HYBRIDIZATION OF BASIC WALLROCKS IN XENOLITHIC IGNEOUS COMPLEXES.

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January 1989

The University of Aston in Birmingham

Summary: Hybridization of basic wallrocks in xenolithic igneous complexes by Andrew Jonathan David Pattie. Ph.D. 1989.

The igneous complexes at Glen Dubh (Isle of Arran), Bolton Hill (Pembrokeshire) and Garabal Hill (Argyllshire) show a variety of basic rock types intruded by later granitic rocks. In each case the basic rocks show evidence of being assimilated by granite producing a range of dark, mottled, heterogenous hybrid rocks of intermediate composition.

Basic rocks show complex veining by acidic material whilst granites contain xenoliths of the basic wallrocks to varying extents before the reaction with the granite took place.
Xenoliths occur in all stages of breakdown, with sharp or diffuse outlines, to xenocrysts or xenocrystic clumps. In places complete equilibrium may produce apparently "normal" intermediate rocks with no evidence of hybridization.

Metasomatism has resulted in the transfer of certain constituents to the wallrocks, changing their chemistry, with the loss or localized distribution of existing constituents and causing zoning and replacement of pre-existing minerals. Geochemical analysis of the rock series show that the intermediate rocks form along generally linear compositional trends on variation diagrams between basic and acidic endmembers for most elements. Hybridization is also demonstrated by the use of statistics and mixing calculations.

Key words: Assimilation, hybridization, metasomatism, mixing, xenolith.

ACKNOWLEDGEMENTS

I am grateful to Professor D.D. Hawkes, in whose Geology Department the work was carried out, for the use of the various forms of Departmental equipment and finance for Neutron Activation Analyses.

I am particularly indebted to my supervisor, Dr. Andy Chambers, for arranging the project and sampling areas, and for much invaluable help and constructive criticism at all stages from the start to completion of the work.

I would also like to thank Mr. Eric Hartland and the various technicians in the Department for general help and technical support, particularly for Thin Section preparation and in the use of equipment such as A.A.S, X.R.F. and X.R.D. I am grateful to Mr. Roger Howell from the Metallurgy Department for help and guidance in the use of the Scanning Electron Microscope and Electron Probe Micro-analyser.

Acknowledgements are also due to Dr. Susan Parry of the Imperial College Reactor Centre at Ascot for Neutron Activation Analyses of the Garabal Hill rocks, and to Dr. Alyn Davies of the Atomic Weapons Research Establishment Reactor at Aldermaston for the Neutron Activation Analyses of the Bolton Hill rocks.

Finally, I am also grateful to Mrs. J. Edelman for an immense amount of work and patience whilst typing the manuscript, and to my family and fiancee for their support and encouragement.

TABLE OF CONTENTS

Page

Page

Page

Page

Table of Contents: contd.

LIST OF TABLES

Page

Tables: contd.

Tables: contd.

LIST OF FIGURES

List of illustrations: contd.

Plates: contd.

LIST OF APPENDICES

APPENDIX 1 - Mineral analysis Page

APPENDIX 2 - Whole rock analysis

APPENDIX 3 - Fluid geochemistry

1. INTRODUCTION

Numerous plutonic rocks have been described which involve the associations of acid, intermediate and basic rocks. Field relations are often complex, but frequently the field evidence suggests that the intermediate members of such complexes have formed by some hybridization process involving the acid and basic end members. The particular concern of this thesis is the reaction between acid magma and basic wallrocks.

From field and petrographic evidence it would appear that intrusion of the acidic magma results in veining and brecciation of the wallrocks, so forming isolated xenoliths which in turn are completely incorporated into the magma. The xenoliths themselves are often broken down into basic xenocrysts which may show progressive re-equilibration textures with the granite magma, due to these basic xenocrysts being unstable in it, this being seen where hybridization has not followed to completion.

The whole process is one of mechanical disintegration of the basic country rocks without the involvement of melting, and is demonstrated by the presence of the xenoliths, xenocrysts and mineralogical zoning.

In addition to mechanical breakdown and subsequent mixing, other processes may also be of significance. The acid magma may itself change progressively in composition due to incorporation of the basic material or loss of volatiles, and the country rocks are modified chemically and mineralogically to varying extents by metasomatic processes involving fluids emanating from the acid magma.

The aim of this study is to confirm that assimilation and the mechanical incorporation of material into a granitic magma has been, in the case of the complexes studied, the principal formational mechanism of dioritic rocks.

To this end field, petrographic, mineralogical and geochemical observations have been used.

In all of the complexes studied there are a wide variety of rock types, and a problem of the presence of a number of basic and acidic rocks as potential end members. A further aim has been to define in each case, which end members have been involved in the hybridization process.

It is also necessary to determine the nature and extent of other contributing processes, in particular the effects of metasomatism. Of particular importance here are the problems of identifying the possible compositions of the aqueous fluids and the consequent behaviour of the elements mobilized by them.

Tentative conclusions have been drawn concerning these matters, based on fluid inclusions and wallrock mineralogical changes.

Such characterisation allows the relatively immobile elements to be identified and used to confirm the mechanism of production of the dioritic rocks by assimilation.

The three complexes chosen for examination each show overwhelming field evidence of the reaction between acid magma and basic wallrocks. They are the Glen Dubh area of the Tertiary Central Ring Complex on the Isle of Arran, the Caledonian Garabal Hill Intrusion to the north of Loch Lomond, Central Scotland, and the Precambrian Johnston Diorite Complex near Haverfordwest in South Wales. Additionally, all these areas have undergone no more than hydrothermal alterations or very low grade regional metamorphism. It is believed that as a consequence of this, their geochemistry, and to a large extent their mineralogy, reflects the original igneous events together with associated metasomatism without a regional metamorphic overprint.

A further factor in choosing these three localities is that all three have been described in terms of their field relations and petrography - Arran (Tyrrell, 1928), Garabal Hill (Nockolds, 1941), Johnston Diorites (Strahan *et al.*, 1914; Cantrill *et al.*, 1916) - but have been subject to only limited if any geochemical or mineralogical investigations (Nockolds, 1941; Thorpe, 1970).

A great deal of pioneering research has been carried out at various periods over past years concerning assimilation, its characteristics, mechanisms and its importance as a petrogenetic process.

The main contributions and landmarks in this history of research are outlined below.

2. HISTORY OF RESEARCH

2.1 Research prior to Bowen, (1928)

The genetic relationships involving acid-basic associations in xenolithic and net veined complexes, have long been the subject of petrological study, pioneered at the turn of the century by the likes of Lacroix (1893), Geikie (1894) and Harker (1904).

Lacroix (1893) produced a comprehensive account of the petrographic features of foreign inclusions in igneous rocks, whilst Harker (1904) reported the existence of many acid-basic intrusions, where reaction between the two types had formed areas of hybrid rock, during his classical work on the Isle of Skye.

Subsequently, similar xenolithic and hybridized intrusions were reported elsewhere particularly in the British Tertiary, e.g. the volcanic centres of the Isle of Mull (Bailey *et al.*, 1924) and the Isle of Arran (Tyrrell, 1928).

Such features were generally believed to have been caused by the assimilation of basic rock by acid magmas although the opposite relations were also suggested (Harker, 1904; Thomas, 1922).

The theory of hybridization came to be regarded by many authors as being the dominant process in the formation of a diverse variety of igneous rocks, having special powers not possessed by other processes. The presence of inclusions was thought to merely represent the remnants of a great host of rock which had been almost completely incorporated into a magma.

Certain authors however, e.g. Harker (1909) proposed that magmas could not possess enough energy for the melting of significant amounts of foreign crystalline material, and that hybridization was strictly localized being confined to the margins of large plutons due to the great deal of superheat required.

Whereas the main area of thinking centred around the assimilation of crystalline inclusions in a magma, the similar process of magma mixing to produce hybrid intermediate rocks was also postulated, initially by Bunsen (1851) in Iceland. Fenner (1923, 1926) was also a great advocate for the mixing of basic and acidic magmas resulting in the formation of intermediate rocks in certain environments.

2.2 The contribution of Bowen (1928)

N.L. Bowen's "The evolution of the igneous rocks" had a huge influence on petrological thinking for another 50 years following its publication, and his work put the special powers of assimilation assumed by earlier workers into a more realistic perspective.

Bowen identified three mechanisms by which magma/rock interactions could occur.

1. Reaction of the melt with unstable minerals higher in the Reaction Series to produce new stable ones (e.g. granitic magma with more basic minerals).
2. Direct solution of unstable minerals, lower in the Reaction Series, into the melt (e.g. basaltic magma with more acidic minerals).
3. Fusion or partial fusion of the xenolith and subsequent mixing with the magma.

He also demonstrated that there was a wide difference between the heat capacity and heat of solution of silicates, so that magmas would require enormous amounts of superheat to melt crystalline material, e.g. a temperature of 300°C. above the liquidus would be required by a magma to assimilate a foreign mass equivalent to itself even if the crystals were already preheated up to melting temperature, but there was no evidence to suggest that magmas contained superheat.

Bowen proposed that whilst allowing for its action in certain cases, assimilation was not a very important petrogenetic process because the energy content of magmas was insufficient to allow them to much, if any, dissolution. Furthermore, the energy for melting or reaction of the magma with the xenolithic material would be supplied by the latent heat of crystallization of the magma itself. Consequently any material able to be digested would occur at the expense of the crystallization of the magma leading rapidly to the production of residual liquids by fractional crystallization.

As a consequence of Bowen's work although a small bastion of support remained in favour of assimilation as a major process, most notably Bowen's adversaries Fenner (1923, 1926) and Daly (1933) (who believed that the field relations which they observed offered more compelling evidence than the more simple systems studied in the laboratory), crystal fractionation became widely acknowledged to be the dominant force in the formation of diverse varieties of igneous rocks, with other processes such as assimilation and magma mixing being relegated to minor significance.

2.3 Research after Bowen (1928)

Despite its dismissal by Bowen (1928), further work was published in the years after "The evolution of the igneous rocks" which showed strong field evidence for the action of assimilation in certain igneous complexes both in the British Isles and abroad.

Brammall & Harwood (1932) described apparently normal igneous rocks being formed at Dartmoor by the breakdown and equilibration of basic xenoliths by granitic magma. Thomas & Smith (1932) reported similar features in the Tregastel-Ploumanac'h granite, Northern France, ultimately producing a series of gabbros-diorites-quartz diorites-granodiorites-granites similar to those believed to form by fractional crystallization in other environments.

A particular supporter of the hybridization theory in the immediate years after Bowen was Nockolds (1934a, 1934b, 1935, 1938) who produced similar convincing arguments in its favour in Britain and Ireland. He suggested that rocks of intermediate composition may even be dominantly formed by assimilation with many of the large diorite-granodiorite plutons, which often show more basic margins, forming in this way even where xenolithic material is not apparent. Nockolds (1934b) pointed out that these intermediate rock types are absent from the large sills and laccoliths which were at the time supposed to show evidence of gravity differentiation.

These early studies were generally based on petrographic and field evidence. In more recent years there has been a resurgence of interest in hybridization, with many more intrusions being documented which show intimate associations between basic igneous wallrocks and granitic or syenitic magmas - e.g. in Ireland (Claxton, 1970), the Channel Islands (Power & Gibbons, 1980) and Greenland (Brown *et al.*, 1978), this later work also offering a great deal of geochemical evidence.

Although it is not as widely believed that suites of igneous rocks evolved as a result of the assimilation of rocks by magmas, these views in favour of the process have been proposed by Middlemost (1985, p.65) as being of no great surprise because no body of magma is ever completely independent of the wallrocks that contain it.

This supposition is also well illustrated by the work of Fratta & Shaw (1974) and Dostal & Fratta (1977), and has been implied by Carmichael *et al.*, (1974) as being a normal accompaniment to igneous intrusion. In addition Hart & Allegre (1980) proposed that it is imperative that late stage effects such as volatile transfer and contamination be understood so that its effects can be accounted for before modelling of primary processes can be carried out.

A great amount of research has also involved the study of magma mixing, e.g. the classical work of Fenner (1938) at Gardiner River, Wyoming, and Wager *et al.*, (1965) on the marscoite of the Isle of Skye. The largest proportion of this work however, has taken place in Iceland (McGarvie, 1984; Mørk, 1984) and Greenland (Brown & Becker, 1986).

A great deal of work has also been carried out recently concerning the thermal, mechanical and chemical constraints of the magma mixing process in the production of homogeneous hybrid or magma-mingled rocks (Sparkes & Marshall, 1986; Frost & Mahood, 1987).

Intermediate xenolithic rocks have also been suggested to form by the partial melting of source material, and the separation from a felsic melt of refractory restite residuum in the form of xenocrysts and inclusions (White & Chappell, 1977; Chappell *et al.*, 1987).

In addition to the routine petrographic observations of assimilation, Nockolds (1933, 1934b) demonstrated the participation of a fluid phase in the process, suggesting its importance during re-equilibriation. This has given rise to many thoughts on the modification of wallrock due to the transportation of constituents by metasomatic fluids.

A number of new ideas have arisen in the last decade involving the occurrence of assimilation (or magma mixing) in combination with other processes such as fractional crystallization or evolution of a gas phase (Taylor, 1980; De Paolo, 1981; Walker, 1983). De Paolo (1981) suggested that the operation of coupled processes is necessary due to the heat required for assimilation being provided for by the latent heat of crystallization of the magma, and that non-linear effects on liquids have been shown from such geochemical models. Taylor (1980) has indeed implied that two component simple mixing lines or hyperbolas may have limited relevance in modelling processes such as assimilation.

The rise of such models has meant that assimilative contamination is being discovered where it was thought to be absent by investigators using more simple models, consequently this multi-mechanism approach has been applied in several complicated geological situations (Walker, 1983).

Interest has also been shown concerning the possible derivation of calc-alkali rock series by such methods as large scale assimilation of crustal rocks by basaltic magmas (Best 1982; Walker 1983), e.g. Grove *et al.* (1982) have shown that the low pressure phase relations relevant to the interaction of high alumina basalt with continental crust contain a reaction point between the liquid fields of the major minerals, this reaction point being the normal termination point of the crystallization of high alumina basalt parent magmas. Grove *et al.* indicated however, that if the parental magmas are suitably contaminated by fused crustal material then fractionally crystallized and re-mixed with fresh magmas, the resulting residual liquids may avoid the termination of their crystallization at this point and produce a spectrum of calc-alkali residual liquids, the fractionation trend of high alumina basalts in oceanic areas (in the absence of continental crust) being a consequence of stagnation at this reaction point.

Walker (1983) has proposed how this view of andesites is consistent with observations on the physical state of lavas, e.g. Eichelberger (1980).

Eichelberger (1974, 1975) had a few years earlier put forward some very convincing evidence for the formation of calc-alkali suites by the intrusion of acidic magma through and hybridization with, thick piles of mechanically weak basalt lavas. Further work carried out in recent times associated with the concept of hybridization revolves around the kinetics of the process. Although rates of diffusion are slow, Watson (1982) showed in his experimental work on the rates of digestion of crustal rock in basaltic magmas that uptake of silica by basalt is rapid, and that certain elements may be selectively introduced by diffusion ahead of others into magmatic liquids. This subsequently alters the chemistry of the magma without leaving visible evidence of contamination.

This "selective contamination" has also been shown by Fratta & Shaw (1974) and Dostal & Fratta (1977), and would be likely to aid such hybridization even where there may be thermal problems.

Selective contamination of magmas may also occur during the melting of less evolved country rocks due to the differing rates of dissolution of particular minerals (Donaldson, 1984a) in basic magmas, i.e. certain minerals may be melted earlier and more rapidly than others by selective dissolution, therefore if equilibration does not go to completion the magma may be contaminated by the constituents of only certain minerals in preference to others.

Possibly one of the most significant aspects that has recently emerged is the recognition of the importance of the study of certain isotopic contents/ratios (McBirney, 1979).

In particular Sr (and also Rb) isotopes have been widely used to show assimilation of crustal material by mantle magmas (Cox *et al.*, 1979; Taylor, 1980; De Paolo, 1981; Dickin *et al.*, 1981). Other radiogenic isotopes have also been used, for instance Pb and Nd (Cox et al, 1979; De Paolo, 1981).

Stable isotopes such as O and H have been used in addition as indicators for the mixing of mantle derived magmas with crustal rocks (Taylor, 1978), occasionally when coupled with other processes (Taylor, 1980).

There are certain shortcomings associated with isotope work (Taylor, 1980) as the interaction of plutons with meteoric water in hydrothermal systems may result in selective changes in some isotopes (particularly Sr). Consequently, observations would need to be treated with caution in altered rocks (this problem is also indicated by the work of Hart & Allegre (1980), Watson (1982) and Fratta & Shaw (1974)).

3. ASSIMILATION - PHYSICAL CONSTRAINTS, MECHANISMS AND RECOGNITION

The concept of assimilation has been shown to be not necessarily as simple a process as originally thought by Bowen (1928). The straightforward two endmember mixing may be complicated by various mechanisms operating along with, or post dating, hybridization (e.g. fractional crystallization, metasomatism - McBirney, 1979; Watson, 1982; Walker, 1983).

In addition certain physical constraints must be taken into account which may impede or reduce the rate and extent of assimilation of country rock, such parameters including energy considerations, temperature contrasts, viscosity differences and rate of magma ascent. Others may aid the process, e.g. mineral dissolution, metasomatism and mechanical breakdown.

The end result of hybridization generally being the production of intermediate rocks, alternative methods of forming hybrids and rocks of intermediate composition (as proposed by other authors) must also be considered.

3.1 Energy considerations

A particularly important factor to consider which would determine whether assimilation is a possibility concerns the country rock temperature (probably low for high level plutons). Cold country rocks would absorb heat from the intruding magma and, whatever the exact mechanism of hybridization, this lost energy would only be produced by the cooling and subsequent crystallization of the magma itself (release of latent heat). Excessive heat loss to the country rocks in raising their temperature towards that of the magma would ultimately prevent effective assimilation and limit its extent.

The dissipation of heat through the wallrocks by conduction or by the action of circulating groundwaters may also have a profound cooling effect on the magma.

The intrusion of magma through originally cold country rocks may in certain intrusions be seen by the presence of chilling around the margins of the pluton.

The rapid crystallization of magma could be avoided if the country rocks are already at a high temperature, thus requiring less energy from the magma.

The only method by which cold wallrocks could be raised in temperature to a significant extent without crystallization of part of the magma body would be if the magma was superheated (i.e. at a temperature well above that at which crystallization begins).

Many arguments have taken place regarding the feasibility of this. Bowen (1928) tended to dismiss the argument, suggesting that magmas are rarely superheated to any degree. Although at great depths in the crust there may be excessively hot material, he indicated that this is "hardly concerned with the matter that comes to the light of day as an igneous rock." Furthermore, Bowen proposed that most magmas come from a zone where the material is already partly crystalline, being at a temperature below its liquidus during intrusion.

In his experimental work, Bowen (1928) pointed out that because of the discrepancies between the specific heats of silicates (0.8 - 1.3 Joules/g degree) and their heats of fusion (270 - 420 Joules/g degree), melting or solution of an equal weight of solid by a magma, even when already at magmatic temperatures, would require approximately 300°C. of superheat. There is no evidence however, to substantiate any theory that magmas contain this amount of superheat.

It is interesting to note however, that the positive melting curve of dry silicates (Harris *et al.*, 1970, Fig. 1a), on increase in pressure means that under dry conditions a magma formed at depth could possibly contain some superheat. With the melting temperatures increasing between 6°C./kbar (basalt) and 12°C./kbar (granite), the curves from Harris *et al* (1970) suggest that a magma derived from approximately 30 km (6 kbar) depth could retain superheat of between 60°C. - 80°C. when reaching shallow levels in the crust. This would have to occur by the magma rising without losing heat to its surroundings, i.e. adiabatically, cooling at a rate of only 1° - 1 1/2° C./kbar, and is perhaps unlikely unless the magma is rising very rapidly.

In his review of Bowen's work, McBirney (1979) also considers superheat to be a relative rarity. He does, however, suggest the presence of superheat in some of the early Cascade lavas (McBirney, 1980) due to the magmas rising very quickly in large volumes, and uses this to explain the lack of xenoliths in those lavas (being assimilated completely by the superheated magma). Meanwhile the presence of many xenoliths in the later granitic plutons in the same area was accorded to their not containing superheat and hence inability to digest foreign inclusions, this being due to the slow rise of these later magmas, during declining activity, and their crystallization below the surface.

Marsh (1978) also indicated that large bodies of rapidly ascending magma have remarkably little thermal interaction with their surroundings, and that they may approach adiabatic conditions (again implications for superheat), although Hildreth (1981) suggests that adiabatic ascent is unlikely except for voluminous basalt eruptions (this itself may be unlikely as De Paolo (1981) has indicated that basalt ascent through silicic crustal rocks is slow because of the low density contrast and reduced buoyancy). The consensus of opinion would seem to be that the presence of significant superheat in rising magmas is unlikely.

If superheat is a rarity then there is still Bowen's original problem of how heat is supplied from the magma to:

(a) heat up the country rocks, and
(b) assimilate the country rocks.

Bowen (1928) showed how the heat supply problem can be successfully overcome by assuming that magma crystallization is going on at the same time, and that the heat source is the latent heat of crystallization of the magmatic phases. This suggestion has also since been demonstrated by O'Hara (1977), Taylor (1980) and De Paolo (1981) in their studies (e.g. Harris *et al.*, 1970). It has been suggested that the heat of crystallization could raise the temperature of a granite by up to 195°C., which would probably be sufficient for some assimilation of wallrock.

It is possible to calculate the approximate amounts of crystallization that would take place, but these would only be approximate because of uncertainties about the exact latent heat of fusion values, and also those of specific heat which in any case change with temperature.

Using typical values (e.g. Best, 1982) -

Granite - latent heat of fusion
280 Joules/g degree
- specific heat
1.0 Joules/g degree
Basalt - latent heat of fusion
400 Joules/g degree
- specific heat
1.2 Joules/g degree

If basalt at 1150°C. intruded granite country rock at 150°C., then to heat 1g of granite requires 1000 Joules (ΔT x Sp. heat).

To dissolve 1 g of granite requires 280 Joules. The total amount of energy is obtained by crystallization of e.g. (1000 + 280)/400 = 3.2g basalt.

If a granite at 800°C intruded basalt country rock at 150°C. to heat 1g of basalt requires 780 Joules. *To dissolve 1g of basalt requires 400 Joules.

This energy would be obtained by crystallization of

(780 + 400)/280 = 4.2g granite

If the country rocks have been preheated to a temperature nearer to their melting point assimilation can take place to a greater extent, with less degree of crystallization of magma, as there will only be the dissolution energy to be overcome.

As will be shown later, when discussing mechanisms of assimilation the partial or total conversion of the wallrock mineralogy by metasomatism to phases in equilibrium with the magma, and the subsequent breakdown of the country rock by mechanical processes, requires less energy. This metasomatic alteration would allow hybridization to go further by reducing the amount of energy needed from the magma, and is probably a more likely process (the three areas described in this study were chosen to demonstrate this). Despite the energy problems associated with assimilation, it is interesting to note that with regard to basic magmas and acidic crustal rocks at least, the conclusion of a number of authors is that partial fusion and hybridization of the lower crust is unavoidable (McBirney, 1980; Hildreth, 1981; Best, 1982).

A point worthy of mention in studies on assimilation concerns the possible operation of convection currents in magmas producing a continuous supply of heat for it to occur. This was put forward by Wilcox (1954), during work on granitic xenoliths in basaltic lavas of Paracutin, who found that heat liberated by the crystallization of minerals was insufficient to melt the xenoliths and postulated that further energy was contributed by a large body of convecting magma at greater depth with no superheat consequently being required. This action of convection currents to supply further heat for assimilation has, however, received little attention in more recent years.

A final point in terms of energy conditions involves the thermal nature of mineral reactions. Bowen (1928) noted that reaction of magmas with phases which could have crystallized earlier in the reaction series (e.g. granite with pyroxene/olivine, etc.) results in exothermic reactions (liberating heat) whereas reactions of a magma with minerals later in the reaction series (e.g. basalt with quartz) are endothermic (absorb heat).

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* Although a granite is incapable of melting basalt, this would be the energy needed if a granite could melt and dissolve a basalt at this temperature. (Obviously further energy would be necessary to heat basalt to its normal melting point, these figures shown are merely semi-quantitative to show roughly the amounts of magma crystallization that are required for this overall process, even where volumes of wallrock are small).

These reactions might be expected to have an influence on whether assimilation occurs (particularly if large amounts of foreign material are involved). However Bowen (1928) suggested that in terms of energy these reactions make little difference to the overall mechanism, as under normal conditions these characteristics are overshadowed by other effects especially where the amount of added material is proportionately large and at a temperature below that of the magma. Under these conditions therefore he proposed how the action of the liquid on relatively cold material is essentially the same regardless of whether the added rock is earlier or later in the crystallization sequence (i.e. the heat is extracted from the liquid, lowering its temperature causing crystal precipitation).

3.2 Kinetics of dissolution

Although much work has been carried out on the thermal aspects of hybridization, studies on the kinetics have only been undertaken in recent years. This mainly applies to the mechanism by which magmas melt unstable, less refractory, minerals and concerns the rates at which dissolution can occur (given the known slow rates of diffusion in silicate liquids).

Insufficient work has currently been done on this subject, but Watson's (1982) examination of the chemical interaction between molten basalt and crystalline felsic material has been important. He demonstrated that dissolution rates for quartz are sufficiently fast that contamination of basalt by quartzose xenoliths can be expected to occur in terms of days to years. This could subsequently produce marked contamination and clearly can result in effective silica contamination of a magma given favourable circumstances. Watson (1982) also observed that selective contamination of a basic melt may occur, particularly by constituents such as K_20 (also Na_20 and Sr) compared with others such as $Si0_2$ and Al_20_3 (diffusion rates have been shown to be much faster for alkalis at 1300°C, approximately 10^{-5} cm ^{2}/s for K_2 0 than silica at the same temperature:- 10^{-9} - 10^{-10} cm ^{2}/s).

Watson 1982) indicated that due to rapid diffusion rates of K_20, the time required for significant K_20 contamination of a magma may be quite small particularly in relation to the probable time scale of a magma body ascent through the crust (see also Marsh 1978).

Due to the slow diffusion rates of a component such as $Si0_2$, its introduction into a basic magma is controlled by the dissolution of xenoliths, therefore selective enrichment of elements like alkalies is likely to be stronger where melting of wallrock is not involved (the slow diffusion of $Si0_2$ also tends to limit the diffusivity of other melt species) and diffusion is therefore operating alone. The effect of Watson's work shows that the interaction of basaltic magmas and continental crust is not a simple 2 endmember mixing process and that where the reaction does not go to completion, the resulting contamination may be complicated.

Donaldson (1984a) examined the dissolution rates of olivines, plagioclase and quartz in tholeiitic basalt and demonstrated (similarly to Watson, 1982) that the timescale is very short (in order of days), although different minerals showed different rates (e.g. labradorite is roughly 30 times faster than olivine) again indicating the possibility of selective contamination (although in mineral rather than atomic terms.)

One disadvantage with these studies by Watson (1982) and Donaldson (1984a) is that on all occasions superheated liquids (up to 200°C of superheat) were used in the experiments whereas under normal conditions this would probably not be the case (as indicated earlier). As pointed out by Donaldson, further work is needed to look at dissolution rates as a function of the amount of superheat or even in sub-liquidus melts.

3.3 The assimilation process

3.3.1 Mechanisms of assimilation

Bowen (1928) outlined three general mechanisms involving the interaction between magmas and wallrocks, the most straightforward being the straight fusion (complete or partial) of wallrock material followed by mixing with the magma by diffusion.

The second method involves the direct solution of unstable minerals into the melt and the third the reaction of the melt with unstable minerals transforming them into stable ones.

The melting of phases occurs when a magma is in contact with minerals with which it is still undersaturated (i.e. one which it may precipitate at a later stage, such as quartz in basalt). If the crystals and magma are at the same temperature, even though these crystals may have melting temperatures greater than that of the magma, they could dissolve (McBirney, 1979; Fig. 10-1). This may be accomplished if the liquid at that particular constant temperature remains on the liquidus surface, and this can only happen by the solution of an equivalent amount of previously-existing crystalline material. The liquid may only be enriched in the new minerals when all earlier crystals have been removed. A consequence of this reaction is an increase in the volume of liquid.

The third proposal of Bowen is relevant to the reaction between magmatic liquids and country rocks of more refractory composition (e.g. granites intruding basic wallrocks). In this case the xenolith/xenocryst material is again out of equilibrium with the liquid, the liquid cannot melt or dissolve the foreign matter but reacts with it. The magma must remain on the liquidus surface, for the reaction to take place. To achieve this as the phase is converted to one in equilibrium with the magma then the magma itself must precipitate this new phase (this is demonstrated in a eutectic system representing the discontinuous reaction series (McBirney, 1979; Fig. 10-1), and a continuous solid solution reaction series by Bowen (1928) and McBirney (1979)). Because of the formation of crystals from the magma due to latent heat effects, the process is exothermic and unless heat is lost the temperature of the system will rise.

Whether any of these processes occur may depend upon the style of pluton emplacement. Rapid emplacement and simple geometric contacts e.g. granitic ring dykes might result in reaction between magma and wallrock but the rapid formation of a margin of protective crystallized magma prevents further reaction. Magmas which stope their way upwards in an irregular fashion have much more opportunity to react with and assimilate roof zone material.

It is interesting to note that Hildreth (1981) argues against partial melting/assimilation of roof rocks on geochemical grounds and the general absence or rarity of xenocrysts in many magmatic rocks. He suggests that assimilation of roof rocks above well established magma chambers is not a continuous process but only occurs during dyking and eruption, however there is little evidence in the areas in this study in agreement with this, as all complexes show extensive areas of xenolithic rock with no indication of the granites having intruded as dykes at very shallow levels during eruption.

3.3.2 The action of volatiles

The involvement of volatiles in assimilation was put forward by Nockolds (1933, 1934b) who noticed the strong presence of hydrous minerals in and around xenoliths, and expressed the idea of the importance of volatiles in the alteration of xenoliths/xenocrysts. This was based on the abundance of hydrous minerals in the xenolithic rocks which were often found to be absent from the uncontaminated host rock.

Volatiles associated with the intrusion of a magma may be important in a number of ways; this applies to both magmatic "water" due to degassing and heated meteoric water.

(1)The "water" may have a thermal effect in pre-heating the country rocks prior to direct contact with the magma, hence less heat needs to be provided from the magma by the crystallization of the mineral phases.

(2)Metamorphic and metasomatic changes may alter the country rock mineralogy.

Korzhinskii (1970) described two ways in which this can occur, with aqueous solutions percolating through country rock by infiltration through fractures etc. (several km's) or by diffusion (m's), the elements migrating in response to concentration or temperature gradients through solutions in rock pores. Didier (1973), in addition, proposed that this could be aided by the appearance of microcavities in xenoliths/wallrock due to dilatation of minerals caused by increased temperature (if wallrocks were previously cold). This would have the effect of opening up a network of microfissures allowing easier and more extensive access for aqueous fluids.

The alteration of wallrock minerals by metasomatic effects may cause its recrystallization, and mechanical breakdown (Eichelberger, 1974, 1975) which can occur by the setting up of stresses in the country rock due to pre-existing minerals being replaced by others of lower density (Brown *et al.*, 1978), with the result of the brecciation and shattering of xenoliths. This also allows further invasion by magma, making assimilation likely to be more extensive.

(3)As outlined later, a metasomatic fluid in equilibrium with the magma would tend to change the mineralogy of the country rocks producing phases in equilibrium with the magma. As these are more stable they would not need to react with the magma and as such much less energy would be required to incorporate xenoliths and xenocrysts, enabling hybridization to take place to a greater extent. Such modified xenocrystal material would be likely to be virtually indistinguishable chemically from phases precipitated by the magma.

(4) Volatiles derived from incorporated xenoliths would reduce magma viscosity enabling the diffusion of components between xenolith and magma (Nockolds, 1933). The constituents entering the inclusions through volatiles would displace those already comprising them, during the alteration of the original mineralogy; these would in turn diffuse out into the magma in a kind of reciprocal reaction (Nockolds, 1933).

The migration of components has been suggested by Watson (1982) to be in response to chemical potential gradients between liquid and xenolith, these components respond by diffusion to equalize their potentials across the system thus stabilizing it.

Evidence for this has been shown by McBirney (1979) at the Skaergaard intrusion with pegmatitic zones being seen around the margins of xenoliths.

3.3.3 Selective contamination

This has been proved experimentally by Watson (1982) with alkalis, Sr and possibly rare earth elements, Zr and Nb being selectively enriched by basaltic magma when rising through continental crust.

Fratta & Shaw (1974) and Dostal & Fratta (1977) have also illustrated selective contamination in a dolerite dyke through wallrocks of various compositions, the elements affected being K, Rb, Tl, Li and Ba, and also suggested that it may occur on a large scale where basic melts ascend through crustal rocks of different compositions. Magmas may also be enriched in particular minerals due to differential dissolution rates (Donaldson, 1984a) in basic melts. There has, however, as yet been no study of selective contamination involving granite magmas intruding basic igneous wallrocks.

3.4 Alternative methods of producing other hybrid and intermediate rocks

3.4.1 Magma mixing

The possibility of the mixing of magmas was first recognized by Bunsen (1851) when proposing that rocks of intermediate compositions between basalt and rhyolite may have formed in exactly this way.

This is a process close to assimilation in terms of chemistry producing what could be called hybrid intermediate rocks.

Other methods have been identified as yielding intermediate rocks (see later) but would be distinguishable from simple assimilation/magma mixing concerning field relations, petrography and chemistry.

Later studies on this subject include those of the Gardiner River Complex, Yellowstone Park, where many hybrids were reported as forming by mixing of rhyolitic and basaltic liquids (Fenner, 1938; Wilcox, 1944).

Of the areas where magma mixing has been recognized the best known, which outcrops as an irregular ring dyke on the Isle of Skye has been termed "marscoite" (Harker, 1904). This is a rock of quartz monzodioritic composition containing xenocrysts and/or phenocrysts of quartz, alkali feldspar and andesine set in a background of oligoclase, alkali feldspar, Fe-Ti oxides, quartz and apatite, which was demonstrated by Wager *et al.* (1965) to have been produced (along with a ferrodiorite) by mechanical mixing of granite and basic liquids by differing convection currents. This has since been complemented by the more recent study by Vogel *et al.*, (1984). Another example of proposed magma mixing in the British Tertiary is that of Vogel (1982) where liquid-liquid relationships were based on the presence of pillow-like xenoliths at the Ardnamurchan Complex. Many studies have particularly been carried out in Iceland where rhyolite-basalt mixing has been widely documented and has received much attention e.g. McGarvie (1984) on the Torfajokull volcano, and Mørk (1984) on the lavas of the Veidivotn Fissure eruption.

