 7 days
- thin section study, to choose samples for analysis : 20 hours
- crushing rocks to powder : 55 hours
- Silica determination (including data processing) : 60 hours
- atomic absorption spectrophotometry : preparation : 40 hours
  - runs : 32 hours
  - data processing : 24 hours
- ferrous iron : 15 hours
- phosphorus : 6 hours
- total water and minus water : 40 hours
- REE : preparation for irradiation : 8 hours
  - counting and data processing : 200 hours
- Microprobe : 20 hours
- writing : 4 weeks

* please note these time estimates are for time spent working in the lab; they do not include heating, cooling, settling etc.

Sources

Location map is modified from Fullager and Bottino (1968)

Sample locality map is from Boucot et al (1974); photocopied by Norman Wade.

All other drafting was done by the author.

Petrography was done by the author, but thin sections were prepared by G. Brown; photomicrographs by F. Stefani.

Microprobe analyses of spherulites in rhyolite and feldspars in ignimbrites were done by the author, using the EDS. R. Mackay analyzed the Nb-rich oxides, with the wavelength system.

Trace element and chemical analyses were done by the author; Dr. Dr. Jagam wrote programs for processing the data.

Typing was done by M. Annand.

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Acknowledgements

Abstract

A chemical study of the ignimbrites of Arisaig, Nova Scotia, was undertaken to determine their geochemical character, any variations within flow units, and their relationship to associated volcanics.

The ignimbrites are rhyolitic in composition and there seems to be no primary chemical variation within individual flow units. The area has been subjected to low-grade regional metamorphism, probably to greenschist facies, which accounts for most of the variation within each ignimbrite.

The rock type previously called "andesite" is found to be more appropriately classified as a spilite.

Some possible indicators of the nature of the rock suite are investigated, including trace- and rare-earth element distributions, and possible interpretations of the origin of this bimodal occurrence are discussed.

The chemical evidence favours a model involving fractional crystallization.

Chapter 1

Introduction

I. Introductory Statement

The coastline of Arisaig, Nova Scotia, provides an excellent ex-
posure of ignimbrites in wavecut cliffs and in the tidal zone, yet they
have not been studied in much detail.

This investigation was undertaken with three objectives in mind:
mainly, to describe the general geochemical character of the ignim-
brites; to search for chemical variation within and between flow units;
to determine their relationships with associated rock types.

II. General Characteristics of Ignimbrites

Before examining this occurrence, a summary of ignimbrite char-
acteristics in general would be useful.

Ignimbrites, following the realization that most of the great
rhyolite and dacite sheets of the world are of pyroclastic origin, have
been recognized in every continent and have been found in geological
series ranging in age from Pre-Cambrian to Recent. Volumes of ignim-
brite deposits may be great. Mackin (1960, p. 83) estimated that the
Great Basin of the western United States alone contains approximately
238,500 cubic kilometres of ignimbrites, and Smith (1960) calls this
figure conservative! Individual ignimbrite formations may be from a
few metres to 500 metres thick and extend for as much as 26,000 square
kilometres.

These rocks which resemble both tuffs and lavas, have long puzzled geologists. Smith (1960) and Ross and Smith (1961) provide good, definitive summaries of ash-flows and ash-flow deposits. This review is taken largely from those papers.

The term "ignimbrite"--"fire cloud rock"--was first defined by Marshall (1932, p. 200) as the rock comprising a nuée ardente deposit, without regard for the degree of welding. In present-day literature the term is used synonymously with ash flows, welded tuffs, glowing avalanche deposits, incandescent tuff flows, to name but a few. Both Smith (1960) and Ross and Smith (1961) have dealt with the problem of nomenclature.

This paper will refer to an ignimbrite as the deposit resulting from the passage of one nuée ardente (Smith, 1960, p. 800).

Even though no large ignimbrite eruptions comparable with those of prehistoric flows (such as at Taupo-Rotorua, New Zealand and those of the San Juan Mountains, Colorado) have been witnessed by man, the mechanism by which the magma is discharged and transported over such large distances seems to have been adequately explained (Fisher, 1966; McTaggart, 1960). Present concepts have been based largely on accounts of the eruption of Mt. Pelée in 1902 and Mt. Katmai in the Valley of Ten Thousand Smokes, 1912. (The deposits at Mt. Pelée are regarded as small and those of the Valley of Ten Thousand Smokes are of moderate volume, 4 cubic kilometres (Smith, 1960, p. 819)). The majority of investigators of ignimbrite formations agree on their deposition as

pyroclastic material from the lower, avalanche part of an incandescent ash "cloud". E. F. Cook describes emplacement by a "hot, rapidly expanding, turbulent, highly mobile, magmatic gas "cloud" (nuée ardente or pyroclastic flow) which carries with it intratelluric crystals, liquid droplets of the exploding magma (and the resulting glass shards), as well as rock fragments torn from the walls of the vent or picked up from the ground surface" (1966a, p. 159).

The main opponents of this mode of emplacement are Soviet scientists, whose hypotheses generally invoke either highly gaseous and/or pumice-charged lava flows, or non-homogenized lava flows. An interesting compilation of their studies has been edited by Cook (1966b).

In the field, non-welded ignimbrites may be confused with air-fall tuff sheets or with lahars, and welded varieties have often been confused with lava flows. They commonly show a gradation from a loose, relatively unconsolidated tuff at the top of the sheet to a thoroughly welded, massive, jointed, lava-like rock toward the base, and often a thinner unwelded tuff at the base (e.g. Gibson, 1970). Ignimbrites are characterized by absence of bedding (within individual units) and/or sorting, and presence of columnar jointing with densely welded textures in the lower part of sections a few hundred feet thick (e.g. Ratté and Steven, 1967). The transition between the soft, unwelded upper part and the hard, jointed, welded lower part is commonly gradational, as mentioned, but only over a very narrow interval, giving the appearance of a contact between two separate layers (Ross and Smith, 1961).

Colours of ash-flow tuffs are variable, but shades of light gray to brown are most common.

The degree of welding of an ignimbrite deposit depends on the temperature of the tuff upon deposition, the amount and composition of volatiles, the composition of the tuff, rate of cooling and crystallization, in conjunction with the weight of the overlying material.

Sheridan and Ragan (1976) delineated three stages responsible for the textures found in ash-flow deposits. The primary stage is that of emplacement from a fluidized cloud, with deflation and degassing, resulting in a poorly-sorted mass with randomly oriented pumice and lithic inclusions. The second stage involves mechanical and welding compaction, resulting in deformed glass shards, flattened, oriented pumice fragments (fiamme) and pressure shadows around lithic clasts. Stage three, with folded foliation and lineation features, occurs in only a few deposits.

Smith (1960, p. 821) reports that before welding or crystallization, most ash-flow deposits consist of: "(1) glass shards and glass dust, (2) pumice or scoria fragments and occasionally bombs, and (3) crystals; glass generally predominates over crystalline materials. Most contain some accidental lithic fragments".

In general, ignimbrites have vitroclastic texture and compaction structure, expressed principally in glass shards and pumice fragments. In strongly welded rocks, this texture may be destroyed.

Ross and Smith (1961) have distinguished two types of crystal-
lization. The first involves devitrification resulting in intergrowths
of cristobalite and alkali feldspar, mainly with spherulitic or axiolitic
textures. The second type--vapor-phase crystallization--is characterized
by growth of alkali feldspar and tridymite in pore spaces.

In older or altered rocks, quartz replaces cristobalite and tri-
dymite, whereas in Pleistocene and Recent samples, quartz has not been
recorded as a primary groundmass mineral.

Nearly all investigators of ignimbrites have identified feldspar
as a major component. Albite, sanidine and orthoclase are the varieties
recognized. Other minerals that have been reported as groundmass con-
stituents include magnetite, biotite, fayalite, hornblende and sodic
amphibole.

Varying degrees of alteration and corrosion due to welding and
crystallization have been observed in phenocrysts of quartz, sanidine,
plagioclase, amphibole, clinopyroxene, orthopyroxene, fayalite and
sphene.

Chemically, ignimbrites are predominantly silicic rhyolites,
quartz latites, rhyodacites and dacites. Andesites and trachytes may
occasionally be found in this form, but basaltic ignimbrites are ex-
tremely rare, if, indeed, they may truly be called ignimbrites.

One of the remaining problems with ignimbrites concerns the
location and kind of eruptive vent and source areas which produce the

sheet deposits of great volume. Recent field studies have shown that many of the ignimbrite sheets were erupted from arcuate fissures around the crests of broadly up-arched domes which subsequently collapsed to form calderas of gigantic size (e.g. Creede Caldera: Ratté and Steven, 1967).

III. Location and Access

The town of Arisaig lies on the shore of Northumberland Strait, approximately 24 kilometres northwest of Antigonish. The area studied extends from Arisaig Pier, north for 600 metres to McGillivray Brook. Arisaig Pier is accessible from the Pier Road, just off Collector Highway 245 (Fig. 1, 2).

IV. Previous Work in the Area

Gesner (1836) was the first to mention the Arisaig rocks and since that time most work has concerned the Arisaig Group, which overlies the volcanic rocks of the present study. The Massachusetts Institute of Technology held a summer school in the area from 1948 to 1960, during which time the coast and brooks of Arisaig were mapped on a scale of 50 feet to the inch. Ziegler, Dewey, and McKerrow mapped the Bears Brook Volcanic Group in the early 1960's. Their work is included in Boucot et al. (1974), which describes the volcanic rocks in some detail, for the first time.

Also, as a result of the M.I.T. summer school, two B.Sc. theses on the Arisaig Igneous Complex were submitted by Ziegler (1950), and

Key For All Figures

Arisaig Volcanics:

    ignimbrites   ⊙ ●

    rhyolite   △

    spilite   ⊡
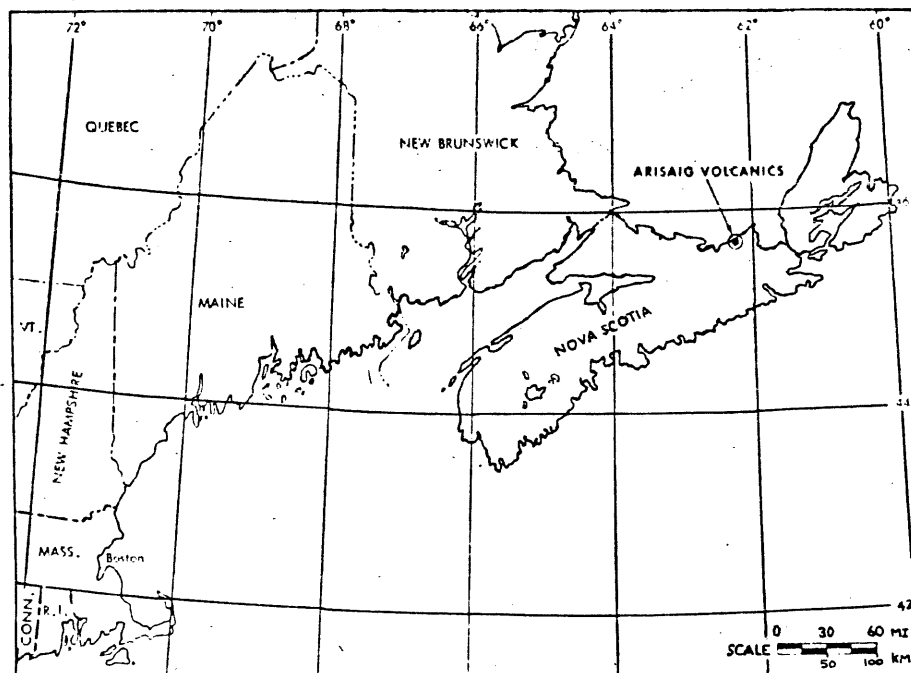
FIG. 1. Map showing the location of the Arisaig volcanics.

Foster, Healy and Lee (1950).

Benson (1970) mapped the Arisaig area on a scale of 1:50,000 (Map 11E/16; edition 2MCE; series A791) and, in 1974, he wrote on the geology of the Antigonish Highlands.

Fullager and Bottino (1968) analyzed twelve whole-rock samples from the Dunn Point Volcanics (see below) for rubidium, strontium and strontium isotope composition.

V. Geological Setting and Igneous History

The ignimbrites analyzed in this study are included in the Dunn Point and McGillivray Brook Formations of the Bears Brook Volcanic Group. The Group consists of the fluviatile Malignant Cove Formation, in addition to the intermediate and silicic volcanic rocks of the Dunn Point and McGillivray Brook Formation.

The Bears Brook Volcanic Group is thought to be of Middle-Late Ordovician age, as determined indirectly by its field relations with associated rocks (Boucot et al., 1974) and by strontium isotope composition (Fullager and Bottino, 1968), which yields a date of 430 ± 15 million years for the Dunn Point Volcanics.

Arisaig is located in the northern Appalachian region which was subjected to two main orogenic events, in Middle-Late Ordovician and in Early Devonian times. The earlier of these two events is known as the Taconian Orogeny.

Ruitenberg et al. (1977) propose that closing of a marginal oceanic basin (between Quebec and the Avalon microcontinent) by subduction during the Ordovician time, led to development of a broad volcanic arc system. The Taconian Orogeny then represents the final closing of that basin. Benson (1974) interprets the Antigonish Highlands block as the site of part of a magmatic arc system during the Cambrian and Ordovician. However, Schenk (1978, in preparation) notes that there is still much confusion as to the nature of the paleoenvironment. In any case, the Bears Brook Volcanic Group is associated with the Taconian Orogeny.

The volcanic group appears to have formed subaerially as shown by the air-fall tuffs, lahars, welded tuffs and lateritic soil profiles (Boucot et al., 1974), and was emplaced on the Brown's Mountain Group.

The volcanic sequence consists of varied lavas and pyroclastics which are predominantly andesitic in the lower part and rhyolitic in the upper part. Benson (1974) gives a very rough estimate of the thicknesses of the two portions: 60 metres for the andesite and 30 metres for the rhyolite and associated tuff. The coastline is parallel with the regional strike and makes a three-dimensional outline of facies variation difficult. The base of the sequence is not exposed.

The igneous portion of the Bears Brook Volcanic Group is divided into the earlier Dunn Point Formation with andesites, rhyolites, ignimbrites and laterites, and the later McGillivray Brook Formation, consisting of silicic lahars, rhyolites, silicic ignimbrites, and laterites (Boucot et al., 1974). The division is based on a laterite bed which

can be traced laterally throughout the section from Arisaig Pier to McGillivray Brook.

Boucot et al. (1974) report the following history for the volcanic formations: andesitic extrusions from the north, in a series of sheets and tongues, with lateritic soil profiles developed between flows; ignimbrite flow (ia) followed by emplacement of rhyolite and development of the laterite marker horizon; ignimbrite flow (ib) followed by rhyolite emplacement; ignimbrite (ic) followed by a slumped laterite and ash-fall sheet; ignimbrite (id) which is succeeded by a thin ash-fall unit; and finally ignimbrite (ie). In the section under study, ignimbrite (ie) is succeeded by conglomerate of the Beechhill Cove Formation. It should be noted that not all the units are present in any one section.

VI. Field Work--Sampling

Samples were collected from May 8 to 14, 1977. The detailed map of Boucot et al. (Plate 3, sections 1 through 5; 1974) was used to determine relative sample locations (Fig. 2).

Of the five ignimbritic flow units recognized in the area, two (ia and ib) were totally submerged during those seven days and as a result, the study is concerned solely with flows ic, id, and ie.

Thin sections of ninety-eight samples were prepared. Of these, nine ignimbrite samples, one rhyolite, and one andesite sample were

ARISAIG POINT

ARISAIG HARBOUR

PIER ROAD

SECTION 1

R

Plate 3. Shore northeast of Arisaig (by A. M. Ziegler and J. Southard, with revisions by (3 parts) J. F. Dewey and W. S. McKerrow).