Brown & Becker (1986) also showed the mixing of basalt and felsic syenite at the Kialineq igneous centre, East Greenland.

Much work has been done recently by Sparkes & Marshall (1986) and Frost & Mahood (1987) on the mixing of magmas to produce hybrid rocks. Sparkes & Marshall (1986) have indicated that magmas may mix and homogenise, or mingle and remain separate depending upon their temperature, volume and compositional features. Whilst working on rocks at St. Kilda, Scotland, they suggested that complete homogenization can only occur where magmas both behave as liquids at the same temperature, whilst xenolith/inclusion formation occurs where there is a large temperature difference during intrusion, i.e. the mafic magma may be at a low temperature and contain sufficient crystals to be essentially a solid, preventing mixing, or be at a higher temperature than the acidic magma causing itself to quench - also preventing mixing. This would produce xenoliths with chilled margins (e.g. Gibson & Walker, 1963).

Frost & Mahood (1987) also proposed that the formation of xenoliths may be caused by the presence of a large proportion of silicic magma in relation to mafic magma, and that typically at least 50% of mafic magma must be present for homogenization. Large proportions of silicic magma may only completely hybridise with more evolved mafic magmas when there is a small compositional difference between them (less than 10% $Si0_2$), e.g. granitic and andesitic liquids.

Sparkes & Marshall (1986) and Frost & Mahood (1987) reported the presence of chilled "pillows" of mafic and intermediate rock net veined by felsic material, the pillows showing a rounded appearance (termed "enclaves" by Frost & Mahood, 1987) in these mixed rocks. These chilled pillows appear to be a feature of magma-mixed rocks, having been reported by other authors - Wager & Bailey (1953), Vogel (1982), Vernon (1984), Brown & Becker (1986).

Mixing may also be prevented by the density contrast between acid and basic liquids (2.7 for basalt, and 2.2 for rhyolite - McBirney (1980)).

If rhyolite overlies basalt, the temperature difference and tendency for the basalt to rise into the rhyolite and mix with it is more than compensated for by this density - hence they may tend to convect separately without mixing.

Mixing may also be inhibited by viscosity contrasts.

The effects of these contrasts have been shown by Yoder (1973) in experimental work where rhyolitic and basic silicate liquids at 1200°C maintained an interface, and their separate identities, for at least limited periods of time without mixing although diffusion of component elements between the two liquids did occur.

This is in accordance with field evidence of co-existing but unmixed basalt and rhyolite. Gibson & Walker (1963) reported the presence in Iceland of such magmas which were simultaneously erupted in varying proportions producing composite lavas fed by composite dykes, the liquid basalt never forming a homogeneous solution with the acidic magma since even small blebs of basalt had a thin glassy protective skin. A similar feature is also seen in the British Tertiary igneous centres with the composite sills and dykes showing little if any mixing (Harker, 1904).

For mixing to be effective it would be reasonable and necessary for it to occur over long time periods at depth, or in violent eruptive episodes where these contrasting magmas could be violently and intimately mixed to overcome these contrasts (McBirney, 1980).

Chemical constraints on magma mixing are also outlined by McBirney (1979, p.328) who has showed that if two liquids are mixed, and each contains crystals which are not in equilibrium with the new mixed liquid, then they will react or be absorbed and depending upon the proportions, the new liquid may be either of the two original liquids with a different amount of the appropriate crystals, i.e. if the mass of crystals is large then the liquid not in equilibrium with the crystals may be entirely consumed in the reaction, and only the other liquid will survive - an intermediate liquid cannot be stable.

This work shows that a mixed liquid may not necessarily have an intermediate composition between the two end members, but this would only occur if one or both original liquids contain crystals not in equilibrium with the opposing endmember (McBirney, 1980). Although Frost & Mahood (1987) indicate that it is not capable of yielding large amounts of silicic intermediate rocks, magma mixing as a major mechanism for producing large volumes of andesitic and dacitic rocks has had its advocates (Eichelberger (1975, 1980), Eichelberger & Gooley (1977)), Sparkes & Marshall (1986) in addition suggest that this is the main mechanism for producing xenolithic rocks, and the overall process has gained favour with recent authors. The process has been used in a modified form to explain observed deviations from curved fractionation paths (Best, 1982, p.328).

O'Hara (1977) has also explained a deviation of rock compositions from a traditional crystal fractionation liquid line of descent as being caused by mixing of successive batches of genetically related magmas in a magma chamber, where the earlier batches have undergone crystal fractionation.

Because of the strong partitioning of some elements into residual liquids this mechanism, if repeated, may have very marked effects on trace element abundances without significantly altering major element contents. Such arguments have been applied to the chemistry of Mid Ocean Ridge Basalts (Huppert & Sparks, 1980).

Despite the force of opinion being against such methods as magma mixing it is interesting to note the absence of intermediate rocks (except those obviously formed by assimilation or mixing) in the Tertiary igneous centres of the British Isles despite the presence of enormous volumes of acidic and basic rock (King, 1982). A possible explanation for this has been indicated by Hildreth (1981) who suggests that the very sparse intermediate rocks in oceanic areas, which otherwise show sharply bimodal eruptive units, are at least in part hybrids. He also proposed that an extensional orogenic environment favours rapid upward transfer of mantle derived basalt and felsic liquid (from crustal melting or fractional crystallization of basalt) to high levels, subsequently suppressing hybridization, whereas in a non-extensional environment the upward movement of magma is slow enough through thick crustal rock, so that fractional crystallization and hybridization may occur, leading to a predominance of intermediate rocks (and accounting for the difference between the absence of andesitic rocks at rifts, e.g. British Tertiary and their abundance at Destructive Plate Margins, e.g. The Andes). Hildreth (1981) in addition emphasized how andesites commonly contain disequilibrium textures and assemblages, and that their heterogeneity attests to a complex history, which indicates that they are generally not of a primary origin. Further evidence of the formation of andesites by hybridization is from Watson (1982) who states that some crustal mixing is unavoidable, with the melting point of basalt being well above that of felsic rock, and with magmas consisting of intermingled basalt/rhyolite being quite common. Indeed Taylor (1980) calculated that a crystallizing basalt magma could generate crustal melts of 10% - 50% of the basic mass, whilst De Paolo (1981) indicated that if the crust is already hot, a melt equivalent to or greater than the basaltic mass may be produced - allowing increased likelihood of hybridization.

3.4.2 Restite Separation

White & Chappell (1977) and Chappell *et al.* (1987) have suggested that many granites and volcanics contain significant amounts of crystals that did not crystallize from a melt. These are "restites" - refractory material remaining during the partial melting of source rocks.

Where the amount of felsic melt is small, a minimum melt may be formed. However where the fraction of felsic melt is large, the rigid restite framework breaks and the whole mass becomes a crystal-rich magma.

The authors proposed that the separation of restite during movement of the granite liquid accounts for the linear chemical variation found in granitoid suites - a form of "unmixing" process, although separation is suggested to be inhibited so some restite remains.

White & Chappell (1977) imply that bulk restite is seen as xenocrysts and small aggregates of crystals rather than large xenoliths, these crystals react with the magma resulting in zoning of the minerals, producing similar overall features to those produced by assimilation.

Although White & Chappell (1977) and Chappell *et al.*, (1987) suggest that magmas are too viscous to allow wallrock assimilation, and that roughly 99% of xenoliths in granite complexes are from restite, they also indicate that the restite model has never become widely accepted and has been criticized in the past.

3.4.3 Production of intermediate rocks (other processes)

Other processes which may result in intermediate rock types are worthy of mention.

These include the primary melting of hydrous peridotites which have been proposed to be able to form andesitic liquids (Mysen, 1982), as has part melting of oceanic crust (Green, 1982). Andesitic liquids have also been said to be derived by fractional crystallization of basalt under specific conditions of oxygen fugacity (Kuno, 1968; Arculus & Wills, 1980), and fractional crystallization combined with assimilation of crustal material (e.g. Grove *et al.*, 1982).

Over recent years the concept of compositionally zoned magma chambers has come to the fore, e.g. Hildreth (1981) described how intermediate magmas may form in zoned chambers by fractional crystallization of basalt followed by assimilation of crustal melts. This zoning has been convincingly demonstrated to apply in acid magmatism by Hildreth and has also been supported by McBirney (1980).

3.5 Additional processes in areas of assimilation

3.5.1 Contemporaneous effect of a magmatic fluid phase

In the areas studied it is likely that the country rocks were affected by a superheated aqueous phase which is likely to be of magmatic origin.

Despite the fact that a great deal of work has been done under water saturated conditions ($P_{H_2O} = P_T$) it is probable that most acidic magmas are not at least initially saturated. If saturated, the solidus curve would be negative and granitic magmas would crystallize not far from their own crustal sources (unless markedly superheated - Harris *et al.*, 1970) but would also, on release of pressure, lose water (and other volatiles) causing extensive metasomatism of wallrock (i.e. the more hydrous a magma the greater its possible metasomatic effects).

If not initially saturated, the magma on ascent reaches conditions where the load pressure is such that $P_{vapour} = P_T$ and the magma evolves a separate aqueous phase at higher levels although its extent of metasomatic alteration on wallrocks would be much less.

A dry granite would, however, rise towards the surface with a consequent reduction of pressure without a change in state (Harris *et al.*, 1970).

The release of an aqueous phase causes crystallization which may raise the temperature of a magma due to the effects of latent heat of crystallization. This may go some way to aiding the hybridization process.

The separation of an aqueous phase from a magma may be seen by the metasomatism of wallrocks, but also by the presence of druses, miarolitic cavities, pegmatites, etc. Also fluid inclusions may be remnants of these fluids trapped during crystallization of the magma.

Concentrations of H_2O (and F, Cl) in the roof zone (cooling surfaces) of a magma body by diffusion down thermal gradients is convincingly argued by Hildreth (1981), although he does not favour a separate aqueous phase; however such a concentration would appear to favour later separation as the magma rises to higher levels of emplacement. Hildreth (1981) has also implied that, due to its low solubility in silicic magmas, bubbles of CO_2 could aid upward transport of H_2O, halogens, etc. through a magma.

The composition of a magmatic vapour phase which evolves from a granite is important particularly with respect to the elements which it may transport: e.g. Hildreth (1981) proposed how certain constituents may be transported by large amounts of F^- whilst others are preferentially transported by Cl^- and CO_2. Burnham (1979a) also indicates how certain complexing agents such as F^- and Cl^- may cause the mobilization of certain elements, although generally some constituents are more susceptible to this than others (see Chapter 3.6).

The important consequences of the action of any vapour phase on rocks prior to assimilation are generally a combination of:

(a) Thermal action - heating up of wallrocks

(b) Mechanical action - the breaking up of wallrocks

(c) Chemical action -changing the crystal composition and mineral assemblage towards equilibrium with the magma

The combination of all these actions would appear to greatly assist the assimilation process.

3.5.2 Contemporaneous effect of a meteoric fluid phase

Meteoric water may possibly enter a magma directly at the walls of the pluton as suggested by Shaw (1974) or by stoping of wet roof-rock material (Taylor, 1974) producing low δO^{18} magmas.

Alternatively, at magmatic or just sub-magmatic temperatures the heat source of the magma is known to drive large scale meteoric convection systems which can affect previously formed hybrid rocks. Such hydrothermal exchanges are indicated by Taylor (1978) as being confined to the epithermal part of a pluton and to decrease with depth. These interactions may produce changes in isotopic and trace element concentrations, and must consequently be taken into account when using geochemical criteria to demonstrate assimilation. The effect is thought to be particularly strong in the roof zone above a magma chamber - Taylor (1978) (this being roughly the area of study in the igneous complexes described here), and has been described by Hart & Allegre (1980) to generally be synchronous with pluton formation.

3.5.3 Late stage secondary alteration

This is associated with relatively low temperatures, and is late stage occurring post-crystallization of the magma. It may also re-arrange element distributions and needs to be taken into account when studying the effects of assimilation. Late alteration is commonly seen in replacement of primary igneous minerals by a secondary assemblage more in equilibrium with the lower temperature conditions. Interaction with late stage hydrothermal fluids is well documented in particular in the British Tertiary (Taylor & Forester, 1971; Dickin *et al.*, 1981; Dickin & Jones, 1983) and other complexes in the U.K. (Nockolds, 1941; Lambert & Holland, 1971), and appears to have taken place at least to a certain extent in the great majority of igneous intrusions.

3.5.4 Metamorphism

In hybrid complexes that have undergone later regional metamorphism, obvious petrographic changes will occur. It is probable that such metamorphism is not entirely isochemical and will therefore overprint and confuse chemical patterns and characteristics established during assimilation and/or mixing.

3.6 Recognition of assimilation

3.6.1 Field evidence

Field evidence for assimilation poses few problems although assimilation of basic material by acidic magma may be so complete as to leave little evidence (i.e. complete re-equilibration of xenoliths and magma). Such features may include complex veining and dyking of country rocks by the magma, the presence of xenoliths with angular to rounded, embayed or corroded edges. These xenoliths may be in various stages of breakdown to clotted xenocrystal material, forming a series of mottled heterogeneous rocks (Tyrrell, 1928; Brown *et al.*, 1978), and may be sharp or diffuse in outline (semi-acidified). Xenoliths may also be surrounded by a marginal pegmatitic zone (McBirney, 1980) and possibly show a recrystallization texture.

The contaminated rock is also generally located between, or at least near the interface between the parent magmatic material and foreign wallrock (Best, 1982).

Where the mixing of magmas is believed to have produced hybrids, the basic member is often seen in the form of "pillows" with curved or cuspate margins and generally chilled, in a net veined matrix of more felsic rock (Blake *et al.*, 1965; Vogel, 1982; Brown & Becker, 1986), the felsic rock having usually been reheated followed by its back-veining into the semi-solidified basic member.

3.6.2 Petrographic evidence

Petrographic features of assimilation involving basic rock and felsic magma are the presence of (occasionally corroded) xenocrysts showing disequilibrium textures, e.g. zoning of minerals and/or reaction rimming of minerals by later ones (with no melting involved). Disaggregation of xenoliths is apparent and certain minerals, e.g. pyroxene can show recrystallization into radiating aggregates.

Magma-mixed rocks have been described by Cox *et al.*, (1979) as being detectable due to the presence of two suites of phenocrysts of types not normally expected to be in equilibrium with each other (e.g. marscoite).

Textures resulting from the reaction between basaltic liquids with acidic rock of lower melting temperature have been shown by McBirney (1979), and during experimental work on dissolution by Donaldson (1984b). Xenocrysts in basic magmas commonly show shallow, broad embayments and rounded corroded margins due to melting.

Phases may also exhibit coronas of other minerals or reverse zoning (such as plagioclase). Dark glossy material can be evident along grain boundaries of xenocrysts, or occurring as seams along cleavages or fractures within them, due to the melting of the respective phases.

3.6.3 Geochemical evidence

A straight line variation in chemistry is most easily explained by mixing of two endmembers; either two magmas or a magma and a solid which has been completed integrated into the magma. Any other explanation of linear trends requires combinations of fractionation, partial assimilation (and/or volatile processes) that are too fortuitous to be realistic when partition coefficients between crystals and liquid are considered (particularly when considering trace elements which are generally much more strongly partitioned into certain mineral phases than are the major elements).

Therefore, linear variation diagrams equate well with a mixing process (Harker, 1904; McBirney, 1979) and contrast with typical trends produced by fractional crystallization, e.g. Best (1982, p. 328) has produced a diagram of $Ti0_2$ concentration versus percentage fractionation for various fractionation trends
(calculated using known partition coefficients) which contrasts markedly with mixing lines.

As suggested earlier (and indicated by Middlemost, 1985, p.69) these types of trends may be more difficult to demonstrate with major elements than with traces due to the usual stronger partitioning of the latter, e.g. REE, however fractional crystallization would be expected to form a curved series (e.g. Middlemost, 1985, p.67).

A number of authors have proposed that assimilation may occur together with fractional crystallization, which would modify the linear variations (O'Hara, 1977; Taylor, 1980; De Paolo, 1981) whilst Best (1982) has also shown diagrammatically the combined effects of the above producing a lens-shaped area of compositions between the lines of mixing and fractionation. These authors do not, however, mention that excluded incompatible elements are probably not affected by fractional crystallization and hence would give a good guide to assimilation.

Taylor (1980, p.245) heavily criticizes the use of simple mixing models as having limited relevance when studying such petrogenetic processes. His (and those mentioned above) arguments tend to involve deeper more extensive systems than those studied here and also generally apply to the reaction between mantle-derived basic magmas with silicic crustal rocks on a large scale (rather than the high level granites assimilating basic wallrocks).

Ideally, the original unaltered rock compositions are required to demonstrate assimilation, however this is rarely achieved due to modification by aqueous fluids. Volatile transfer (Hart & Allegre, 1980) is a process which can cause deviation from a linear pattern particularly for elements like K, Rb, etc., depending on the nature of the volatile phase, as may selective contamination (Fratta & Shaw, 1974; Dostal & Fratta, 1977; Watson, 1982). The occurrence of phenocrysts with vastly differing dissolution rates (Donaldson, 1984a) would also produce a possible non-linear pattern of certain mineral constituents if equilibrium is not reached. Hence non-linear trends for such elements do not necessarily preclude assimilation.

Due to alteration being a common occurrence in igneous rocks, a large amount of literature has been published in an attempt to distinguish mobile elements from immobile ones which tend to remain unaffected by late stage fluids.

The mobility of elements has been examined under conditions of metamorphism, metasomatism and particularly hydrothermal alteration. These studies having been carried out on rocks of a great variety of compositions including submarine basalts (Philpotts *et al.*, 1969), alkali rocks (Kogarko, 1974), greenstones (Condie *et al.*, 1977), basic lavas (Thompson 1982), oceanic basalts (Humphris & Thompson, 1978), skarns (Giere, 1986), basic sills (Dickin & Jones, 1983), granodiorites (Muecke & Clarke, 1981) and granites (Exley, 1980; Baker, 1985).

Although conflicting arguments and opinions occur from author to author, certain groups of elements e.g. the High Field Strength Elements, Zr, Y, Nb, Ti, Sc and REE are generally reported to be immobile whilst others (in particular the alkali elements) are mobile. As hydrothermal interaction modifies rock chemistry, Hart & Allegre (1980) suggest that caution is needed in the use of mobile elements and that a larger role should be given to studies involving these non-mobile elements. However, a certain degree of care is still necessary even when modelling processes with the High Field Strength Elements which have been shown to be mobile under certain special conditions when the aqueous fluids involved are of a particular composition (Bandurkin, 1961; Balashov & Krigman, 1975; Fryer & Edgar, 1977; McLennan & Taylor, 1979).

Whereas linear trends of variation would be expected in a rock series formed by assimilation, it must be pointed out that this may not necessarily be the case with a magma-mixed series. If one or both liquids contain large proportions of phenocrysts (off the linear trend in composition) which are out of equilibrium and hence react or are absorbed, this can change the bulk composition depending upon the proportions of liquid and solid it incorporates. Such a hybrid may not be a simple intermediate mixture of the two end members (Middlemost, 1985).

3.6.4 Isotopic evidence

The effects of assimilation coupled with fractional crystallization have been modelled using isotopic data to place constraints on the rates and extent of assimilation and the liquid phases involved. A number of isotopes have been used, e.g. De Paolo (1981) showed that a correlation exists between country rock age and ^{143}Nd/^{144} Nd ratios in continental igneous rocks which is suggestive of crustal contamination being important.

In general Sr and (to a lesser extent) Pb have had a major impact on research concerned with mantle derived magmas and crustal contamination (Taylor, 1980; De Paolo, 1981; Dickin *et al.*, 1981), although Sr data have also been indicated to be selectively changed during interaction of plutons with meteoric water, and may therefore give misleading results. Little if any work on this subject has been done concerning the assimilation of basic wallrocks by acidic magmas, the dominant work being orientated towards deeper large scale crustal assimilation.

Oxygen isotopes have also been of significance in investigating the reactions of magmas with high $^{18}0$ crustal rocks, particularly when combined with other isotopes, e.g. Taylor (1978) used 0 and H isotopes to show how many magmas may be strongly affected by the widespread melting and assimilation of hydrothermally altered roof-zone rocks above a magma chamber, whilst Taylor (1980) has indicated how correlations between initial $^{87}Sr/^{86}Sr$ and $^{18}0$ values show mixing of mantle magmas with high $^{18}0$ and high ^{87}Sr crustal metamorphics in the formation of certain Italian plutons. In his study, Taylor (1980) also concluded that "combined assimilation - fractional crystallization" effects in magmas will in many cases produce clear cut signatures when using 0 combined with Sr isotope data.

3.7 Conclusions

Assimilation is by no means a straightforward process and confirmation of it as a mechanism is often made difficult by simultaneously operating, or late stage processes which complicate matters.

The complexes studied in this work have been done so on the following grounds:

(1) All the areas show field relationships on all scales indicative of assimilation, consequently they all appear to be good candidates for study by geochemistry and mineral chemistry. Any deviations from those expected for assimilation must be explained by reference to additional processes.

(2) All the areas involve the assimilation of basic igneous wallrocks by acid magmas. Therefore the systems involve "simple" igneous chemistry (no sediments with odd compositions are involved), and because of the lower melting and crystallization temperature of the acid magma (below that of the wallrock) no actual melting of the country rock is involved. What is being seen therefore, is the reaction of crystals with the magma (and volatiles), and at the most the only melting of lower temperature material would be that of interstitial zeolites. This means that the overall assimilation process is clearer, especially in terms of field relations, than if a basic magma were involved when extensive melting could occur as well as reaction.

(3) The areas were chosen to minimize regional metamorphic effects, also to reduce as much as possible complications caused by hydrothermal alteration (although this is unavoidable).

(4) Small high level hybrid complexes were chosen where extensive (if any) fractional crystallization can probably be ruled out (note that the combined action of assimilation/fractional crystallization described in literature - O'Hara, 1977; Taylor, 1980; De Paolo, 1981 - has generally occurred during reaction between basic magmas and solid acidic crustal rocks), this would again allow as clear as possible a look at the simple hybridization process.

Despite all the precautions in choosing the areas, additional effects are inevitable particularly those involving a volatile phase. Such geochemical effects must be identified, explained and "removed" to reveal the geochemical characteristics of assimilation.

4. FIELD RELATIONS AND GEOLOGICAL SETTING

The complexes examined in this study were done so on the basis of a number of points outlined in Chapter 3.

(1) Notably they show strong field evidence for assimilation with xenoliths, veining and dyking being commonly seen (this is indicative of a "stoping" style of magma emplacement whereby any protective crystalline barriers are breached, allowing greater opportunity for assimilation due to increased magma/wallrock contact, compared with plutons with simple geometric outlines which offer less possibility for reaction).

Other factors include:

(2) The simplicity of the systems (i.e. one acidic magma assimilating basic wallrock) with the result that no melting is involved.
(3) Limited alteration is seen in the complexes.
(4) The small size and apparent high level emplacement of the complexes imposes thermal limitations which would probably rule out large scale coupled processes and the formation of zoned magma chambers. A further factor is that despite their small size, the complexes show evidence of additional processes such as the evolution of a magmatic hydrous phase which is known to play an important part in the assimilation process, allowing it to occur to a greater extent.

4.1 Glen Dubh, Isle of Arran

Early work on the Arran rocks in general was carried out by Gunn (1903) whose mapping of the whole island produced a framework for later advances such as that of Tyrrell (1928), who performed the first detailed work on the Central Ring Complex. He first noted the presence of heterogeneous intermediate rocks at Glen Dubh and proposed their origin was by reaction between granitic magma and gabbro.

Since this classical account, the only detailed work concerning the Central Ring Complex has been the description of the rock types and structure of the area around Ard Bheinn (King, 1955). This also included the first detailed geochemical study of some of the rocks. Other literature touching on the Glen Dubh area largely includes a number of regional and excursion guides, e.g. Gregory & Tyrrell (1924), Tomkeieff (1961), Macgregor (1965), although some studies have been made on hybrids and hybridization associated with some composite intrusions on the island in recent years, e.g. King (1982),

Kanaris-Sotiriou & Gibb (1985). These later studies are mainly thought to involve mixing of magmas.

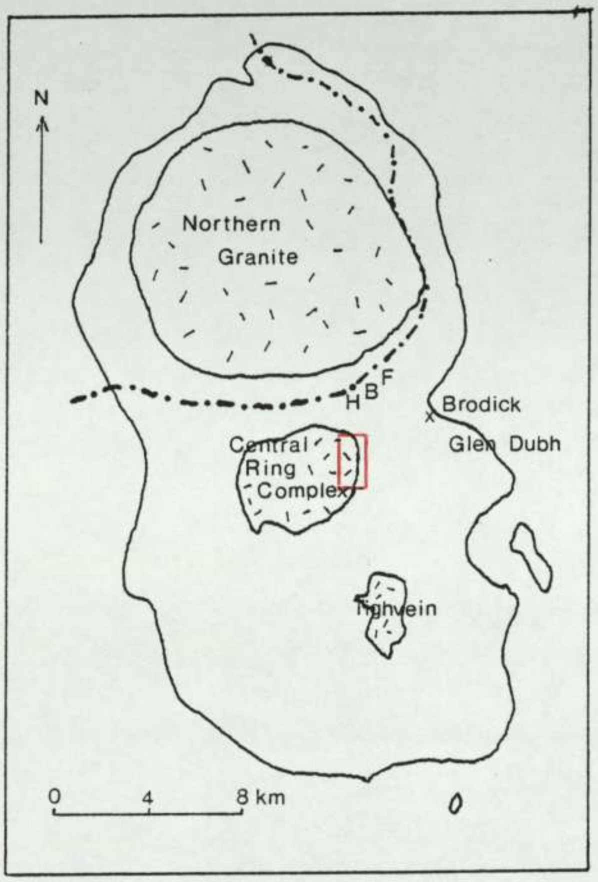
The classic hybrid locality of Glen Dubh is situated in the south eastern margin of the Central Ring Complex (Tyrrell, 1928), which is the smaller of two igneous centres on the Isle of Arran (Fig. 1). The Central Arran granite has been $^{40}Ar/^{39}Ar$ age dated as 58.3 ±4.4 Ma (Evans *et al.*, 1973) and it is assumed that the Central Ring Complex as a whole is of similar age.

The complex itself consists of a wide range of rock types in juxtaposition, but is dominantly granitic with some marginal areas of more basic rock of which Glen Dubh is one. It intrudes through Devonian sandstones which dip steeply away from the main Northern granite.

Glen Dubh is a complicated region of gabbros, granites and mottled heterogeneous rocks of intermediate composition, faulted and cross cut by dolerite dykes. Detailed field relationships are difficult to establish due to poor exposure although in places the gabbros are visibly cut by a network of thin acidic veins forming an extensive series of xenolithic and contaminated hybrid rocks. One of these net veined xenolithic areas was termed "Hybrid Hill" (Tyrrell, 1928).

There is much evidence for the incorporation of gabbro by the granite. Xenoliths up to 10 cm in length are exposed in various stages of modification from sharply defined basic inclusions to diffuse clotted xenocrysts in contaminated granite. Some xenoliths show angular margins whilst the more modified ones commonly exhibit rounded and corroded margins due to increased reaction with the acid material. Many xenoliths also show an

FIG. 1 MAP OF THE ISLE OF ARRAN SHOWING THE POSITION OF THE CENTRAL RING COMPLEX AND GLEN DUBH



The area of Glen Dubh studied is shown in red.

increase in grainsize around their margins due to this reaction.

Veining of the basic rock occurs by thread-like "stringers" which gradually widen out to form veinlets and veins of granite up to 2 cm in width.

These in turn broaden into larger granitic patches often containing numerous xenocrysts: however some areas appear homogeneous due to equilibration between acidic and basic material ultimately producing dioritic/granodioritic rock.

Whereas most granite veinlets show some degree of reaction with wallrock, a number of apparently late stage veins sharply cross cut all other rock types although these veins are largely aplitic in nature.

It proved impossible to map the area accurately into separate diorites, granodiorites and granites due to their variable nature and the complex and intimate associations between the rock types.

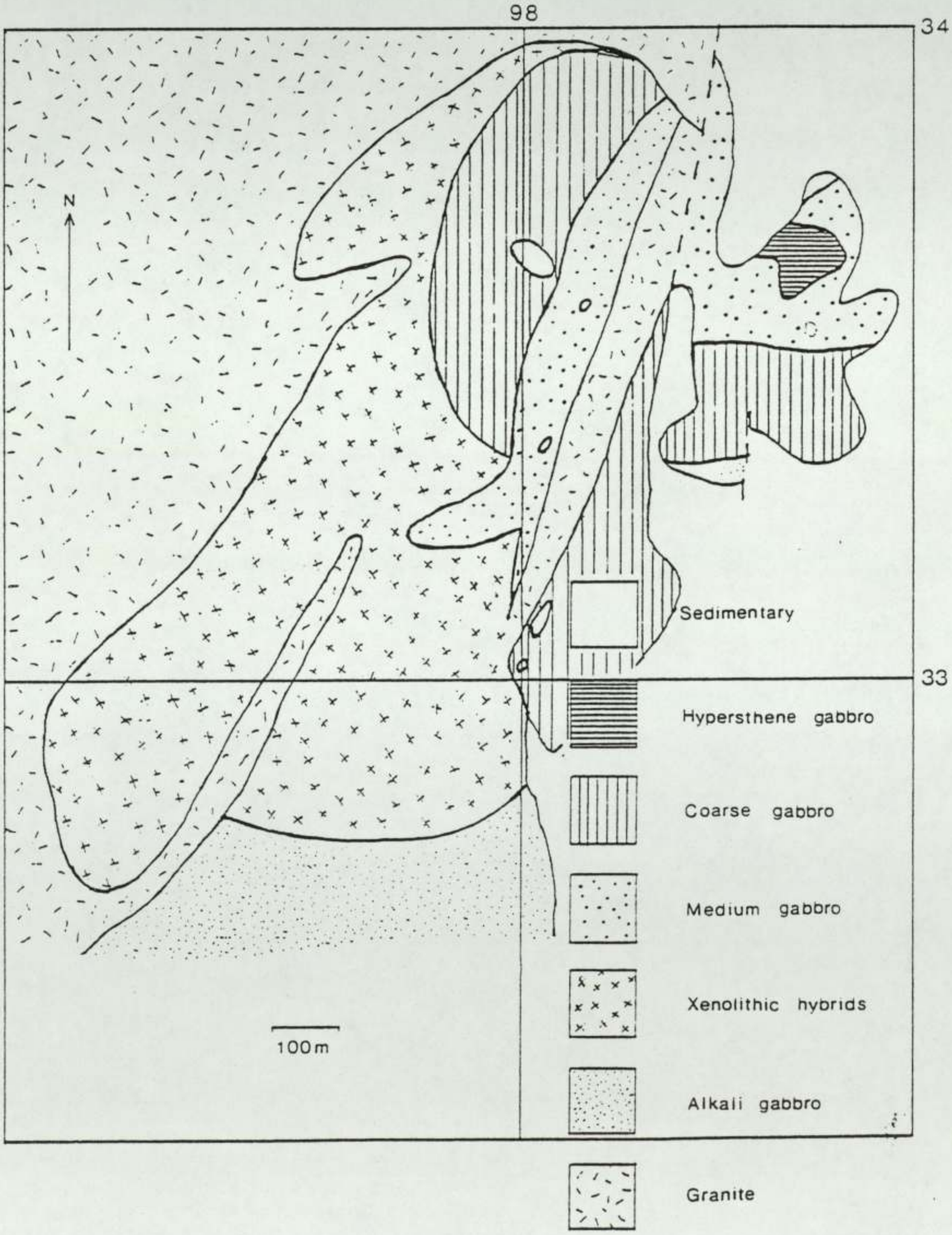
However, it was possible to demonstrate the existence of a number of gabbros (Fig. 2) in various stages of hybridization with granite and a tentative suggestion has been made as to the position of the boundaries of the gabbros before hybridization took place.

4.2 The Johnston Diorite Complex (Pembrokeshire)

The Johnston Diorites (Strahan *et al.*, 1914) are just one group of a great number of Precambrian igneous rocks first described in Pembrokeshire at the turn of the century. These early accounts were largely pioneered by the work of Hicks (1877) with the first descriptions of rocks termed the "Pebidian" and "Dimetian" in the St. Davids area, followed by petrographic and structural descriptions of similar rocks by Green (1908); Thomas & Jones (1912) and Williams (1934).

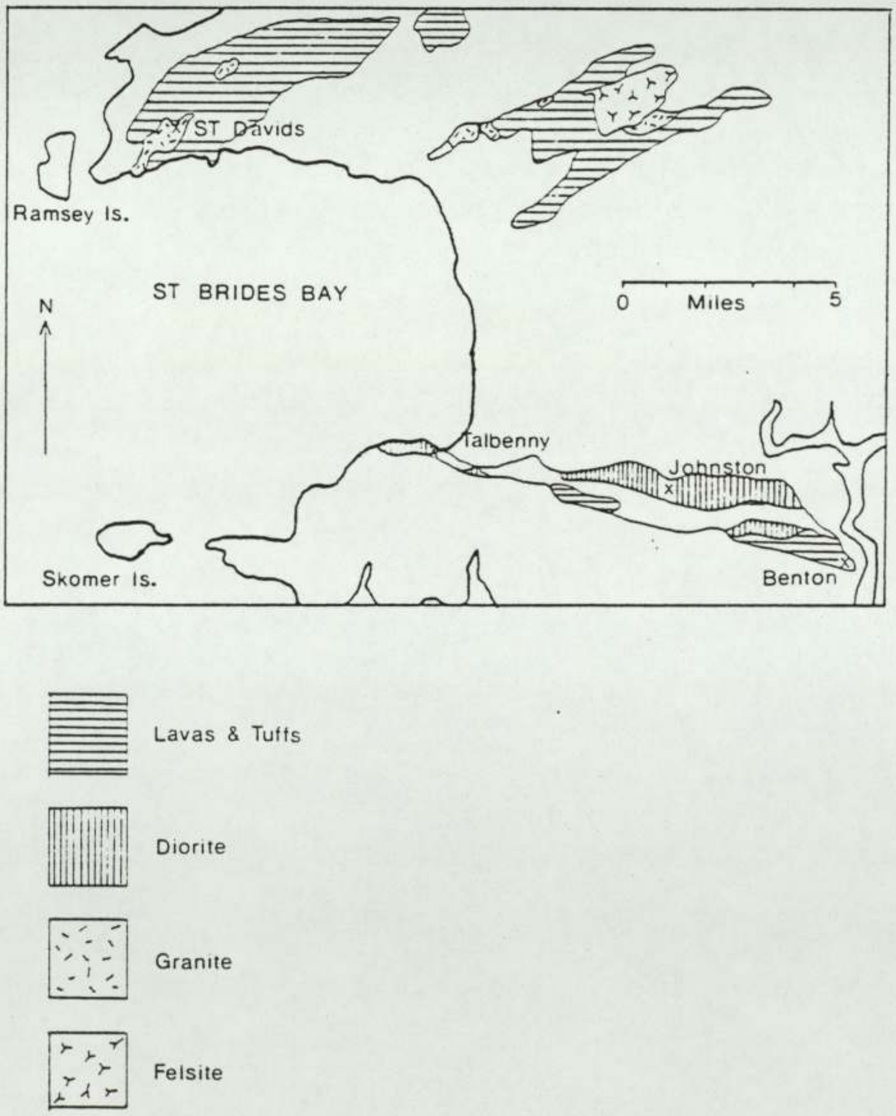
The Johnston Diorites themselves belong to a faulted, sporadically exposed belt of igneous rocks in Pembrokeshire, isolated from the Pebidian and Dimetian of St. Davids, and outcropping from St. Brides Bay at Talbenny east-south east through to the villages of Johnston and Benton (Fig. 3).

FIG. 2 GEOLOGICAL MAP OF THE AREA AROUND GLEN DUBH



(in part after Tyrrell, 1928)

FIG. 3 OUTCROP PATTERN OF THE PRECAMBRIAN IGNEOUS ROCKS OF PEMBROKESHIRE



(in part after Thomas & Jones, 1912)

The plutonic diorites are associated with Precambrian volcanics (the Benton Series) and show faulted contacts with sedimentary rocks of Silurian to Carboniferous age.

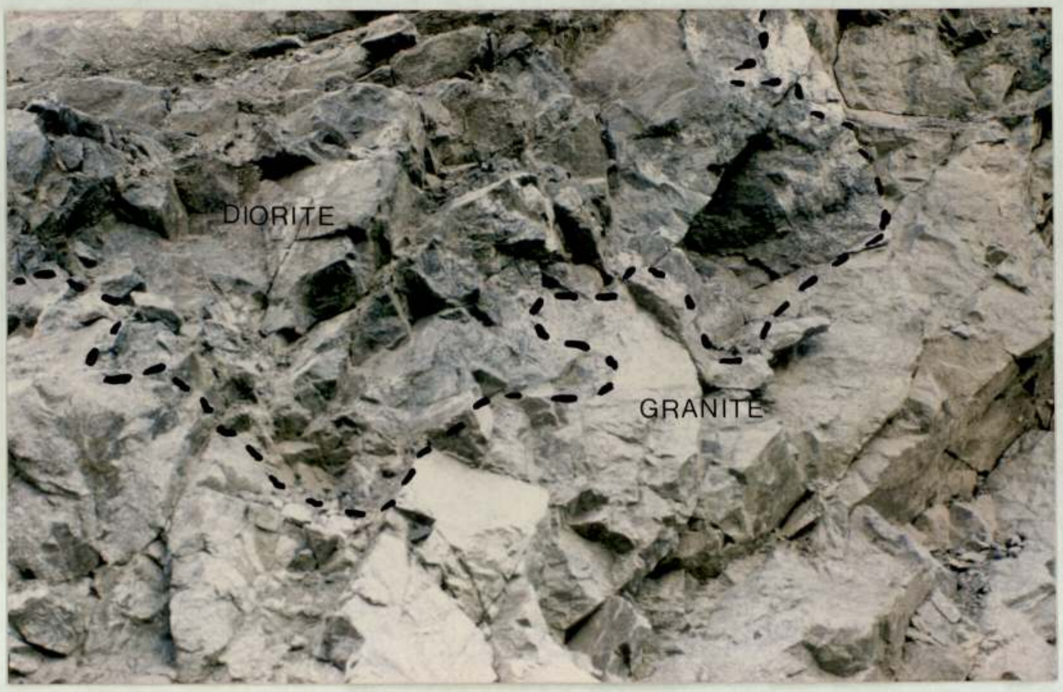
The earliest detailed observations on the Diorites were described in the Geological Survey Memoirs by Strahan *et al.*, (1914) who established the presence of a number of rock types and commented on their intimate associations and complexity. This work was reinforced by the later study of Cantrill *et al.*, (1916).

More recent years have seen an increase in literature published concerning the Johnston Diorites, most notably by Wright (1968, 1969) who first suggested that some of the rock types were formed by hybridization although other origins were also proposed (Claxton, 1963; Thorpe, 1970, 1972). Other studies have been largely general descriptions (Rast & Crimes, 1969; Baker, 1971; Shackleton, 1975; Thorpe, 1974, 1982) and various regional guides (George, 1970; Baker, 1982) which refer to the complex. A limited amount of geochemical work on the Johnston Diroites has also previously been carried out (Thorpe, 1970, 1972).

The Diorites are generally very poorly exposed, the best exposures being found along the coast and in the large quarry at Bolton Hill (grid ref. SM 9170 1140) near the village of Johnston where they form the largest inland outcrop. The rocks are exclusively fault bounded with no intrusive contacts which has led to some uncertainty in the past as to their age. Recently, however, Patchett & Jocelyn (1979) have dated the whole series using U/Pb zircon ages at late Precambrian (643^{+5}_{-28} Ma).

The diorites are similar to some of the Dimetian intrusions of St. Davids, and have been suggested to be comparable (George, 1970), although it is generally believed that the two series are not correlated (e.g. Baker, 1971). The appearance, composition and structure of the Diorite complex is however more markedly similar to the late Precambrian complex of the Malvern Hills (Wright, 1969; Thorpe, 1972, 1974), the two igneous series possibly being related.

PLATE 4.1 CONTACT BETWEEN DIORITE AND INTRUSIVE PALE GRANITE AT BOLTON HILL

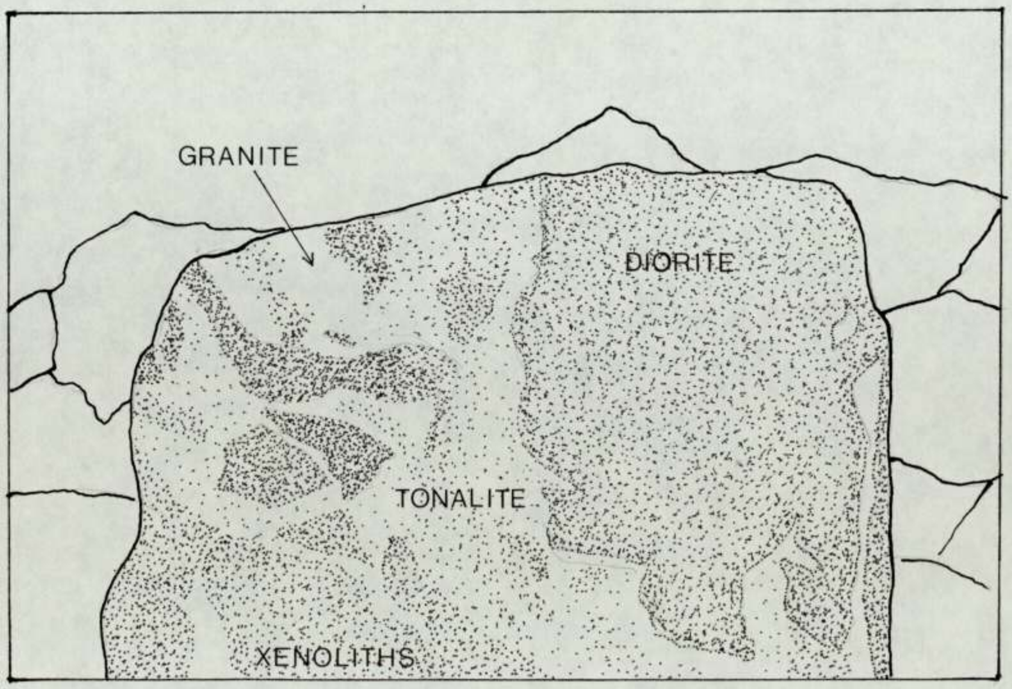


Diorite appears dark, granite appears pale, intruding from below.
Field width 4 metres.

PLATE 4.2 VEINLETS OF PALE GRANITE FORMING A NETWORK, SHARPLY INTRUDING DIORITE. (Bolton Hill)

PLATE 4.3 <u>XENOLITHS OF DIORITE IN GRANITE</u>. (Bolton Hill)

The granite shows all stages of reaction with diorite to form irregular areas of quartz diorite and dark contaminated granite.



At Bolton Hill Quarry the dominant rock type is a dark medium grained diorite intruded by pale medium grained granite. Contact relations between the two are very intricate (Plate 4.1) with granitic veins and veinlets commonly forming a network through the host diorites (Plate 4.2). Veins vary from a few mm up to 1 m. in thickness and may sharply cut the diorites or show some reaction with them.

Xenoliths of diorite in granite are common, some show sharp contacts with the granite whilst others appear more diffuse and
gradational (Plates 4.3 and 4.4) with irregular patches of hybrid material.

Many xenoliths show almost complete equilibration with the granitic material due to acidification, ultimately losing their identity to merge with the host rock (Plate 4.5).

Such equilibration between diorite and granite results in the formation of a series of intermediate, largely heterogeneous, hybrid rocks (Plate 4.6) ranging from quartz diorite to tonalite in composition, although complete reaction commonly removes all traces of xenoliths and xenocrysts to produce homogeneous varieties.

All rocks may be cut by later granitic or pegmatitic veins which show no form of hybridization on contact with the earlier types (Plate 4.7). The quarry is traversed by find grained subvertical doleritic dykes from 1 - 3 m. in width (Plate 4.8). These dykes are occasionally bifurcated and show chilled margins against the earlier plutonic rocks, having intruded after the hybridization process took place.

A very weak foliation is apparent in the diorites which may be brecciated and cut by secondary veinlets of epidote. A stronger
foliation is present in the Johnston Diorites near Talbenny where the rocks were named "The Dutch Gin Schists" (Claxton, 1963). It has since been shown that these are merely intensely sheared diorites brought about by internal thrusting at the sole of a major Hercynian Thrust fault (Baker *et al.*, 1968), the weak foliation visible at Bolton Hill being presumably a reflection of the distance from a major thrust plane.

PLATE 4.4 DIORITE XENOLITHS WITH SHARP OUTLINES CONTAINED IN MODIFIED GRANITE. (Bolton Hill)

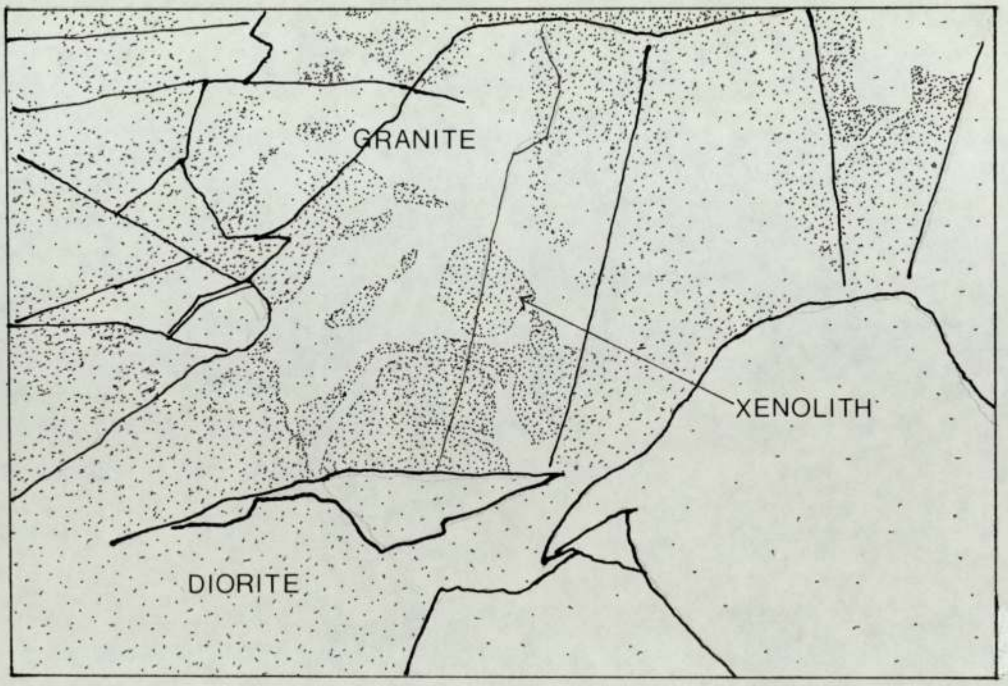
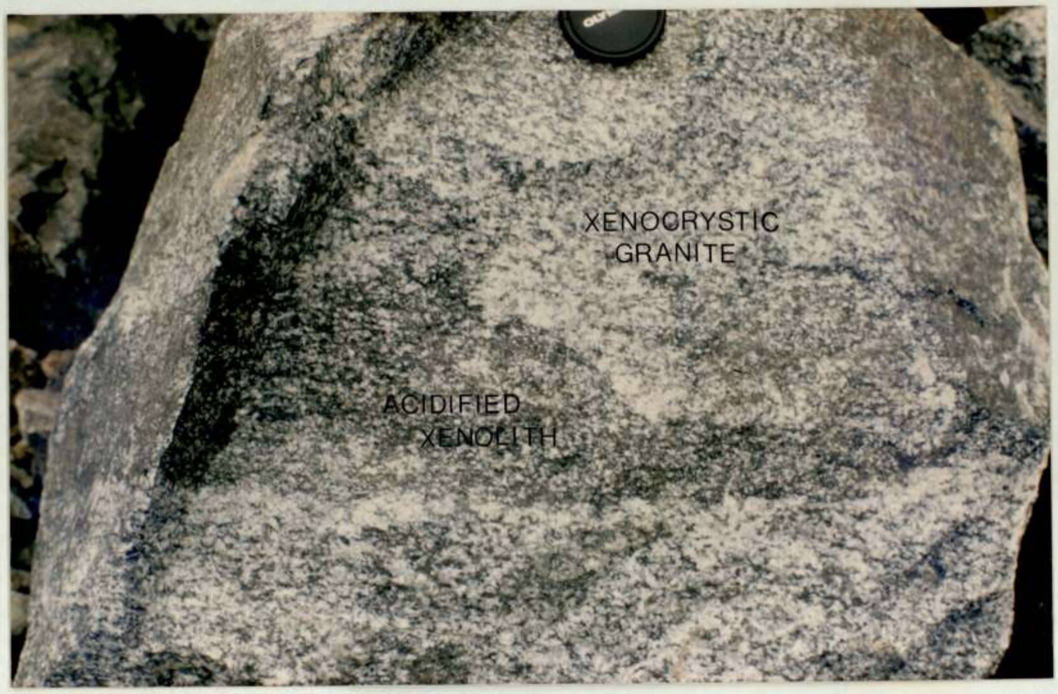


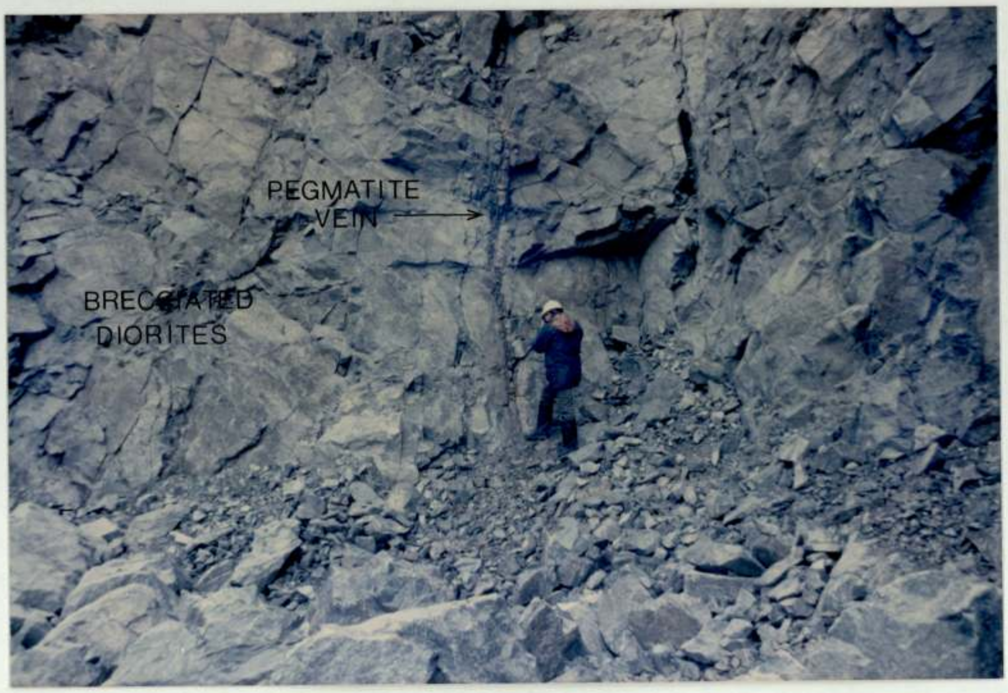
PLATE 4.5 DIORITIC XENOLITH SHOWING DIFFUSE, GRADATIONAL OUTLINES, AND INVASION BY ACID MATERIAL. (Bolton Hill)



Xenolith shows almost complete equilibration with the surrounding magma.

PLATE 4.6 XENOLITHIC, HETEROGENEOUS INTERMEDIATE HYBRID ROCKS DUE TO REACTION BETWEEN DIORITE & GRANITE. (Bolton Hill)

PLATE 4.7 RED FELDSPAR-RICH PEGMATITE VEIN CUTTING THROUGH DIORITES (Bolton Hill)



The vein cuts through sheared, brecciated diorites with no reaction between it and the diorites.

PLATE 4.8 BASALT DYKE CUTTING JOHNSTON DIORITES.

The 3 metre wide dyke shows bifurcation and is distinguished from the other plutonic rocks in the quarry by its darker appearance.

Looking South.

4.3 The Garabal Hill Complex (Argyllshire)

The intrusive complex of Garabal Hill is situated in the Southern Highlands of Scotland near the northern shore of Loch Lomond, Argyllshire. The complex stretches from the village of Ardlui, westwards to Glen Fyne and intrudes through Dalradian schists.

It was first studied and mapped by Dakyns & Teall (1892), with some later work concerning the more basic rocks by Wyllie & Scott (1913), although little attempt was made to separate the various rock types in either account.

The whole complex was subsequently examined and mapped in much greater detail in the classical work of Nockolds (1941), who commented on the presence of a great number of different rock types ranging from granites through to ultrabasics. He included detailed petrographic descriptions and, to date, the only geochemical analyses carried out on the rocks. In addition Nockolds (1941) noticed the existence of xenolithic rocks and was the first to propose the possibility of some of them forming by hybridization.

The Garabal Hill intrusion was suggested to be of Lower Devonian age (Nockolds, 1941) and has since been dated at 406±4 Ma by Rb/Sr dating on mineral separates (Summerhayes, 1966), apparently confirming this suggestion.

The particular rocks studied outcrop around Garabal Hill itself which rises 425 metres from the shores of Loch Lomond at the eastern margin of the complex. The area is geologically complicated, consisting of a huge variety of igneous rocks centred around an elongate body of ultrabasics (peridotites, pyroxenites, hornblendites) and associated gabbros, surrounded by a later granodiorite.

The granodiorite shows extensive evidence of reaction with the more basic rocks, which are seen to be veined in places although exposure is poor. The veins range from 5 cm. in width to minute veinlets less than 1 mm. in diameter.

Between the basic and acidic rocks is an area of variable width of heterogeneous, xenolithic intermediate rock caused by intrusion of acidic magma into the basic core, resulting in the breaking off of xenoliths of gabbro and incorporation into the magma. Most xenoliths show

PLATE 4.9 BASIC XENOLITH SHOWING BREAKDOWN AND VEINING BY GRANODIORITE (Garabal Hill)

The xenolith is cut by thin granitic "stringers" which widen out to form irregular patches of hybrid material.

some veining by, and reaction with, the granodiorite (Plate 4.9). Xenoliths may also have sharp angular outlines or, more commonly, gradational ones with the granodiorite producing marginal areas of dioritic material (Plate 4.10).

Extensive acidification by acidic magma may result in xenoliths becoming very diffuse in outline (Plate 4.11), ultimately completely merging with the contaminated host rock. This may take on a mottled appearance due to the presence of numerous xenoliths in various stages of breakdown to xenocrysts (Plate 4.12).

Complete equilibration between wallrock and intrusive magma may result in the formation of apparently "normal" homogeneous dioritic rocks. These may occur dominantly with the heterogeneous intermediate types in a zone between the basic rocks and the granodiorite (Fig. 4), and are hybrids of the two. The wallrocks, in addition, show strong evidence of metasomatic alteration close to the contact zone with the formation of hornblende gabbros.

Late stage acidic veins are seen cutting sharply through the earlier rocks, and occasional dolerite dykes occur up to
1 m. in width.

4.4 Discussion

The complexes are remarkable similar in terms of field relations, being characterized by the presence of acidic magma intruding through and reacting with basic wallrock.

Veining of the wallrock occurs in each case with the formation of xenolithic rocks, in which xenoliths show various stages of breakdown and reaction with the magma, ultimately completely equilibrating with it to produce homogeneous intermediate varieties. Xenoliths range from having sharp, angular contacts with granite to rounded, diffuse outlines which are difficult to identify due to their acidification by the granitic material, and may be of variable size down to little more than small clusters of xenocrysts.

All the complexes consequently show a series of hybrid rocks, according to the degree of reaction between the basic and acidic endmembers, all intermediate in composition between

PLATE 4.10 BASIC XENOLITH SHOWING SHARP AND GRADATIONAL BOUNDARIES WITH GRANODIORITE (Garabal Hill)

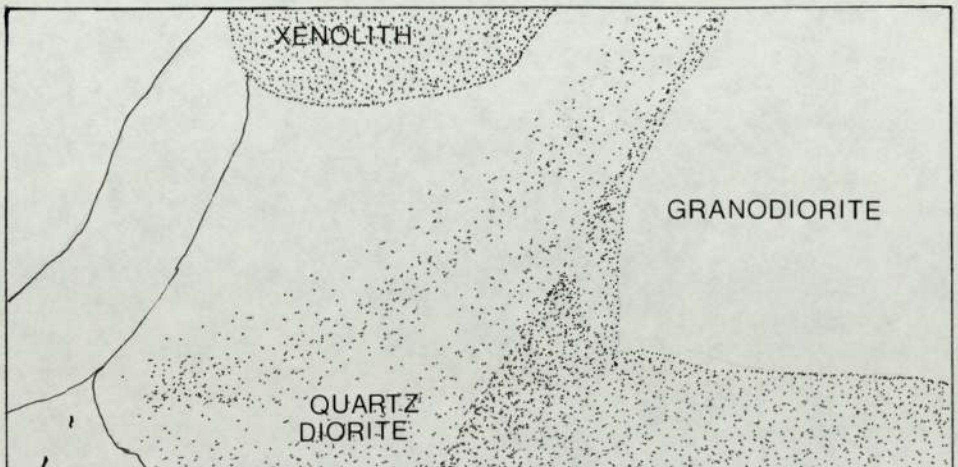


PLATE 4.11 GRANODIORITE CONTAINING ONE SHARP XENOLITH AND ANOTHER MORE ACIDIFIED, DIFFUSE VARIETY (Garabal Hill)

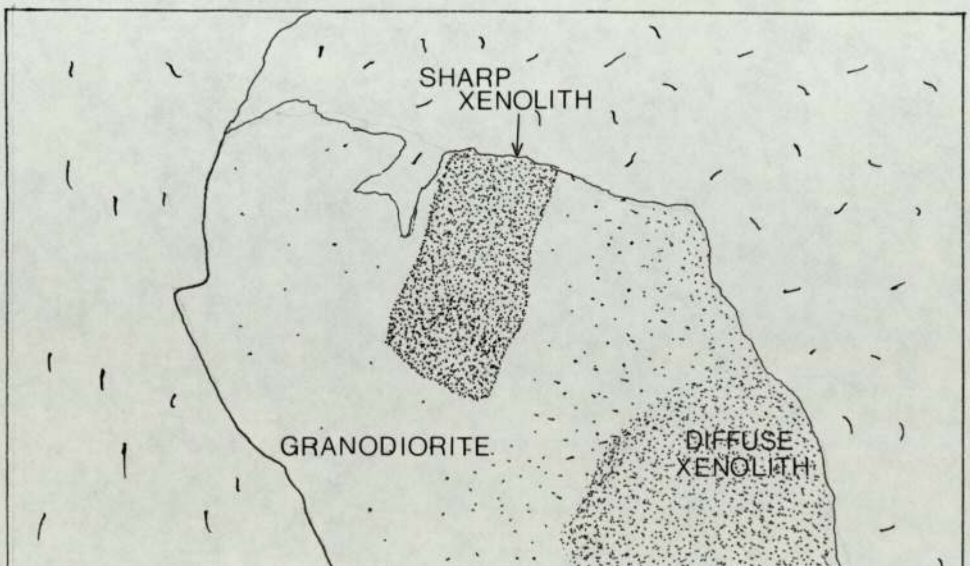
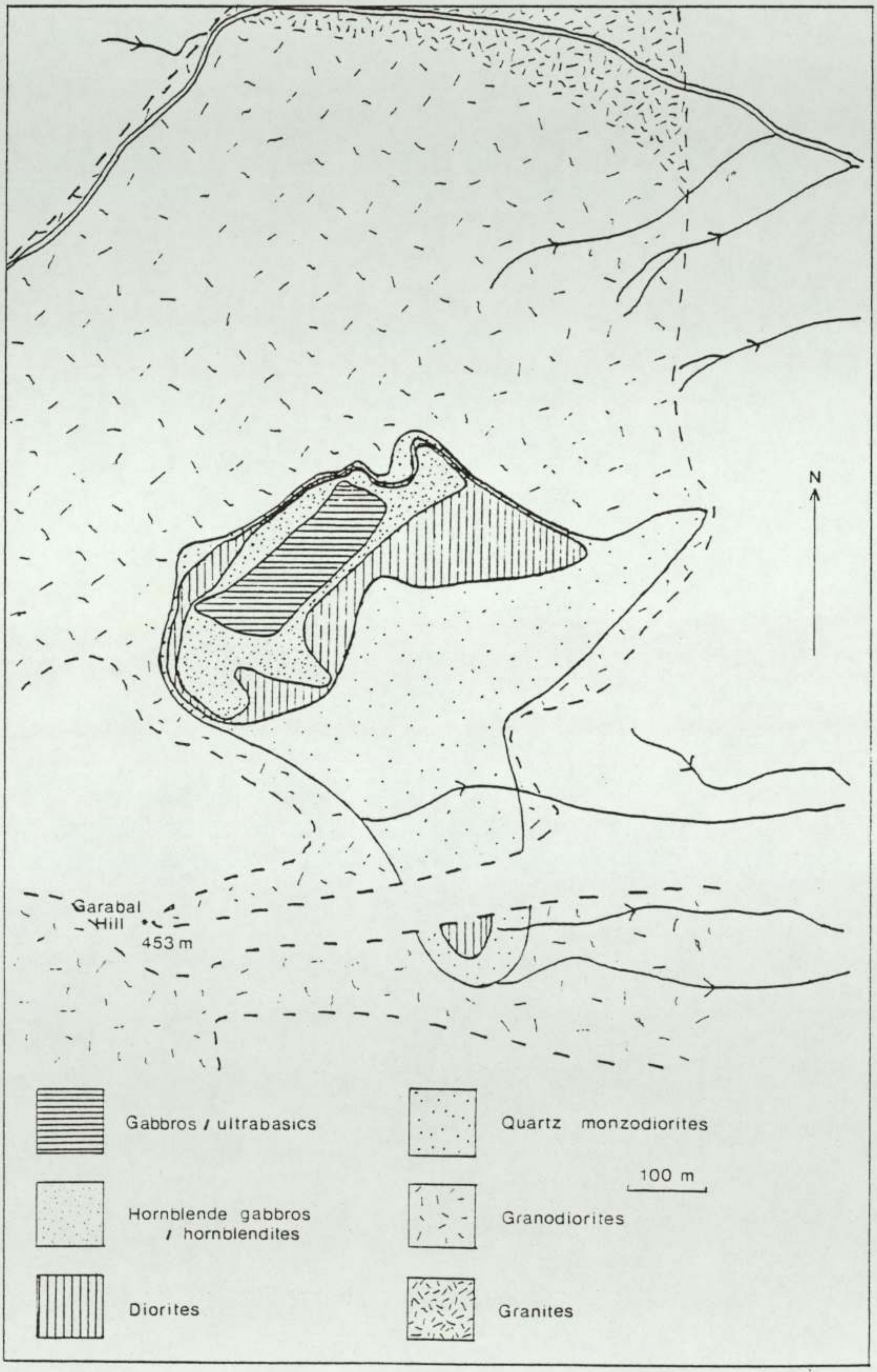


PLATE 4.12 MOTTLED HETEROGENEOUS GRANODIORITE SHOWING VARYING DEGREES OF BREAKDOWN AND INCORPORATION OF XENOLITHS, WITH THE FORMATION OF BRONZE-COLOURED BIOTITE

FIG. 4 GEOLOGICAL MAP OF THE AREA AROUND GARABAL HILL



(in part after Nockolds, 1941)

these respective endmembers.

These features would appear to provide overwhelming field evidence of assimilation having occurred on a relatively small scale in these areas, with the formation of apparently typical intermediate igneous rocks, in addition to the mottled heterogeneous types "frozen" in time before it could continue to completion.

5. PETROGRAPHY

The rock types in each of the complexes are divided into their constituent acidic and basic endmembers, and the resultant hybrid intermediate, xenolithic rocks.

5.1 Glen Dubh, Isle of Arran

5.1.1 Gabbros

The gabbros of Glen Dubh can be distinguished on petrographic criteria and classified as one of four types.

(a) Alkali gabbros
(b) Hypersthene gabbros
(c) Coarse gabbros
(d) Medium gabbros

All the gabbros contain pyroxene in varying proportions. The Alkali gabbros are distinguished by the presence of pale purple-brown titanaugite whilst the remaining three varieties contain colourless to pale green augite, often in the form of euhedral 8-sided crystals.

In addition, the Hypersthene gabbros are particularly characterized by the occurrence of lozenge-shaped crystals of pale pink to pale green pleochroic hypersthene - a mineral not present in the other gabbroic rocks.

Plagioclase is of a bytownite composition in the Alkali gabbros, whereas in the others it occurs as subhedral laths of labradorite (An_{67}) up to 2.5 mm., and often in a sub-ophitic relationship with augite.

Altered remnants of olivine occur only in the Alkali gabbros, and are mainly pseudomorphed by greenish-yellow serpentine, green chlorite (penninite) and magnetite.

Minor amounts of brown hornblende and dark brown biotite are seen bordering augite, and are presumably indicative of incipient alteration preceding the assimilation process.

Accessory minerals are dominantly magnetite and ilmenite with few squat crystals of apatite. Magnetite and ilmenite form both discrete grains, and minute inclusions in augite, the magnetite often showing exsolution lamellae of ilmenite.

The rocks all show alteration of pyroxene to uralitic amphibole, yellow epidote and green penninitic chlorite. Plagioclase alters to epidote and sericite. Veinlets and patches of calcite, epidote and fluorite are also abundant (Plate 5.1). Much of this alteration is a result of hydrothermal alteration post dating the main hybridization event.

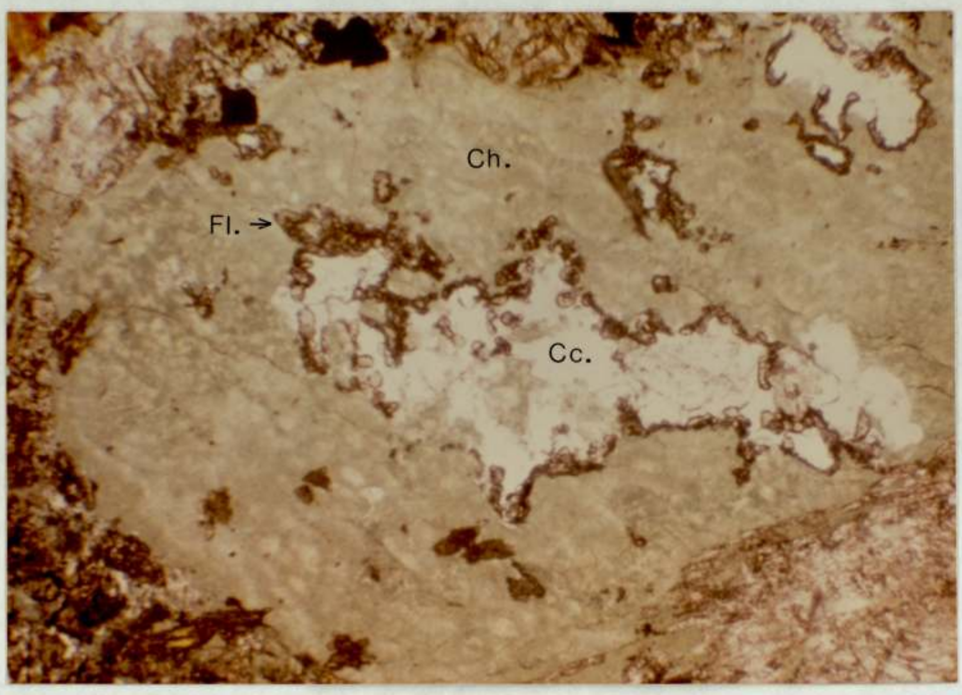
5.1.2 Granites

The medium grained granites consist dominantly of clear quartz and turbid orthoclase feldspar in variable proportions, and often in the form of a coarse granophyric intergrowth moulded around plagioclase feldspar although discrete crystals also occur.

The plagioclase varies inversely in proportion with the quartz/orthoclase content. It is mainly of oligoclase composition although occasionally crystals are zoned to more calcic andesine cores (An_{46}). The plagioclase tends to form euhedral or subhedral laths.

Mafic minerals are mainly altered green hornblende and brown biotite, the hornblende often being found rimming remnant grains of colourless augite. The accessory minerals are apatite and colourless or pale brown euhedral zircon which, where it is present in biotite forms pleochroic haloes. Colourless euhedral epidote and pale brown to black, strongly pleochroic allanite are also both abundant as small crystals, often forming clearly defined boundaries with each other. Pale brown sphene is present usually in close association with ilmenite and magnetite, suggesting that it formed by reaction from Ti-bearing phases. Pyrite and chalcopyrite are the dominant sulphide minerals.