Key: Rm   Recent mudflow
      Sb   Beechhill Cove Formation
      Sbc   Beechhill Cove Formation (conglomerate)
      7Oka, 7Okb, 7Okc, 7Okd, 7Oke ignimbrites
      7Ora, 7Orb, 7Orc, 7Ord, 7Ore, 7Orf,
      7Org, 7Orh, 7Ori rhyolites
      7Olf   felsite
      7Ol   laterite slump sheet
      7Ot   laterite
      7Oc   cinerite
      7Olu   lahar
      7Os   sericitic quartzite
      7Oa   andesite
      7Au   intrusive andesite
      7Aap   porphyritic andesite
      fb   fault breccia

SECTION 2

N

SECTION 3

FRENCHMAN'S BARN

SECTION 4

SECTION 5

Mill Brook

C

Scale in Feet

• SAMPLE

Ⓝ ANALYZED SAMPLE
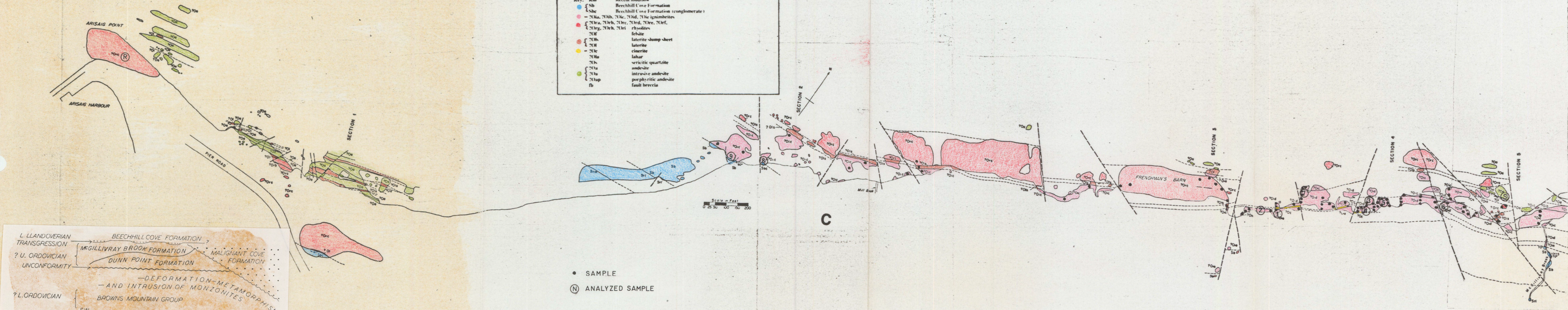
L. LLANDOVERIAN
TRANSGRESSION ———— BEECHHILL COVE FORMATION

——— McGILLIVRAY BROOK FORMATION ——— MALIGNANT COVE
FORMATION

? U. ORDOVICIAN
UNCONFORMITY ———— DUNN POINT FORMATION

—DEFORMATION—METAMORPHISM—
—AND INTRUSION OF MONZONITES—

? L. ORDOVICIAN   BROWNS MOUNTAIN GROUP

SW   NE

Figure 2. Stratigraphic relations of the Malignant Cove Formation, the McGillivray Brook Formation, and the Dunn Point Formation of the Bears Brook Volcanic Group.

FIG. 2 SAMPLE LOCALITIES

FROM : BOUCOT AND OTHERS, PLATES 3, 4
        Geological Society of America Special Paper 139

chosen for chemical analysis. The choice was made according to the freshness and homogeneity of the sample. Lithic and pumicious fragments were difficult to avoid because they were very abundant. However, the nine samples chosen had relatively small fragments (less than 10 mm in length). The rhyolite and andesite samples were included for comparison.

The analyzed rhyolite was taken from the collection at Dalhousie University, because the only rhyolite sample collected was considerably altered. The sample from the Dalhousie collection is known to be from Arisaig Pier.

Please note also that only one andesite sample was collected and, as such, may not be truly representative.

Chapter 2

Mineralogy and Petrography

I. <u>General Description</u>

Thin-section descriptions and photomicrographs of the nine analyzed samples are given in Appendix B.

The ignimbrites at Arisaig are essentially phenocryst-poor, eutaxitic, welded tuffs. Lithic clasts are abundant in the lower portions of the flows and flattened pumice fragments, or fiamme, are common in the middle and upper portions.

In the field, the ignimbrites are mainly deep red-brown as a result of the ubiquitous hematite dust. The lower portions of flows ic and id consist of approximately 75 centimetres of angular breccia, grading rapidly into very dense, flinty, welded tuff. The breciatted portion of flow ie appears to have been removed by the sea. The densely welded middle and upper portions of all three flows are characterized by columnar jointing (maximum diameter measured 1.5 metres) and the presence of fiamme. The fiamme show a great range in sizes: from microscopic to 43x7 centimetres. The top 50 to 75 centimetres of the flows, where visible, are only partially welded and do not exhibit columnar jointing. Veins of chlorite, calcite, and quartz are abundant in the less consolidated zones.

Mineralogically and petrographically, there appears to be no difference between flows ic, id, and ie. There are also no regular lateral trends evident.

A summary of the post-extrusion processes that have affected the Arisaig samples is given in Table 1. The samples appear to have been subjected to low-grade regional metamorphism, possibly to greenschist facies, and devitrification has occurred in all but the andesite sample. These factors have made optical identification of minerals rather difficult. Thin sections of the nine samples that were selected for chemical analysis were examined with the aid of the electron microprobe. However, most of the microprobe analyses of feldspars gave low totals because they are sericitized and chloritized.

II.   Basal Portion

Sections of the basal 75 centimetres consist of 50 to 75% lithic clasts. These clasts include laterite pebbles, angular andesite fragments, subangular sericitized quartzite (probably from the Brown's Mountain Group), fragments of welded tuff, and in one instance, spherulitic rhyolite. In thin section, the clasts ranged in size up to 10 x 5 millimetres. In the field, laterite and andesite cobbles of 5 x 3 centimetres were observed. There is no evidence of flattening of the clasts, but in most cases a faint linear orientation is discernible.

All sections are deep red-brown due to the laterite inclusions and hematite granules in the matrix. The hematite is believed to have two sources: (1) oxidation of iron within the ignimbrite, and (2) derivation from the laterites, as the nuées ardentes ploughed over them.

Table 1: Post-Extrusion Alteration

Process	Andesite	Rhyolite	Ignimbrites	Evidence
deuteric oxidation	-	X	X	reaction rims and halos of iron oxide grains; abundance of hematite
deuteric reaction with fluids	-	X	X	extensive chloritization and sericitization
devitrification	-	X	X	spherulites; micro-crystalline groundmass
low-grade, regional metamorphism	X greenschist facies (including possible spilitization)	X	X	chlorite-epidote-albite in andesite; chlorite-albite-quartz in rhyolite and ignimbrites, and association with andesite; quartz and calcite veins in fissures
weathering	X	X	X	field observations: presence of laterite soils between flows; discoloured and iron-stained weathering surfaces; clay minerals in fractures and cavities.

The matrix generally consists of an unresolvable mass of hematite grains, clay minerals, and quartz.

The clasts are usually surrounded by chlorite and, less commonly, sericite, displacing the iron oxide grains into rims surrounding the halos. The halos are approximately 0.2 to 0.3 millimetres wide.

Quartz has crystallized along cracks and fissures in the rocks.

No sample of the basal breccia was submitted for bulk rock analysis.

III. Middle, Welded Portion

Samples from the middle, densely welded zone are characterized by a eutaxitic texture, mainly due to fiamme.

The fiamme are basically lens-shaped, with stretched, flame-like ends. In these samples, the larger pumice fragments consist mainly of coarse, strain-free quartz grains with inter-granular chlorite and hematite. This coarse-grained crystallization of quartz within pumice lapilli is characteristic of vapour-phase crystallization (Smith, 1960).

The matrix is a microcrystalline combination of quartz and alkali feldspar, probably as a result of devitrification. These sections are also red-brown in colour, as a result of finely disseminated hematite within the matrix. Opaque grains may constitute as much as 15% of the groundmass.

Since the groundmass is microcrystalline in the large majority of samples, the electron microprobe was used to obtain its composition. Analyses show mainly orthoclase with quartz, but reveal the presence of patches of albite with quartz, also. Results of the microprobe study are given in Table 2.

Microprobe analyses of optically determined "possible" feldspars show both albitic and orthoclase feldspars with extensive sericitization. As a result of the alteration, the analyses yielded low totals (approximately 97%), but they do indicate two distinct types of feldspar are present (Table 2).

Microprobe analyses of the oxides indicate they are dominantly members of the ilmenite-hematite solid-solution series, with some rutile, or brookite, probably as a result of alteration of ilmenite. It is interesting to note the presence of niobium in the rutile/brookite grains. The first report of such an occurrence in Nova Scotia was by Dwyer (1975). There are also Nb-rich grains present, that appear to be members of the columbite-tantalite group. The analyses of the grains (Table 3) show presence of titanium also, which might indicate an intergrowth of ilmenite and rutile phases.

IV. Top Portion

Sections from the top metre of flows ic, id, and ie look quite similar to those from the middle portion. However, the eutaxitic texture is less pronounced, with abundant chlorite, calcite, and

Table 2

Electron Microprobe Analyses of Feldspars

	1	2	3	4	5	6	7
SiO_2	68.63	68.76	68.55	63.46	67.57	70.88	69.07
TiO_2	-	-	-	-	-	0.06	-
Al_2O_3	19.61	19.46	19.62	17.47	16.59	14.06	19.79
FeO	0.33	0.22	0.09	0.94	0.45	0.14	0.13
CaO	-	-	0.14	-	-	-	0.10
Na_2O	11.08	10.65	10.82	-	1.96	-	10.81
K_2O	0.13	0.23	0.59	15.09	12.25	13.57	0.05
Total	99.78	99.32	99.81	96.96	98.82	98.71	99.95

1. ignimbrite from flow ic; lab no. 8; field no. 11-2

2. ignimbrite from flow ic; lab no. 9; field no. 11-1

3. ignimbrite from flow id; lab no. 6; field no. 8-3B(T)

4. ignimbrite from flow id; lab no. 5; field no. 9-5c

5. ignimbrite from flow id; lab no. 4; field no. 12-6B(T)

6. average of three spherulite analyses of rhyolite; sample no. R

7. average of three feldspar phenocryst analyses of andesite, sample no. A

"-" indicates zero

Table 3

Partial Microprobe Analyses of

Nb-rich Oxides in an Ignimbrite Sample

	1	2	3
TiO_2	43.63	21.57	72.32
FeO	12.14	1.31	9.52
NbO_2	28.62	38.83	6.24
CaO	.00	5.89	.00
Total	84.39	67.60	88.09

All three analyses are from flow id; lab no. 6; field no. 8-3B(T)

quartz veins precipitated in cracks and fractures. Pumice fragments are not as flattened as in the middle sections and are surrounded by black, opaque oxidation halos, in most cases.

The matrix is characterized by a microcrystalline, felsitic texture that reveals the same bimodal composition found in the middle portion by electron microprobe analysis; i.e. dominantly orthoclase and quartz with albite and quartz.

Similarly, feldspar analyses shows both orthoclase and albitic compositions, though extensively sericitized.

In two thin sections, iron oxide grains (3 to 5%) are more abundant than in lower portions.

V.   Rhyolite

Only one section of rhyolite was examined. It is 70% spherulitic: bands of closely-packed spherulites alternate with bands of devitrified growths of quartz and alkali feldspar. These crystals appear to have grown outward from narrow lines of iron oxide grains.

Broad-beam electron microprobe analyses of the spherulites yielded compositions of orthoclase and quartz (Table 2). It is interesting that no sodium was detected. Kesler and Weiblen (1968, from Smith, 1974, p. 585) in their study on spherulites in andesites from Haiti, noted that potassium preferentially enters the spherulite about four-fold, relative to the groundmass.

The outer rims of the spherulites appear to be coated with hematite dust.

VI. Andesite

Only one section of andesite was examined. It consists of clusters of subhedral to euhedral albite phenocrysts, partly sericitized, within a fine-grained pilotaxitic groundmass. Intergranular chlorite is present. Small stringers of epidote and calcite were observed in the field. Minor amounts (approximately 2-5%) of epidote and calcite can also be seen in the thin section.

Electron microprobe analyses of feldspars confirm their albitic composition (Table 2).

The phases identified - chlorite - epidote - albite - are diagnostic of greenschist facies metamorphism.

Chapter 3

Chemistry

I. Methods Used

Descriptions of the analytical methods and their accuracy will be found in Appendix C. Provided here is a brief summary of the methods used.

Element	Method
Si	neutron activation
Al, Fe $_{total}$, Mg, Ca, Na, K, Ti, Mn	atomic absorption spectrophotometry
Fe^{2+}	titration
P	spectrophotometry
H$_2$O total	Penfield Tube
H$_2$O$^-$	weight loss of dried sample
* Trace Elements \} Rare-Earth Elements	instrumental neutron activation

II. Major Elements

Whole-rock analyses of the nine ignimbrites, one rhyolite, and one andesite are shown in Table 4. A potassic rhyolite and an average andesite are included for comparison. The calculated C.I.P.W. norms are also presented in Table 4.

_____

* only samples 5, 8, R, and S were analyzed

Table 4. Major Element Chemistry and C.I.P.W. Norms[*]

	1	2	3	4	5	6	7	8	9	10	11	12	13
SiO_2	79.24	77.28	76.19	76.39	76.75	77.93	77.32	76.28	76.86	49.05	76.37	73.76	58.17
TiO_2	0.15	0.16	0.15	0.17	0.16	0.16	0.16	0.16	0.17	2.53	0.19	0.12	0.80
Al_2O_3	11.38	11.19	10.86	12.06	11.54	11.96	11.29	11.69	11.52	15.75	12.65	11.98	17.26
Fe_2O_3	0.08	1.31	2.35	1.51	1.89	0.65	1.47	2.57	2.28	12.13	0.82	1.14	3.07
FeO	0.73	0.57	0.86	0.52	0.47	0.52	0.43	0.43	0.49	2.62	0.40	2.40	4.17
MnO	0.005	0.003	0.016	0.005	0.006	0.006	0.008	0.005	0.004	0.196	0.004	-	-
MgO	0.04	0.04	0.11	0.07	0.06	0.07	0.04	0.07	0.11	4.64	0.07	0.76	3.23
CaO	0.04	0.01	0.01	0.02	0.01	0.02	0.18	0.01	0.02	3.13	0.02	0.32	6.93
Na_2O	3.10	2.68	0.27	1.65	0.71	2.07	2.12	1.89	2.73	7.24	0.97	0.53	3.21
K_2O	4.70	5.34	7.63	6.84	8.11	5.60	5.83	6.04	4.71	0.29	8.01	7.38	1.61
P_2O_5	0.01	0.01	0.02	0.02	0.02	0.02	0.01	0.01	0.01	0.51	0.01	-	0.20
H_2O^+	0.73	0.68	1.14	0.90	0.80	0.90	0.77	0.98	0.89	2.88	1.33	1.75	1.24
H_2O^-	0.22	0.22	0.02	0.09	0.21	0.11	0.27	0.10	0.21	0.60			
other	-	-	-	-	-	-	-	-	-	-	-	0.34	-
total	100.43	99.49	99.63	100.25	100.74	100.02	99.90	100.24	100.00	101.57	100.84	100.48	99.89
Q	43.01	41.52	46.08	43.80	41.88	44.64	42.84	42.18	43.62	-	40.32		
or	27.83	32.29	45.65	40.64	47.87	33.40	35.07	36.18	27.83	1.67	47.32		
ab	26.22	23.08	2.10	14.16	5.77	17.83	17.83	16.26	23.08	56.9	8.39		
an	0.27	-	-	-	-	-	0.83	-	-	10.02	-		
ne	-	-	-	-	-	-	-	-	-	1.91	-		
di	-	-	-	-	-	-	-	-	-	1.73	-		
hy	1.02	0.10	0.30	0.20	0.20	0.33	0.10	0.20	0.30	-	-		
ol	-	-	-	-	-	-	-	-	-	7.6	-		
mt	0.23	1.39	2.32	1.16	0.93	0.93	0.93	0.93	1.16	1.85	0.93		
il	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	4.86	0.30		
ap	-	-	-	-	-	-	-	-	-	1.36	-		
hm	-	0.32	0.80	0.80	1.28	-	0.80	1.92	1.44	11.02	0.16		
C	1.12	0.92	2.24	1.94	1.63	2.45	1.22	2.03	2.04	-	2.45		

1. Sample No. 1; Field No. 14-10A(T); ignimbrite from flow ie
2. Sample No. 2; Field No. 14-11B(M); ignimbrite from flow ie
3. Sample No. 3; Field No. 12-6B(B); ignimbrite from flow id
4. Sample No. 4; Field No. 12-6B(T); ignimbrite from flow id
5. Sample No. 5; Field No. 9-5C; ignimbrite from flow id
6. Sample No. 6; Field No. 8-3B(T); ignimbrite from flow id
7. Sample No. 7; Field No. 14-9F; ignimbrite from flow id
8. Sample No. 8; Field No. 11-2; ignimbrite from flow ic
9. Sample No. 9; Field No. 11-1; ignimbrite from flow ic
10. Sample No. S; Field No. A; "andesite"
11. Sample No. R; Field No. R; rhyolite
12. Potassic Rhyolite, quoted from Hatch, Wells, and Wells (1973, p. 239)
13. Average of 1775 andesites, Chayes (1969, p. 2; in Hatch, Wells, and Wells, 1973, p. 321)

"-" indicates zero

[*] C.I.P.W. Norms calculated following Johannsen, 1939 (2nd edition), p. 89.

The silica value of the so-called andesite (Boucot et al., 1974) sample is very low. In fact, it is within the basalt range. Andesites with SiO_2 less than 50% are included in Chaye's (1969, in Hatch, Wells, and Wells, 1973) average, but there is question as to their validity as true andesites.

The "andesite" sample also displays a low potash value, more characteristic of a basalt. Similarly, the iron, magnesia, and titanium values are basaltic. Table 5 compares the Arisaig "andesite" with an average tholeite and a tholeitic lava.

The CaO value for the "andesite" is notably depleted. Small calcite veins (generally less than 5 millimetres wide) and nodules (largest measured 4 millimetres in diameter) were observed in the "andesite" outcrop. Stringers of epidote further indicate mobility of calcium in solution.

The soda content of the "andesite" sample is significantly enriched. In thin section, and in field observation, the sample is notable for its abundance of albite phenocrysts. These two characteristics suggest the rock type, spilite.

Lyttle (1972, p. 18; unpub. M.Sc. thesis) proposed a working definition for the term "spilite": "a rock of approximately basaltic composition, characterized by the presence of sodic plagioclase, chlorite, a high soda content, and generally exhibiting textures typically found in basalts and diabases". The Arisaig "andesite" fulfills these requirements.

Table 5

A Comparison of the Major Element Chemistry of the

Arisaig "Andesite" with Tholeites and Tholeitic Lava.

	Arisaig "Andesite"	Average of 3 Tholeites[1]	Tholeitic Lava[2]
SiO_2	49.05	49.78	50.83
TiO_2	2.53	0.68	3.44
Al_2O_3	15.75	15.69	12.67
Fe_2O_3	12.13	2.73	3.10
FeO	2.62	9.20	11.39
MnO	0.196	0.35	0.25
MgO	4.64	7.79	4.19
CaO	3.13	11.93	8.18
Na_2O	7.24	1.21	3.24
K_2O	0.29	0.29	0.87
P_2O_5	0.51	0.07	0.75
H_2O^+	2.88	-	-
H_2O^-	0.60	-	-
other	0.00	0.29	0.94
total	101.57	100.01	99.85

1. H. Kuno (1960, p. 141; in Hatch, Wells, and Wells, 1973)

2. I. Carmichael (1964, p. 439)

"-" means not determined

Battey (1974) notes that "the overwhelming majority of spilites are pre-Tertiary in age and have been buried under later strata. Their mineralogy is consistent with zeolite facies metamorphism, but the differences in bulk composition from basalt imply an open system and some external source of Na during the process". The Arisaig "andesites" are thought to be of late Ordovician age and have certainly been buried by later strata. Petrographic study of the sample identified the green-schist facies mineral assemblage: albite-epidote-chlorite. Sodium may have been introduced from seawater. It is also interesting that the overlying ignimbrites and rhyolites, especially, have very low soda contents.

It should be noted that the sample was taken from an outcrop which is completely surrounded by sea water. This might account for some of the enrichment of Na_2O.

All factors discussed above, combined with the petrographic observations, strongly suggest that the Arisaig "andesite" is in fact, a spilite, which has formed from the low-grade metamorphism of a tholeitic lava. The sample previously named "andesite" will henceforth be named "spilite".

The silica values for the rhyolite and ignimbrite samples are not unusual. SiO_2 values generally show an increase from spilite to rhyolite to ignimbrite.

Alumina values decrease slightly with increasing silica content. The presence of normative C in all samples but the spilite (Table 4) is best explained by the removal of alkalies to the spilite.

Titanium, ferrous iron, magnesia, and lime contents decrease as a result of the early crystallization of the mafic minerals.

The Fe_2O_3/FeO ratio of the spilite is high, owing to the oxidation of iron from ferrous to ferric state. The slight enrichment of Fe_2O_3 in the ignimbrites is probably due to the presence of finely disseminated hematite within the groundmass, as noted earlier.

Magnesia values decrease from the spilite to the rhyolitic samples, as expected, though the $MgO/(FeO+Fe_2O_3)$ ratio of the spilite is low. This depletion is probably due to the aforementioned Fe_2O_3 enrichment, coupled with the tendency of Mg to be taken up by early crystallizing phases. These phases may then become separated from the melt.

CaO values show a similar pattern decreasing from basic to more silicic compositions. The presence of calcite veins, attesting to the mobility of calcium, explain its low absolute abundance.

The general Na_2O-depletion and K_2O-enrichment was noted above. This pattern results in a large difference in K_2O/Na_2O ratios between the spilite and rhyolitic rocks. The ratios for the spilite, rhyolite, and average "middle-zone" ignimbrite are 0.04, 8.23, and 3.49, respectively. Possible causes of the variation are: (1) presence of

sericite, particularly in the rhyolite; (2) the tendency of potassium to stay in residual liquid fractions (ionic radius of K^+ is 1.33 $\overset{o}{A}$, compared with Na^+, 0.95$\overset{o}{A}$) and (3) diffusion of sodium into basalt during low-grade metamorphism (spilitization ?).

TiO_2, MnO, P_2O_5, and H_2O values are not remarkable. It may be noted that the highest total H_2O value was detected in the least welded ignimbrite sample (number 3). H_2O^+ probably represents the extent of sericitization within that sample.

The AFM diagram (Fig. 3) shows that the suite of Arisaig volcanics falls within the area defined by Nockolds and Allen (1953) as being characteristic of calc-alkaline suites. This suggests a liquid trend of fractionation.

However, drawing any conclusions from this diagram is hazardous. At least part of the trend is likely the result of alteration: although sodium and potassium have moved, the total alkali content has not, except for the spilite. The enrichment of sodium has pulled the spilite point toward the alkali apex. The AFM diagram effectively illustrates the bimodal character of the Arisaig volcanic suite.

Lipman (1966) applied Tuttle and Bowen's (1958) experimental data to ash flows of southern Nevada to determine water pressures during differentiation and crystallization of the magma. His method was to plot bulk-rock compositions of a rock series presumed to be related by a single line of liquid descent, establishing a differentiation trend.
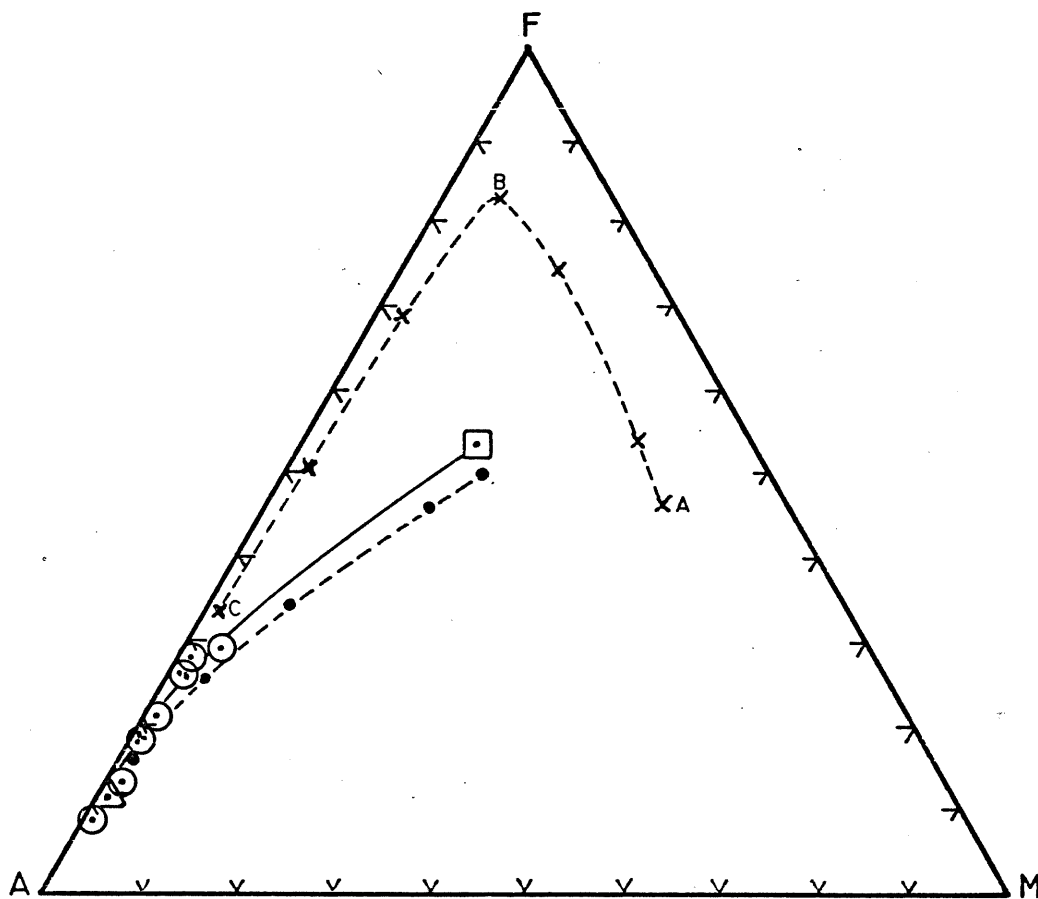
Fig. 3 AFM diagram for Arisaig volcanic suite. ● = points on calc-
        alkaline trend, from Nockolds and Allen, 1953; X = samples
        from Skaergaard Intrusion: A , marginal gabbro (assumed
        parental magma); B - C , late granophyric liquid fractions;
        from analyses given in Carmichael, Turner and Verhoogen, 1974,
        p. 477.

This trend may indicate a certain water pressure either by intersecting the line of isobaric minima or by bending to follow an isobaric line towards its minimum. Lipman (1966) said that if the points were scattered, equilibrium was achieved by some means other than crystal-liquid equilibrium.

Tuttle and Bowen's (1958) experimental system may be applied to natural rocks, only if they may be adequately represented by the components: Q, ab, or.

The rhyolite and ignimbrites of Arisaig may be approximated by the Q-ab-or system, as the sum (Q + ab + or) is greater than 94% for all samples. They are plotted in Figure 4 with one of Lipman's rhyolitic suites. Lipman interprets such a scattering of points as being indicative of an alteration process, such as volatile transfer.

The Arisaig data points are displaced towards the Q apex, or away from the Ab apex. Initially, the rhyolitic liquid was following the feldspar-quartz cotectic line towards the thermal minimum. The displacement may be explained in three ways: (1) quartz veins effectively pull the data points towards the Q apex; (2) loss of sodium during metamorphism moves the points away from the Ab apex; (3) a combination of the above.

III. Trace Elements

The trace elements studied include Ta, Sc, Sb, Cs, Cr, Hf, Co,

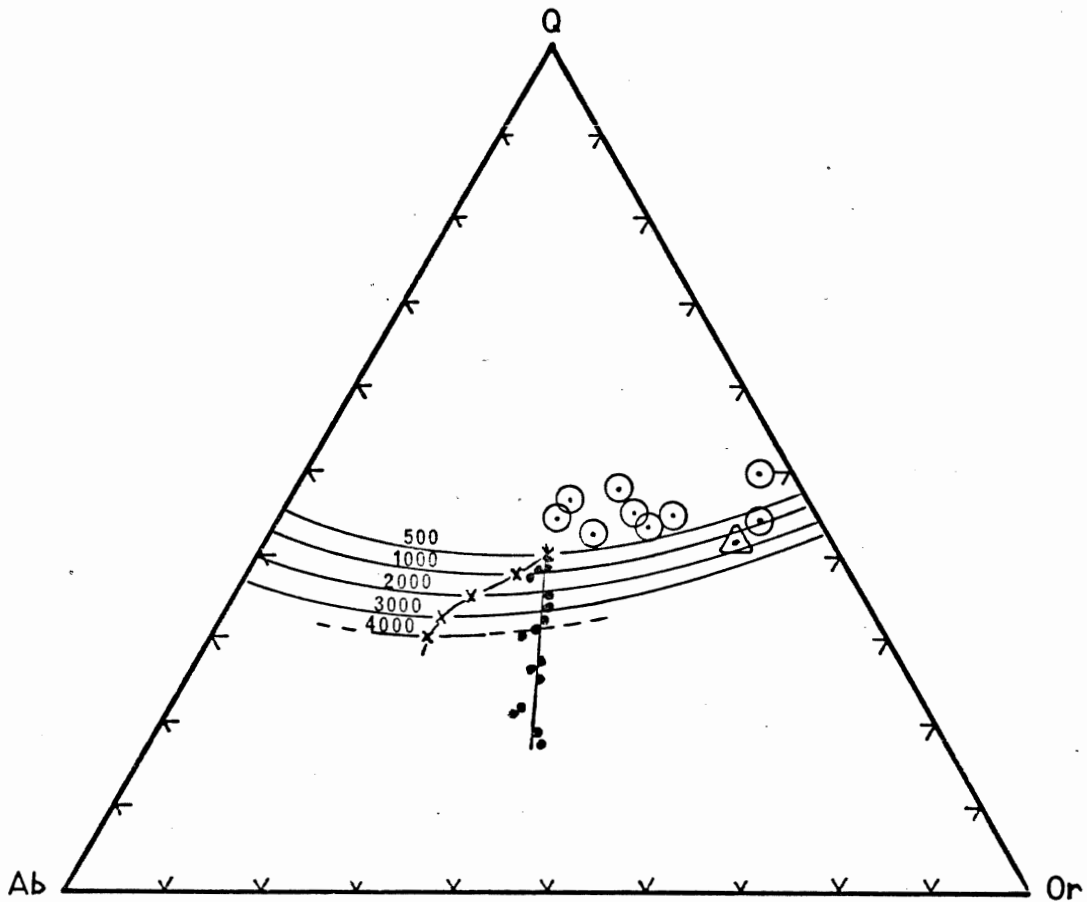Fig. 4 Petrogeny's Residua System. (Modified from Tuttle and Bowen,
        1958, p. 75). Isobaric lines mark positions of the quartz-
        feldspar boundary at various water pressures. **x** marks the
        location of the thermal minimum on each isobar. ● = samples
        from rhyolitic Topopah Spring tuffs, showing approximate trend
        of differentiation (Lipman, 1966, p. 815).

Ba, Th.   These are the trace elements that are normally detected with
the neutron activation equipment; other methods, such as x-ray
fluorescence, were not used.   Results are presented in Table 6, arranged
in order of increasing ionic radius.

Here again, the spilite values are indicative of a more basic
rock type than a true andesite.   This is shown by the low abundances
of elements which are typically concentrated in the later stages of
magmatic differentiation: Ba and Th.   Also, the ferromagnesian ele-
ments, Sc and Cr, are slightly enriched.   Despite these characteristics,
Hf and Cs, which tend to be incompatible, are enriched relative to
basalt, and even the true andesite.   Table 7 permits comparison of the
Arisaig spilite with an average New Zealand andesite and an average
basalt.

The change in trace-element concentrations from spilite to
rhyolite to ignimbrites suggests an increasing differentiation.   The
ions with large valence charges and/or large radii, such as Cs^+,
Th^{4+}, Hf^{4+}, Ta^{5+} are incompatible and so stay in residual liquids
(Ringwood, 1955).   They are found significantly enriched in the rhyo-
lite-ignimbrite analyses.   In contrast, ions such as Sc^{3+} and Cr^{3+}
may be found within ferromagnesian minerals and are noticeably depleted
in the more acid rocks.   Similar depletions are recorded by Haskin
et al. (1966).