PLATE 5.1 ALTERATION PATCH IN AN ARRAN GABBRO SHOWING A CENTRAL AREA OF CALCITE BORDERED BY YELLOW FLUORITE AND GREEN MARGINAL CHLORITE (SPECIMEN 46)



Field of view 3.4 mm

PLATE 5.2 HORNBLENDE IN ARRAN HYBRID ROCK SHOWING OPTICAL ZONING FROM A BROWN CORE TO A GREENISH RIM (SPECIMEN BA7)

Field of view 3.4 mm

The presence of apparently xenocrystic andesine and augite crystals suggests that even the granites themselves have undergone a certain degree of contamination by basic material.

5.1.3 Intermediate hybrids

The intermediate rocks are of very variable composition. They grade from partially assimilated gabbro or dolerite xenoliths through a mafic diorite to quartz diorites, monzodiorites and granodiorites.

Plagioclase feldspar is the most abundant mineral throughout the intermediate series showing very strong marginal zoning from labradorite or andesine to oligoclase. The zoned feldspar overgrowths result in an increasingly euhedral character for the plagioclase laths. These laths are xenocrystal in origin and the strongly zoned margins represent additional growth of the crystals in the acidic magma.

Colourless or pale green augite is present and is variably replaced by hornblende with the following pleochroism.

α = Yellow
β = Pale green
γ = Brownish green

The hornblende increases in proportion relative to augite in the more acidic rocks. It displays a more euhedral tendency when in contact with quartzo-feldspathic material due to further growth of the xenocrysts in the acid magma prior to its crystallization.

The hornblende is also zoned from brownish-coloured cores to more greenish margins (Plate 5.2). In certain rocks (generally the more acidic types), the hornblende completely replaces pyroxene, whereas in others the pyroxene occurs as relic cores within the amphibole. Biotite occasionally replaces both augite and hornblende and is strongly pleochroic from dark brown to yellow.

α = Straw yellow
$\beta = \gamma$ = Dark brown

Biotite also forms independent crystals unconnected with the earlier mafic minerals (as does hornblende), although they may be associated with magnetite.

The proportions of quartz and orthoclase feldspar vary from small interstitial crystals between the grain boundaries of the more basic minerals to patches showing coarse granophyric intergrowths. Orthoclase generally is of a turbid appearance whilst quartz is clear.

Apatite is the commonest accessory mineral and is extremely abundant in the form of short euhedral crystals or long, thin, often hollow, needles (Plate 5.3) reaching lengths of up to 3 mm. These needles cross cut all other minerals but are particularly common in hornblende, biotite and zoned plagioclase (the minerals thought to form during the assimilation process). Apatite is far more abundant in these intermediate rocks than in either the basic or acidic end members thought to be involved in this process.

Pale brown euhedral zircon is a minor phase in the more granitic rocks along with colourless euhedral epidote, pale brown sphene
and strongly pleochroic allanite with the following colour scheme.

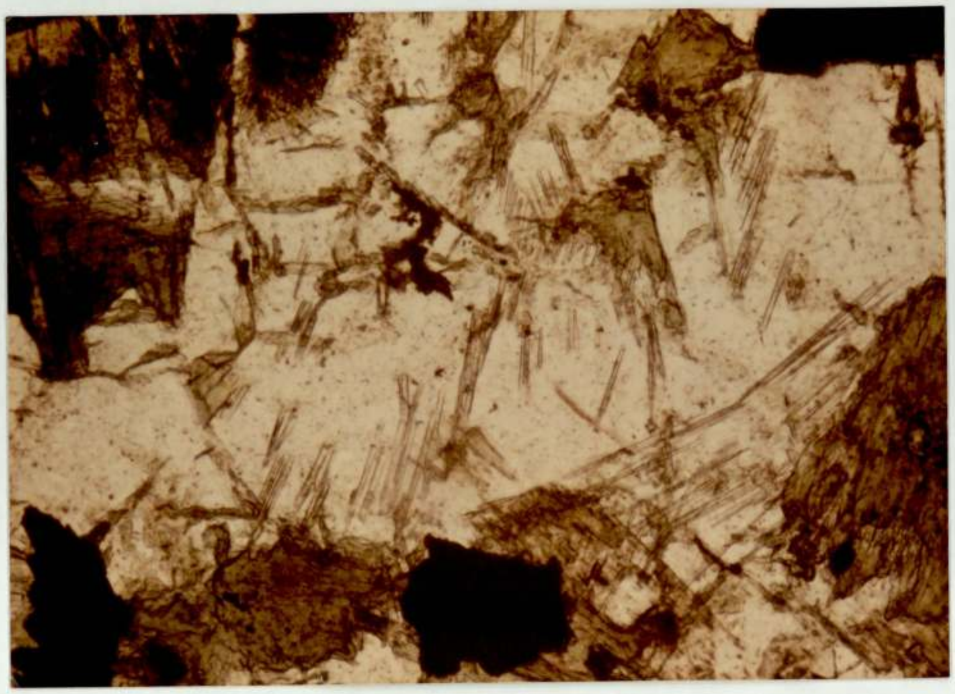
α = Reddish brown
β = Brownish yellow
γ = Black

Sphene is again associated with ilmenite and magnetite, which are in turn found in the vicinity of other mafic minerals.

The Fe-Ti oxide inclusions present in augite do not occur in the replacing hornblende presumably due to Fe and Ti being incorporated within the amphibole structure (see Chapter 6.).

The marked abundance of apatite appears to be a characteristic feature of hybrid and xenolithic intermediate rocks, and has been reported by numerous authors, e.g. Harker

PLATE 5.3 "SWARMS" OF APATITE NEEDLES IN AN ARRAN HYBRID



Field of view 2.2 mm (Specimen 26)

Note the presence of needles traversing earlier-formed pyroxene.

(1904), Nockolds (1933, 1941), Claxton (1970), Miyashiro (1970), Brown *et al.,* (1978), Brown & Becker (1986).

5.1.4 Xenoliths

Xenoliths are abundant and can be seen in various stages of breakdown and alteration by contaminated granites. The least altered xenoliths are recrystallized, with colourless to pale green augite seen breaking up into a mosaic of irregular rounded granules radiating from a common source, along with plagioclase laths which combine to produce an often striking reticulate pattern. In contrast, some of the xenoliths exhibit marked evidence of metasomatism associated with the invasion of the granite, with augite altering to green-brown hornblende and green or brown biotite, and labradorite replaced by andesine.

The metasomatism of the xenoliths and their constituent minerals has the effect of largely destroying their original metamorphic texture. It is non-uniform, being extensive in some xenoliths whilst virtually absent from others. Also it is not of a uniform occurrence within individual xenoliths as it may be seen to be present in parts but not in others.

In certain xenoliths all the augite is seen to have been replaced by hornblende and biotite. The hornblende/biotite ratio is also variable and is unrelated to the ratio in the surrounding granite, nor is it dependent upon the amount of acidic material which has entered the xenolith.

Large numbers of apatite needles cross cut the xenoliths, whilst colourless euhedral epidote and pale brown sphene may occur in their vicinity.

Both are more abundant than in either the basic rocks or the "uncontaminated" granites. The invasion of the xenoliths by granite causes an increase in grainsize of the constituent minerals and the development of a more euhedral character for both the feldspars and hornblende when compared with their irregual anhedral nature in the metasomatized xenoliths. The invasion of the xenoliths by granitic magma also marks the beginning of their breakdown and disintegration into individual xenocrysts, subsequently contaminating the magma.

5.1.5 Hydrothermal alteration

All of the rock types at Glen Dubh have suffered from post-crystallization alteration with the result that augite is at times replaced by pale greenish yellow, fibrous, uralite of actinolitic composition, and yellow granular epidote.

Hornblende alters to pale green "penninitic" chlorite and yellow epidote, whilst biotite is replaced by chlorite, epidote and granules of sphene.

Plagioclase may be extensively altered to sericite, calcite and epidote, whilst ilmenite is commonly bordered by sphene and magnetite by haematite.

Intergrowths of pyrite, chalcopyrite, sphalerite, bornite and chalcocite occur in intensely altered rocks as granular aggregates, and the rocks may also be traversed by veinlets and patches of calcite, epidote and yellow fluorite although this is non-uniform in distribution. It is probable that these later hydrothermal changes are isochemical but possible introduction or removal of certain elements should be borne in mind when chemical variation in the rocks is assessed (Chapter 7).

5.2 The Johnston Diorites

5.2.1 Diorites

The basic diorites at Bolton Hill are of two petrographically distinct types:

(a) Dark diorites
(b) Pale diorites

(a) Dark diorites

These are medium grained rocks comprising variable proportions of hornblende and plagioclase feldspar, and ranging from hornblende diorite to a more feldspathic diorite (Williams, (1934) noticed a similar wide variation in the proportions of these minerals in the Hollybush Diorite, N. Pembrokeshire). Plagioclase is of an andesine composition (An_{47}) although fresh crystals are uncommon due to its intense alteration.

Hornblende forms anhedral, interlocking crystals showing strong pleochroism:

α = Yellow
β = Olive green
γ = Green/brown

These hornblende crystals combine to form a framework separating areas of formless plagioclase (Plate 5.4). A pale green to colourless twinned cummingtonitic amphibole is also present, partly replaced by hornblende. This replacement occurs as distinct, sharp and irregular patches of hornblende both in the cummingtonite and rimming it. Both amphiboles are in optical continuity, a feature described by Iwao (1937) and Kuno (1938) in dacites from Japan.

Magnetite is present as discrete grains, but may also occur as tiny crystals between the grain boundaries of hornblende and within cummingtonite. Ilmenite forms discrete crystals rimmed by sphene and occurs as exsolution lamellae in the magnetite. Apatite needles are common within some of the hornblendes whilst other accessory minerals are marcasite and chalcopyrite.

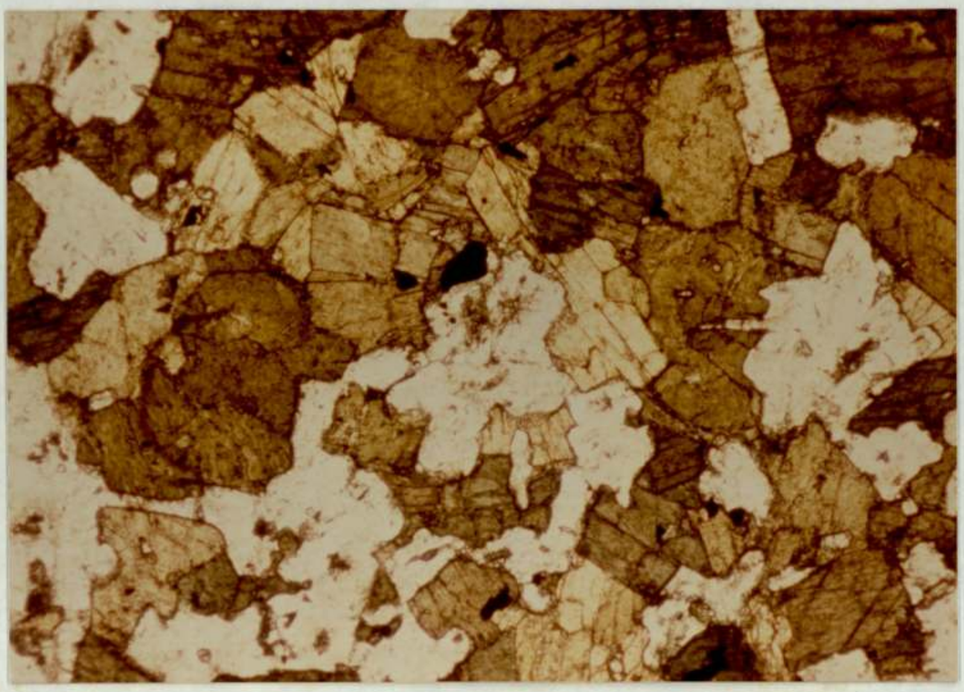
(b) Pale diorites

The pale diorites are very similar in appearance to the Dark diorites, the main difference being the hornblendes which are paler and more green rather than green-brown (Plate 5.5). The colour scheme of the pale hornblendes is as below:

α = Yellow
β = Pale blue-green
γ = Green

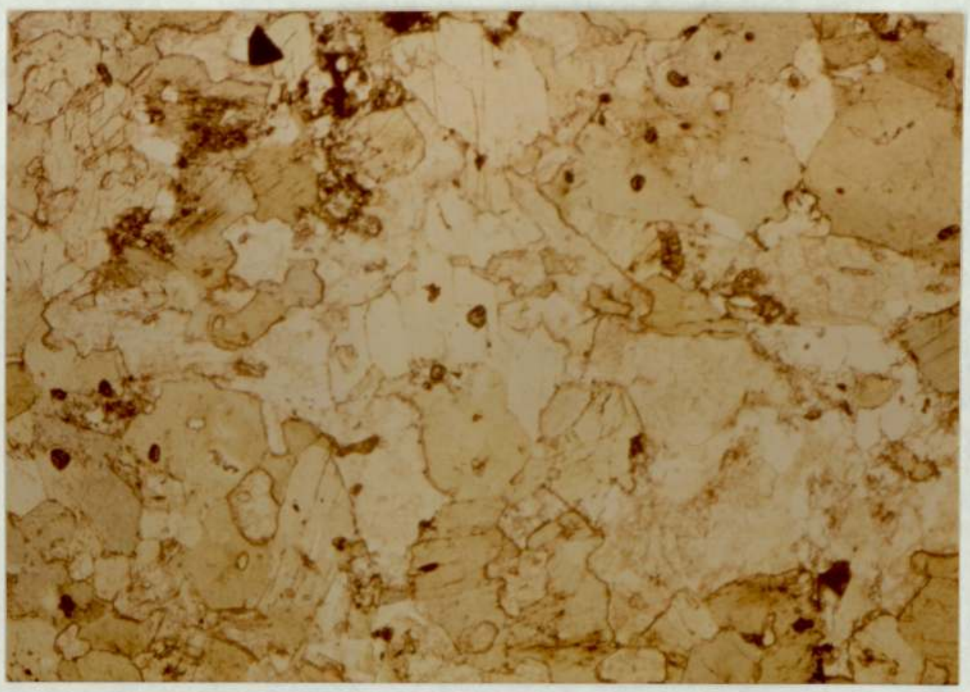
Another major difference between the diorites is the absence of cummingtonite in the Pale variety.

PLATE 5.4 BOLTON HILL DARK DIORITE



Field of view 3.4 mm (SPECIMEN BH 114X)

PLATE 5.5 BOLTON HILL PALE DIORITE



Field of view 3.4 mm (SPECIMEN BH 100)

Plagioclase of andesine composition is the only other major constituent of the diorites. It forms the centres of frameworks of hornblende crystals although it may be extremely altered and often pseudomorphed. Magnetite, ilmenite and apatite are all less abundant than in the darker diorite.

The other accessory minerals include pale brown sphene rimming ilmenite whilst marcasite and chalcopyrite are the dominant sulphides.

The textural appearance of the diorites as an anhedral framework of plagioclase and hornblende tends to indicate that they are not true diorites (this is confirmed by chemical analysis of the rocks and discussed in Chapter 7).

5.2.2 Granites

Two separate types of granite also outcrop at Bolton Hill and can easily be distinguished on petrographic criteria.

(a) Albite granite
(b) Microcline granite

(a) Albite granite

The Albite "granite" is a medium to coarse grained rock composed almost totally of quartz and plagioclase feldspar.

Quartz may form up to 50% of the total rock and generally shows undulose extinction, evidence of strain and recrystallization. The quartz also occurs as distinct individual crystals as does plagioclase which varies in composition from albite (An_5) to occasionally more calcic oligoclase (An_{16}), and constitutes 50% - 60% of the rock. The feldspar is also strained and recrystallized with deformed and fractured twin planes.

Alteration of the plagioclase in these granites is much less intense than in the diorites due to their more sodic nature. A few altered remnants of mafic minerals may occur largely represented by green penninitic chlorite.

Pale brown euhedral zircon, colourless euhedral epidote and needles of apatite are the main minor phases, although small amounts of pale brown sphene may be present with altered remnants of opaque oxide material. Zircon sporadically causes the formation of pleochroic haloes in chlorite.

A number of albite pegmatites are associated with the granites, which are similar in terms of mineralogy but coarser grained being composed almost entirely of intimate intergrowths of quartz and albite (although a few contain largely quartz and epidote). The granites and pegmatites often show zones of crushing and shearing.

(b) Microcline granite

The microcline granite is also medium to coarse grained but differs from the albite granite in containing two feldspars, a plagioclase of albite or oligoclase composition and a less abundant coarsely perthitic microcline.

The microcline occurs interstitially between plagioclase and quartz and shows exsolution of albite. It also exhibits strain features and evidence of recrystallization. Plagioclase and quartz form separate crystals rather than intergrowths, and are strained and recrystallized showing undulose extinction similar to that seen in the albite granites.

Minor epidote and zircon are present, the zircon forming pleochroic haloes in altered remnants of mafic minerals. Sphene is also apparent and is far more abundant than in the albite granites. Brown allanite, absent from the albite granites, occurs in very minor amounts together with sporadic needles of apatite.

The microcline granites are associated with microcline- bearing pegmatites in which the microcline occurs in coarse granophyric intergrowths with quartz, albite being completely absent.

Both the granites and pegmatites show shear and crush zones.

5.2.3 Intermediate hybrids

The hybrid rocks range from quartz diorites to tonalites due to impregnation and assimilation of both the pale and dark diorites by the albite granite, the process occurring to differing extents.

All the hybrids contain dark or pale hornblendes, of largely or exclusively xenocrystal origin, which decrease in proportion in the more acidic rocks. The hornblendes become coarser in grain size, and are more euhedral, when in contact with the acidic material as a consequence of further growth of the crystals in the granitic liquid (in contrast to the smaller anhedral hornblendes in the diorites).

The dark hornblendes show a slight degree of optical zoning in the intermediate rocks from brown-green cores to green margins, whilst the pale hornblendes show a complete absence of zoning.

Plagioclase also becomes coarse and euhedral in the acidic hybrids, this being as a result of further growth of the xenocrystic feldspars in the granitic environment, resulting in zoning of the andesine to margins of more sodic oligoclase or albite.

Quartz increases in abundance from small interstitial crystals in the quartz diorites to large clear patches in the tonalites where it comprises up to 40% of the rock mineralogy. Both quartz and plagioclase are fractured and recrystallized.

Significantly, microcline is not present in any of the intermediate hybrid rocks indicating that the microcline granites have not reacted with, or hybridized, the diorites.

Cummingtonite is partially replaced by a dark hornblende in some of the hybrids (Plate 5.6). The presence of pale green or colourless cummingtonitic amphiboles has been reported in hybrid complexes by other authors (Nockolds, 1934a; Deer, 1935; Read, 1935; Iwao, 1937; Kuno, 1938; Lambert & Holland, 1971; Ishizaka & Yanagi, 1977). Almost always it is found in association with hypersthene which it is seen to replace. Deer *et al.*, (1963a) also describe its presence in hybrid rocks as a common occurrence, being the middle member of the reaction series:

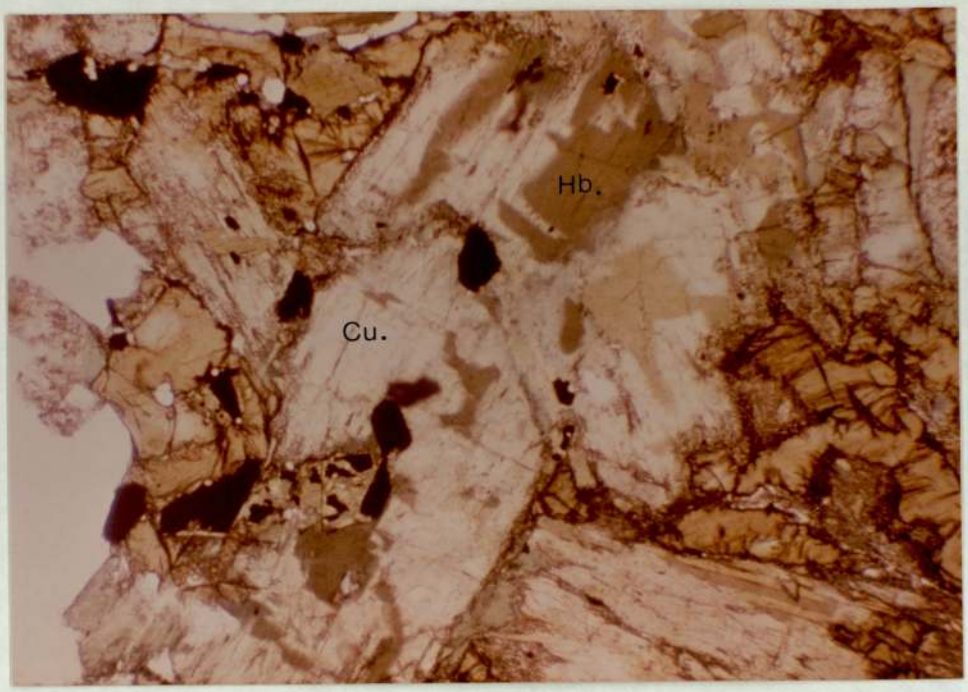
Orthopyroxene→

Cummingtonite → Hornblende

and suggest it is due to the effect of volatiles reacting with the orthopyroxene under favourable conditions. Mongkoltip & Ashworth (1986) also report its presence replacing orthopyroxene in a complementing fashion to that of hornblende replacing clinopyroxene.

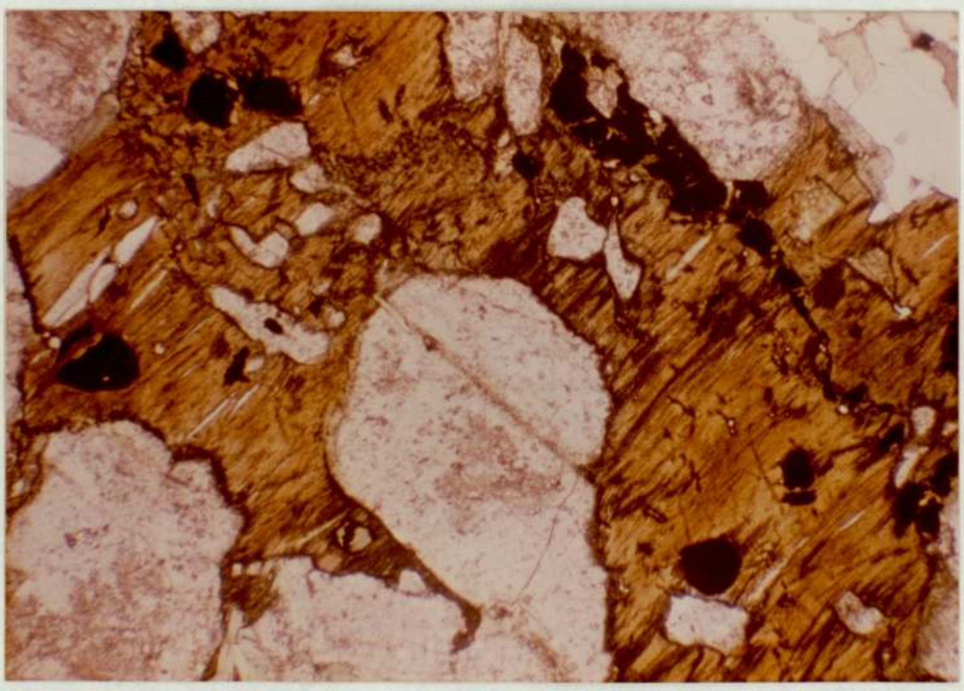
The pale and dark hornblendes are often found partly or almost completely replaced by a brown platey mineral, confirmed as a variety of chlorite by Electron Probe Micro-analysis.

PLATE 5.6 COLOURLESS CUMMINGTONITE SHOWING PARTIAL REPLACEMENT BY GREEN HORNBLENDE



Field of view 3.4 mm (SPECIMEN BH128)

PLATE 5.7 ORANGE-BROWN HIGH RELIEF CHLORITE IN A BOLTON HILL GRANITIC ROCK



Field of view 2.2 mm (SPECIMEN BH 128)

The chlorite (of a "Brunsvigite" composition) forms large strained and crenulated flakes up to 2 mm. in length with a very high Refractive Index, very low birefringence (anomalous) and strong pleochroism from brown to orange-brown or yellow (Plate 5.7).

Occasionally a dark green, weakly pleochroic variety of this "high relief" brunsvigite chlorite is seen (Plate 5.8). The brunsvigite replaces hornblende more extensively in the quartz-rich granitic and tonalitic rocks, and is also seen to form at the expense of cummingtonite (Plate 5.9) in some of the dark diorite hybrids. It also occurs less commonly as discrete crystals (although this may be due to its complete replacement of an earlier mafic mineral). The brunsvigite is believed to have formed during the hybridization process in place of biotite due to the very potash-poor nature of the hybridizing granite (indicated by the absence of K-feldspar). This would subsequently prevent the crystallization of biotite and allow brunsvigite to form in its place from the previously existing amphiboles.

Vast numbers of apatite needles are present in the hybrid rocks in both quartz and plagioclase, and especially in the vicinity of hornblende and where brunsvigite replaces hornblende. This apatite is more abundant than in either the diorite or granite end members, and is commonly in association with colourless euhedral epidote (which is itself in greater concentrations in these rocks than in either of the end members of the assimilation process).

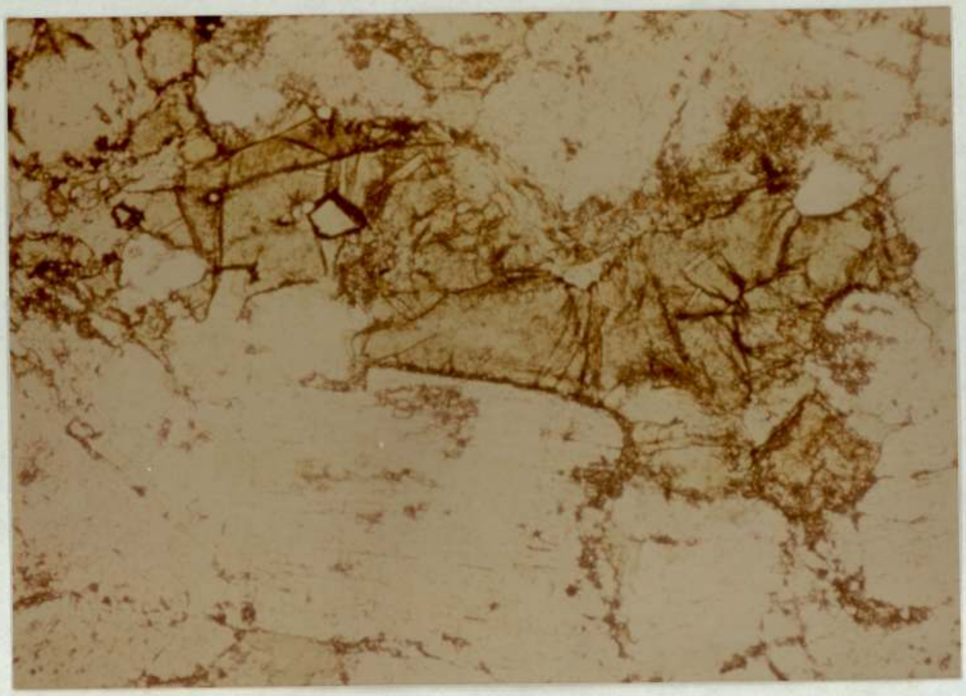
Other accessory minerals include euhedral zircon, which may occasionally be found as very large grains (Plate 5.10), magnetite with ilmenite exsolution lamellae, and ilmenite bordered by sphene. Zircon is often seen forming pleochroic halos in the brunsvigite.

Xenoliths in the hybrid rocks are disintegrated and occur merely as xenocrystal concentrations of hornblende and andesine in modified granite.

5.2.4 Hydrothermal and metamorphic alteration

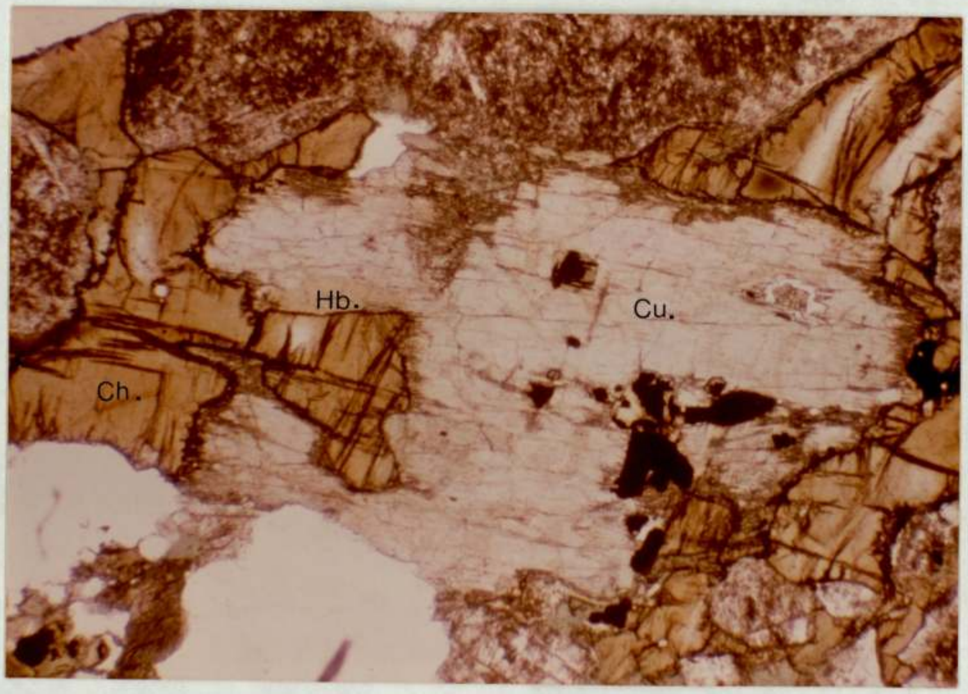
The diorite series shows evidence of late stage alteration which has resulted in the primary

PLATE 5.8 GREEN HIGH RELIEF CHLORITE FROM BOLTON HILL



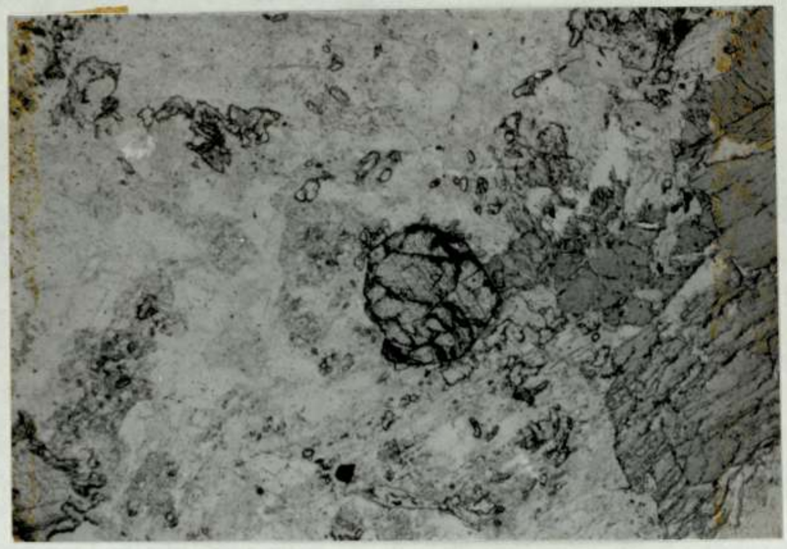
Field of view 3.4 mm (SPECIMEN BH 126)

PLATE 5.9 CUMMINGTONITE SHOWING MARGINAL REPLACEMENT BY BROWN CHLORITE



Field of view 2.2 mm (SPECIMEN BH 126)

PLATE 5.10 <u>LARGE ZIRCON CRYSTAL IN THE JOHNSTON DIORITES</u>



Field of view 1.76 mm (SPECIMEN BH 100)

minerals being replaced by secondary phases.

Plagioclase is intensely altered to sericite, epidote and clinozoisite, and is often pseudomorphed by these minerals in the more basic rocks. However the more sodic feldspars in the granitic rocks are affected to a much lesser degree.

Hornblende shows some alteration to yellow-green penninitic chlorite and yellow granular epidote. In certain areas the brown or dark green brunsvigite chlorite may be wholly or partly replaced by yellow-green penninitic chlorite, yellow epidote and brown granules of sphene.

Uralite is absent from the altered diorites. It is a pyroxene replacement product, and pyroxene is not present in these rocks.

A second phase of alteration is seen to post-date the first, and consists of veinlets of albite, calcite and prehnite. These veins can be seen to cross cut all the features described above and periodically widen out into alteration patches.

Prehnite replaces hornblende and plagioclase, whilst the albite may form sharp rims around pre-existing calcic or sodic plagioclase crystals where such veins cut through earlier magmatic feldspar.

In earlier petrographic descriptions on the diorites, prehnite was mistakenly identified as white mica (Cantrill *et al.*, 1916). Where this mineral replaces hornblende, rod-shaped crystals of magnetite are produced due to the inability of prehnite to accommodate the excess Fe. These veinlets and alteration patches are believed to have been introduced by (Na and Ca)-rich fluids during a phase of metamorphism after crystallization of the magma and termination of hybridization. The association noted above of prehnite, calcite and albite has been described elsewhere in igneous rocks in Pembrokeshire (Roach, 1969; Bevins, 1978) and has also been ascribed to a phase of low grade metamorphism (Oliver, 1978; Bevins, 1978; Bevins *et al.*, 1981; Roberts, 1981; Bevins & Rowbotham, 1983).

At Bolton Hill this metamorphism is believed to be associated with thrust-faulting and rock deformation.

5.3 Garabal Hill.

5.3.1 Ultrabasics and gabbros

The ultrabasic rocks include a combination of peridotites with up to 50% unaltered olivine, and pyroxenites which comprise up to 85% augite and hypersthene. The latter phase can be seen to replace olivine in places.

The pyroxenites exhibit varying degrees of replacement by hornblende, ultimately producing a series of "hornblendites" (the "davainites" of Wyllie & Scott, 1913). In these ultrabasics the remainder of the rock mineralogy generally includes variable, but low, concentrations of plagioclase, magnetite and ilmenite.

Olivine is colourless, highly fractured and at times altered.

Augite is colourless or pale green, often euhedral, and slightly pleochroic. It generally contains abundant Fe-Ti oxide inclusions and needles (magnetite and ilmenite) exsolved along three crystallographic orientations.

Plagioclase is of labradorite composition (An_{60}) but may show zoning to andesine (An_{41}) in certain rocks. The feldspars are usually anhedral and appear to have formed interstitially between the euhedral pyroxenes.