The relatively incompatible ion, Ba^{2+}, is enriched in the silicic
compositions.   This is a result of the size effect: although Ba has the

Table 6

Trace-Element Concentrations (ppm)

| Element | Ionic Radius (Å)[1] | Spilite | Rhyolite | Ignimbrites | |
				Sample 8	Sample 5
Cr	0.69	108.55	1.33	1.05	1.82
Ta	0.73	1.42	5.43	14.88	15.18
Co[2]	0.74	72.22	91.83	99.14	104.18
Sb	0.76	0.25	0.90	1.20	0.33
Sc	0.81	36.89	1.36	0.55	0.21
Hf	0.81	3.15	9.99	40.33	40.31
Th	0.95	2.50	17.93	34.79	35.31
Ba	1.35	260.07	2489.97	1363.86	909.96
Cs	1.69	2.19	3.05	3.29	5.58

1. Ionic radii from Sargent-Welch Scientific Company Chart (except Sb, from Ahrens, 1953; in Taylor and White, 1966).

2. Co values should be ignored, as they are the result of contamination from the tungsten-carbide swing mill.

Table 7

Comparison of Trace-Element Concentrations in the

Arisaig Spilite with an Andesite and an Average Basalt (ppm)

Element	Arisaig Spilite	Andesite[1]	Basalt[2]
Cr	108.55	70	200
Sb	0.25	0.18	0.2
Sc	36.89	25	38
Hf	3.15	3.0	2
Th	2.50	4.7	2.2
Ba	260.07	290	250
Cs	2.19	1.0	1.0

1. New Zealand Andesite, from Taylor and White (1966).

2. Average Basalt, from Taylor and White (1966).

same charge as the calcium ion, its radius is similar to that of the potassium ion. Ba^{2+} shows a very high concentration in the rhyolite, with decreasing amounts in the ignimbrites. Barium favours liquid over plagioclase crystals, but it tends to prefer alkali feldspar phenocrysts over liquid (Smith, 1974), so much of the Ba substitutes for K in the crystallizing rhyolite, leaving less for the ignimbrites to inherit. The result is that Ba^{2+} concentrations increase with differentiation to a maximum and then rapidly decline in the more extreme differentiates.

Plotting Ba/K values versus K (Fig. 5) produces a correlation which may be interpreted as one of fractionation.

K/Cs values were also calculated and plotted with respect to potassium concentration (Fig. 6). Both the potassium ion and the cesium ion have large ionic radii (1.33 $\overset{\circ}{A}$ and 1.69 $\overset{\circ}{A}$, respectively) and so tend to end up in late liquids (Cesium is slightly more incompatible than potassium). There is a positive correlation between the K/Cs values and K concentration which could be a possible indicator of fractionation. Note also that the values of K/Cs of the ignimbrites are slightly less than that of the rhyolite, as a result of higher Cs concentrations. The lower ratios suggest a higher degree of differentiation.

Hf^{4+} and Ti^{4+} have the same charge, but the ionic radius of Ti^{4+} (0.68 $\overset{\circ}{A}$) is less than that of Hf^{4+} (0.81 $\overset{\circ}{A}$); hence, a plot of Hf/Ti values versus Ti concentrations showing high ratios corresponding with low Ti^{4+} values could indicate fractionation. The Arisaig suite exhibits this type of correlation (Fig. 7).
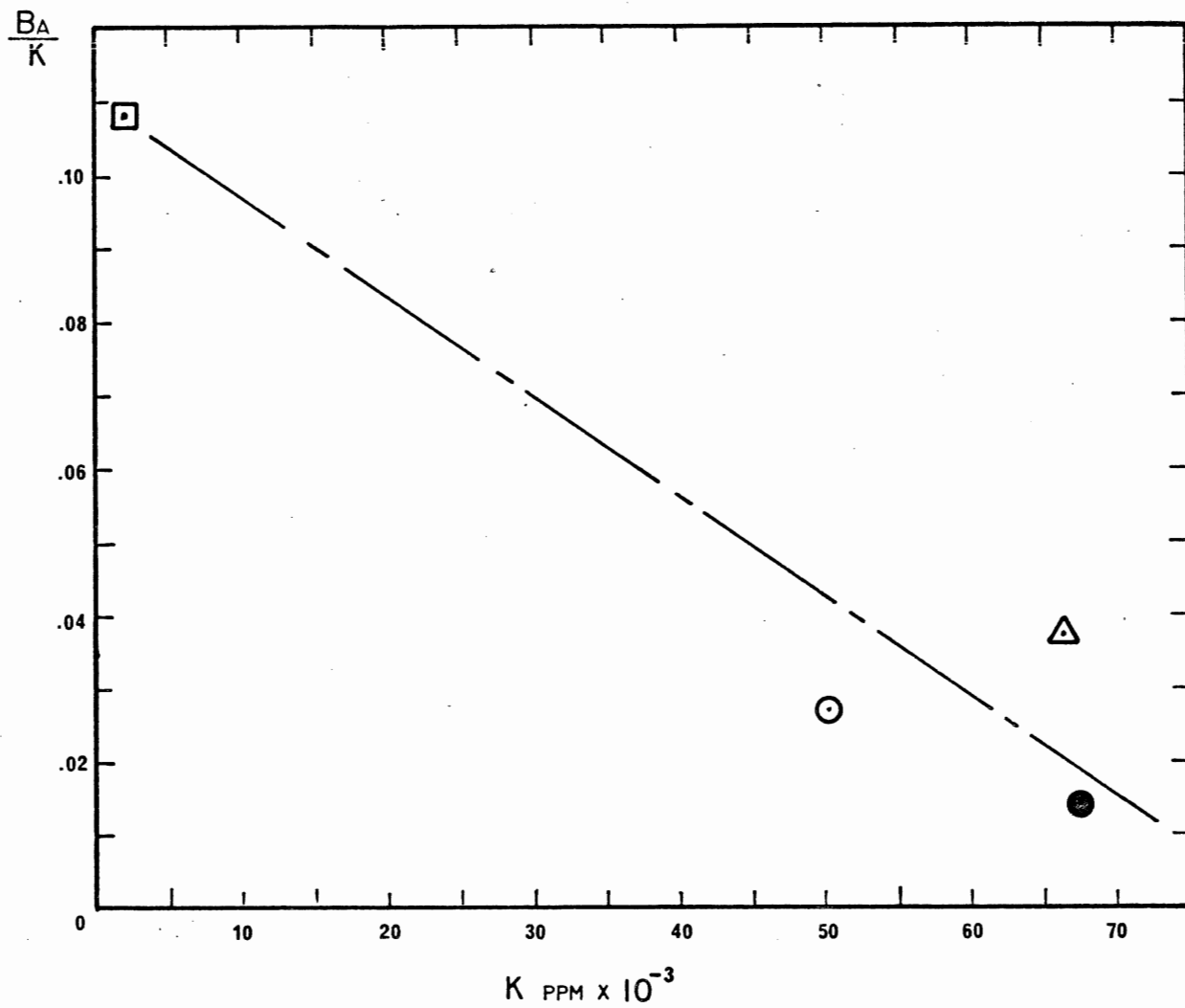
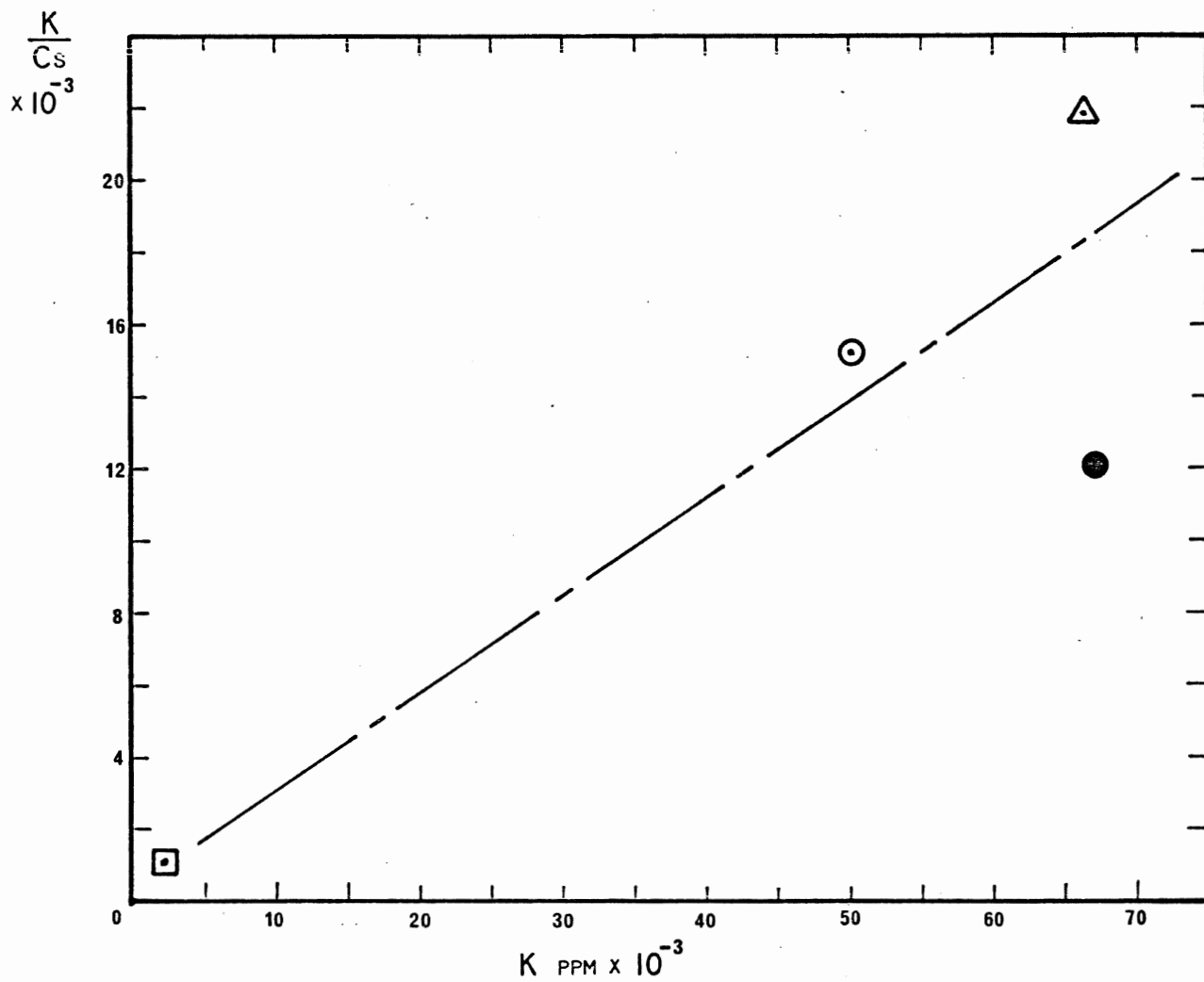Fig. 5 ^{Ba}/K versus K. The plot may be attributed to fractionation.

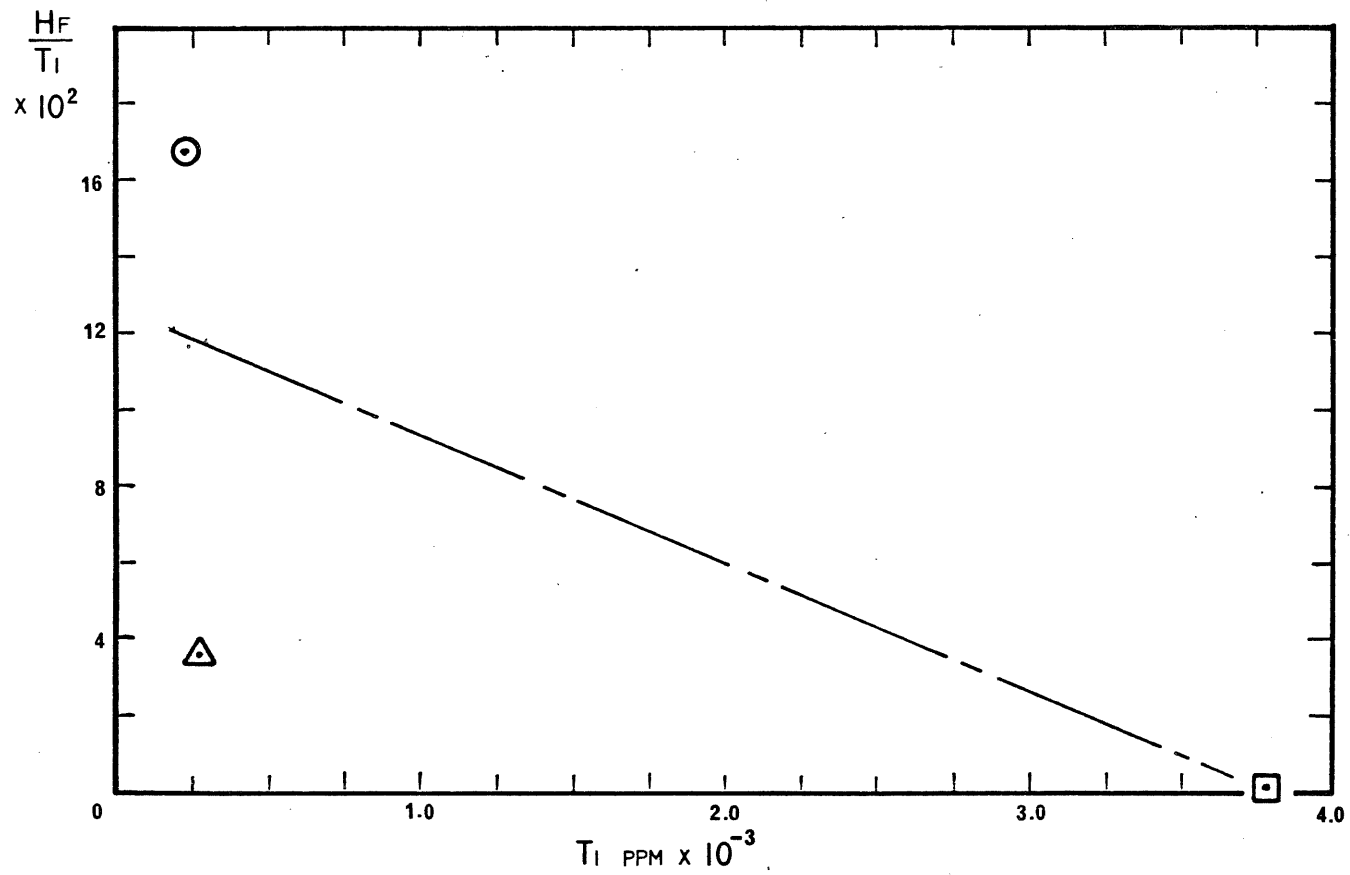Fig. 6 K/Cs versus K. Positive slope could indicate fractional crystallization.

Fig. 7 Hf/Ti versus Ti. Hf/Ti values increase with increasing dif-
ferentiation.

The plot of $^{Sc}/Fe_T$ values with respect to Fe_T, where Fe_T = total iron calculated as Fe_2O_3, illustrates the ferromagnesian character of the scandium ion (Fig. 8). During magmatic crystallization, scandium preferentially enters the early ferromagnesian minerals occupying the Mg-Fe positions, thereby becoming impoverished in residual magmas. Ringwood (1955, p. 199) notes that Sc^{3+} probably becomes concentrated at the expense of Fe^{2+}, rather than Mg^{2+}.

It is hazardous to draw any firm conclusions based on these trace element plots because of the lack of data points, but it can be stated that the patterns shown by the Arisaig volcanics do not clash with predicted fractionation trends.

III-A. Additional Note on Trace Elements of the Arisaig Volcanics

Fullager and Bottino (1968) analyzed twelve whole-rock samples for rubidium, strontium, and strontium isotopic composition. They reported three initial strontium isotope ratios: 0.7065 ± 0.002, for analyses done at the Massachusetts Institute of Technology and obtained by visual vest-fit isochron plot; 0.7075 ± 0.012, when calculated by least-squares method on the M.I.T. analyses; 0.707 ± 0.002, for analyses done at the Goddard Space Flight Center and obtained by visual best-fit. Unfortunately, the range of their results--0.6955 to 0.7195-- is much too large to allow any interpretations regarding origin of the Arisaig rock suite. Also, the scatter of points on the isochron plots suggests the samples have not remained closed with respect to Rb^{1+} and Sr^{2+}.
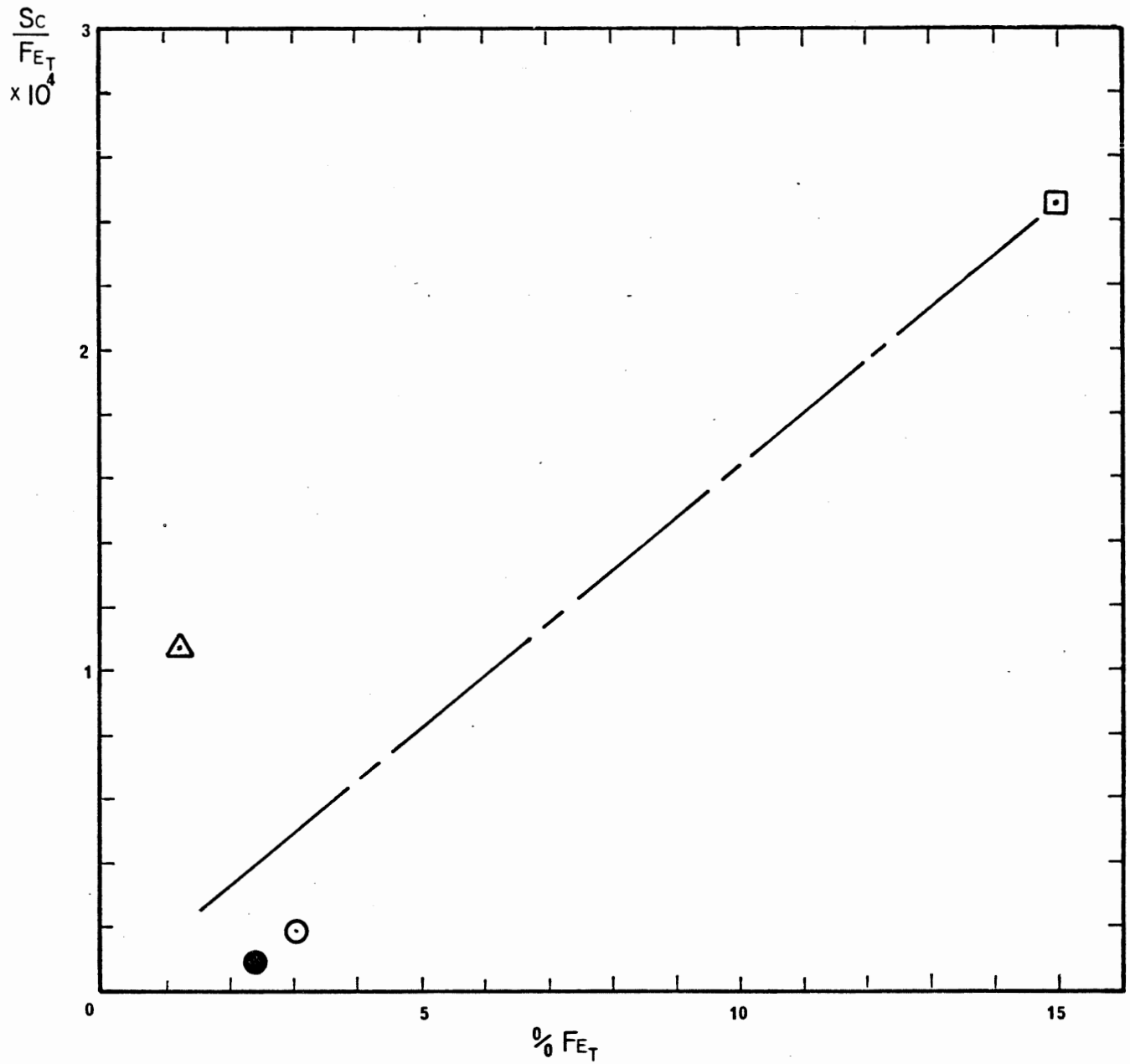
Fig. 8 Sc/Fe versus Fe. This plot illustrates the ferromagnesian
character of scandium.

IV. Rare-Earth Elements

Six rare-earth elements were analyzed: La, Ce, Eu, Tb, Yb, Lu.
Results are given in Table 8, according to atomic number.

The total of the rare-earth elements studied, shows progressive
enrichment from spilite to rhyolite to ignimbrite. The low total
for ignimbrite sample number 8 is due solely to the extraordinary Ce
value. This concentration is very low and though checked carefully
several times, remains an anomaly.

All other values increase with "acidity" of the rock type, with
the notable exception of Eu, resulting in a negative anomaly.

These characteristics are seen clearly in a plot of chondrite-
normalized (Table 9) REE concentrations of the four samples versus
atomic number (Fig. 9).

Ringwood (1955) included the REE in the group of incompatible
elements and, as such, predicted them to be enriched in a residual
liquid.

The rhyolite and ignimbrite patterns show generally greater REE
abundances (except Eu) than the spilite pattern.

The REE distribution pattern for the mineral plagioclase, parti-
cularly the sodic members, displays a prominent positive europium
anomaly (Haskin et al., 1966), indicating that Eu^{2+} is accommodated

Table 8

Rare-Earth Element Concentrations (ppm)

| Element | Spilite | Rhyolite | Ignimbrites | |
			Sample 8	Sample 5
La	15.46	18.71	20.37	42.04
Ce	38.66	41.62	18.47	94.63
Eu	2.48	0.42	0.60	0.76
Tb	0.86	0.85	3.52	3.86
Yb	2.79	4.16	14.29	17.0
Lu	0.34	0.51	2.07	2.48
Total	60.59	66.07	59.32	160.77

Table 9

Composite Chondrite Values[1] (ppm)

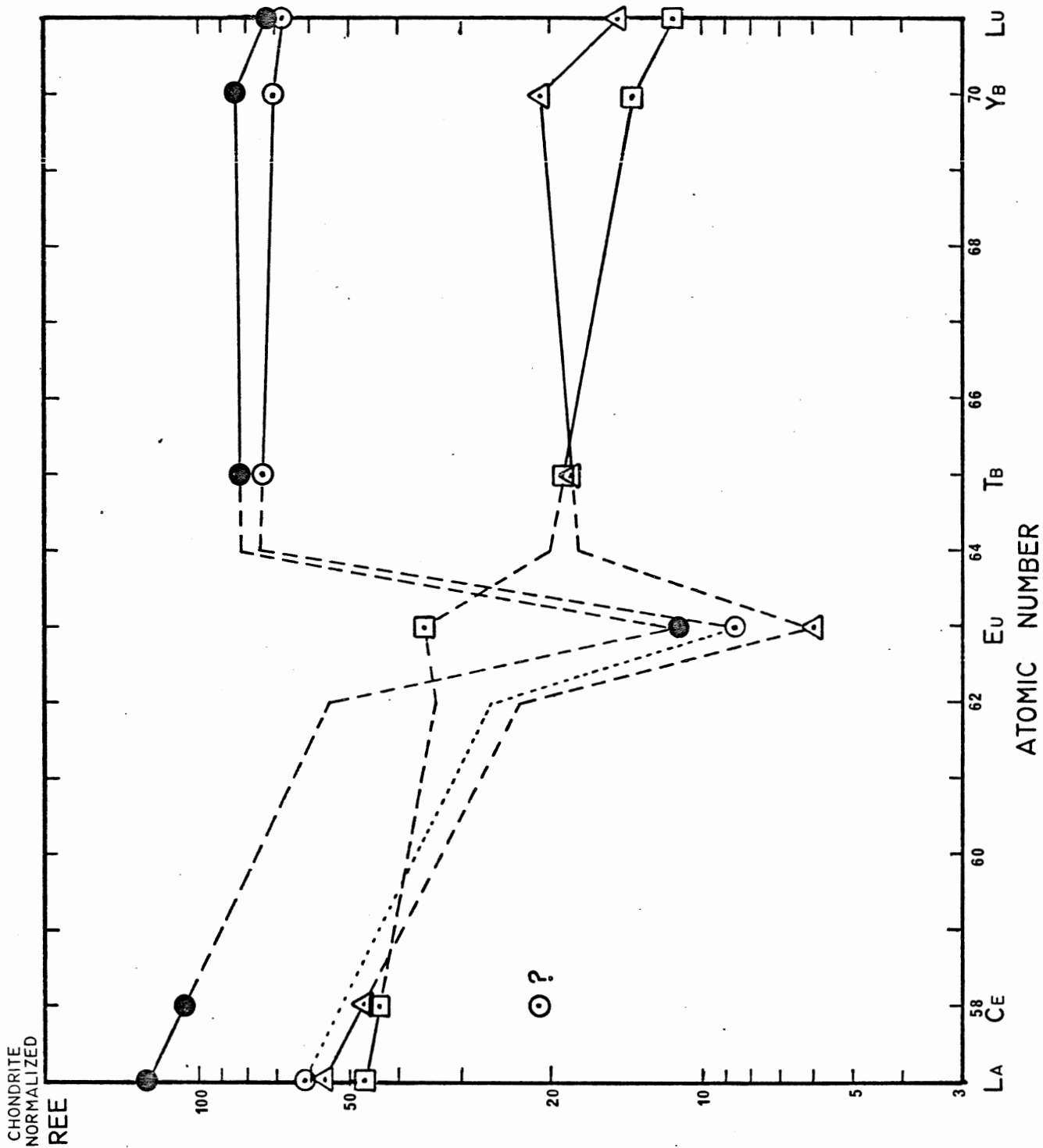|	
La	0.330 ± .013
Ce	0.88 ± .01
Eu	0.069 ± .001
Tb	0.047 ± .001
Yb	0.200 ± .007
Lu	0.034 ± .002

1. Values are from Frey et al. (1968)

Fig. 9 Rare-earth element distribution patterns. Normalized REE
values use chondritic values from Table 9.

preferentially in the crystalline plagioclase phase. Eu may substitute

for Ca^{2+} in plagioclase, when it is reduced to Eu^{2+} by redox conditions

in the magma (the ionic radius of Eu^{2+}, 1.12 $\overset{o}{A}$, is similar to that

of Ca^{2+}, 0.99 $\overset{o}{A}$). The solid/liquid distribution coefficient, Do, for

europium is a measure of this property: 0.5 to 5.0 (Schnetzler and

Philpotts, 1970).

There seem to be three possible explanations for the presence of

negative europium anomalies. The first,involves partial melting

of a source rock, in which plagioclase remains in a refractory residuum.

The second suggestion is simple, but extensive,plagioclase fraction-

ation; and the third possibility, proposed by Beeson and Goles (1968,

p. 339), is a "multi-stage process in which transport of Eu-depleted

rare earths along with,and complexed by,volatile components is re-

sponsible for these and other observed Eu anomalies". This latter

hypothesis merely shifts the problem to the origin of the original

"Eu-depleted rare earths".

The writer believes the Arisaig suite, spilite-rhyolite-ignimbrite,

is related by fractional crystallization. Being at opposite ends of a

differentiation trend, the spilite and rhyolitic samples could show

complementary patterns, if fractional crystallization is the process

relating them. Figure 9 shows that this is possible. The slight

positive europium anomaly of the spilite pattern is due to the presence

of an excess of feldspar phenocrysts, removed from the parent magma.

This subtraction of plagioclase results in negative europium anomalies in the later fraction and so will characterize rocks crystallized from it.
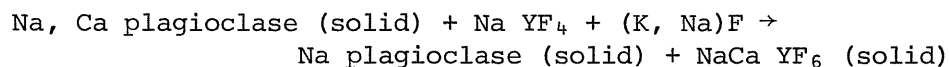
To evaluate the role of fractional crystallization of a magma, experimental models have used REE distribution patterns (e.g. O'Nions and Clarke, 1972). In this case, however, the lack of control points (especially Sm and Gd, on either side of Eu) and the anomalous Ce value for one of the samples renders such a test highly questionable.

Haskin et al. (1966) report that Russian experiments with REE distribution patterns of alkaline massifs with $((Na+K) < Al)_{mol}$ have shown that these massifs tend to concentrate the heavy REE toward the end of magmatic differentiation, while the opposite was true for those with $((Na+K) > Al)_{mol}$. Similarly, the Arisaig ignimbrites and rhyolite, with $((Na+K) < Al)_{mol}$, are enriched in the heavy rare earths relative to the more basic sample.

A measure of this tendency would be the $^{La}/Yb$ ratios: spilite, 5.54; rhyolite, 4.45; ignimbrites, 2.47 and 1.42. These ratios suggest increasing relative enrichment of the heavy rare-earth elements.

Mineyev (1936) associated this trend with high volatile content. He proposed that REE fractionation is caused by migration of REE in the form of complex alkali fluorides, coupled with regular variation in the acidity of postmagmatic solutions. For instance, with albitiza-tion, the sodium ion in the solution would be used up forming plagio-

clase and would cause precipitation of the insoluble, complex fluorides:

$$Na, Ca \text{ plagioclase (solid)} + Na\ YF_4 + (K, Na)F \rightarrow$$
$$Na \text{ plagioclase (solid)} + NaCa\ YF_6 \text{ (solid)}$$

The weakest, light REE complexes would dissociate first, so the residual solution would become relatively enriched in the heavier REE.

Haskin et al. (1966) notes that this could provide a plausible method for deriving a heavy REE-enriched (relatively) pattern from that of a silicate melt which is characteristically enriched in the light REE.

As rhyolites and particularly, ignimbrites are associated with high volatile contents, the process described by Mineyev could apply to the Arisaig samples.

V.   Vertical Variation Within One Flow Unit

Investigation of vertical variation within one flow unit has been investigated in unit id. Sample 3 was collected approximately 1 metre from the bottom of the flow; sample 5, approximately 7 metres from the bottom; sample 6, approximately 1 metre from the top. Total thickness of unit id, in this area, is estimated to be 18 metres.

The AFM diagram (Fig. 10) reveals a distinct trend of iron en-richment towards the bottom of the flow, coupled with alkali depletion. It is believed that the variation is due to post-extrusion processes, rather than any original variation within the magma itself, particularly
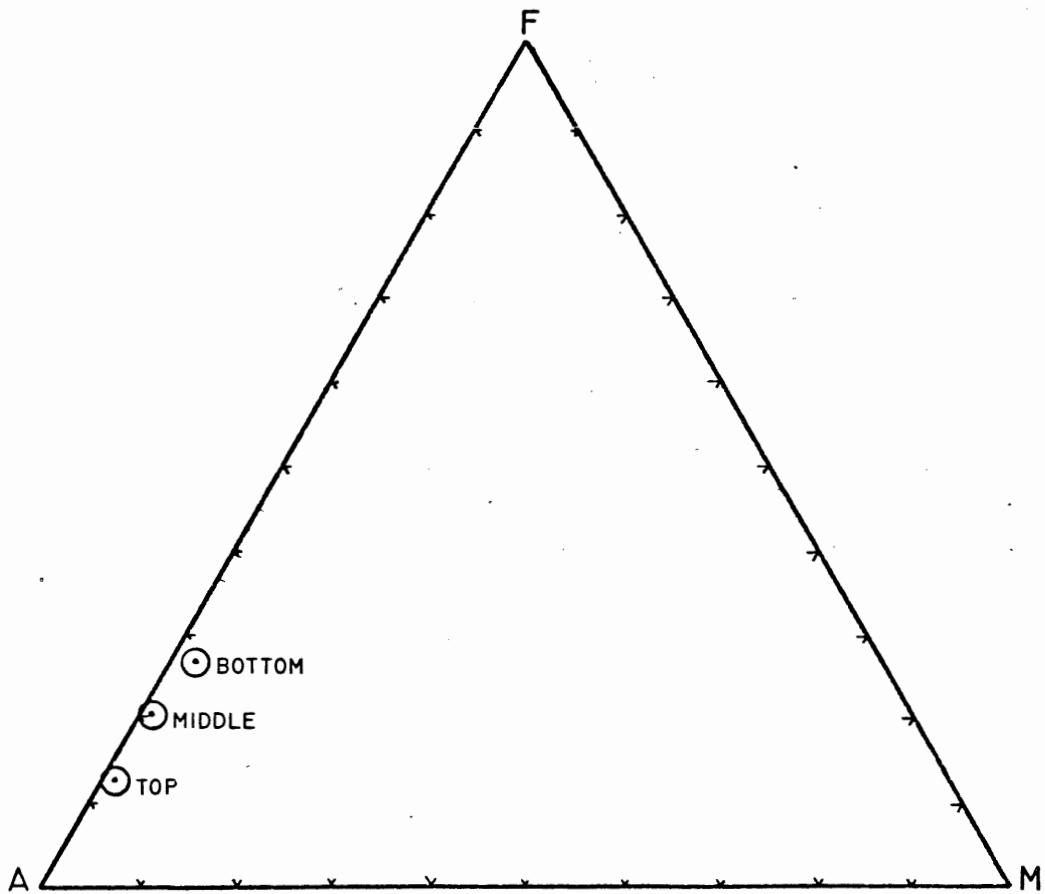
Fig. 10   AFM diagram showing vertical variation within ignimbrite, id.

as the ignimbrite is quite thin (18 metres) and is of Ordovician age.