Hypersthene, strongly pleochroic from pale pink to pale green, occurs in wide ranging proportions from 0% - 40%. It is present as lozenge-shaped or granular crystals in large clusters associated with much magnetite, possibly due to the replacement of original Fe-rich olivine.

A whole series of different rock types is present due to the varying proportions of these minerals in the rocks. An increase in plagioclase content results in gabbroic rather than ultrabasic rocks. The absence of hypersthene results in normal gabbros, and its presence a gradation from hypersthene gabbros to norites (in which hypersthene becomes the dominant pyroxene).

Dark brown hornblende replaces pyroxene in many of the ultrabasics and gabbros. The hornblende is anhedral and strongly pleochroic with the following colour scheme:

α = Yellow
β = Dark brown
γ = Dark red-brown

It is seen to become the dominant mafic mineral in some rocks, with pyroxenes merely as remnant cores rimmed by the amphibole. These rock types have been termed hornblende gabbros, or hornblendites where they have replaced pyroxenites.

Magnetite and ilmenite are common. Both form abundant small grains and inclusions in augite (occasionally also some occur in hypersthene) which are largely resorbed on replacement of the pyroxene by hornblende (Plate 5.11).

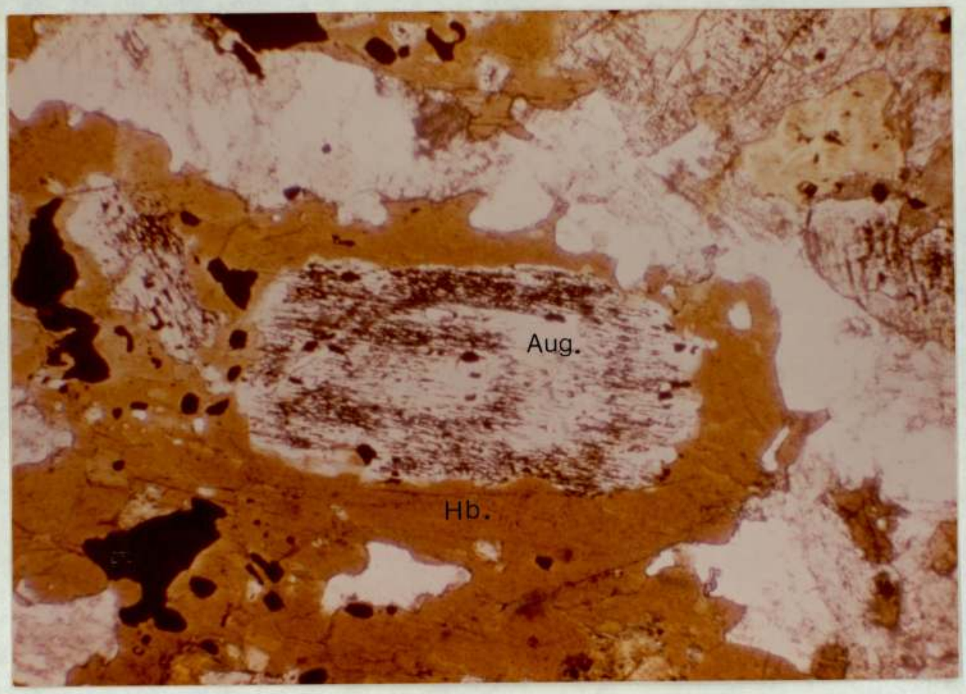
The needles of magnetite and ilmenite in pyroxene are believed to have formed by exsolution of Fe and Ti oxides from the pyroxene structure during crystallization (Nockolds, 1941). Some of the magnetite crystals also themselves show exsolution lamellae of ilmenite.

Biotite replaces augite and hornblende but only constitutes up to 10% of the rock mineralogy. It is strongly pleochroic.

α = Yellow-brown
$\beta = \gamma$ = Orange (Plate 5.12)

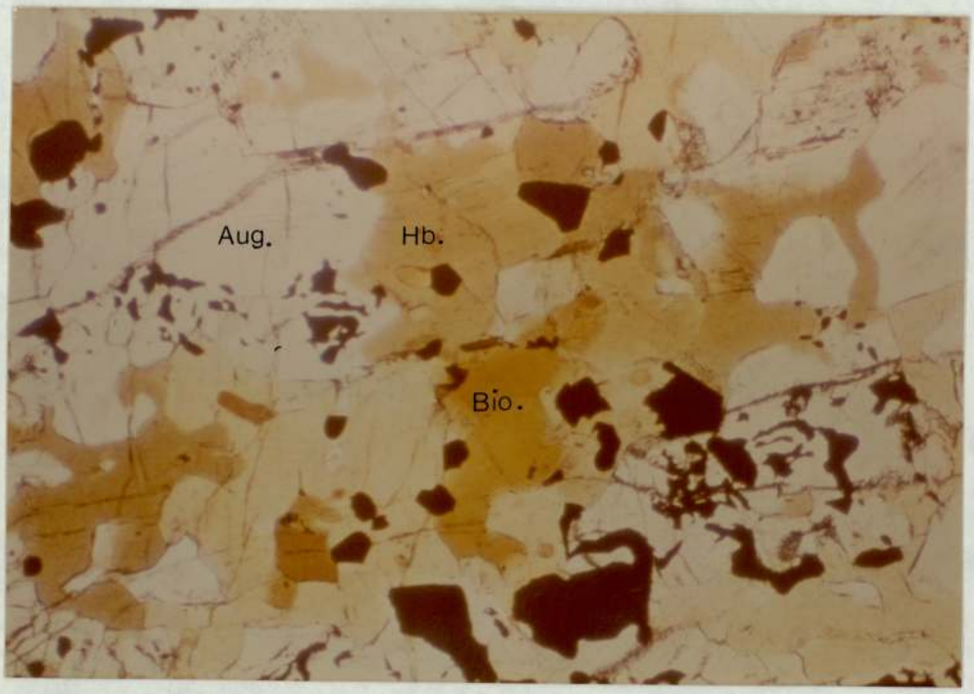
Hornblende in the gabbros generally contains minute but abundant opaque needles. These would appear to be of rutile and/or ilmenite, and occur along three crystallographic

PLATE 5.11 GARABAL HILL AUGITE SHOWING RESORPTION OF Fe-Ti OXIDE NEEDLES DURING ITS REPLACEMENT BY DARK BROWN HORNBLENDE



Field of view 3.4 mm (SPECIMEN GH 7)

PLATE 5.12 ORANGE-BROWN BIOTITE REPLACING HORNBLENDE & AUGITE IN A METASOMATIZED GARABAL HILL GABBRO



Field of view 2.7 mm (SPECIMEN GH 14)

orientations within the hornblende. These are likely to be remnants of the Fe-Ti oxide inclusions exsolved from the pyroxenes, which were unable to be accommodated into the hornblende structure on its replacement of the pyroxene. These rutile needles are further resorbed on replacement of hornblende by biotite. Other minor phases include pyrite, chalcopyrite, green spinel and occasional large crystals of apatite.

There is strong evidence of mineralogical alteration in the basic wallrocks close to the contact with the later acid material, this is seen by the increased replacement of pyroxene by hornblende and biotite towards the contact zone with the surrounding granodiorite. This results in the presence of a zone of hornblende gabbros near the contact zone.

Olivine also suffers from some degree of alteration and is partly replaced by a platy mineral showing one strong cleavage and vivid pleochroism from orange to bright green (Plate 5.13), although it has proved unidentifiable.

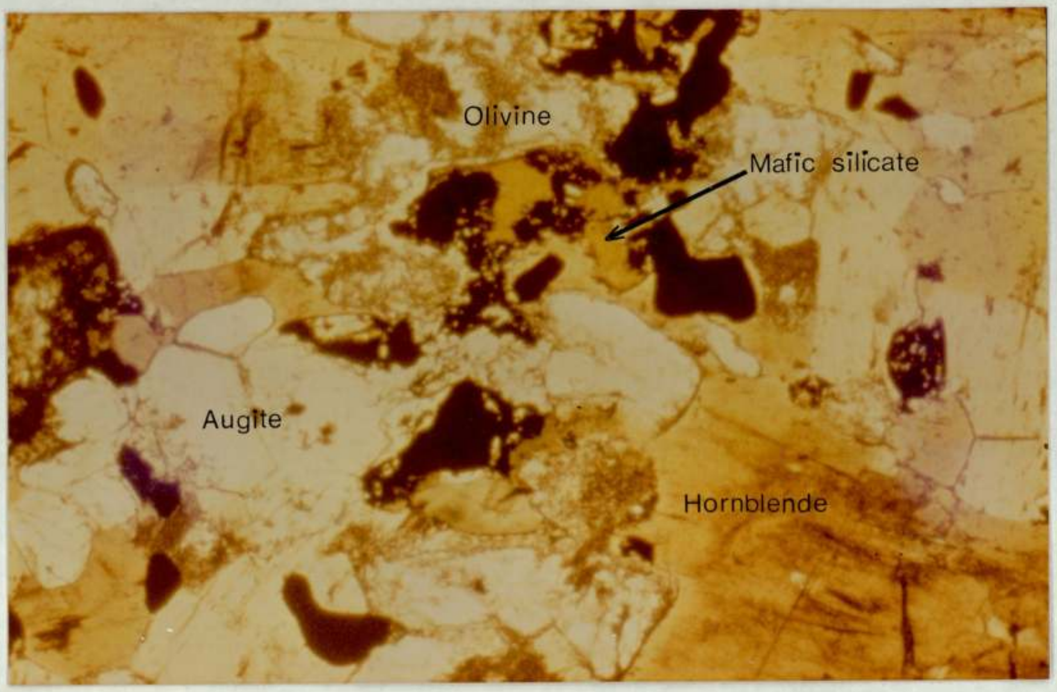
Alteration has also caused the replacement of labradorite by andesine on a large scale at the immediate contact zone, forming diorites at the expense of the original gabbros. Away from the contact zone the effects of alteration fall off rapidly, shown by the decrease in hornblende, biotite and andesine towards the centre of the basic mass where the normal gabbros and ultrabasic rocks outcrop.

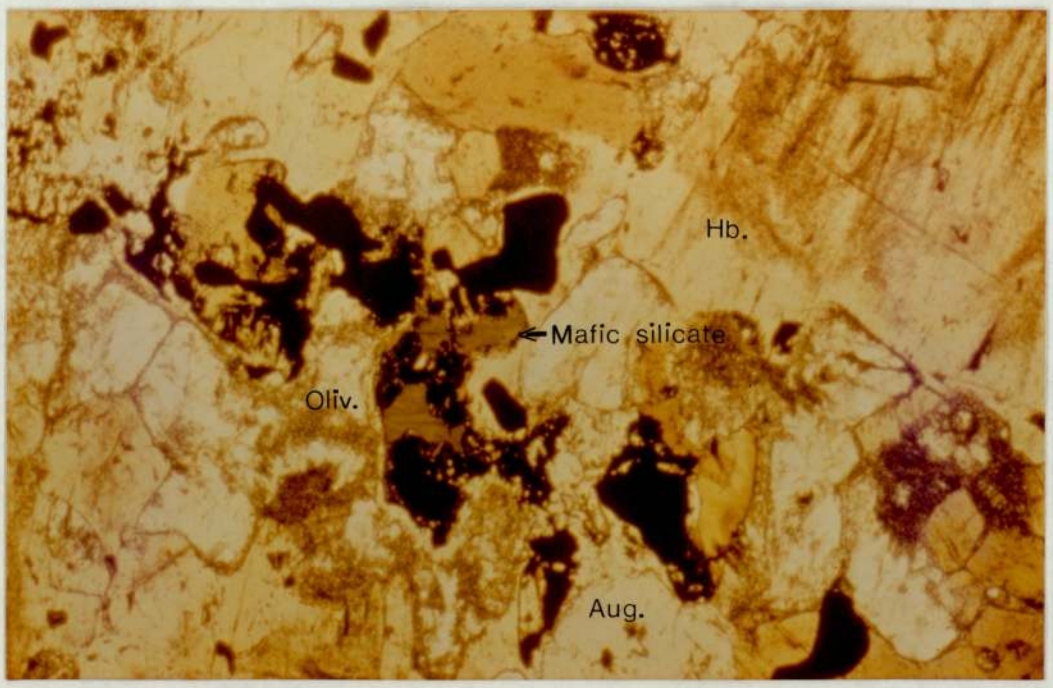
5.3.2 Granodiorites/granites

Plagioclase feldspar in the granodiorites is largely oligoclase in composition (An_{27}), occasionally showing andesine cores, and occurs as subhedral lath-shaped crystals. Clear undulose quartz and turbid orthoclase feldspar are the other felsic minerals. The orthoclase is perthitic and occurs in approximately equal proportions with plagioclase. The dominant mafic mineral is a biotite with pleochroism:

α = Straw yellow
$\beta = \gamma$ = Dark brown

PLATE 5.13 Fe-Mg SILICATE REPLACEMENT PRODUCT OF OLIVINE FROM A METASOMATIZED GARABAL HILL ULTRABASIC ROCK, SHOWING VIVID ORANGE TO LIGHT GREEN PLEOCHROISM





Fields of view 2.2 mm (SPECIMEN GH 111)

This biotite is often seen replacing a euhedral, strongly pleochroic hornblende with the following colour scheme:

α = Yellow
β = Pale blue-green
γ = Green

Pale brown euhedral sphene is common in association with these mafic minerals, particularly where biotite replaces hornblende.

Zircon is common, forming pleochroic halos where it occurs in biotite and hornblende, whilst apatite and colourless epidote are also particularly abundant in the near vicinity of these minerals. Indeed, apatite produces pleochroic halos in a similar fashion to zircon.

Allanite is a common accessory mineral, and is strongly pleochroic.

α = Pale pink-brown
β = Pale brown
γ = Orange-brown

It is also of a metamict nature.

Magnite and ilmenite constitute the oxide minerals.

5.3.3 Intermediate hybrids

The intermediate rocks are mineralogically and texturally variable, ranging in composition from quartz diorites through quartz monzodiorites and xenolithic granodiorites.

Plagioclase is ubiquitous and is the dominant mineral in all the rock types, being strongly zoned from andesine cores to rims of oligoclase, and shows a lath-shaped, subhedral appearance.

Augite is common as colourless xenocrysts in many of the diorite rocks, and contains abundant Fe-Ti oxide inclusions. The augite is extensively replaced by hornblende which, in turn, is strongly zoned from brown cores to brown-green or green margins (Plate 5.14).

Amphibole increases in proportion relative to augite in the more granitic rocks and has a tendency to form euhedral crystals when in contact with acidic material. These strongly zoned hornblendes are xenocrystal in origin and may have been incorporated as amphibole or as augite, before being converted to amphibole by the granite magma.

Dark brown biotite with pleochroism as follows is present:

α = Straw Yellow
$\beta = \gamma$ = Dark brown

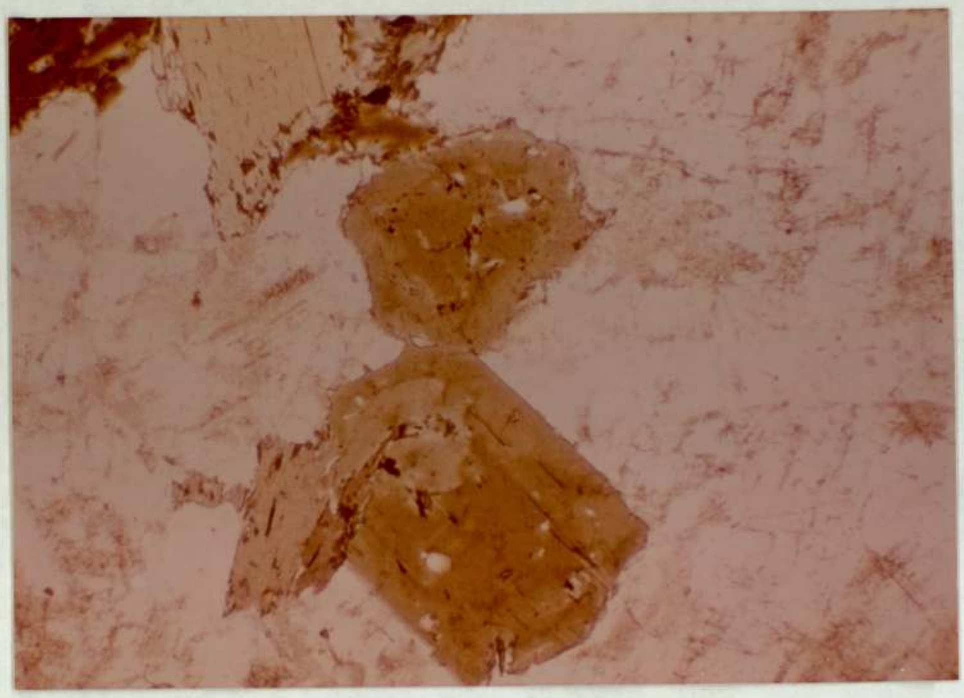
This is of a different colour from that in the gabbros and forms at the expense of the other mafic minerals (Plate 5.15), becoming dominant over hornblende in the majority of the hybrid rocks.

Euhedral sphene is very common in the vicinity of the mafic minerals, occurring together with large numbers of crystals of colourless epidote and particularly apatite. These accessory minerals are especially numerous in the hybrid xenolithic rocks. Quartz and orthoclase increase in concentration in the more granitic hybrids to form areas of a coarse granophyric intergrowth mantling plagioclase, whilst in the more basic hybrids the felsic minerals occur interstitially, between grain boundaries of earlier minerals, as individual crystals.

Fe-Ti oxides occur as needle like inclusions and as small grains in augite, which are largely resorbed during its replacement by hornblende or biotite, although tiny needles of rutile may remain in these minerals.

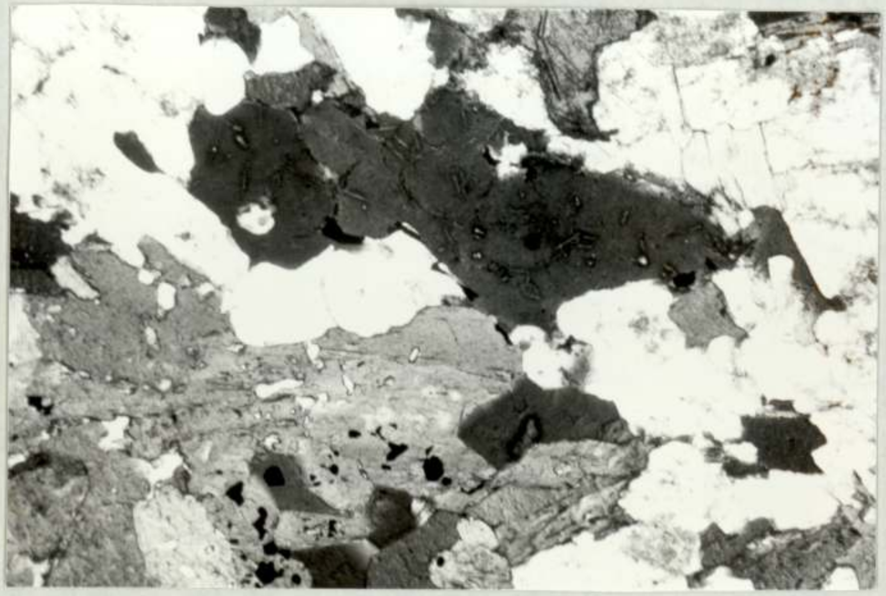
Allanite and zircon are present albeit in lower concentrations than in the granodiorites. Zircon, and to a lesser extent apatite, form pleochroic halos in biotite. Chalcopyrite and pyrite are the dominant sulphides.

PLATE 5.14 HORNBLENDE FROM A GARABAL HILL HYBRID ROCK SHOWING OPTICAL ZONING FROM A BROWN CORE TO A PALER BROWNISH GREEN RIM



Field of view 2.2 mm (SPECIMEN GH3)

PLATE 5.15 DARK BROWN BIOTITE, IN A GARABAL HILL INTERMEDIATE ROCK, CONTAINING ABUNDANT NEEDLES OF APATITE



Field of view 3.4 mm (SPECIMEN GH3)

5.3.4 Hydrothermal alteration

Hydrothermal alteration has resulted in the replacement of augite by pale green fibrous uralite, and hypersthene by fine grained masses of serpentinous material and magnetite.

Plagioclase shows clouding due to its replacement by sericite and yellow granular epidote, whereas hornblende and biotite suffer extensive alteration to green penninitic chlorite, yellow epidote and granular sphene.

Ilmenite is often marginally altered to sphene and rutile. Olivine can be extensively replaced by serpentine and red-brown oxides/hydroxides (possibly "iddingsite"). This secondary alteration is non-uniform in distribution being particularly associated with faulting, the rocks sporadically being traversed by veinlets of yellow epidote and calcite which widen out into alteration patches. The development of veinlets would appear to suggest that new material was introduced during the alteration phase, whilst it is also likely to be partly caused by re-allocation of existing chemical constituents.

5.4 Discussion

5.4.1 Petrographic criteria for assimilation

The reaction between granitic magma and basic wallrocks in the three areas of study is characterized by an abundance of xenolithic and xenocrystic intermediate rocks of variable composition. The hybrid rocks all show strong evidence of disequilibrium (as indicated by the work of Bowen, 1928; and Best, 1982), these features being:-

(a) Zoning of plagioclase feldspar from basic calcic cores to sodic margins
(b) Zoning of hornblende
(c) Replacement and rimming of pyroxene by amphibole
(d) Replacement of pre-existing mafic minerals by biotite
(e) Growth of euhedral crystals into areas of quartz/alkali feldspar (ie acidic magma)
(f) Abundance of apatite and epidote in hybrid rocks in relation to potential endmembers.

Most of these features occur, although there are subtle differences, between the complexes studied.

The Bolton Hill complex in particular is slightly different from those of Glen Dubh and Garabal Hill due to the absence of pyroxene cores rimmed by hornblende. This is believed to be due to the replacement of all previously existing pyroxene by hornblende before hybridization took place. In addition, the absence of biotite replacing hornblende is of note. This is due to the potash-poor nature of the rocks inhibiting the formation of biotite, but resulting in the replacement of hornblende by brunsvigite in place of the biotite.

Other subtle differences occur between the complexes. The Bolton Hill plagioclase feldspars show less intense zoning than those of the other complexes due to their less calcic nature in the endmember diorites (andesine rather than labradorite).

The optical zoning of the hornblendes differs between the complexes, being stronger in those of Garabal Hill, less strong at Glen Dubh, and weakest at Bolton Hill. This difference is due to compositional differences, the dark brown nature of the Garabal Hill hornblende being due to the high Ti content, whilst the brown-green appearance at Glen Dubh and green nature at Bolton Hill is caused by, in turn, lower concentrations of this element. The subsequent zoning to green margins in the hybrid rocks is due to re-equilibration of the hornblendes with the Ti-poor granitic magma, and is comparable to that reported from other hybrid complexes (Brown *et al.*, 1978). The replacement of pyroxene by hornblende and biotite is due to the instability of the mineral being replaced, in the new acidic environment.

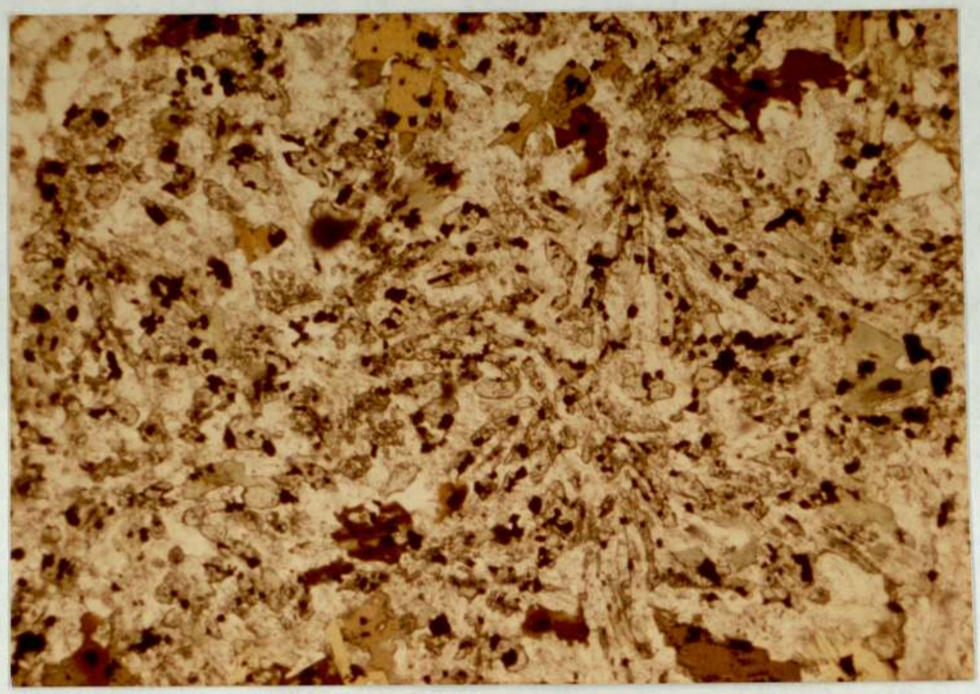
The other characteristics mentioned above occur in each of the complexes in a similar fashion. The presence of numerous apatite and epidote crystals where pyroxene alters to hornblende and biotite is believed to be caused by reaction of released constituents (e.g. Ca) with volatiles associated with metasomatism.

5.4.2 Recrystallization textures

The xenoliths in the Glen Dubh hybrid rocks show a variolitic texture, with small granules of pyroxene in a reticulate pattern of amphibole and feldspar. This is believed to have been caused by recrystallization of the xenoliths (Plate 5.16), and has been interpreted as such by other authors studying other complexes (Nockolds, 1935; Richey, 1937). It is interesting to note that similar textures have been described in other igneous complexes, where they have been attributed to the chilling of a basic magma in a more acidic host, and have subsequently been used to demonstrate the co-existence and mixing of two magmas (Wager & Bailey, 1953; Vernon, 1984; Brown & Becker, 1986). It may be that some of the supposed "chilled margins" are due to a recrystallization process.

To complicate matters, Reynolds (1951) has attributed the formation of a similar texture to the passage of gas-charged magmas through a wallrock, resulting in the melting of certain minerals. It may also be that similar textures may be formed by more than one process.

PLATE 5.16 RECRYSTALLIZED ARRAN XENOLITH, COMPOSED OF ROUNDED OR ELONGATE GRANULES OF AUGITE IN A RADIATING PATTERN PARTLY REPLACED BY HORNBLENDE & BIOTITE.



Field of view 2.2 mm (SPECIMEN 43)

This recrystallization texture is absent from the xenoliths at Garabal Hill and Bolton Hill. This may be caused by a dry acidic magma assimilating basic igneous wallrock with minimal metasomatism at Glen Dubh (i.e. dry metamorphism), whereas the other two complexes appear to involve appreciable metasomatism so that recrystallization textures are replaced by metasomatic textures (i.e.wet metamorphism). This would change the mineralogy of the wallrocks which may approach equilibrium with the ascending magma, preventing the formation of recrystallization textures.

5.4.3 Endmember compositions

Examination of petrography enables the endmembers, in the hybridization process, in each of the complexes to be identified.

At Glen Dubh, four basic rock types are present, three of which may be eliminated on petrographic grounds - the Hypersthene gabbros due to the absence of hypersthene, and the Alkali gabbros due to the absence of minerals such as titanaugite, in the hybrids. The coarse gabbros are ruled out due to their coarse nature.

At Bolton Hill both diorites are seen to be assimilated although only one of the granites (albite) has reacted with them. The absence of microcline in the hybrids indicates that the microcline granites play no part in the process.

In the Garabal Hill complex, the ultrabasic rocks may also be ruled out of the hybridization process due to their occurring towards the centre of the main mass of wallrock, some distance from the intruding granite (e.g. Fig. 4).

The use of petrography has also shown however, that what appear to be the extreme endmembers on field and hand-specimen criteria, may show evidence of being hybrids themselves albeit marginal hybrids, e.g. the granite at Glen Dubh shows pyroxene and plagioclase xenocrysts, whilst those at Bolton Hill and Garabal Hill contain zoned "laths" of plagioclase which may also be xenocrysts. In addition, the basic rocks may show zonation of plagioclase and amphibole and occasionally tiny amounts of quartz and alkali feldspar.

5.4.4 Post-crystallization alteration

The presence of secondary minerals in the rocks is indicative of their undergoing late stage alteration which may have altered the whole-rock chemistry. In particular, although it is likely that much of the secondary mineral assemblage has resulted largely from the breakdown and redistribution of existing whole-rock constituents, the occurrence of secondary veinlets traversing the rocks would suggest that certain elements may have been added to the rocks by the percolating hydrothermal solutions. This would be contemporaneous with the removal of certain constituents from the rock (i.e. the alteration process was non-uniform), and would therefore have implications for the whole-rock geochemistry.

All of the rock types named above are according to the classification scheme of Streckeisen (1976).

6. MINERAL CHEMISTRY

The study of the mineral chemistry in the three hybrid complexes has been restricted to the analyses of the mafic phases. The felsic mineralogy is plagioclase in the more basic rocks in the complexes, showing typical NaSi - Ca Al substitution, together with quartz and alkali feldspar in the acidic rocks.

The mafic phases are those most markedly affected by reactions during assimilation and related processes, and some idea of the variation in mineralogy and mineral chemistry is a necessary framework from which changes in whole-rock chemistry can be examined.

A description of the chemistry of the original phases (olivine, clinopyroxene, orthopyroxene) is given together with data on minerals formed during the assimilation process (amphiboles, biotite, chlorite). These phases are formed either by reaction and equilibration with the invading acidic magma, or by reaction with a hydrous fluid phase associated with intrusion of such a magma.

The chemistry of allanite is discussed due to it being the major repository of the rare earth elements. The chemistry of these relatively immobile elements is of particular importance during the assimilation process (see Chapter 7).

Implications of the changes in mineral chemistry are discussed at the end of the chapter and are of consequence when consideration is given to whole-rock changes.

All mineralogical analyses were carried out by Wavelength- Dispersive Electron Probe Micro-analysis using a Cambridge Instruments Microscan 5 analyzer. The analytical conditions and detection limits for the various elements are described in Appendix 1.1. Analyses of minerals from Glen Dubh, Bolton Hill and Garabal Hill are tabulated in Appendix 1 (Tables 4 - 17).

6.1 Olivine

Olivine is only present in the peridotites at Garabal Hill where it falls between Fo_{76} and Fo_{79}, giving the composition of chrysolite (Deer *et al.*, 1962a) (Table 1).

A strongly pleochroic orange to green mineral is seen to replace the olivine in Garabal Hill peridotites and gives variable analytical results, dependent upon its apparent orientation (Table 1). This mineral is of a similar composition to the olivines being replaced, being rich in magnesium and iron, the only other major constituent being silicon. The main difference from olivine is its probably hydrous nature and the presence of minute amounts of alkalis. It is also slightly poorer in Mg). Comparisons between compositions of these minerals are shown below (the analyses of the alteration product being of different mineral orientations).

Table 1: Typical compositions of olivine and its alteration product

	Olivine	Alteration product	
%			
$Si0_2$	38.89	46.51	38.65
Al_20_3	0.02	1.65	0.52
$Ti0_2$	0.06	0.02	0.04
Fe0	21.32	19.03	27.23
Mg0	38.18	21.79	18.52
Ca0	0.07	0.30	0.56
Mn0	0.47	0.05	0.13
Na_20	-	0.07	0.20
K_20	-	0.15	0.25
	99.01	89.57	86.10

The alteration mineral is platey in appearance. This and its composition tend to suggest that it is formed during the assimilation process rather than hydrothermally, hence forming at the same time as brown hornblende and orange biotite (described later). Neither the chemical composition nor an X-ray diffraction trace (Appendix 1.4) give any indication as to the identity of the mineral, although it does not appear to be a typical replacement product of olivine.

6.2 Pyroxenes

All clinopyroxenes are classified according to the diagram of Poldervaart & Hess (1951).

Orthopyroxenes are classified according to Deer et al, (1963a).

6.2.1 Glen Dubh

The Arran clinopyroxenes are mainly augite in composition, although some containing slightly higher Ca contents may be classified as salite (Table 6).

The pyroxenes of the Hypersthene gabbro plot as ferroaugite and ferrohypersthene, the difference between these and those of the normal gabbros being their higher Fe content.

6.2.2 Garabal Hill

Both ortho and clinopyroxenes are represented in the wide range of basic and ultrabasic rocks. The orthopyroxenes are quite iron poor, plotting between 70 - 76 atomic % Mg (i.e. of a "bronzite" composition). (Table 7).

They show little chemical variation in composition apart from the slightly varying Mg/Fe ratios.

The orthopyroxene is associated with abundant magnetite, the presence of which may be due to the replacement of original, more Fe-rich, olivine (Bowen & Schairer, 1935b).

Clinopyroxenes in Garabal Hill are also Fe poor, and augitic, with a varying Ca content grading into salite. The augites are slightly more Ti and Al rich than those of Arran and are poorer in Fe than the Arran augites (Table 8).

6.3 Amphiboles

The amphiboles are classified according to the recommendations of the I.M.A. Sub-committee on Amphiboles Report (Leake, 1978). This method is briefly summarized in Appendix 1.3.

The analyses of amphiboles from Glen Dubh, Bolton Hill and Garabal Hill are presented in Tables 9 - 12 respectively.

A full discussion of the problems of calculating the Fe^{2+}/Fe^{3+} ratio is given in Appendix 1.2.

6.3.1 Glen Dubh

Hornblende in the gabbros in close contact with the granite magma and in the xenoliths, is generally a brown "magnesiohornblende" with a slightly variable Si content.

These brown hornblendes show lowest Si contents down to 6.7 Si cations per unit cell. These hornblendes also show low Fe contents (to 1.9 Fe cations per unit cell) but high Ti (up to

0.25), Mg (2.8) and A-site alkalis (up to 0.8) contents per unit cell.

The brown hornblendes show zoning where in contact with the acidic material suggesting growth in equilibrium with this material. In the more granitic rocks they zone to a brownish-green or green colour.

This change in colour occurs together with an increase in the Fe/Mg content resulting in a gradation to amphiboles of ferrohornblende composition, in which Fe exceeds Mg in the number of cations per unit cell.

Zoning also results in amphiboles which show an increase in Si content towards the margins (up to 7.5 cations per unit cell) with a corresponding decrease in A-site alkalis, Ti and tetrahedral Al (Fig. 5). Octahedral site Al increases throughout whilst Ca remains constant; (these variations are described on the basis of total Fe as Fe^{2+} - see Appendix 1.2). The decrease in Ti accounts for the colour change from brown cores to more greenish-brown margins, and has been described from other localities (Deer, 1938; Kuniyoshi & Liou, 1976; Brown *et al.*, 1978).