A combination of alkali leaching and oxidation of iron by per-
colating fluids probably accounts for the variation. The bottom unit
is much more susceptible to these processes as a result of its un-
consolidated nature, than are the upper units. Iron oxides, mostly
hematite, fill joints and small voids, and coat glass shards and
phenocrysts in the more porous lower zone.

Gravity could be proposed as a factor, with the heavier mafic
minerals and lithic fragments settling to the bottom. However, the
effect of gravity is severely limited by the rapid cooling of the
ignimbrites.

Lipman and Christiansen (1964) found little chemical variation in
a thin, simple cooling unit of the Piapi Canyon Formation in Nevada.
They concluded the ignimbrite lost most of its deuterically active
fluid by evaporation into the atmosphere or much of its original heat
during transportation before welding.

Scott (1966) attributed vertical chemical variation within
ignimbrites of the Grant Range, Nevada, to deuteric alteration and
weathering. The units he studied varied in thickness, due to topo-
graphy, but were greater than 60 metres.

VI. Lateral Variation Within One Flow Unit

Two pairs of samples from ignimbrite id have been studied for
indications of lateral variation. Samples 5 and 7 were each collected

about 7 metres from the bottom of the unit; sample 7, approximately 107 metres west of sample 5. Similarly, samples 4 and 6 were each taken approximately 1 metre below the top of unit id; sample 4, about 100 metres west of sample 6.

There does not seem to be any regular variation along the unit. For a comparison, see Table 10. Presence of both positive and negative percentage differences indicates that any variation is random.

Scott (1966), in a study of the chemical variations within ignimbrite sheets of east-central Nevada, also could not recognize any lateral trends.

VII.   Variation Between Flow Units

Samples 1, 4, and 9 were taken approximately 1 metre from the tops of flow units ie, id, and ic, respectively.

The AFM diagram (Fig. 11) illustrates the variation between these units. The trend is not due to an enrichment in alkali content, but rather a depletion of $(FeO+Fe_2O_3)$ and MgO. The (Na_2O+K_2O) values are given, to show their consistency.

The points may describe an increasingly fractionated liquid. The trend of a fractionated calc-alkaline suite, as determined by Nockolds and Allen (1953), is included in the AFM diagram to show the similarity.

Table 10

Lateral Variation Within Ignimbrite "id",

Expressed as Percentage Difference from West to East.

Element	First Pair[1] West − East (%)	Second Pair[2] West − East (%)
SiO_2	+0.01	−0.02
TiO_2	−0.02	+0.01
Al_2O_3	−0.29	+0.86
Fe_2O_3	−0.09	0
FeO	−0.50	0
MnO	+0.94	0
MgO	+0.67	−0.25
CaO	−0.39	+0.18
Na_2O	0	+0.06
K_2O	+0.25	−0.20
P_2O_5	−1.0	0
H_2O^+	−0.04	0
H_2O^-	+0.22	−0.22

1. First pair consists of ignimbrite samples 5 and 7.

2. Second pair consists of ignimbrite samples 4 and 6.

Data for the Arisaig points are as follows:

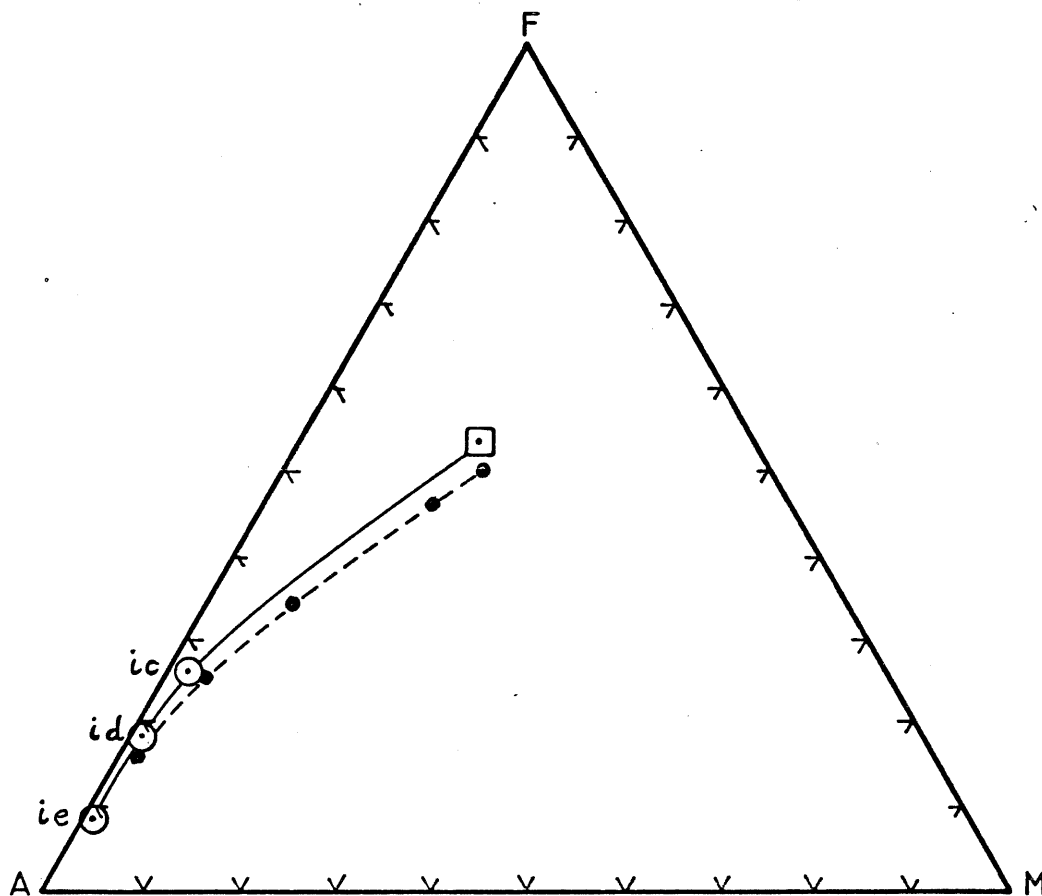|	Spilite	Ignimbrites *ic* / 9	*id* / 4	*ie* / 1
Na_2O+K_2O	7.53	7.44	8.49	7.80
Fe_2O_3+FeO	14.75	2.77	2.03	0.81
MgO	4.64	0.11	0.07	0.04

Fig. 11 AFM diagram showing variation between flow units ic, id, and ie. ● = points on the calc-alkaline trend, from Nockolds and Allen (1953).

Chapter 4

Discussion and Conclusions

The spilite-rhyolite-ignimbrite suite at Arisaig has been sub-
jected to low-grade regional metamorphism. It is proposed that the
sample from the outcrop previously called "andesite" should actually
be termed a spilite, formed as a result of greenschist facies metamor-
phism of basaltic lava, with introduction of sodium from seawater and
the leaching of overlying silicic volcanics.

Chemically, the ignimbrites are rhyolitic in composition and have
been subjected to deuteric oxidation, deuteric reaction with fluids,
devitrification, and weathering, in addition to metamorphism. The
effects of these processes account for most of the vertical chemical
variation within individual flow units, especially as they are quite
thin. No regular lateral variation, both within and between ignim-
brites, was recognized.

However, in spite of the alteration processes that have been
active, there is still chemical variation within the suite which con-
forms to the expected original chemical trends.

The silica values increase from spilite to rhyolite to ignimbrite,
with a corresponding decrease in alumina. Similarly, the titanium,
total iron, manganese, magnesium and calcium values decrease from basic
to silicic samples. The K/Na ratio increases with increasing silica
content, as expected, but cannot be relied upon, as the alkalies have

certainly been involved in post-extrusion alteration processes.

The trace element plots also show possible fractionation trends, with Ta, Hf, Th, and Ba enriched in the rhyolitic samples, relative to the spilite. Sc and Cr, being ferromagnesian in character, are more abundant in the spilite.

The absolute abundance of REE increases from spilite to rhyolite to ignimbrite.

These trends may all be attributable to original, igneous chemical variation.

There is a problem, however, in explaining the extrusion of a basic lava, followed by such silicic volcanics, with no associated intermediate members. Three possible working hypotheses are presented below.

Yoder (1969) shows experimentally that basaltic and rhyolitic magmas could be maintained separately in a magma chamber, and he proposes a partial-melting hypothesis for the generation of two contrasting, homogeneous liquids from a common parental source rock, without producing liquids of intermediate composition. Yoder notes that the volume of a single eruption would rarely exceed 2 cubic kilometres. So, for small occurrences, such as at Arisaig, of basalt-rhyolite, this tentative model might work.

An hypothesis which has been used to explain many ignimbrite occurrences (e.g. Taupo volcanic zone, New Zealand), is that of contact

anatexis, where heat brought up by ascending basalt may determine melting of sialic material.

The presence within the rhyolitic volcanics of two distinct feldspar types, albite and orthoclase, suggests that the Arisaig ignimbrites belong to the category proposed by Carmichael (1963, p. 126) of either (1) a basaltic magma contaminated with sialic material which fractionates to produce a potassic acid liquid; or (2) direct sialic fusion. The high strontium isotope ratios support the crustal contamination model.

However, chemically, the suite conforms broadly to the conventional model of differentiation of a series of increasingly alkaline and siliceous melts possibly from some sort of parent tholeitic basalt. As only a very limited section is exposed, the intermediate members may well be expected to occur. The major element variation trends and trace element plots, which provide support for this hypothesis, have been discussed above. Also, the complementary REE patterns of the spilite and rhyolitic samples may be attributed to fractional crystallization.

The age (Middle-Late Ordovician) and character of the volcanic suite (the acidic rocks being typical of convergent plate margins), suggest that they are associated with the development of a volcanic arc system during the opening of the Paleozoic Atlantic. The closing of the marginal ocean basin between the North American continent and

the Avalon micro-continent corresponds to the Taconian Orogeny.

In summary, the analyses of nine ignimbrite samples, one rhyolite, and one spilite sample from the Arisaig volcanics have lead to these conclusions:

(1) The suite has been subjected to low-grade regional metamorphism, probably to greenschist facies.

(2) The previously-termed andesite is, in fact, a spilitized basalt.

(3) Vertical chemical variation within each ignimbrite is a result of post-extrusion processes.

(4) No regular lateral trends are apparent.

(5) The chemistry of the volcanic suite favours an origin by fractional crystallization of a basaltic magma, probably associated with the Taconian Orogeny.

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Appendix A

Hand Specimen Descriptions

Note: All sample locations may be found in Fig. 2.
       All analyses are given in Table 4.

<u>Sample 1</u>; Field No. 14-10 A (T); collected May 14, 1977

General Characteristics: massive; pink-brown; dense; flinty with

    irregular and conchoidal fractures; numerous inclusions.

Components: impossible to identify individual components of ground-

    mass in hand specimen; 5-10% lithic fragments and fiamme.

Texture: pyroclastic rock that is flinty with a dull sheen; thin

    (< 1 mm) reaction rims surround xenoliths and iron oxide grains

    in cryptocrystalline, felsitic groundmass.

Inclusions: elongated pumice fragments, or fiamme (maximum measured

    2 mm x 2 cm), are coarser-grained with anhedral quartz crystals,

    iron oxides, and epidote readily visible; rim surrounding fiamme

    is deep red and glassy; fiamme are elongated in one direction,

    giving the rock a eutaxitic texture; small spilite (?) xenoliths

    (maximum measured: 3 x 4 mm) are also present, surrounded by

    pink-red rims.

Weathered Surface: buff-coloured with iron-staining; maximum thickness

    of buff-coloured layer is 3 mm.

Aggregate Composition: salic

Identification: ignimbrite

Sample 2; Field No. 14-11B (M); collected May 14, 1977

General Characteristics: massive, deep red-brown; dense ; sharp;

   irregular fractures with slight conchoidal characteristic;

   inclusions common.

Components: impossible to identify individual components of ground-

   mass in hand specimen; various inclusions make up 5-10%; black

   specks, barely visible with hand lens (iron oxides?) 10%

Texture: pyroclastic rock with xenoliths, amygdules, and iron oxide

   specks in cryptocrystalline groundmass; fiamme are elongated in

   one preferred direction, resulting in a eutaxitic texture;

   reaction rims (approximately 0.5-2 mm) surround xenoliths.

Inclusions: fiamme: maximum dimensions, 3 mm x 6 cm; quartz crystals

   up to 1.5 mm are readily visible. Reaction rim is dark cherry-

   red; two xenoliths (3 x 3 mm) in this specimen appear to be of

   earlier ignimbrite; reaction rims (1 mm) surrounding xenoliths

   are dark, almost black; cavities exposed in this specimen are

   filled with euhedral quartz crystals.

Weathered Surface: buff-colour to a depth of 2 mm with a very thin

   (<< 1 mm) light green coating, possibly epidote.

Aggregate Composition: salic

Identification: ignimbrite

Sample 3; Field No. 12-6B (B); collected May 12, 1977

General Characteristics: massive, deep purple-red; dense; sharp,

   irregular fractures, many with conchoidal characteristics; few

   inclusions

Components: impossible to identify individual components of ground-
mass in hand specimen; inclusions, approximately 5%.

Texture: flinty rock with various inclusions within cryptocrystalline
groundmass; deep cherry-red reaction rims (approximately 1 mm)
surrounding xenoliths and fiamme are elongated in one preferred
direction.

Inclusions: fiamme dimensions; maximum measured 4 mm x 2 cm; crystals
of quartz are visible (< 1 mm); small lithic fragments (2 x 2 mm)
appear to be basaltic (spilite?).

Weathered Surface: fracture surface shows yellow to red iron staining.

Aggregate Composition: salic

Identification: ignimbrite

Sample 4; Field No. 12-6B (T); collected May 12, 1977.

General Characteristics: dense; massive; purple-red; irregular
fractures, some showing conchoidal characteristics; occasional
lithic fragments present.

Components: impossible to identify individual components of ground-
mass in hand specimen; inclusions make up less than 1%.

Texture: cryptocrystalline groundmass with lithic fragments and
narrow (maximum: 0.5 mm) quartz veins cutting specimen in random
directions; reaction rims are not visible in hand specimen.

Inclusions: lithic fragments are of flow-banded rhyolite and basalt
(spilite?); maximum dimensions: 1 cm x 6 mm.

Weathered Surface: buff-colour to a depth of 4 mm; surface has a
micaceous sheen.

Aggregate Compositiion: salic

Identification: ignimbrite

Sample 5; Field No. 9-5C; collected May 9, 1977.

General Characteristics: massive; purple-red; dense; sharp, irregular
fractures; numerous inclusions and occasional amygdules.

Components: impossible to identify individual components of ground-
mass in hand specimen; inclusions make up 5%.

Texture: pyroclastic rock with xenoliths and small iron oxide grains
within cryptocrystalline groundmass; surrounded by thin (<< 1 mm)
reaction rims; two narrow (0.5 mm) quartz veins cut this sample;
fiamme are elongated in one common direction.

Inclusions: maximum dimensions of fiamme: 1 mm x 3.5 cm; small
dark grains (maximum 1 x 2 mm) surrounded by pink rim (<< 1 mm)
appear to be iron oxide; two amygdules of epidote and a clay
mineral are present (maximum 3 x 4 mm).

Weathered Surface: slickensiding with epidote and iron staining on
surface.

Aggregate Composition: salic

Identification: ignimbrite

Sample 6; Field No. 8-3B (T); collected May 8, 1977.

General Characteristics: light brown to buff-coloured; massive; dense;
sharp, irregular fractures, some with conchoidal characteristics.

Components: impossible to identify individual compoents of groundmass
     in hand specimen; inclusions 5-10%.

Texture: cryptocrystalline groundmass with few lithic fragments,
     surrounded by large reaction rims (up to 1 cm).

Inclusions: maximum dimensions of fiamme: 2 mm x 1.5 cm, elongated
     in one preferred direction; thin reaction rims (< 1 mm) are
     present; a large (1.2 x 1 cm) lithic fragment is exposed by
     weathering, with a reaction rim that grades from off-white to dark
     brown away from the fragment. The fragment now contains hematite
     and epidote.

Weathered Surface: thin (< 1 mm) pink to buff-coloured coat with black
     dendritic patterns of iron oxide on the surface.

Aggregate Composition: salic

Identification: ignimbrite

Sample 7; Field No. 14-9F; collected May 14, 1977.

General Characteristics: deep purple-red; massive; dense; few small
     lithic fragments; one quartz vein (1.5 mm wide) cuts the specimen;
     irregular fractures, some conchoidal.

Components: impossible to identify individual components within the
     groundmass; inclusions make up less than 1%.

Texture: cryptocrystolline groundmass with few lithic fragments, sur-
     rounded by thin reaction rims (< 1 mm) of iron oxides; no linear
     orientation is discernible.

Inclusions: the small lithic fragments (maximum dimensions: 2 x 2 mm)
     are hard to identify, probably basalt and laterite grains; no
     fiamme are exposed.

Weathered Surface: buff-coloured layer approximately 1 mm thick; dendritic iron oxide pattern on the surface; a thin (<1 mm) coat of hematite is visible on one fracture surface.

Aggregate Composition: salic

Identification: ignimbrite

Sample 8; Field no. 11-2; collected May 9, 1977

General Characteristics: deep purple-red; massive; sharp, irregular fractures; many irregular inclusions and many minute (<< 1 mm) quartz veins are present.

Components: impossible to identify the individual components within the groundmass; inclusions make up 15-20%.

Texture: abundant lithic fragments, surrounded by thin (< 1 mm) iron oxide reaction rims, are set in a cryptocrystalline groundmass. No preferred orientation is apparent.

Inclusions: the lithic fragments measure up to 2 x 1 cm, and consist of pumice, basalt (spilite), rhyolite and earlier ignimbrites; no fiamme are visible.

Aggregate Composition: salic

Identification: ignimbrite

Sample 9; Field No. 11-1; collected May 11, 1977.

General Characteristics: massive; dense; deep purple-red; sharp, ir-regular fractures, some with conchoidal characteristics; fiamme and lithic fragments are common; one amygdule is visible.

Components: impossible to identify individual components within the groundmass; inclusions make up 5-10%.

Texture; inclusions, surrounded by cherry-red reaction rims (1-2 mm), are common within a cryptocrystalline groundmass; the fiamme are flattened and elongated, resulting in a eutaxitic texture.

Inclusions: maximum dimensions of fiamme: 2.5 mm x 2.5 cm; quartz crystals within the fiamme occur up to 1.5 mm in length; the lithic fragments are generally basalt, rhyolite, and quartzite (?); only one cavity is visible in this specimen: the walls of the void (1.5 cm x 5 mm) are encrusted with euhedral quartz crystals.

Weathered Surface: thin (<< 1 mm) coat of hematite on fracture surface

Aggregate Composition: salic

Identification: ignimbrite

Sample S; Field No. A; collected May 13, 1977

General Characteristics: massive; dark gray; fine-grained; irregular fractures; occasional amygdules (maximum diameter in this sample, 2 mm).

Components: individual components are difficult to identify; feldspar laths barely visible with 10X hand lens, amount to approximately 50%; the remaining 50% consists of iron oxides, calcite, epidote and possibly amphibole.

Texture: aphyric, holocrystalline, slightly amygdaloidal.

Weathered Surface: iron-stained; thin (0.5 mm) light gray to red-brown layer.

Aggregate Composition: basic

Identification: basalt

Sample R; Field No. R; collected May 10.

General Characteristics: pink to buff-coloured with obvious banding: individual deep red to black bands, < 1 mm, grouped in bands up to 2 cm wide; fractures tend to follow banding; fracture surfaces across banding are irregular, whereas fracture surfaces that follow banding are smooth, occasionally showing slickensiding; iron staining may be present on some surfaces.

Components: 50% feldspar; 40% quartz; 10% oxides (hematite lens, 1 mm thick, 3 cm long) and micaceous flakes along slickensides.

Texture: flow structure is the most obvious textural feature, consisting of dark bands within buff-coloured felsic mass; the very fine-grained to aphanitic dark bands appear glassy; minute anhedral quartz grains and micaceous flakes are the only positively identifiable grains.

Inclusions: occasional lithic fragments are present: maximum size, 3 x 2 mm; they appear to be basaltic; there are also fragments that are less dense and more coarsely-grained, predominantly quartz; these are possibly pumice fragments.

Aggregate Composition: salic

Identification: rhyolite

Appendix B

Thin Section Descriptions

Sample 1; field no. 14-10A (T): ignimbrite (flow ie): devitrified, microcrystalline groundmass with inclusions up to 4 mm long, representing small pumice fragments which have been flattened and stretched into one preferred direction.

The groundmass is felsitic, consisting mainly of quartz and alkali feldspar, with iron oxides, chlorite, sericite, calcite, epidote, and possibly biotite and zircon. Hematite specks give the section its red-brown colour. The sample is cut by a narrow (0.2 mm) quartz vein. In one area, a cavity (3 x 1 mm) seems to have been filled with a clay mineral and a dark halo, resulting from the displacement of iron oxides, surrounds it. Lenses representing flattened pumice fragments consist of anhedral medium-grained quartz with small magnetite grains. Some chlorite and zircons were also identified.

Sample 2; field no. 14-11B (M): ignimbrite (flow ie): devitrified, microcrystalline mass with red-brown hue.

The groundmass consists of quartz and alkali feldspar, showing a preferred orientation, with magnetite grains and hematite dust. Minor chlorite, sericite, epidote and zircons were tentatively identified. The section includes

a large cavity (8 x 5 mm) filled with a pale green clay
mineral, and surrounded by iron oxide granules. (Plate I).

Sample 3; field no. 12-6B (B): ignimbrite (flow id): pumice fragment
and lithic fragment within a cryptocrystalline groundmass.

Devitrified groundmass constituents are unresolvable, ex-
cept for presence of hematite dust and black opaque grains.
Large pumice fragment (20 x 5 mm) has deep red-brown colour
and consists basically of euhedral quartz crystals with
finely disseminated hematite, chlorite, magnetite, and
epidote. (Plate II).

Sample 4; field no. 12-6B (T): ignimbrite (flow id): devitrified
micro-cryptocrystalline groundmass, showing relict eutaxitic
structure.

The section consists mostly of an unresolvable mass of
quartz/alkali feldspar crystals and hematite dust, resulting
in its deep red-brown colour. Microcrystalline patches of
quartz/feldspar are bent and stretched in one preferred di-
rection. The section is cut by stringers of quartz, with
chlorite and iron oxides. (Plate III).

Sample 5, field no. 9-5c: ignimbrite (flow id): red-brown, crypto-
crystalline mass, cut by small quartz and calcite veins.

Constituents of the cryptocrystalline groundmass are un-
identifiable, but presence of hematite dust is evident by

its colour. There are areas of fine-grained quartz and/or feldspar that have the same orientation as the one flattened pumice fragment (10 x 0.5 mm). The fragment consists mostly of medium-grained quartz with iron oxide grains, chlorite, and sericite. At one end of the fragment the quartz/feldspar light areas of the matrix are bent around it. (Plate IV).

Sample 6; field no. 8-3B (T): ignimbrite (flow id): devitrified microcrystalline mass with one flattened pumice fragment, or fiammé, and one foreign lithic clast.

Granophyre of quartz and alkali feldspar generally shows no flattening of grains or elongation of crystals, except one area near the lithic clast. Here, the quartz/feldspar grains are flattened and bent around one corner of the clast, which consists of quartz, chlorite, and a clay mineral. Fine hematite dust gives the slide its light red-brown colour. (Plate V).

Sample 7, field no. 14-9F: ignimbrite (flow id): devitrified micro-crystalline mass with light red-brown hue.

The section consists mainly of microcrystalline quartz and feldspar with finely disseminated hematite lending its colour to the sample. Minor amounts of chlorite, sericite, and magnetite were observed. Two small (3 x 0.4 mm) flattened pumice fragments were included and several thin quartz and calcite stringers cut the section. (Plate VI).

Sample 8; field no. 11-2: ignimbrite (flow ic): devitrified micro-
crystalline to cryptocrystalline mass.

The section is essentially felsitic quartz and alkali
feldspar with finely disseminated hematite. Chlorite,
sericite and magnetite have also been identified. The
section is cut by a narrow (0.2 mm) quartz vein, with areas
of calcite within it. A faint, preferred orientation within
the quartz and feldspar matrix is visible. (Plate VII).

Sample 9; field no. 11-1: ignimbrite (flow ic): flattened and
elongated pumice fragment (20 x 2 mm) within a devitrified,
microcrystalline groundmass.

The groundmass is essentially quartz and alkali feldspar
in a granophyric texture, with finely disseminated hematite,
resulting in a deep, red-brown colour. Other minerals
tentatively identified within the matrix are chlorite,
sericite, magnetite and calcite. Small veins, larger quartz
and feldspar crystals, and patterns of the hematite dust
suggest a lineation concordant with the fiamme. The pumice
fragment itself consists of coarse, subhedral quartz grains
with radial growths of an undetermined mineral, probably
quartz, coated with iron oxide grains. Interstitial chlorite,
sericite, calcite, and zircons were also identified.
(Plate VIII).

Sample S; field no. A: spilite: holocrystalline; fine to medium-
grained; euhedral; glomeroporphyritic.

Clusters of euhedral albite (?) phenocrysts, with some
sericitization, are found in a fine-grained, pilotaxitic
groundmass mainly of small feldspar laths and opaques with
some epidote and chlorite. Two small (0.3 mm) calcite
nodules are present (Plate IX).

Sample R; field no. R: rhyolite: devitrified; holocrystalline;
fine-grained; spherulitic.

Spherulites of microcrystalline quartz and alkali feldspar
are dominant. The devitrified matrix consists of quartz,
alkali feldspar, hematite, magnetite, chlorite, and sericite.
Hematite specks rim some spherulites. The section is cut
by several veins of quartz with iron oxides. Banding is
observed as a result of areas with higher amounts of iron
oxides. Also, bands of closely packed spherulites alter-
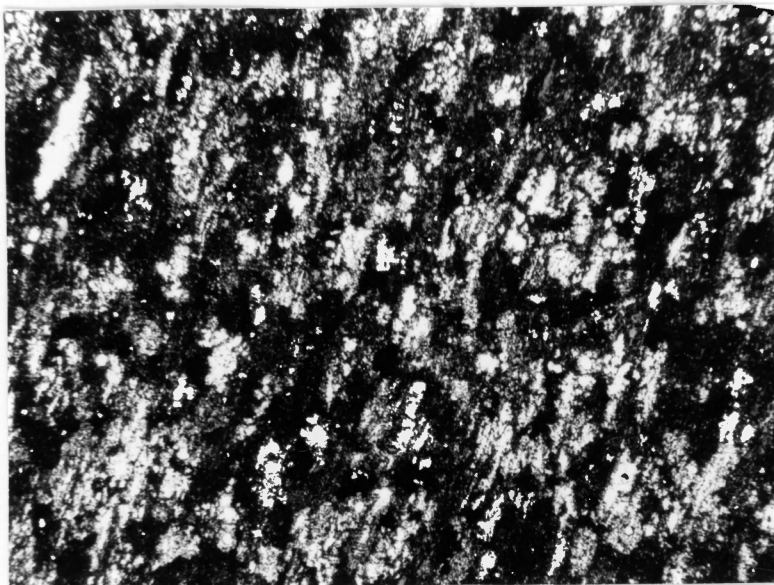nate with the felsitic matrix. (Plate X).

Plate I.   Lab no. 2; field no. 14-11B (B); (x 2.5, crossed polars).
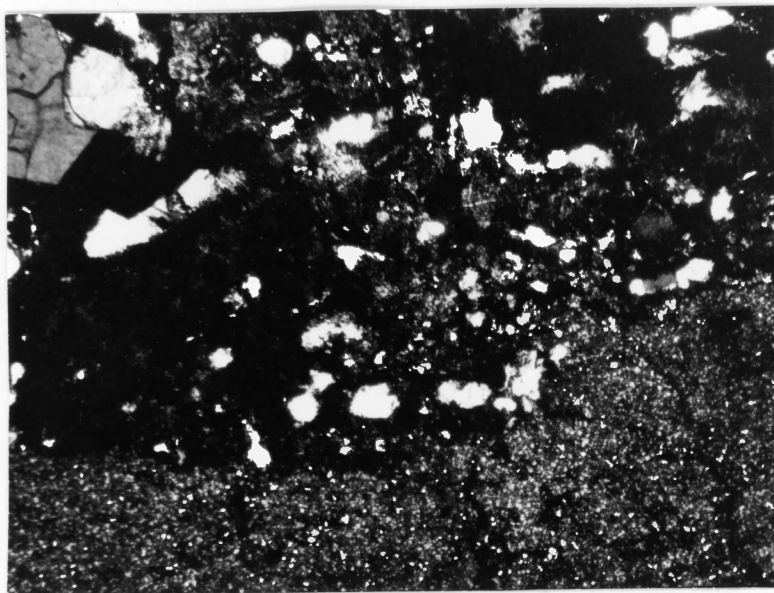Devitrified groundmass of ignimbrite from flow ie.