The rise in Fe concentration is likely to be responsible for predominance of the green colour over brown at the margins of the crystals.

The variation in chemical composition of a zoned hornblende is shown in an Electron Probe Line Scan for SiO_2, FeO, MgO, Al_2O_3, TiO_2, Na_2O and K_2O (Fig. 5a).

The variation in Arran amphibole compositions is controlled by a number of substitution reactions. The dominant substitution appears to be the coupled substitution:

$$(Na,K)_A + Al^{3+}_T \_\_\_ [\ ]_A + Si^{4+}_T$$

This substitution accounts for the decrease in total A-site and tetrahedral Al with a corresponding increase in Si. Dominance of the substitution involving A-site and Al_T would be indicated by an increase in these cations by a ratio of 1:1 between the core and marginal hornblende analyses. The actual ratio is approximately 1.07:1, suggesting that the common substitution, often seen in hornblendes, involving Al_T and Ti would not appear to occur in the

FIG. 5 CHEMICAL ZONING OF ARRAN HORNBLENDES SHOWN IN TERMS OF THE ATOMIC VARIATION OF ELEMENTS AGAINST Si

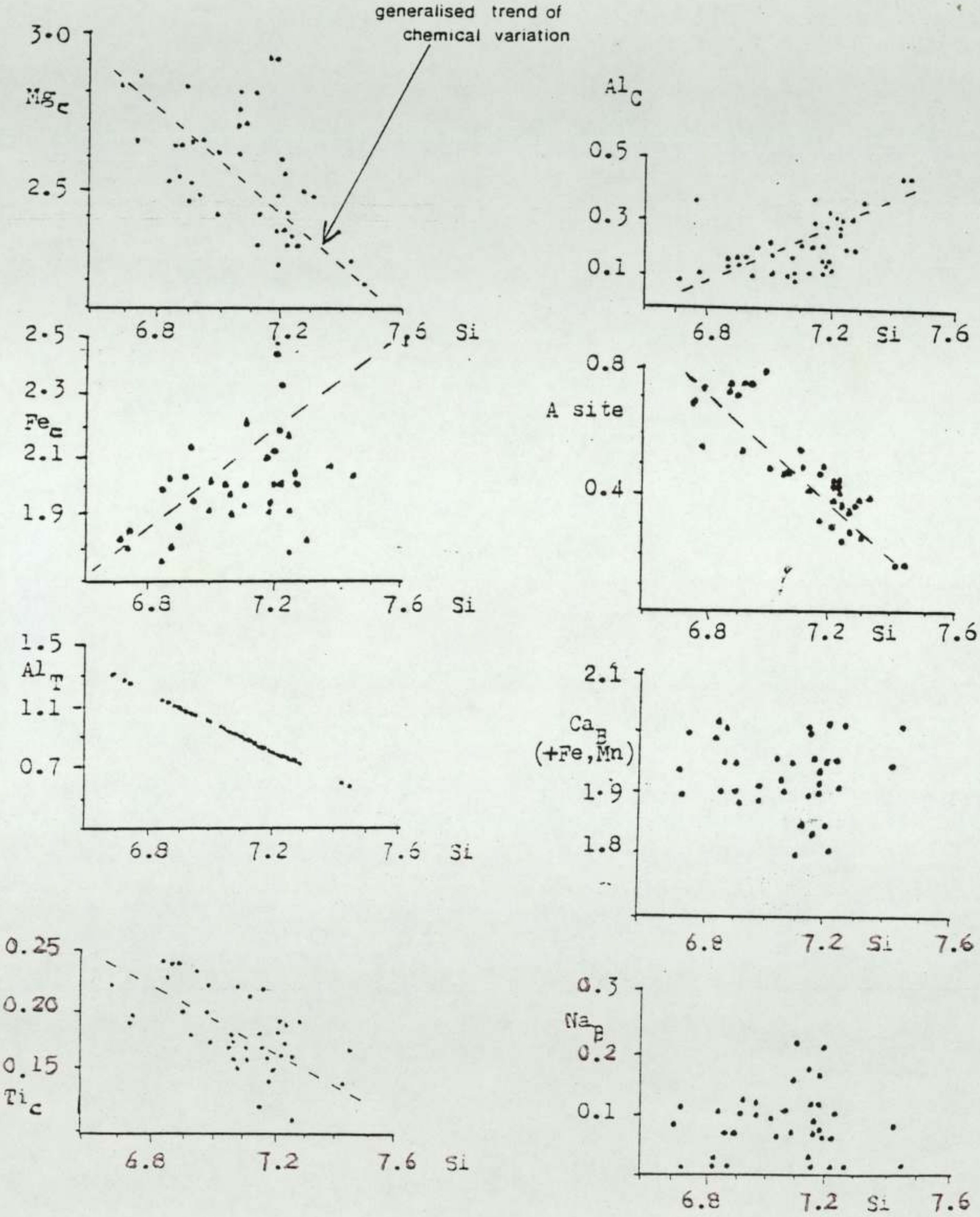
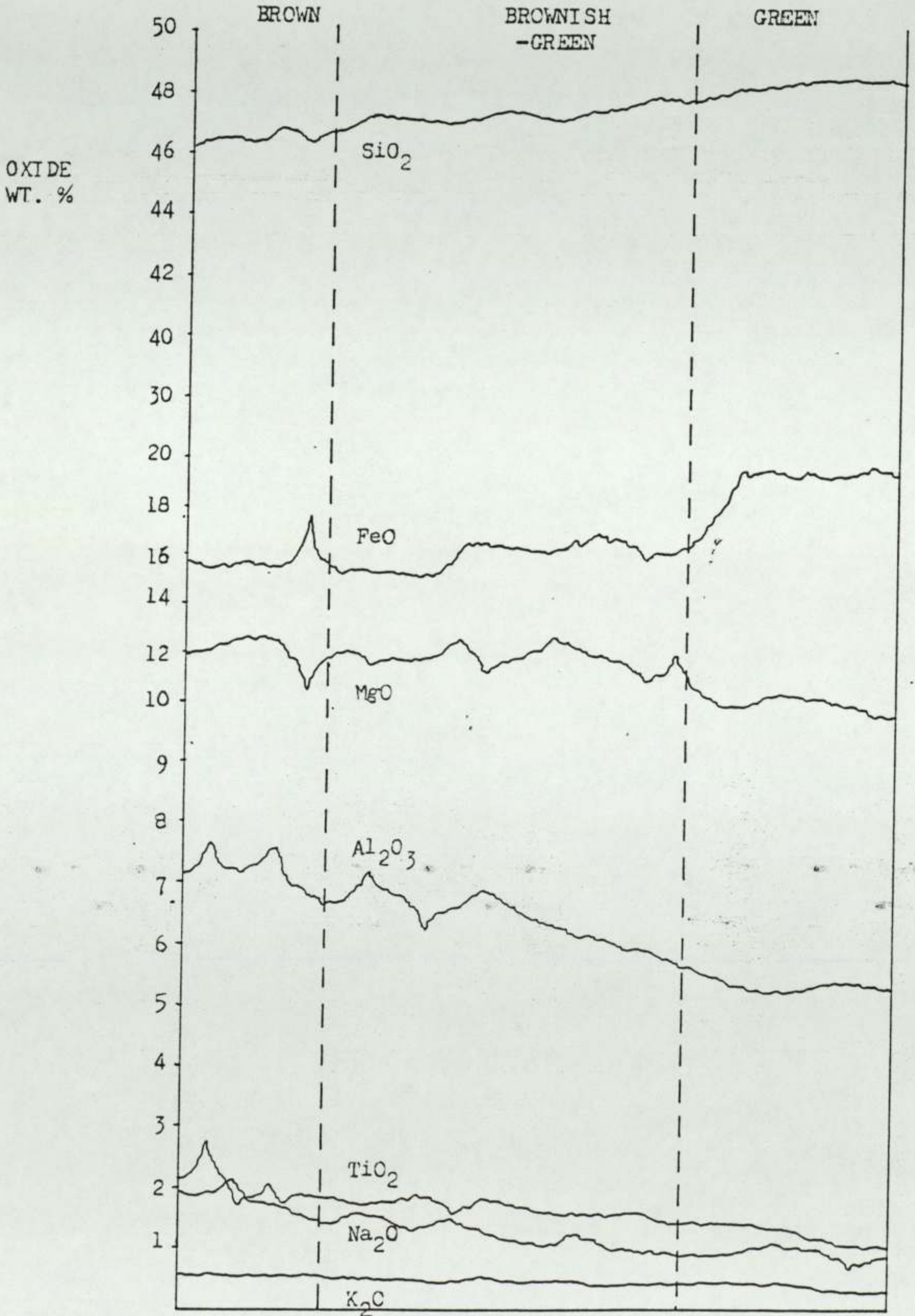


FIG. 5a ELECTRON PROBE LINE SCAN OF COMPOSITIONAL ZONING IN AN ARRAN HORNBLENDE



Arran hornblendes. Here all tetrahedral Al variation is compensated by A-site variation in the substitution shown above.

This is also seen by the larger variation in tetrahedral Al over Ti between the cores and margins of the hornblendes. The ratio of increase in $\mathrm{Al_T}$:Ti is 7.8:1. Any significant coupled substitution involving a combination of these elements would produce a much lower ratio (Brown *et al.*, 1982).

The decrease in $\mathrm{Mg_C}$ and $\mathrm{Ti_C}$, and the increase in $\mathrm{Al_C}$ and $\mathrm{Fe_C}$ may be as a result of the coupled substitution of

$$\mathrm{Mg}^{2+}_{C} + \mathrm{Ti}^{4+}_{C} \;\text{—}\; 2\mathrm{Al}^{3+}_{C}$$

combined with $\mathrm{Mg}^{2+}_{C} \;\text{—}\; \mathrm{Fe}^{2+}_{C}$,

or the operation of the substitution,

$$\mathrm{Mg}^{2+}_{C} + \mathrm{Ti}^{4+}_{C} \;\text{—}\; \mathrm{Al}^{3+}_{C} + \mathrm{Fe}^{3+}_{C} \text{ alone.}$$

6.3.2 Johnston Diorites

Compositions of hornblendes in the Johnston Diorites differ between the pale and dark hornblendes. The hornblendes from the pale diorite are of a "magnesiohornblende" composition due to Mg exceeding Fe (Tables 10a - 10b).

The pale hornblendes show very low TiO_2 contents (generally 0.6% - 1%) which is responsible for their green colour, whilst their pale nature can also be attributed to the relatively low FeO content (15% - 18%). The low A-site content is related to their high Si, whilst the low concentration of Ti is responsible for the complete absence of optical zoning in the hornblendes (due to the lack of substitution involving Ti and Al_T), unlike the Arran and Garabal Hill amphiboles.

The dark diorites contain hornblendes with the composition "ferrohornblende" due to their higher FeO content than the pale hornblendes (18% - 20%). The dark hornblendes are also very low in TiO_2, although slightly richer in this element than the pale hornblendes (generally between 0.9% - 1.4% TiO_2). The higher TiO_2 would account for their more brownish appearance than the pale hornblende, whilst their higher FeO concentrations cause their darker green nature. As would be expected, the dark hornblendes also show lower MgO than the pale varieties (8% - 11.5% compared with 10.5% - 13.5%) (Tables 10c - 10d). The dark hornblendes are similar to the paler ones in having very low A-site alkali contents (complemented by the reciprocally high Si and low Al_T), however the dark hornblendes do show faint optical zoning (presumably due to their higher Ti content).

Within the group the amphiboles show little variation in composition, the main differences being slightly varying Mg/Fe ratios.

The absence of optical zoning in the hornblendes (or its limited occurrence) is likely to be due to the lack of Ti, unlike the Arran hornblendes which contain higher amounts of this element and consequently stronger zoning. In addition the high Si prevents any coupled substitution involving Al and A-site alkalis, consequently reducing their possible range in composition even further.

The Johnston Diorites contain a colourless to pale green, slightly pleochroic, optically positive amphibole. This is an Fe-rich cummingtonite, showing a slightly variable composition (Table 11).

The cummingtonite contains between 52 and 54 atomic percent Fe/(Fe+Mg). This high Fe content is also seen in the dark
hornblendes which are associated with these cummingtonites.

Many of the crystals contain high concentrations of MnO, and high contents of SiO_2 corresponding with low Al_2O_3 are an additional feature.

Cummingtonite has often been reported occurring as a replacement product of orthopyroxene in xenoliths and hybrid rocks - Nockolds (1934a, 1941); Deer (1935); Read (1935); Iwao (1937); Kuno (1938); Ishizaka & Yanagi (1977); Deer *et al.*, (1963a) and the replacement has been demonstrated experimentally by Bowen & Schairer (1935a).

Bowen & Schairer (1935a) indicated that excess Fe is released during replacement of orthopyroxene by cummingtonitic amphibole. This could be an explanation for the presence of magnetite inclusions in the cummingtonite. This process has also been recognized and advocated by Mongkoltip & Ashworth (1986). It is therefore likely that in the Bolton Hill Dark Diorites, cummingtonite has replaced an original orthopyroxene of probably ferrohypersthene composition.

6.3.3 Garabal Hill

Hornblende analyses are displayed in Tables 12a - 12e. The hornblendes of the amphibolitized gabbros range between the fields of "tschermakite" and "tschermakitic hornblende", with total Si cations below or just above 6.25 per unit cell.

The dark red-brown colour of these basic hornblendes is caused by their very high Ti content (up to 4.5%). Slightly lower concentrations of this element may, in places, give a more green-brown colour.

These amphiboles are also characterized by their high A-site alkali occupancy (up to 0.7 cations per unit cell), high Al_T (up to 1.8 cations per unit cell) and low Si (to 6.2 cations).

In the more intermediate and granitic rocks, the hornblendes show very marked optical zonation to marginal brown-green, green and pale green varieties as a consequence of equilibration of the tschermakitic varieties with the granitic magma. The colour change shown by these amphiboles is associated with extensive chemical variation, the most striking of which are the increased Si content (from 6.2 to 7.8 cations per unit cell), and decreased tetrahedral Al (from 1.8 to 0.1 cations) and Ti (from 0.5 to 0.1 cations) in the more acidic hornblendes. The rapid increase in Si results in a change from "tschermakitic hornblende" through "magnesio-hornblende" and "actinolitic hornblende", ultimately to "actinolite" where Si exceeds 7.5 cations per unit cell.

The associated rapid decrease in Ti causes the loss of the brown colouration of the amphiboles, which subsequently become green. The variable Fe content causes a pale or dark green appearance, increased Fe content giving the darker green amphiboles. This variation in the Fe content of the hornblendes in the intermediate and granitic rocks is a result of similar variation in the original brown tschermakitic varieties which preceded these hornblendes. This may in turn be partly due to their formation by replacement of original pyroxenes of differing Fe contents.

The rapid drop in Ti content of the more acidic hornblendes during equilibration has been suggested by Helz (1973) as being in response to increased oxygen fugacity, and appears to be a common feature of hybrid rocks.

The great variation in SiO_2 concentration throughout the amphibole range has allowed their change in composition to be shown by plotting the number of Si cations per unit cell of each amphibole against those of other elements (Figs. 6a and 6b). (In addition an Electron Probe Line Scan has been made of the zoning of an individual amphibole (Fig. 6c)).

From Figs. 6a and 6b, two separate amphibole compositional trends can be recognized. The

FIG. 6a CHEMICAL ZONING OF GARABAL HILL HORNBLENDES SHOWN IN TERMS OF THE ATOMIC VARIATION OF ELEMENTS AGAINST Si

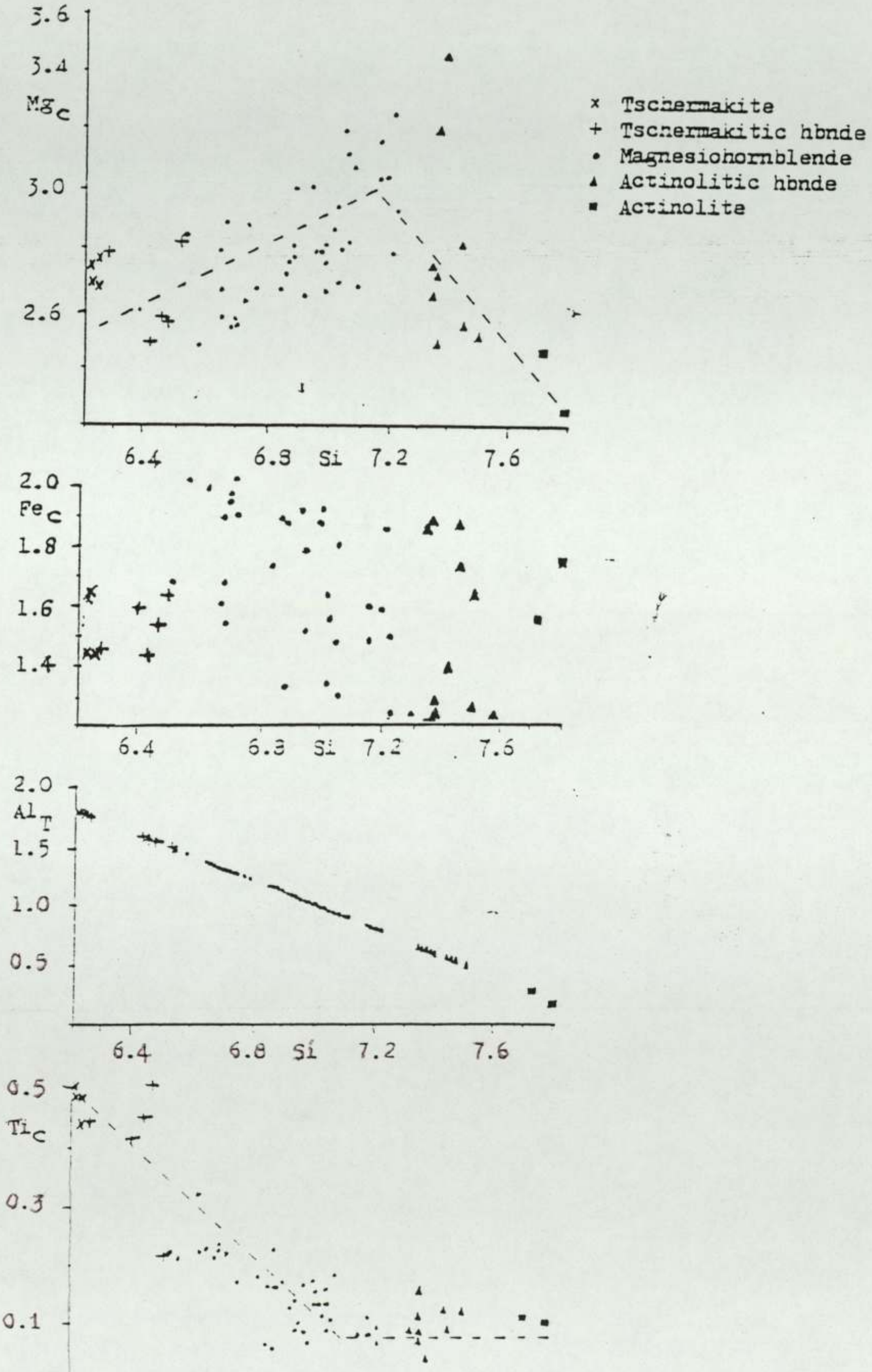


FIG. 6b CHEMICAL ZONING OF GARABAL HILL HORNBLENDES SHOWN IN TERMS OF THE ATOMIC VARIATION OF ELEMENTS AGAINST Si

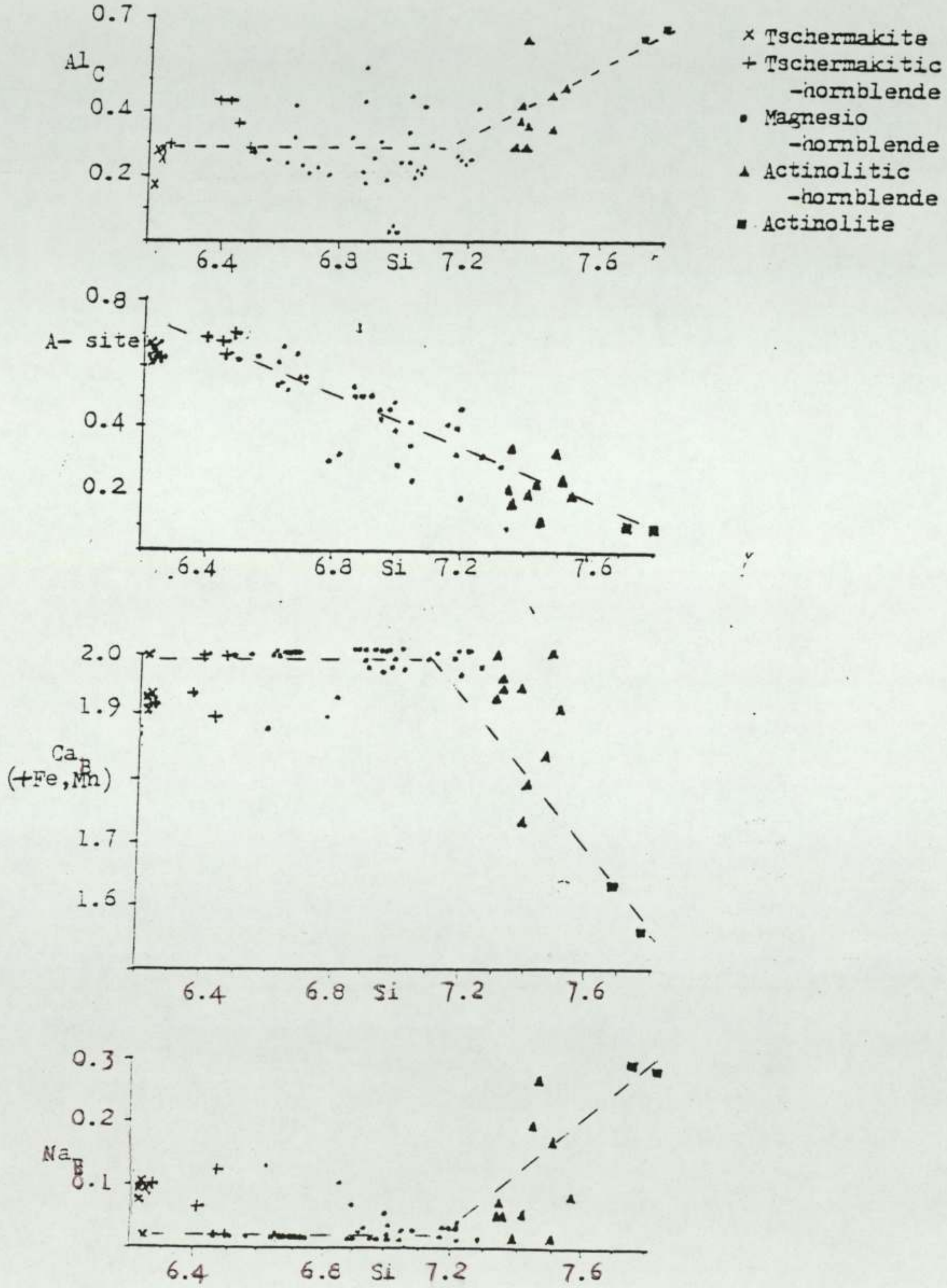
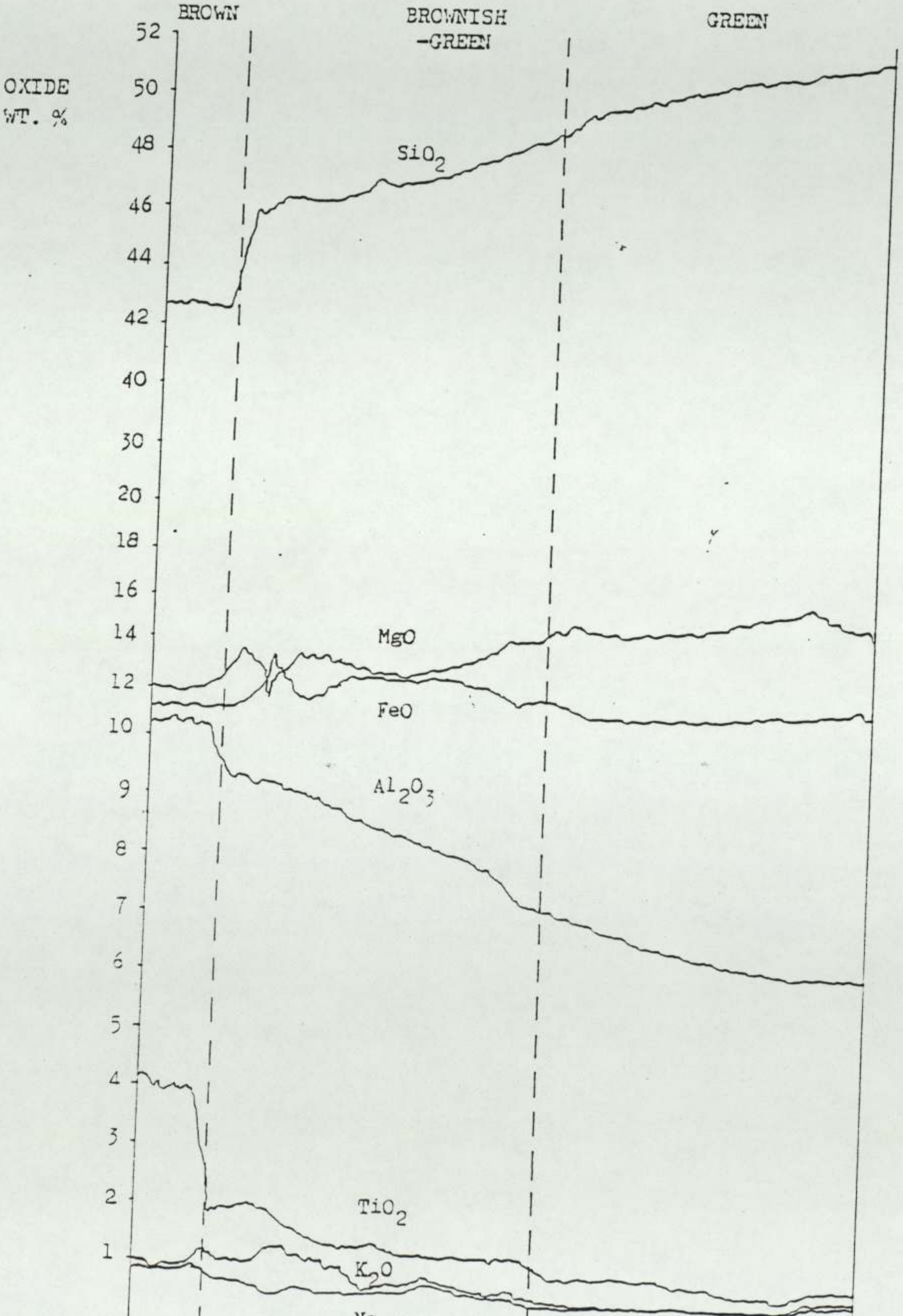


FIG. 6c ELECTRON PROBE LINE SCAN OF COMPOSITIONAL ZONING IN A GARABAL HILL HORNBLENDE



first is shown by the basic tschermakitic amphiboles and those of up to 7.1 Si cations per unit cell. In contrast, amphiboles with greater than 7.1 cations, occurring in the more granitic rocks, follow a totally different trend.

The trend shown by the more basic amphiboles consists of an increase in Si and Mg, with corresponding decreases in Al , A-site alkalis and Ti. The more important changes would appear to involve a combination of the coupled substitutions:

$$(\mathrm{Na, K})_A + \mathrm{Al}^{3+}_T \;\underline{\hspace{2em}}\; [\,]_A + \mathrm{Si}^{4+}_T \quad \text{.......} \; (1)$$

$$(\mathrm{Al, Fe})^{3+}_C + \mathrm{Al}^{3+}_T \;\underline{\hspace{2em}}\; (\mathrm{Mg, Fe})^{2+}_C + \mathrm{Si}^{4+}_T \quad \text{.......} \; (2)$$

$$\mathrm{Ti}^{4+}_C + 2\mathrm{Al}^{3+}_T \;\underline{\hspace{2em}}\; (\mathrm{Mg, Fe})^{2+}_C + 2\mathrm{Si}^{4+}_T \quad \text{.......} \; (3)$$

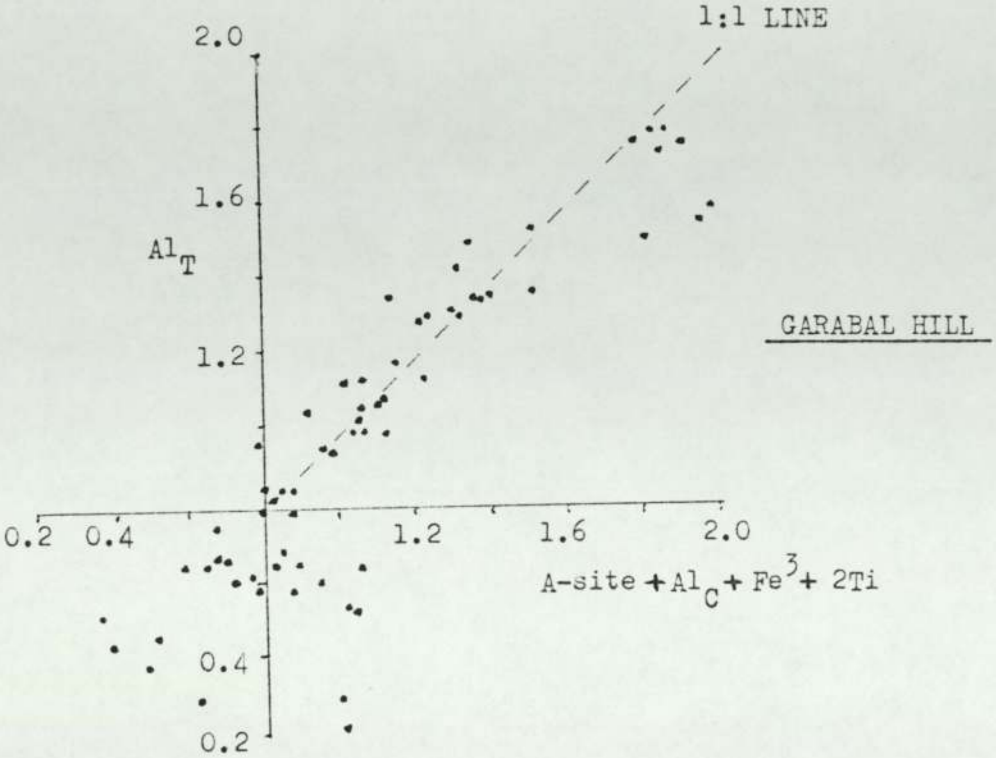
Robinson *et al.,* (1971) noted that the combination of these substitutions would lead to a 1:1 slope when (A-site + Al_C + Fe^{3+}_C + 2Ti) is plotted against Al_T .

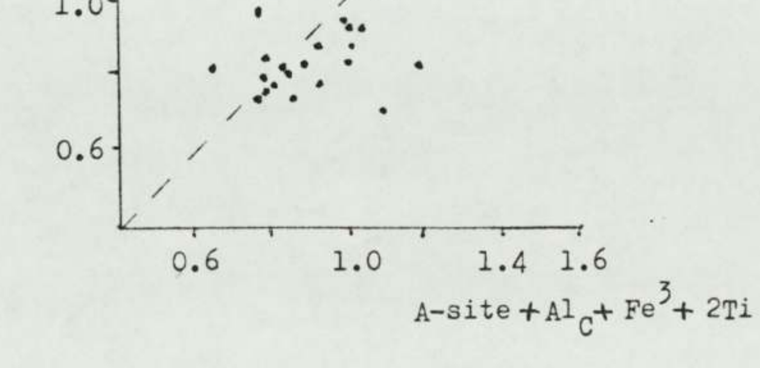
This relationship is demonstrated for the Garabal Hill hornblendes in Fig. 7, and shows a good 1:1 slope with a correlation coefficient of 0.941. Consequently it is reasonable to assume that these are the main substitutions involved. A similar plot for the Arran amphiboles (Fig. 7) shown no systematic relationships and hence indicates that these substitutions do not all occur in those amphiboles (as suggested in Chapter 6.3.1).

Of these substitutions operating in the Garabal Hill amphiboles, the dominant ones are likely to be substitutions (1) and (3) due to the sharp fall apparent for Ti, Al_T and total A-site, also the increase in Si and Mg (also as the Fe^{3+} content is unknown). The importance of these coupled substitutions in zoning was also suggested for the Kialineq amphiboles (Brown & Becker, 1986).

Substitution (2) appears to be of least importance due to the absence of any decrease in octahedral Al. Ferric iron may occur in small concentrations in the octahedral sites and allow substitution (2) to take place to a minor extent. Although Fe^{3+} has not been analyzed, its presence may be indicated in Fig.7 by points lying slightly to the left of the 1:1 slope. These suggest that the total of (A-site + Al_C + Fe^{3+} + 2Ti) is very slightly low in relation to Al_T

FIG. 7 TETRAHEDRAL Al PLOTTED AGAINST Al_C, Fe^3, 2Ti AND TOTAL A- SITE ALKALIS FOR GARABAL HILL & ARRAN HORNBLENDES





content of the same amphiboles. The presence of small amounts of Fe^{3+} would tend to shift the trend more towards the 1:1 slope.

The same trend for the Arran hornblendes show a marked scattering of points indicating that a combination of these substitutions does not take place.

For Garabaal Hill amphiboles, the substitution of Al coupled with both A-site alkalis and Ti are indicated by plotting A-site vs Al_T (Fig. 7a).

If Al_T were coupled solely with A-site cations, a 1:1 ratio would be expected (e.g. at Arran, 1.13:1). The Garabal Hill line, however, shows an excess of Al_T over that needed to combine with alkalis and a ratio of 1.66:1 (correlation coefficient 0.600). This excess Al substitutes with Ti.

Brown *et al* (1982) have proposed how Ti and Al_T can be substituted by Mg and Si as in substitution (3) mentioned above or, alternatively, the following substitution could take place.

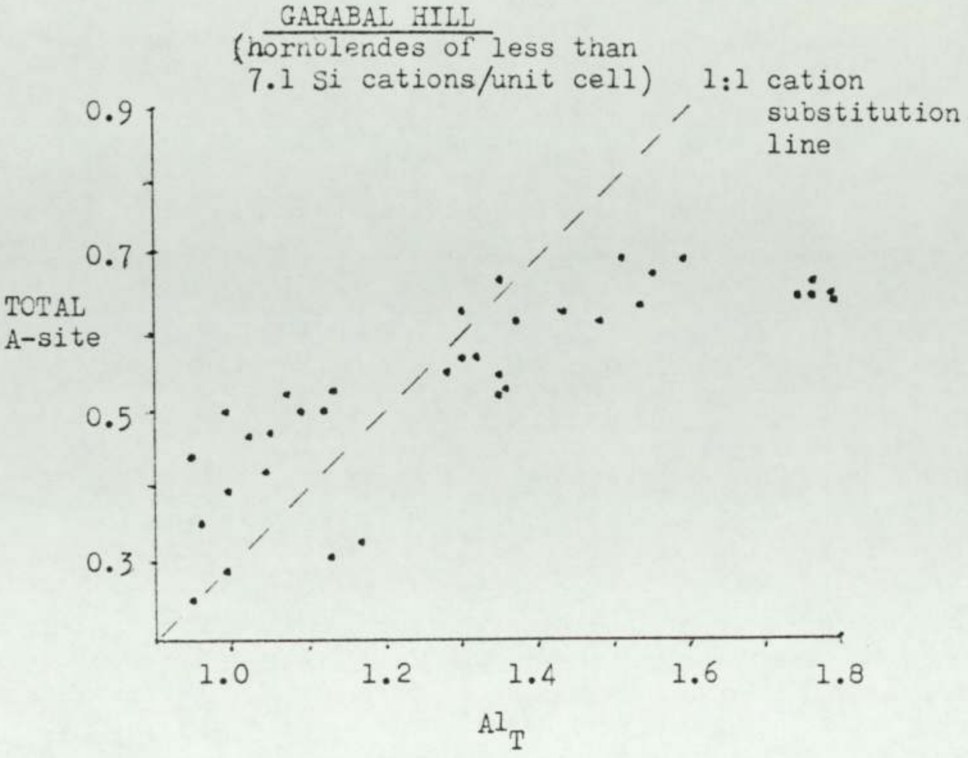
$$Ti^{4+}_{C} + Al^{3+}_{T} \;\underline{\hspace{1cm}}\; (Al, Fe^{3+})_{C} + Si^{4+}_{T}$$

However, this substitution appears to be unlikely due to the absence of any increase in octahedral Al or Fe^{3+}. If this substitution is significant it would also result in a Al_T :Ti ratio of below 2:1. In contrast the sole operation of substitution (3) would give a ratio of exactly 2:1, whereas a combination of this and substitution (1) would produce a ratio in excess of 2:1 (Brown *et al.*, 1982).

The Garabal Hill ratio is 2.25:1, again consistent with the operation of substitutions (1) and (3). The same ratio in the Arran amphiboles is 7.8:1, consistent with substitution (1) being the dominant type.

For the Garabal Hill amphiboles the operation of substitution (3) is shown by plotting Ti_C against Mg_C. This plot can be seen in Fig. 7b and shows a trend following roughly around the 1:1 slope. The degree of scattering present on the diagram may be accounted for by the

FIG. 7a TOTAL A- SITE ALKALIS vs Al_T FOR GARABAL HILL AND ARRAN HORNBLENDES



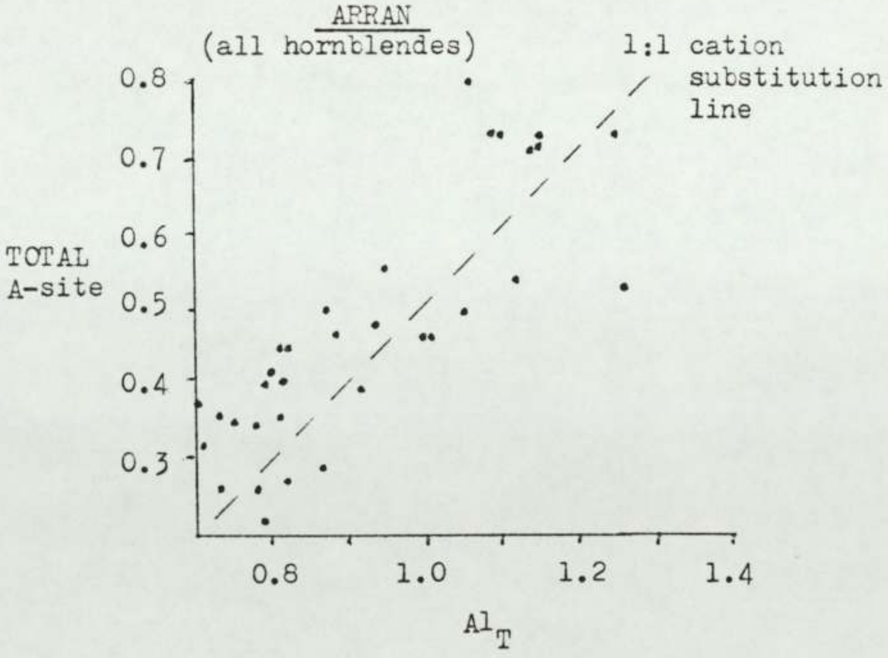
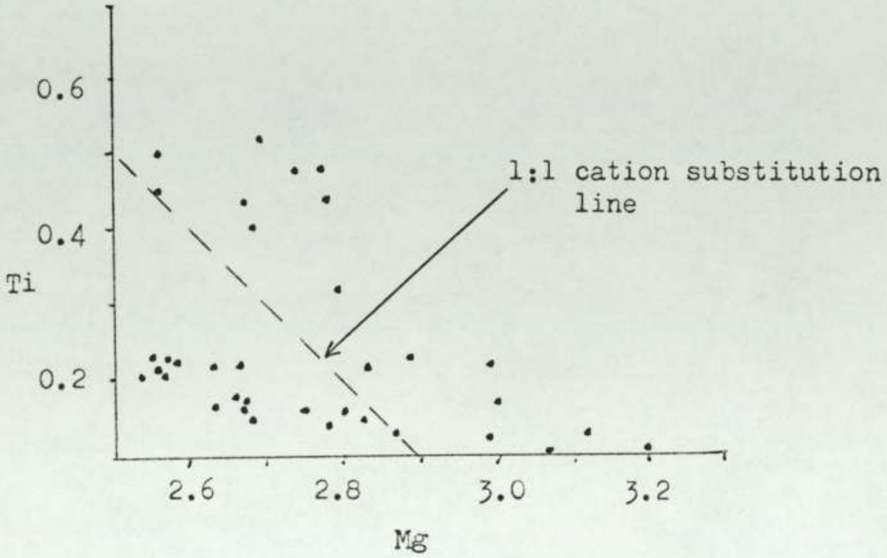


FIG. 7b PLOT OF Ti_C vs Mg_C FOR HORNBLENDES FROM GARABAL HILL

(hornblendes with less than 7.1 Si cations/ unit cell)



inevitable and coincident substitution of Mg for Fe^{2+} .

In the amphiboles with greater than 7.1 Si cations per unit cell, occurring in the more granitic rocks at Garabal Hill, the trend caused by this series of substitutions is seen to be replaced by a second contrasting trend. This is particularly evident by reference to Figs. 6a and 6b, but is also shown by the scattering of points of the granitic hornblendes and actinolitic hornblendes in Fig. 7.

These amphiboles show an increase in the content of Si, Al_C and B-site Na, and a decrease in Al_T , Mg and B-site Ca and A-site alkalis. Fe and Ti remain more or less constant.

The dominant substitution in these acidic amphiboles would appear to be the coupled substitution:-

$$Al^{3+}_{T} + Ca^{2+}_{B} \_\_\_ Si^{4+}_{T} + Na^{+}_{B}$$

the same as that described for the Borgtinderne alkali amphiboles (Brown *et al.*, 1978).

From this coupled substitution, the total number of Ca cations replaced by Na in the B-site is balanced by equal numbers of Al cations replaced by Si in the tetrahedral site (Fig. 7c). Tetrahedral Al and Si in excess of that needed to balance Na/Ca and A site substitute with Mg and Al_C in the coupled substitution:-

$$Al^{3+}_{T} + 2Mg^{2+}_{C} \_\_\_ Si^{4+}_{T} + Al^{3+}_{C}$$

This coupled substitution is indicated by Fig. 7d, a plot of $1/_2\ Mg_{C}^{+}$ vs Al_C. This substitution in the Si rich analyses involves deviation from amphibole stoichiometry.

A good 1:1 negative correlation is seen (correlation coefficient -0.859), suggesting this to be a major substitution in the zoned hornblendes and actinolitic hornblendes in the more granitic rocks.

6.3.4 Discussion

The main substitution reactions in the zoned amphiboles would appear to be as follows. In the

FIG. 7c PLOT OF Al_T + $(Ca,Fe,Mn)_B$ AGAINST Si_T + Na_B FOR GARABAL HILL HORNBLENDES

(hornblendes of greater than 7.1 Si cations/ unit cell)

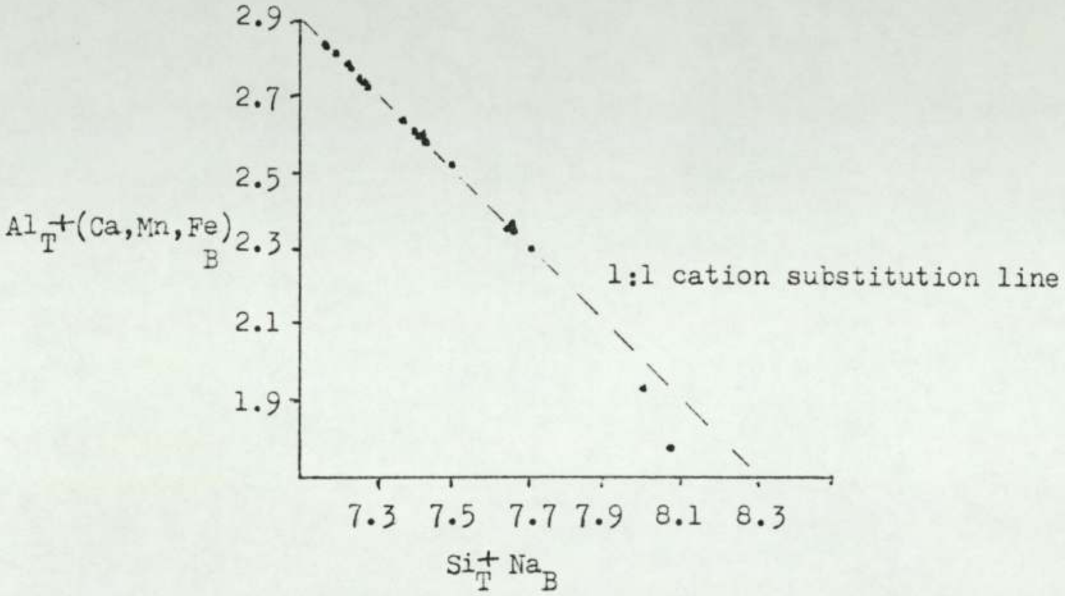
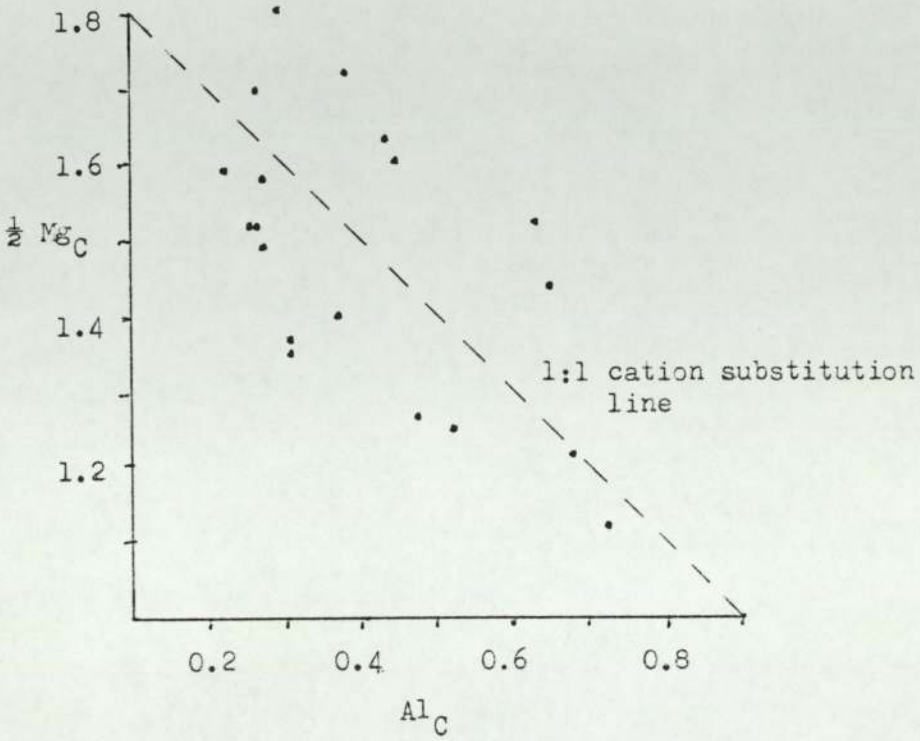


FIG. 7d PLOT OF $\frac{1}{2}$ Mg_C AGAINST Al_C FOR HORNBLENDES FROM GARABAL HILL

(hornblendes of greater than 7.1 Si cations/ unit cell)



Arran hornblendes:-

$$(\mathrm{Na,\ K})_A + \mathrm{Al}^{3+}_T \text{ ——— } [\ ]_A + \mathrm{Si}^{4+}_T\ ,$$

$$\mathrm{Mg}^{2+}_C \text{ ——— } \mathrm{Fe}^{2+}_C$$

$$\mathrm{Mg}^{2+}_C + \mathrm{Ti}^{4+}_C \text{ ——— } \mathrm{Al}^{3+}_C + \mathrm{Fe}^{3+}_C$$

or possibly

$$\mathrm{Mg}^{2+}_C + \mathrm{Ti}^{4+}_C \text{ ——— } 2\mathrm{Al}^{3+}_C$$

In the Bolton Hill hornblendes, zoning is not apparent with the probable exception of

$$\mathrm{Mg}^{2+}_C \text{ ——— } \mathrm{Fe}^{2+}_C$$

The Garabal Hill amphiboles, two contrasting substitution trends are apparent. The first involves the substitutions:-

$$(\mathrm{Na,\ K})_A + \mathrm{Al}^{3+}_T \text{ ——— } [\ ]_A + \mathrm{Si}^{4+}_T$$

$$(\mathrm{Al,Fe})^{3+}_C + \mathrm{Al}^{3+}_T \text{ ——— } (\mathrm{Mg,\ Fe})^{2+}_C + \mathrm{Si}^{4+}_T$$

$$\mathrm{Ti}^{4+}_C + 2\mathrm{Al}^{3+}_T \text{ ——— } (\mathrm{Mg,\ Fe})^{2+}_C + 2\mathrm{Si}^{4+}_T$$

The second zonation trend would appear to involve:-

$$\mathrm{Al}^{3+}_T + \mathrm{Ca}^{2+}_B \text{ ——— } \mathrm{Si}^{4+}_T + \mathrm{Na}_B$$

$$\mathrm{Al}^{3+}_T + 2\mathrm{Mg}^{2+}_C \text{ ——— } \mathrm{Si}^{4+}_T + \mathrm{Al}^{3+}_C$$

Some substitution involving

$$\mathrm{Mg}^{2+}_C + \qquad \text{ ——— } \mathrm{Fe}^{2+}_C$$

is also likely with $\mathrm{Al}^{3+}_T + (\mathrm{Na,K})^{+}_A$ ——— $\mathrm{Si}^{4+}_T + [\ ]_A$. However the second trend is speculative as Fe^{3+} is not known but is likely to occur.

The amphiboles from the different areas show significant differences in concentrations of elements even though all three areas show acid magma assimilating basic wallrocks.

Certain differences in composition are easily spotted optically. In particular, the Ti content of the amphiboles causes a brown colouration to the hornblendes if present in high concentrations. This is shown in the presence of high Ti in the dark brown hornblendes at Garabal Hill (up to 0.5 cations per unit cell) whereas the more green-brown hornblendes at

Arran show lower totals of this element (0.25). This is further seen by the green colour of the Bolton Hill hornblendes which are very low in Ti (approximately 0.1 cations per unit cell). The change to a green colour in low-Ti hornblendes is believed to be due to the presence of Fe in preference to the brown caused by Ti.

Higher concentrations of Fe are seen to give darker green colours to the amphiboles, particularly in the Bolton Hill rocks where the dark green hornblendes of the dark diorites show much higher Fe concentrations than the pale green hornblendes in the pale diorites.

The zonation of hornblendes from brown to green has also been described in may other hybrid complexes (Brown *et al*, 1978).

The Garabal Hill hornblendes show lower Si contents, and higher Al and alkalis than those of Arran and Bolton Hill. The Si concentration ranging from6.2 to 7.8 cations per unit cell compared with 6.7 - 7.5 (Arran) and 6.9 (Bolton Hill). The tetrahedral Al varies inversely, that at Garabal Hill being from 0.2 to 1.8 cations per unit cell, whilst those at Arran and Bolton HIll are 0.6 - 1.4, and 1.1 respectively.

The A-site alkali contents of the Garabal Hill and Arran hornblendes are higher than those of Bolton Hill. The Garabal Hill A-sites vary from 0.1 - 0.8 cations per unit cell (identical with Arran). Those of Bolton Hill contain approximately 0.05 cations per unit cell. The Al_T and A-site cations tend to decrease as amphiboles become more greenish in colour, whilst Si increases.

In the Arran hornblendes, Fe increases in the more acidic hornblendes whilst Mg decreases. In the Garabal Hill hornblendes Fe remains roughly constant whereas Mg increases before falling in the acidic amphiboles.

The absence of elemental zoning in Bolton Hill hornblendes is
presumably due to their high initial Si (which is generally involved in most reactions).

Garabal Hill and Arran amphiboles are similar in showing coupled substitutions between Al_T, A-site and Si, and substitution between Fe and Mg. However they differ in respect of substitutions involving C-site elements such as Fe, Mg, Ti and Al. In addition the Garabal Hill amphiboles show two separate zonation trends whilst the Arran hornblendes show only one.

The differences in chemistry of the amphiboles between the various complexes are due largely to the differences in composition and mineralogy of the original basic wallrock, e.g. high Ti amphiboles in Garabal Hill rocks and lower Ti amphiboles at Arran and Bolton Hill, resulting from the abundance of Fe-Ti oxide inclusions at Garabal Hill and their paucity in the basic rocks of the latter.

In turn the original composition of the basic amphiboles produces different element substitutions and differing compositional variations during zoning.

The nature of metasomatic fluid phase may possibly cause some variations between the complexes, such as differing Na/K ratios in the amphiboles.
In addition, differences in composition of the zoned amphiboles between the complexes may be a result of their
reaction with granitic magmas resulting in their showing subtly different element concentrations and ratios.

As suggested earlier, the most striking difference between the amphiboles of each complex is the Ti content, which is believed to be dependent upon the abundance of Ti in the original pyroxenes, either incorporated in the pyroxene structure or as exsolution lamellae and granules of Fe-Ti oxides. These are more common in the Garabal Hill rocks than those of Arran and Bolton Hill (which show green hornblendes, whereas those of Garabal Hill are brown). The equilibration of these with granite results in decrease in Ti, and zoning to green margins. Other elements also vary in the zonal amphiboles which do not produce optical zoning. The Garabal Hill hornblendes and tschermakitic hornblendes show high A-site contents coupled with high Al and low Si in the tetrahedral site. In contrast, both Arran and Bolton Hill hornblendes show lower A-site content and Al_T , but much higher Si in the tetrahedral site.

The Si content of the amphiboles, and hence the A-site content, may itself be dependent upon their Ti content particularly where this is high.

Verhoogen (1962) suggests that Ti^{4+} results in Al replacing tetrahedral Si, the solubility of Ti increasing with the amount of Al substituting for Si in silicate minerals. The increase in Si in the more acidic amphiboles may reflect equilibration with the granitic SiO_2-rich magma (and subsequently any substitutions involving Si also).

The cause of the many oxide inclusions in the augites is the very low solubility of Ti in pyroxenes at temperatures below the magmatic range (Verhoogen, 1962). Verhoogen also states that Fe-bearing pyroxenes contain low contents of Ti; higher contents of this element causing their breakdown to ilmenite. This may be an explanation for the Fe-poor augites at Garabal Hill, containing abundant Fe-Ti oxide inclusions formed from original Ti-rich augites, whereas the inclusion-poor augites from Arran are richer in Fe (i.e. Ti-rich silicates are commonly Fe-poor). In accordance with this, the low Ti hornblendes in the Johnston Diorites contain the highest Fe concentrations of all three complexes.

The presence of Ti in place of Fe and Mg (Verhoogen, 1962) results in the low (Fe + Mg) totals of the octahedral sites of the Garabal Hill hornblendes in comparison with the higher totals of those from Arran and Bolton Hill.

6.4 Biotite

The structural formulae of micas is based on the presence of 24 (0,0H,F) atoms and probe analyses recalculated on the basis of 22 oxygens (Deer *et al.*, 1962b). Analyses of biotites from Arran and Garabal Hill are presented in Tables 13 and 14.

The classification of the biotites is carried out according to the scheme of Foster (1960).

6.4.1 Glen Dubh

The micas in the Arran basic rocks and xenoliths is an "Mg-Fe biotite", in which the number of Mg and Fe cations are approximately equal. Some variation in the Mg/Fe ratio occurs between those in the more basic and the more granitic hybrid rocks, but the micas all show fairly high contents of Ti and low Al. Minor amounts of Ca and Mn also occur.

6.4.2 Garabal Hill

The biotites from Garabal can be separated into two distinct types
- the variety formed by the action of aqueous fluids on the basic rocks, and the more normal biotites formed magmatically by replacement of other mafic minerals in the hybrid and granitic rocks.

The biotite formed in the basic rocks is a "Mg-biotite" containing high concentrations of Mg and Ti (Mg up to 3 cations per unit cell, Ti up to 0.7 cations per unit cell).

The high Ti content of these biotites is responsible for their orange-brown colouration (Deer *et al.*, 1962b). They also show a low Fe/Mg ratio (0.57) which is a reflection of the low ratio in the previously existing mafic minerals in the basic rocks.

This high Ti and the high Mg/Fe concentrations are characteristic of the biotites in these basic rocks, in a similar fashion to the red-brown hornblendes in the same rocks.

The presence of low Fe in Ti-rich silicates is in accordance with the work of Verhoogen (1962) (see Chapter 6.3.4).

Si and alkali contents are also low, with the twelve-fold co-ordination site significantly less than 2.

The biotites change in composition in the granitic hybrid rocks to more "Fe-biotites", with Fe/Mg ratios of up to 1.02. These biotites contain lower Ti, Al and Mg, but higher Fe, Mn and alkalis with the twelve-fold co-ordination site approaching 2.

The lower Ti concentration of these biotites results in their darker brown colour in comparison with the orange-brown colour of those in the basic rocks. Between the two extreme compositions outlined here there are a series of biotites of intermediate composition.

The lower Ti content of the dark biotites is due to their equilibration with, and crystallization in the Ti-poor granitic magma, whilst the orange varieties replaced existing Ti-rich mafic minerals in the basic wallrock.

6.5 Chlorite

The structural formulae of the chlorites have been calculated on the basis of 28 oxygen equivalents (Deer *et al.*, 1962b). They are classified according to the scheme of Hey (1954).

Chlorite is a particularly important phase in one of the three areas studied, the Johnston Diorites of Bolton Hill where biotite is absent, and analyses of the chlorites are shown in Table 15.

This orange to pale brown, strongly pleochroic, micaceous mineral from the Johnston Diorite hybrids, described as biotite in previous descriptions (Cantrill *et al.*, 1916), was shown to be an Fe-rich chlorite with the composition "brunsvigite" (Hey, 1954).

Occurring in both the pale and dark diorite hybrids it shows slight chemical variation, ranging around the formula:-

$(K_{0.1}\ Ca_{0.3}\ Mg_{3.5}\ Fe_{5.3}\ Ti_{0.3}\ Al_{2.2})_{11.7}\ (Si_6\ Al_2)\ O_{20}\ (OH)_{16}$

Indeed, the analyses are almost identical in composition to the brunsvigite described in the literature by Battey (1956).

The high refractive index of the chlorite is due to its high iron content (much higher than typical penninitic chlorites), and this can account for its very strong pleochroism (Deer *et al.*, 1962b).

The Fe-rich brunsvigites described in earlier work have generally been green in colour (Nockolds & Richey, 1939; Battey, 1956; Nicholls, 1958). This may be a result of a high content of ferric iron which is known to produce a green colouration in other silicate minerals such as pyroxenes and micas. Green varieties are represented in the Johnston Diorite series although brown chlorites are far more abundant.

The noticeable feature of the green chlorites described in previous literature is their low Ti content (approximately 0.3% TiO_2). This is much lower than the Ti content of the brown brunsvigites from Bolton Hill which contain up to 3.3% TiO_2 . This high concentration of Ti is likely to be the cause of the unusual orange-brown colour and would be similar to that of minerals such as pyroxene, hornblende and biotite. It would appear that in the brunsvigite described for the Johnston Diorites, the brown colour, caused by high Ti, masks the effect of high ferric iron.

The low octahedral site totals of 11.5 - 11.7 seen in these brunsvigites (rather than the expected 12) may be explained by the chlorite having been oxidised, with the formation of Fe^{3+} from previously existing Fe^{2+}, rather than the Fe^{3+} being of primary origin. The associated substitution in the oxidised chlorites is 0^{2-} for $(OH)^-$ which, when formulae are calculated according to 28 oxygen equivalents, results in low octahedral totals (Deer, 1962b).

The chlorite replaces hornblende in a similar way to biotite. The latter is absent due to the K_20-poor nature of the invading granite magma Chlorite however is stable under these conditions.

Brown or green chlorite has been identified as a magmatic mineral elsewhere (Battey, 1956, Nicholls 1958), in contrast to its more usual hydrothermal origin as penninite. The brunsvigite at Bolton Hill itself shows late stage alteration to this more typical Mg-rich variety of chlorite. During its replacement by this yellowish green penninite, granules of epidote and sphene were formed. This is caused by the high concentrations of Fe and Ti present in the brunsvigite and unable to be accommodated in the replacing penninite structure. The penninite always shows an association with epidote and sphene whereas the higher relief brunsvigite does not.

6.6 Allanite

The allanites contain the vast majority of the rare earth elements in the granitic rocks, in particular the light rare earth elements (La-Sm). No evidence was found for the presence of rare earth elements in other minerals such as apatite, zircon or sphene.

Allanite is common in the acidic rocks but absent from the basic varieties. In the Johnston Diorites the mineral is only found in the microcline granites, and is absent from the albite granites and their corresponding hybrid rocks.

Analyses of allanites are shown in Table 16 for all three complexes.

Analytical problems occur due to interferences in the determinations of the rare earth elements caused by line overlap. The interferences are of:-

La L on Pr L
Ce L on Nd L
Ce L on Sm L
Nd L on Gd L

Despite interferences, consistently good totals were obtained with the exception of those for the Garabal Hill allanites. This can be explained by their metamict nature, caused by high Th and U contents. The large concentrations of Ti and Fe of the Arran allanites result in dark brown to black pleochroism, whereas the Bolton Hill and Garabal Hill allanites are much paler in colour with a correspondingly lower content of these elements.

6.7 Prehnite

The colourless radiating aggregates seen in the late stage alteration veinlets, together with calcite and albite, in the Johnston Diorites are confirmed as being prehnite, showing high Fe concentration. (Table 17).

6.8 Elemental transitions involved in the replacement of pyroxene by amphibole and mica and implications for the whole rock chemical variation.

6.8.1 Pyroxene-amphibole transitions

The replacement of pyroxene by amphibole in wallrocks is accompanied by numerous chemical changes. In particular, in mineral terms, hornblende shows an increase in volatile content (approximately 2%) and alkali content. Hornblende generally shows higher contents of Fe, Ti and Al than the replaced pyroxene but correspondingly lower Si and Ca. The increase in volatiles and alkalis would seem to have been caused by introduction of these constituents into the wallrock.

The increased concentrations of Fe and Ti in the amphiboles are controlled by Fe-Ti oxides present in the original pyroxenes (Brown *et al.*, 1982). This is a very common occurrence being caused by the resorption of the oxides magnetite, ilmenite and rutile; it is also clearly seen petrographically. It has been suggested that the high temperature hornblendes contain a high Ti content which on cooling is exsolved (along with some Fe) to produce the Fe-Ti oxide inclusions often seen in hornblendes.

However, the differences between the Ti content of the hornblendes at Garabal Hill, Arran and Bolton Hill and the abundance of Fe-Ti oxide inclusions suggest, in these instances this is not the case. It is more likely to be a result of the content of Fe-Ti oxide inclusions in original pyroxenes which have been replaced by the hornblendes, rather than a function of their temperature of formation.

As with Fe and Ti, other elements involved in the transformation may also originate from other mineral phases, i.e. other minerals are involved in the pyroxene-hornblende reaction.

This is shown below using average chemical compositions of the
mafic minerals from the complexes to form balanced reactions of the transformation.

$$\underset{\text{PYROXENE}}{1.4\ Ca_3Mg_2Fe^{2+}Si_6O_{18}} + \underset{\text{ILMENITE}}{0.2\ FeTiO_3} + \underset{\text{MAGNETITE}}{0.1\ Fe_3O_4} + \underset{\text{ANORTHITE}}{1.175\ CaAl_2Si_2O_8}$$

$$\underbrace{+\ 1.85\ NaO_{\frac{1}{2}} + H_2O}_{\text{FLUID PHASE}}$$

$$\Downarrow$$

$$\underset{\text{HORNBLENDE}}{Na_{0.5}(Ca_{1.9}Na_{0.1})(Mg_{2.8}Fe^{2+}_{1.8}Fe^{3+}_{0.1}Ti_{0.2}Al_{0.1})Si_7AlO_{22}(OH)_2}$$

$$\underset{\text{ALBITE}}{1.25\ NaAlSi_3O_8} + 3.475\ CaO + 0.025\ O_2\uparrow$$

This reaction indicates how pyroxene may react with Ca plagioclase and a small quantity of Fe-Ti oxides in the presence of an alkali-rich fluid phase to produce a typical Arran hornblende, sodic plagioclase and a Ca-rich fluid phase.

This would tend to show that most elements remain in the rock with the possible exception of Ca^{2+} (although some of this may combine with any Si^{4+} to produce sphene from ilmenite. Some of these features, e.g. calcic plagioclase altering to sodic plagioclase, the resorption of Fe-Ti oxides by hornblende, and the formation of sphene may be seen petrographically. A similar equation may also be produced for the alteration of pyroxene to hornblende at Garabal Hill (although the mineral formulas are approximate):-

$$0.933\,\underset{\text{PYROXENE}}{Ca_4Mg_3Fe^{2+}Si_8O_{24}} + 0.5\,\underset{\text{ILMENITE}}{FeTiO_3} + 0.022\,\underset{\text{MAGNETITE}}{Fe_3O_4}$$

$$+\ 2.016\,\underset{\text{ANORTHITE}}{CaAl_2Si_2O_8} + \underbrace{2.633\,NaO_{\frac{1}{2}} + H_2O + 0.045\,O_2\uparrow}_{\text{FLUID PHASE}}$$

$$\downarrow$$

$$\underset{\text{HORNBLENDE}}{Na_{0.7}(Ca_{1.9}Na_{0.1})(Mg_{2.8}Fe^{2+}_{1.3}Fe^{3+}_{0.2}Ti_{0.5}Al_{0.2})Si_6Al_2O_{22}(OH)_2}$$

$$+\ 1.833\,\underset{\text{ALBITE}}{NaAlSi_3O_8} + 3.85\,CaO$$

This reaction also indicates the participation of an alkali rich fluid phase in the pyroxene-hornblende transition, in which Fe-Ti oxides are accommodated by the hornblende. Calcic plagioclase alters to sodic plagioclase with the apparent release solely of Ca^{2+}.

In comparison with the same transformation of the Arran minerals, those of Garabal Hill show a greater concentration of Fe-Ti oxides involved in the reaction (due to their greater abundance in the Garabal Hill pyroxenes than the Arran pyroxenes).

A similar balanced reaction cannot be made for the Bolton Hill minerals due to the absence of pyroxene at the complex, however it is likely that a closely comparable reaction would have taken place at Bolton Hill although with a lesser involvement of Ti.

At Bolton Hill it is also likely that cummingtonite formed from orthopyroxene in a similar fashion due to the introduction of a fluid phase.

6.8.2 Hornblende-biotite/brunsvigite transition

The replacement of hornblende by biotite results in an increase in volatile content of the mineral phase (4% - 5%, Deer *et al.*, 1962b), and particularly K. Other constituents in biotite compared with hornblende include Fe, Ti and Al whilst Ca and Si decrease.

The higher content of Ti in biotite in relation to hornblende is caused by resorption of the rutile needles present in the hornblende. This Ti was in excess of that able to be accommodated in the particular hornblende, but not in the case of the newly-formed biotite. This is clearly demonstrated at Garabal Hill where magnesio- hornblendes contain abundant rutile needles which are absent from the replacing biotite. An increase in Fe in the biotites also indicates resorption of some Fe oxides.

Balanced reactions may be made for the hornblende-biotite transition.

$$Na_{0.5}(Ca_{1.9}Na_{0.1})(Mg_{2.8}Fe^{2+}_{1.8}Fe^{3+}_{0.1}Ti_{0.2}Al_{0.1})Si_7AlO_{22}(OH)_2$$

HORNBLENDE

$$+\ 0.3\,TiO_2 \quad +\ 0.183\,Fe_3O_4 \quad +\ 1.425\,CaAl_2Si_2O_8$$

RUTILE MAGNETITE ANORTHITE

$$\underbrace{+\ 2.85\,(K/Na)O_{\frac{1}{2}} \ +\ H_2O}_{\text{FLUID PHASE.}}$$

$$\Big\downarrow$$

$$(K/Na)_2Mg_{2.8}Fe^{2+}_{2.45}Ti_{0.5}Si_6Al_2O_{20}(OH)_4$$

BIOTITE

$$+\ 1.45\,(K/Na)AlSi_3O_8 \ +\ 3.325\,CaO \ +\ 0.1165\,O_2\uparrow$$

ALKALI FELDSPAR

This equation would appear to show that an alkali-rich fluid phase may cause the hornblende to alter to biotite with the resorption of Fe-Ti oxides, the formation of alkali feldspar from plagioclase. All these features may be seen petrographically.

As was seen in the pyroxene-hornblende reaction, Ca^{2+} appears to be released. However Si^{4+} may combine with some of the Ca^{2+} to produce sphene from ilmenite (also seen petrographically), although it is likely that there is an excess of Ca^{2+} even after taking this into account, and this may form epidote in the hybrid rocks.