Plate II.   Lab no. 3; field no. 12-6B (B); (x 2.5, crossed polars).
Boundary between devitrified groundmass and fiamme in
ignimbrite from flow id. Note subhedral quartz crystal
in the lower right hand corner.
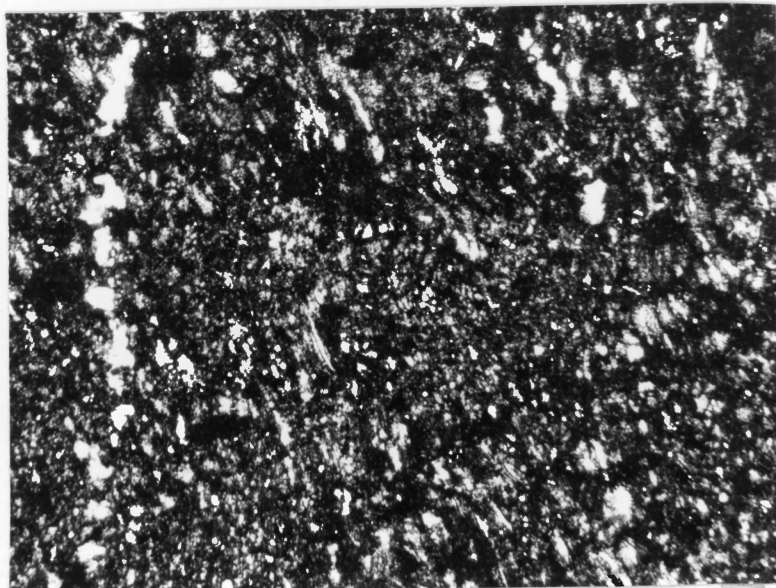
Plate III.   Lab no. 4; field no. 12-6B (T); (x 2.5, crossed polars).
             Devitrified groundmass of ignimbrite from flow id.
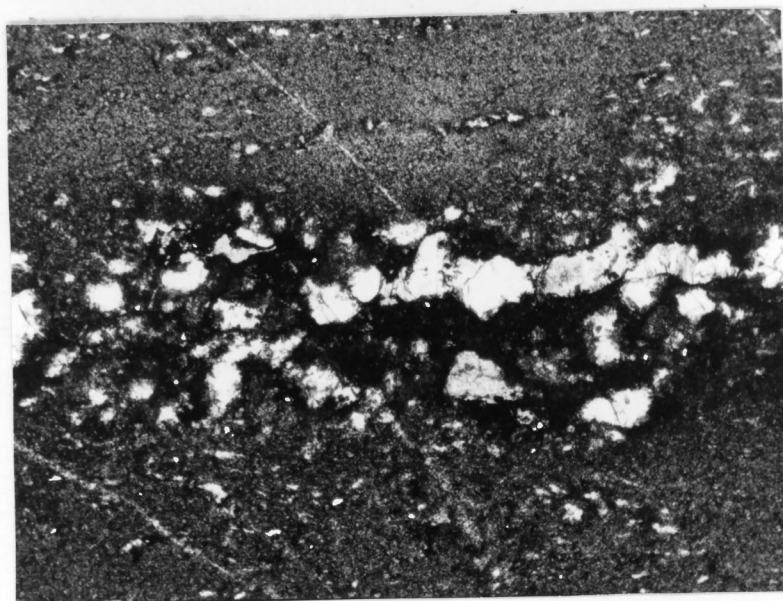

Plate IV.   Lab no. 5; field no. 9-5c; (x 2.5, plane polarized light).
             Fiamme within ignimbrite from flow id. Note the coarse
             vapour phase crystallization within the fiamme, compared
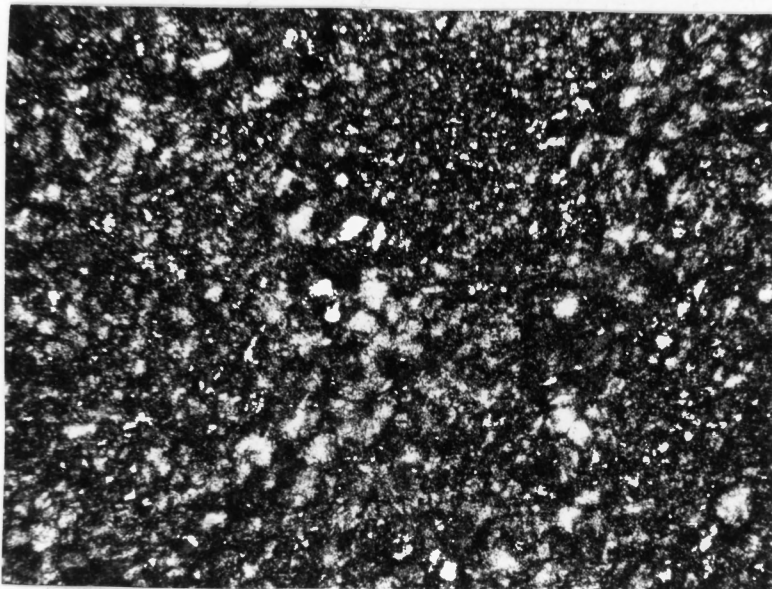   with the microcrystalline devitrified groundmass.

Plate V.   Lab no. 6; field no. 8-3B(T); (x 2.5, crossed polars).
           Devitrified groundmass of ignimbrite from flow id.
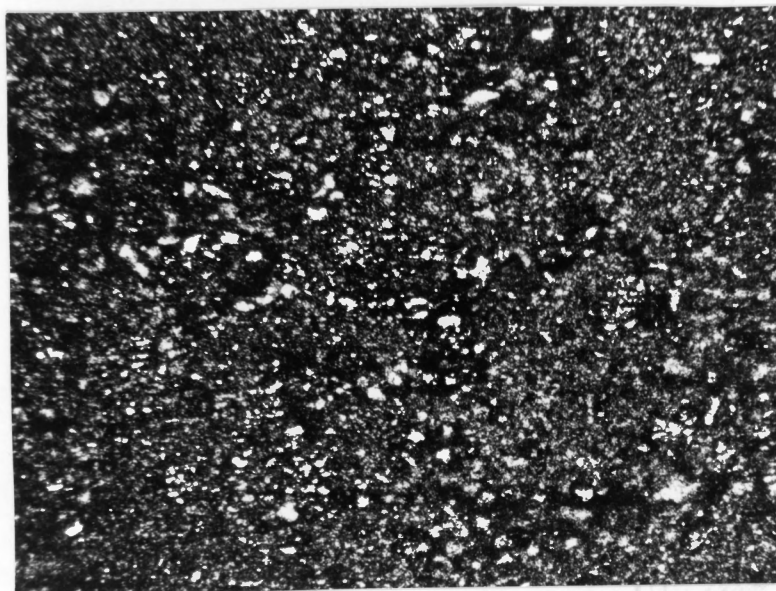

Plate VI.   Lab no. 7; field no. 14-9F; (x 2.5, crossed polars).
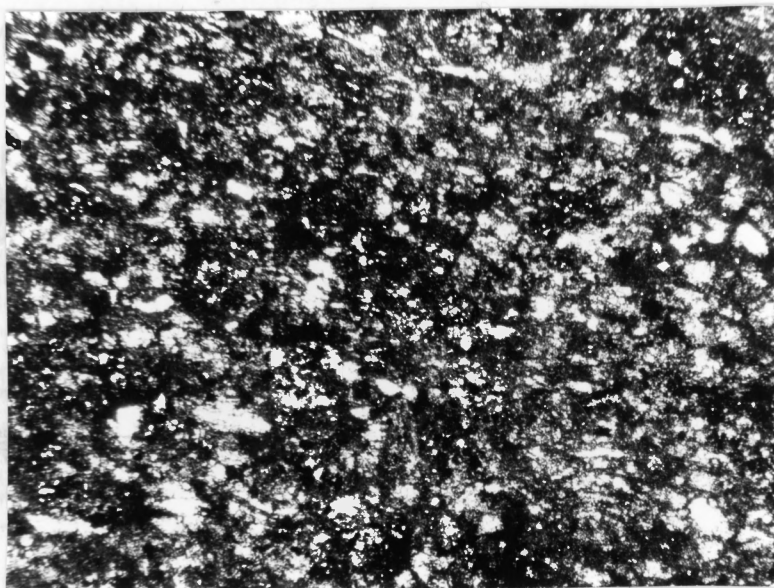   Devitrified groundmass of ignimbrite from flow id.

Plate VII.   Lab no. 8; field no. 11-2; (x 2.5 crossed polars).   De-
vitrified groundmass of ignimbrite from flow ic.
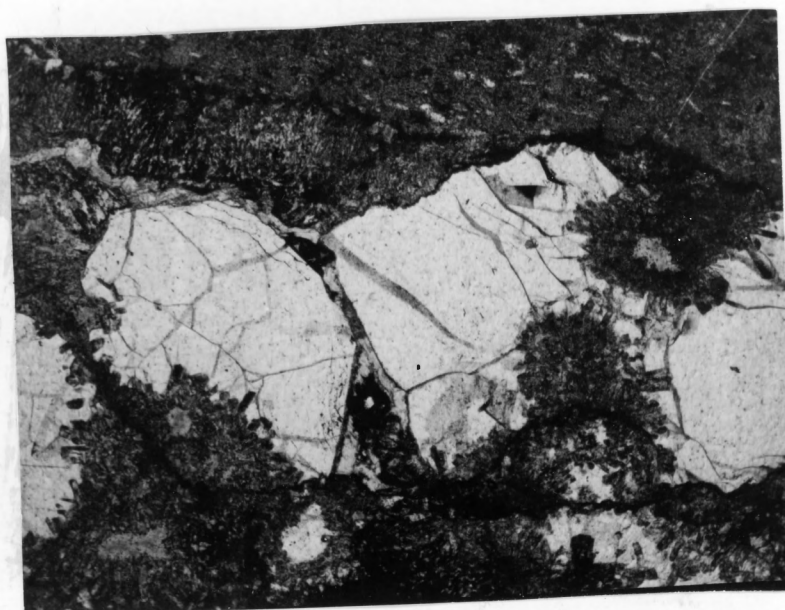
Plate VIII.   Lab no. 9; field no. 11-1; (x 2.5, plane polarized light).
Part of fiamme within ignimbrite from flow ic. Note the
coarse vapour phase crystallization within the fiamme,
compared with the microcrystalline groundmass in the
upper portion of the photomicrograph.

Plate IX.   Sample no. R; (x 2.5, crossed polars).   Spherulitic
            rhyolite.

Plate X.   Sample no. A; (x 2.5, crossed polars).   Spilite.   Feldspar
           phenocrysts within pilotaxitic groundmass.

Appendix C

Analytical Methods
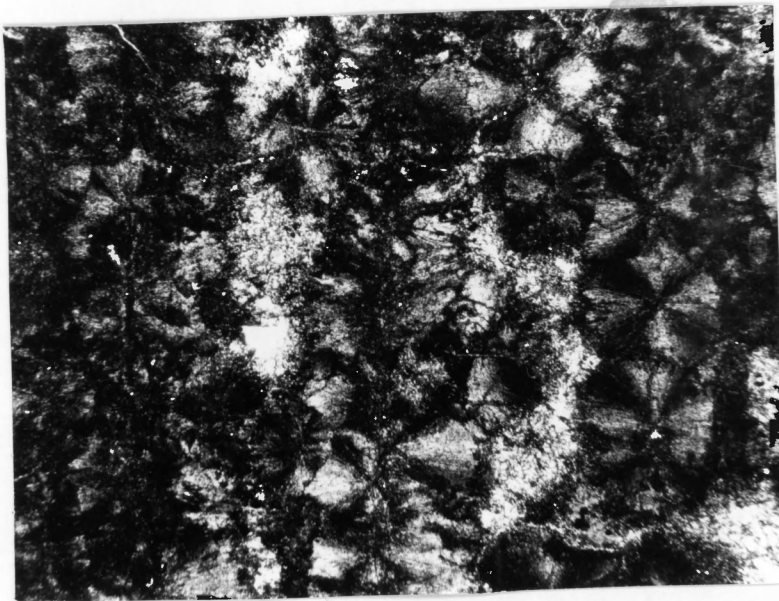
I. Sample Preparation:

Samples were washed and scrubbed with a nylon-bristled brush, rinsed with distilled water, then broken into approximately 2 centimetre cubes, using an hydraulic rock splitter. Weathered surfaces were discarded. The cubes were then reduced to pea-sized pieces with a ceramic-plated jaw crusher. These pieces were ground to -100 mesh size in a tungsten carbide swing mill and the resulting powders were split, using a linear trough splitter.

II. Major Elements:

1. Silica: Silica was determined by fast neutron activation. Samples were irradiated for 30 seconds; delay time was 90 seconds; counting time was 200 seconds.

2. Aluminum, Total Iron (as Fe_2O_3), Sodium, Potassium, Calcium, Magnesium, Manganese, Titanium: These elements were determined by atomic absorption on the Perkin-Elmer Model 503 Spectrophotometer. A nitrous oxide-acetylene flame was used in the determination of aluminum, and an air-acetylene flame for the other elements. 0.5 gram rock powder samples were decomposed with 2.5 ml. nitric acid, 20 ml. of a 1:4 mixture of perchloric and hydrofluoric acid, heated, then 5 ml concentrated hydrochloric acid and 15 ml 5% boric acid were added, heated, then cooled to room temperature and diluted to 250 ml.

3. Ferrous Iron: Ferrous iron was determined by the Wilson Method (Jeffery, 1970, p. 270).

4. Ferric Iron: Ferric iron was obtained by subtracting ferrous iron from total iron (as Fe_2O_3).

5. Phosphorus: Phosphorus was determined on the Bausch and Lomb Spectronic 70 Spectrophotometer. Samples were prepared following the method outlined in Jeffery (1970, p. 367).

6. Total Water: Total water was determined by the Penfield Tube Method (Volborth, 1969), using the following flux: 2 parts lead dioxide: 1 part lead chromate: 1 part sodium tungstate.

7. Minus Water: Samples were weighed, then dried for two hours at 105°C and weighed again. The difference in weight is minus water.

8. Plus Water: Plus water was obtained by subtraction of minus water from total water.

9. Results for External Standards: The United States Geological Survey Standards G-2 (granite) and GSP-1 (granodiorite) were included in analysis of aluminum, iron, sodium, potassium, calcium, magnesium, manganese, titanium and phosphorus.

Standard USGS-G-2 (Wt%)

	Eames 1978	Abbey 1972	Flanagan 1972
Al_2O_3	14.62	15.33	15.40
Fe_2O_3	1.02	1.01	1.08
FeO	1.52	1.45	1.45
MgO	0.72	0.77	0.76
CaO	1.92	1.98	1.94
Na_2O	4.14	4.06	4.07
K_2O	4.53	4.49	4.51
TiO_2	0.49	0.48	0.50
MnO	0.035	0.04	0.034
P_2O_5	0.13	0.14	0.14
Total Fe (as Fe_2O_3)	2.53	2.67	2.65

Standard USGS-GSP-1 (Wt.%)

	Eames 1978	Abbey 1972	Flanagan 1972
Al_2O_3	14.23	15.18	15.25
Fe_2O_3	1.71	1.60	1.77
FeO	2.36	2.34	2.31
MgO	0.90	0.98	0.96
CaO	1.98	2.06	2.02
Na_2O	2.76	2.77	2.80
K_2O	5.38	5.50	5.53
TiO_2	0.64	0.65	0.66
MnO	0.04	0.04	0.042
P_2O_5	0.28	0.28	0.28
Total Fe (as Fe_2O_3)	4.05	4.26	4.33

III.   Rare-Earth Elements and Trace Elements;

1.   Method

Instrumental neutron activation analysis with high-resolution
lithium-drifted germanium detectors was used to determine the rare-
earth elements; La, Ce, Tb, Eu, Yb, Lu, and the trace elements, Ta,
Sc, Sb, Cs, Cr, Hf, Co, Ba, Th.

Approximately 0.1 grams each of two ignimbrite samples (lab
number 5 and lab number 8) and the spilite and rhyolite samples were
sealed in silica glass vials and irradiated at McMaster University
for twelve hours.

Two counts were made, using two Ge(Li) detectors. The first
count was taken three weeks after irradiation. Samples were counted
for two hours at a distance of one centimetre from the detectors.
Lanthanum, lutetium and barium were counted. The second count was
begun five weeks after irradiation. Samples were counted for five
hours, at a distance of one centimetre from the detector. Cerium,
terbium, europium, ytterbium, tantalum, scandium, antimony, cesium,
chromium, hafnium, cobalt, and thorium were counted.

2. Precision

Standard deviations of six duplicate AGV-1 samples for seven ele-
ments have been computed. Values for the other elements are in
preparation. However, standard deviations are generally 6% to 10%
(Jagam, personal communication).

Element	Standard Deviation (%)
Sc	2
Ce	5
Hf	4
Co	3
Eu	3
Lu	6
La	3

IV. Microprobe Analysis

1. Method

Analyses were carried out on the Cambridge Mark V Electron Microprobe. Polished thin sections were prepared in the standard manner. The Ortec Energy Dispersive System was used for all analyses except those of the niobium-rich oxides, which were run by Bob MacKay on the Wavelength System. Operating conditions were 15 KV at 15×10^9 amps. Spherulites in the rhyolite sample were analyzed by broad beam. The standards that were used are listed below.

Natural Minerals:	Albite
	Kakanui Kaersutite
	Sanidine
	Ilmenite
	Magnetite
Synthetic:	$NaNbO_3$

2. Accuracy

For comparison of the Wavelength and Energy Dispersive systems, two pyroxene analyses are shown below. The wavelength system is

generally accurate to $\pm$ 1% (MacKay, personal communication).

	λ 1.	EDS 1.	λ 2.	EDS 2.
SiO_2	47.85	47.58	45.59	45.35
TiO_2	1.41	1.49	1.88	1.92
Al_2O_3	7.86	8.03	9.99	10.18
FeO	7.19	7.25	7.34	7.27
MgO	12.97	12.96	11.74	11.58
CaO	22.03	22.12	22.36	22.50
Na_2O	0.71	0.35	0.81	0.53