The replacement of Garabal Hill hornblendes by biotite may also be shown in a balanced equation using their typical chemical compositions, although again these compositions are merely approximate due to their variable nature.

$$\underbrace{1.107\, Na_{0.7}(Ca_{1.9}Na_{0.1})(Mg_{2.8}Fe^{2+}_{1.3}Fe^{3+}_{0.2}Ti_{0.4}Al_{0.2})Si_{6}Al_{2}O_{22}(OH)_{2}}_{\text{HORNBLENDE}}$$

$$+\underbrace{0.1572\, TiO_2}_{\text{RUTILE}} + \underbrace{0.08\, Fe_3O_4}_{\text{MAGNETITE}} + \underbrace{0.334\, CaAl_2Si_2O_8}_{\text{ANORTHITE}} + \underbrace{1.828\,(K/Na)O_{1/2} + 0.893\, H_2O}_{\text{FLUID PHASE}}$$

$$\Downarrow$$

$$\underbrace{(K/Na)_2Mg_{3.1}Fe^{2+}_{1.8}Fe^{3+}_{0.1}Ti_{0.6}Si_{5.5}Al_{2.5}O_{20}(OH)_4}_{\text{BIOTITE}}$$

$$+\underbrace{0.603\,(K/Na)AlSi_3O_8}_{\text{ALKALI FELDSPAR}} + 2.437\, CaO + 0.2102\, O_2\uparrow$$

Biotite is formed with alkali feldspar from original hornblende, rutile, calcic plagioclase and alkali-rich fluid phase. Again excess Ca^{2+} is produced although some of this may combine with silica to form sphene from ilmenite. Despite this, it would appear that Ca^{2+} is present in excess of that needed to form sphene, and may produce epidote also.

These reactions tend to show the necessity of incorporating alkalis from a fluid phase, and of releasing Ca^{2+} to the fluid phase in the hornblende-biotite transition. This is aided by involving other phases in the reaction which may be seen petrographically, e.g. zonation of calcic plagioclase to alkali feldspar, and incorporation of Fe-Ti oxides into the biotite.

In the Bolton Hill rocks, hornblende alters to brunsvigite in place of mica due to the deficiency of K . This may also be shown in a balanced reaction using average mineral compositions.

$$1.65\,\underbrace{(K/Na)_{0.1}(Ca_{1.7}Na_{0.3})(Mg_{2}Fe^{2+}_{1.7}Fe^{3+}_{1.0}Ti_{0.1}Al_{0.2})Si_{6.8}Al_{1.2}O_{22}(OH)_{2}}_{\text{HORNBLENDE}}$$

$$+\,0.135\,\underbrace{FeTiO_3}_{\text{ILMENITE}} + 0.17\,\underbrace{Fe_3O_4}_{\text{MAGNETITE}} + 2.5725\,\underbrace{CaAl_2Si_2O_8}_{\text{ANORTHITE}} + \underbrace{2.895\,(K/Na)O + 6.35\,H_2O}_{\text{FLUID PHASE}}$$

$$\Downarrow$$

$$\underbrace{(K/Na)_{0.1}(Ca_{0.4}Mg_{3.3}Fe^{2+}_{4.0}Fe^{3+}_{1.1}Ti_{0.3}Al_{2})Si_{6}Al_{2}O_{20}(OH)_{16}}_{\text{BRUNSVIGITE}}$$

$$+\,3.455\,\underbrace{(K/Na)AlSi_3O_8}_{\text{ALKALI FELDSPAR}} + 4.9775\,CaO + 0.2225\,O_2\uparrow$$

An Na-rich fluid phase may react with a typical Bolton Hill hornblende, calcic plagioclase and Fe-Ti oxides to produce brunsvigite, sodic plagioclase and epidote, with the release of Ca^{2+}.

Similarly with Arran and Garabal Hill, these features may be seen petrographically with brunsvigite replacing hornblende, the zonation of calcic plagioclase to more sodic varieties, and the formation of much epidote.

Sphene also occurs due to the reaction of some of the released Ca^{2+} with Si^{4+} and ilmenite, although Ca^{2+} would appear to be in excess of that needed to form this mineral, and may also produce epidote etc.

6.8.3 Formation of apatite.

The apparently large amounts of Ca^{2+} lost during the formation of hornblende or biotite/brunsvigite from earlier mafic minerals, are partly responsible for the huge numbers of apatite needles seen in xenolithic and hybrid basic rocks.

Phosphorus, the other component of apatite, is probably transported by the migrating fluid phase out of the granitic magma and into the basic wallrocks. The Ca^{2+} and P^{5+} subsequently combine to form apatite in these modified and acidified gabbros. The apatites are particularly abundant in the hornblende, biotite and zoned plagioclase.

This theory would appear to be supported by the detection of P along with other volatiles in volcanic gases (Carmichael *et al.*, 1974) and hydrothermal liquids (Froelich *et al.*, 1982).

The hornblendes in the Bolton Hill diorites themselves contain numerous apatite needles which may be a further indication of their having formed by complete replacement of pre-existing pyroxenes, although no remnants of the pyroxenes occur.

6.8.4 Late stage alteration (hydrothermal and metamorphic)

All the complexes show hydrothermal veining involving epidote, calcite, chlorite etc., whilst the Bolton Hill complex also shows metamorphic veining involving prehnite, albite and calcite. This is an indication of how certain elements may be mobilized by late stage fluids, e.g. Ca^{2+}, although some workers suggest that even where hydrothermal alteration is extensive, the only truly mobile component is water, all the other elements being very locally redistributed on a mm. scale.

With the possible exception of Ca, there seems no reason to suspect that the majority of elements are significantly affected by any process except that of assimilation, other than the elements Na, K and P (and possibly associated elements such as Rb). These being introduced into the rock via a fluid phase whilst some Ca may migrate out of the rock via the same fluid phase (i.e. metasomatic elements), other elements are merely redistributed by the fluids.

This has implications for the next chapter where acidic magma may react with basic wallrock during, or post, metasomatism by the aqueous fluids.

7. WHOLE ROCK GEOCHEMISTRY

7.1 Introduction

The study of whole rock geochemical variation is important for a thorough understanding of the assimilation process and to show its possible occurence. It is also essential for establishing which endmembers are involved in the overall assimilation process, where a number of possible endmembers exist, in addition, the role of other processes such as metasomatism, crystal fractionation, hydrothermal alteration.

7.2 Analytical techniques

Major and trace elements were analyzed by XRF using a Philips PW 1400 Wavelength Dispersive X-Ray Spectrometer - fused discs for major elements and "pressed powder briquettes" for trace elements (see Appendix 2 for procedures and conditions). Rare Earth Elements were analyzed by Neutron Activation Analysis using reactor facilities at Ascot (Imperial College Centre) and Aldermaston (AWRE). Additional elements (e.g. Sc) were also analyzed at Aldermaston (see Appendix 2) for procedures and conditions).

7.3 Presentation of data

7.3.1 Use of the variation diagram and choice of abscissa

Plotting major element oxides and trace elements versus silica on the traditional Harker diagrams should define a straight line (Harker, 1909; Cox *et al.*, 1979) for a rock suite of hybrid origin if the acidic and basic endmembers are of fixed composition, and not affected by other contemporaneous processes. This has been demonstrated experimentally by Yoder (1973), who remarked that hybridization is not necessarily confined to producing liquids along normal lines of descent resulting from fractional crystallization.

In contrast, a rock series produced by a process such as fractional crystallization will plot as a gently curved liquid line of descent for many elements with partition coefficients removed from unity (i.e. greater or less than 1: Harker, 1904; Wahlstrom, 1961; Walker, 1983). These curved trends are a result of partition coefficients between silicate liquid and crystals, resulting in compatible or incompatible behaviour and producing either rapid depletion in the liquid, or alternatively, concentration in late stage liquids. Additional deviation from linear behaviour can be due to changes in proportion of the extracted crystals during the evolution of the liquid. Only a delicate and constantly changing balance of crystal phase extraction can result in linear variation of the liquid in an open system (Eichelberger, 1974). The operation of such conditions would be a rare event. The expected curved trends of chemical variation, of fractionally crystallized liquids, has also been shown by detailed field observations during the crystallization of the Alae Lava Lake in Hawaii (Wright & Peck, 1978).

Many of the variation diagrams shown in this study have been compared and contrasted with trends of rock series convincingly demonstrated to have formed by fractional crystallization. Lassen Peak data (King, 1955) or East Iceland data (Wood, 1978) are the two used.

Yoder (1973) suggests that Partial Melting is also no more likely to form a linear trend than fractional crystallization, as it is a discontinuous process with a break in melting following the exhaustion of a phase in the source material, i.e. melts would not vary continuously in composition as many rock series are seen to do. Once again, partitioning of elements in favour of melt or solid phase would also result in non-linear behaviour, even with continuous melting of a phase.

Silica has been used as abscissa on the variation diagrams because it shows a wide variation in composition between the rock types. However, the suitability of $Si0_2$ as an index to demonstrate the process of assimilation should be examined.

Whether Si is mobile during alteration is problematical, but it shows good correlation with many immobile elements (e.g. Zr, Y, etc.) with very little scatter (see later). Therefore the scatter shown by certain other elements is likely to be due to their own behaviour. This is suggested by Power & Gibbons (1980).

Considering other possible processes, it has also been indicated by Vernon (1976) that elements such as Si show negligible diffusion rates under conditions of metamorphism due to high charge. This is in contrast to the low charge ions which diffuse more readily (Fyfe *et al.*, 1962). Mongkoltip & Ashworth (1986) also imply that Si diffuses extremely slowly, due to its high charge, in relation to other elements such as Mg, Ca and Fe.

Could metasomatism result in mobility of Si? Henderson (1982) reported that volatiles lost from a magma are largely represented by volcanic sublimates which are mainly composed of compounds of Na, K, Ca, Mg, Al and Fe. Si apparently is absent. Evidence gained from study of the petrography and mineral chemistry of the three areas covered in this work suggest that the metasomatic/metamorphic reactions observed could be adequately explained without the input or removal of Si.

This evidence tends to imply that Si is generally immobile and is consequently a reasonable element (oxide) to use as an abscissa to demonstrate the process of assimilation.

Whilst mixing may be shown by linear plots on element-element diagrams, Langmuir *et al* ., (1978) have shown that data consistent with mixing may lie along a hyperbolic curve when using element-ratio or ratio-ratio plots. However, endmember compositions may be more accurately identified using actual values on diagrams rather than ratios. In addition, element-element diagrams also provide evidence for the operation of processes such as metasomatism and late stage alteration, which cannot be shown using ratio diagrams.

Ratio diagrams have therefore not been used in this study because the author believes they would show no more evidence for assimilation than variation diagrams (although they may be useful for isotopic data).

7.3.2. Effects of alteration on geochemical trends.

Many of the rocks sampled from all three complexes show some evidence of interaction with an aqueous fluid phase. This could have been primary metasomatic alteration or more frequently, late stage hydrothermal alteration. The metasomatic alteration may occur prior to or during the assimilation process.

Such processes are known to result in the secondary mobilization of certain elements, and can affect the primary (mixing) trends displayed by rock series and distort linear relationships. Study of so-called immobile elements will help to demonstrate the mixing process, whereas study of mobile element behaviour may well assist in the understanding of other important processes taking place.

Henderson (1982) states that "the addition or removal of major and trace elements is dependent upon the mineralogy of the original rocks and the composition of the metasomatizing fluids, and therefore no all-embracing statement on element mobility is possible". Despite this comment, Large Ion Lithophile Elements (L.I.L.E.) such as the alkalis are all generally acknowledged as being easily added to rocks or removed from them during alteration (e.g. Philpotts *et al.*, 1969; Cann, 1970; Wood *et al.*, 1976; Condie *et al.*, 1977; Cox *et al.*, 1979; Dickin & Jones, 1983; Baker, 1985). Dickin & Jones (1983) indicate also that the variable mobility of these elements is explained by the differing ease with which they are incorporated into the new mineralogy of the rock, and that certain elements can be highly mobile during alteration of some rocks but not others. Nevertheless, the alkali elements are not regarded as being particularly reliable indicators of magmatic processes in altered rocks.

Other elements such as Ca, Mg and Fe are variably described in past literature, being reported as mobile by some authors but immobile by others.

Strontium is often described as a mobile element (Philpotts *et al.*, 1969; Condie *et al.*, 1977; Thompson, 1982). More recently however, Dickin *et al.* (1984) have indicated that this element in particular shows variable behaviour and is mobile during alteration of certain rocks such as gabbros, but not in others such as granites.

The mobility of certain elements, such as alkalis, is due to their low charge and ionic radius. This means that they are easily substituted into the lattices of many common silicate minerals. When replaced during alteration their low charge means that these elements are easily transported by hydrothermal fluids to be incorporated in any new minerals. Elements such as Mg and Fe have slightly higher charges and are subsequently less mobile.

Generally, the most reliable elements for demonstrating a particular magmatic process are the High Field Strength Elements such as Ti, Zr, Nb, Y, V which are regarded as being strongly immobile (Butler & Smith, 1962; Parker & Fleischer, 1968; Cann, 1970; Pearce & Cann, 1973; Wood *et al.*, 1976; Winchester & Floyd, 1977; Pearce & Norry, 1979; Muecke & Clarke, 1981; Thompson, 1982; Baker, 1985). Because they are unaffected by later aqueous fluids they are often used for the purpose of discriminating rocks from different tectonic settings.

These "immobile" elements are stable when incorporated into minerals. This is because they are generally incompatible and do not fit easily into the lattices of the common silicate minerals. This is due to either charge or size difference preventing substitution for common elements such as Ca^{2+}, Mg^{2+}, Fe^{2+} and alkalis in the common mineral structures. Hence these incompatible elements tend to occur in oxides (e.g. Ti, V, Nb) or, if in high concentrations, in their own minerals (e.g. Zr in zircon).

The Rare Earth Group of elements are particularly important as they are all small ions of high ionic charge. Consequently, as with the elements mentioned above, they are also unable to be accommodated in major silicates and occur often, as a group in independent LREE or HREE-bearing minerals (with the exception of divalent Eu). Consequently these elements can be expected to be unaffected by normal hydrothermal alteration of the common rock-forming minerals. The chemistry of these independent rare earth minerals and the whole rock REE chemistry is not changed. Certain other elements (e.g. Nb, Y) also occur in these rare earth minerals and are also resistant to most aqueous fluid reaction.

The REE's, due to their supposed immobility, are often used for petrogenetic modelling in rocks where some alteration is apparent (Philpotts *et al.*, 1969; Pearce & Cann, 1973; Wood *et al.*, 1976; Thorpe *et al.*, 1977; Exley, 1980; Thompson, 1982; Thurston & Fryer, 1983). However, a great deal of work has been done in recent years showing that they can be mobilized under certain specific conditions of alteration. This is particularly the case in the presence of F^- in aqueous hydrothermal solutions (Bandurkin, 1961; Balashov & Krigman, 1975; Fryer & Edgar, 1977; Flynn & Burnham, 1978; Humphris, 1984; Giere, 1986). Martin *et al.*, (1978) also report the REE's as being mobilized during fenitization, which again may well involve a fluoride-rich aqueous phase.

In addition, the presence of F^- is also believed to result in transport of otherwise immobile elements such as Y and Nb in the form of fluoride complexes (Parker & Fleischer, 1968; Muecke & Clarke, 1981).

Humphris (1984) in her study concludes that no simple rules exist to predict the transport of REE's during metamorphism, weathering or hydrothermal alteration, and that data from rocks affected by such processes should be used with extreme caution in petrogenetic modelling. Nevertheless, of the three complexes studied here only Glen Dubh, Arran shows evidence for a possible F -rich fluid being active, with the development of secondary fluorite. The other two complexes show no indications of aqueous F -rich fluid activity and REE concentrations in these rocks and are not believed to have been affected by any post-crystallization alteration.

7.3.3. Mixing calculations and the interpretation of the geochemical data.

To further test the possibility of mixing producing the intermediate rocks at each of the complexes, use was made of the "least squares" approximation program of Bryan *et al.*, (1969), provided by M. J. Le Bas (Leicester University), and performed on a BBC Microcomputer.

The program tests an intermediate rock composition against the closest hypothetical mixture of two possible endmembers. It must be emphasized however, that the program merely tests the numerical fit between actual and estimated trends and (as with other statistical methods) does not give conclusive proof of hybridization having occurred. It merely serves to help identify, or rule out, possible endmembers and suggest whether such a process is feasible or unlikely.

The calculations may also show which elements cause significant deviation from the predicted trend and are probably influenced by other processes such as hydrothermal alteration. The calculations have been commonly used to show assimilation or fractional crystallization in other igneous complexes (Wright, 1974; Brown *et al.*, 1978; Kyle, 1981; Brown & Becker, 1986), and have been used to show whether hybridization is feasible in each of the complexes studied here.

In the calculations, the squares of the differences between the predicted and observed values for the concentrations of each element oxide in the hybrids are added together to give an overall total. Lower sums of squares of residuals indicate a better match between the observed and predicted trends and consequently a value approaching 1 is a good fit, e.g. the classic hybrid rocks at Marsco, Isle of Skye, analyzed by Wager *et al.*, (1965) have been shown to give a value of 1.592 by Brown *et al.*, (1978). An ideal value would be close to zero although 1 has been found to be reasonable by some previous authors.

7.4 Major element geochemistry

7.4.1 Glen Dubh, Arran.

Major element analyses of the Isle of Arran suite and their normative values are tabulated in Appendix 2, Tables 29-34. Silica varies between 45% - 76% for the whole rock series and the hybridization trend shows a decrease in $Mg0$, $Fe0$, $Ca0$, Al_20_3, $Mn0$ and $Ti0_2$, and increases in alkalis with increasing $Si0_2$ content (Figs. 8 - 10).

Below 57.5% $Si0_2$ content the plots on variation diagrams show some scattering due to the presence of a number of gabbroic rock types in the area, but above this silica content many elements exhibit sharp linear trends due to reaction of the granite endmember with only one of the gabbros.

The alkali gabbros are nepheline and strongly olivine normative. They plot entirely separately, for most elements, from the main hybridization trend and are seen not to be

FIG. 8 MAJOR OXIDE VARIATION AGAINST SILICA FOR THE ROCKS FROM ARRAN

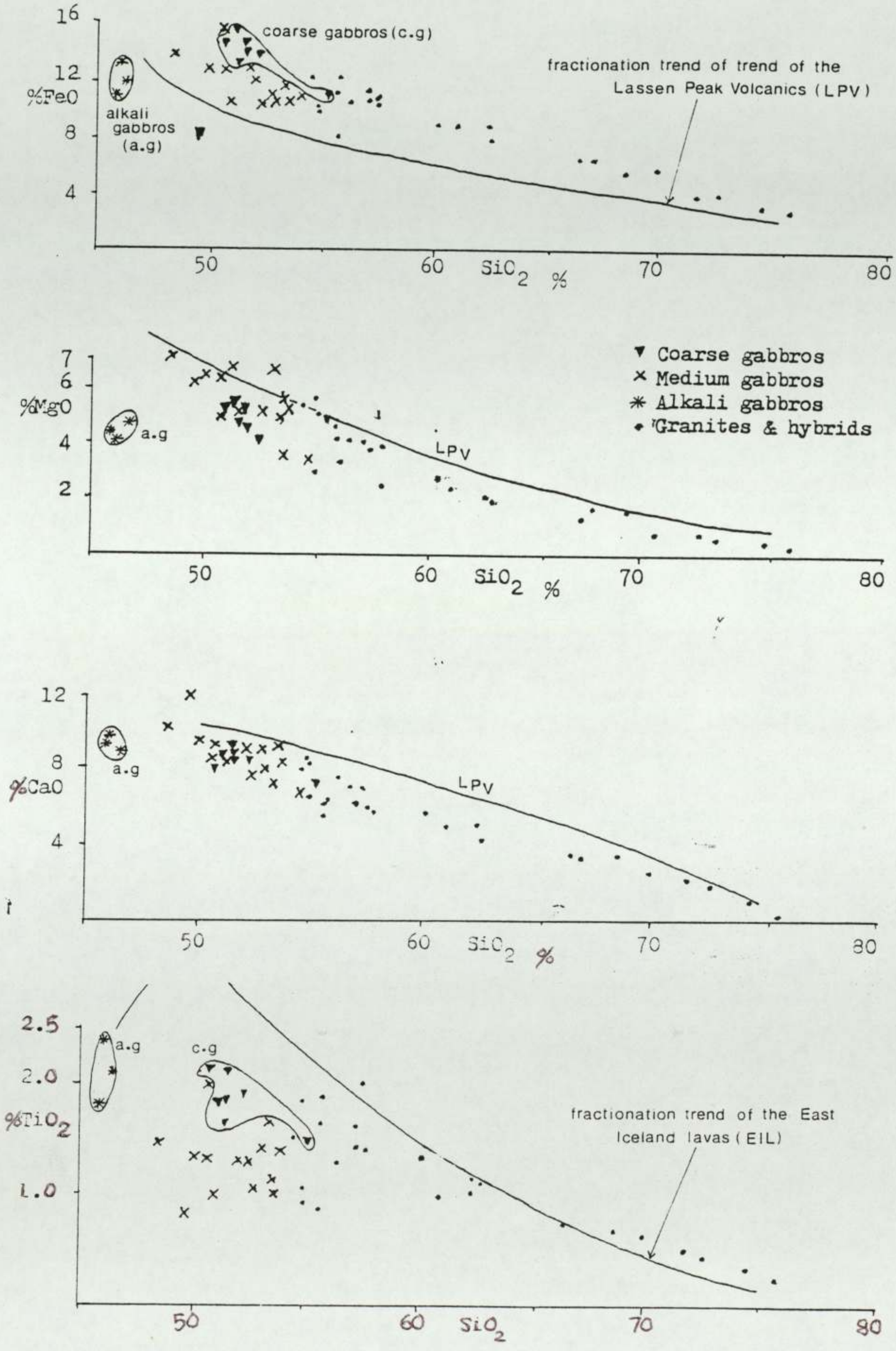
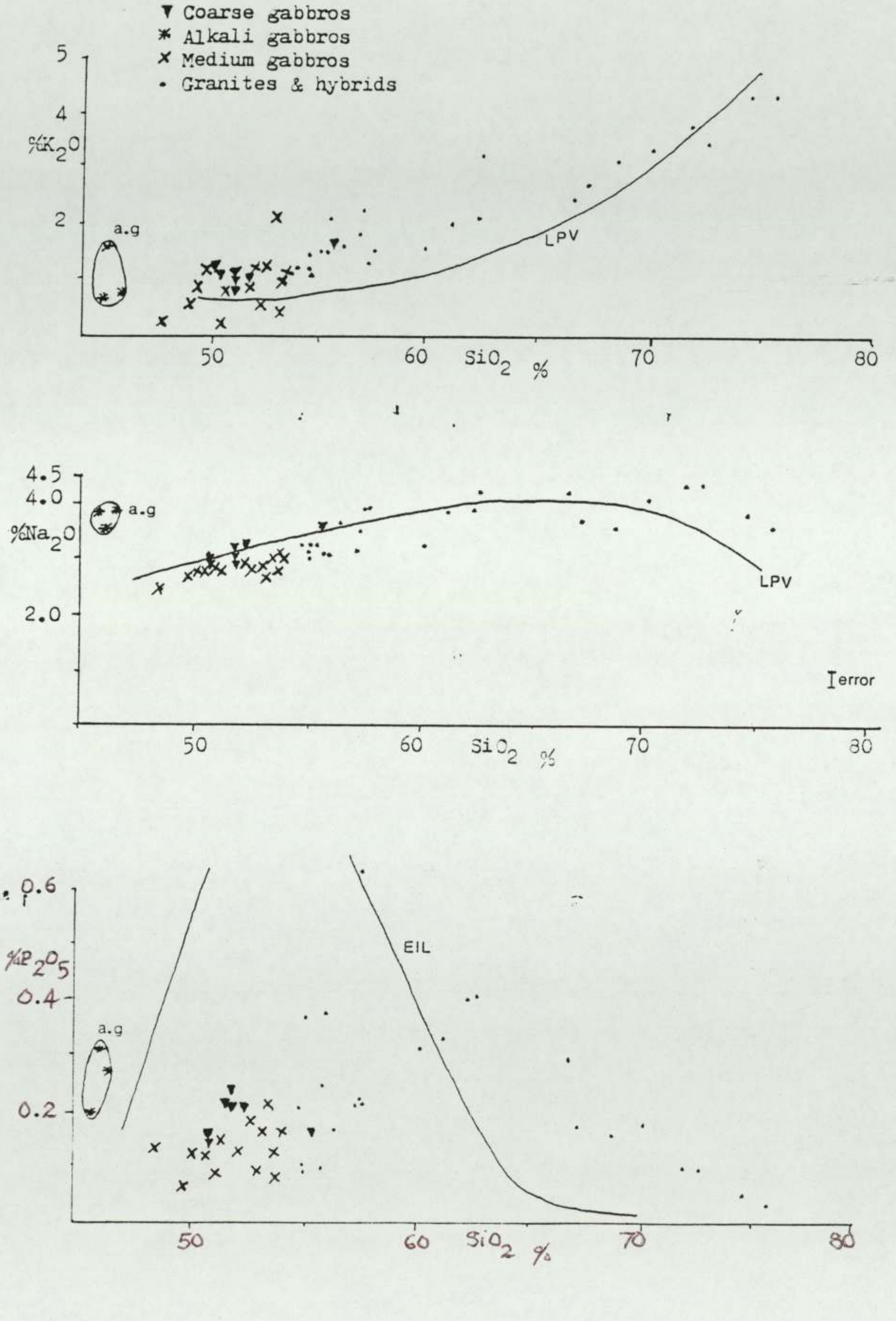


FIG. 9 MAJOR OXIDE VARIATION AGAINST SILICA FOR THE ROCKS FROM ARRAN



involved in it. They are richer than the other gabbros represented, in alkalis, TiO_2 and P_2O_5 whilst being poorer in MgO and SiO_2 . The other gabbroic rocks are quartz normative.

The coarse gabbros present in the complex show high TiO_2 (2.2%) and FeO (16%) contents due to the consistent presence of large Fe - Ti oxide crystals. This is also reflected in the high normative magnetite and ilmenite values when compared to the remaining varieties (Table 29c, Nos 18-BC3). These high Fe and Ti contents tend to show that these gabbros also do not represent the basic endmembers in the hybridization process.

For the remaining quartz-normative medium gabbros and hybrid rocks FeO, MgO and CaO show linear trends with SiO_2, with good correlation coefficients of 0.971, 0.917 and 0.967 respectively, suggesting that these gabbros represent an appropriate basic end member.

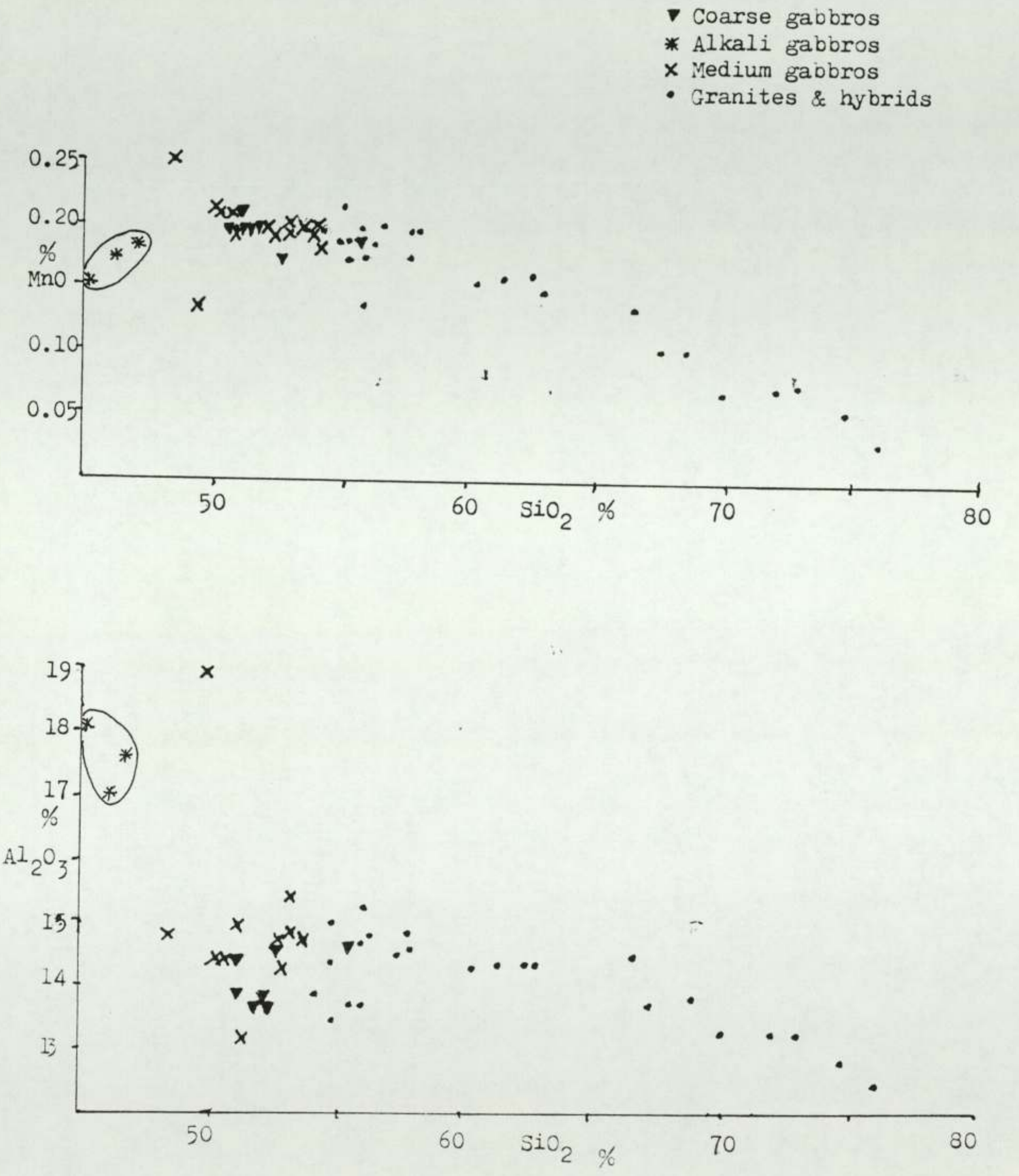
Manganese and Al_2O_3 also show good linear correlation coefficients with SiO_2 (0.938 and 0.922 respectively) indicating a good linear trend between granite and medium gabbro. In the case of Al_2O_3 , the coarse gabbros plot generally lower than most of the other gabbros. The alkali gabbros plot separately for both elements on the diagrams.

Potash and Na_2O show some degree of scattering of points caused by late stage alteration, but still have reasonable correlation coefficients (0.932 , 0.787). These elements increase in concentration in the granitic rocks due to their presence in sodic plagioclase and alkali feldspar.

The granites tend to be corundum normative.

Phosphorus differs from the other major oxides in forming a maximum concentration in the xenolithic and intermediate rocks (0.6%) when compared with both granitic and gabbroic endmembers (0.2% for both). This corresponds with an increase in modal proportions of apatite. This is a significant and dramatic increase in phosphorus and must

FIG. 10 MAJOR OXIDE VARIATION AGAINST SILICA FOR THE ROCKS FROM ARRAN



indicate concentration of at least this element by some process during the assimilation event.

Burnham (1967) has suggested that the establishment of a temperature gradient of 500°C-700°C in aqueous systems in contact with felsic rocks leads to a large scale transfer of certain consitituents. P^{5+} may be mobilized this way, and carried in an aqueous phase from the granitic magma, before combining with Ca^{2+} lost from altering mafic minerals in the basic wallrocks. P^{5+} has already been proposed to be an element easily transported in aqueous fluids (Burnham 1979b), This apparent rise in P_20_5 content of the hybrid rocks was also noted in the Kialineq Complex of Greenland and led Brown & Becker (1986) to the suggestion that fractionation was also involved in their production rather than solely hybridization. There is no evidence that this is the case here, however.

The intermediate and xenolithic rocks also tend to have slightly higher volatile contents than the gabbros and granites, an indication of the importance of volatiles in the alteration and breakdown of xenoliths and wallrocks. Although a number of basic rocks are present at Glen Dubh, the normal gabbros would appear to be the best candidates for hybridization (from geochemical and petrographic evidence).

Reasonable results were obtained using mixing calculations for a number of intermediate rocks when using an average granite composition and average normal gabbro, the sums of squares of the residuals varying between 0.73 - 2.71 (Tables 35a - c).
These results seem particularly reasonable when taking into account the extensive alteration seen in the complex.

For comparison, the same intermediate rocks were tested against, in turn, granite-coarse gabbro and granite-alkali gabbro mixtures. The sums of squares of the residuals varied from 0.68-9.68 for the coarse gabbros (Table 35d) and 0.49-9.91 for the alkali gabbros (Table 35e), and are unacceptably high when referring to such mechanisms as assimilation. Those of the normal gabbros compare favourably with these, and the results appear to indicate that hybridization between the normal gabbros and granitic magma is more likely to have produced the rocks of intermediate composition, i.e. in accordance with variation diagrams.

7.4.2 The Johnston Diorites

The major element analyses of the Bolton Hill rocks are tabulated in Tables 30a-f together with their normative values.

The two potential endmember basic diorites at Bolton Hill can be distinguished from each other on the basis of geochemistry, similarly with the two granite types.

The SiO_2 values of the diorites (down to 45%) are very low, almost to the average composition of many ultrabasic rocks. This is further evidence for the rocks not being true diorites (normally about 55% SiO_2) but metasomatized basic rocks. This low SiO_2 content is reflected in high normative olivine (up to 10%) in the rocks.

The dark diorites are slightly more olivine normative than the pale diorites, and some are also slightly nepheline normative.

The pale diorites can be distinguished from the dark diorites on variation diagrams of FeO, MgO, MnO and TiO_2 against SiO_2. The dark diorites have higher concentrations of FeO, MnO and TiO_2. This is a reflection of the mineralogy, with higher contents of these elements in the respective hornblendes and a greater abundance of modal magnetite and ilmenite (Tables 30d-f). The pale diorites in contrast contain higher MgO reflecting the increased MgO content of these hornblendes in comparison with the dark diorites.

Alumina and CaO are roughly equal in both diorites, occurring in plagioclase and hornblende of which the diorites are equally comprised.

The granites of the complex can also be clearly distinguished in terms of K_2O content, which is considerably higher in the microcline granites (Table 30b). This higher K_2O concentration in these granites is also reflected by their higher normative orthoclase feldspar. The albite granites, in contrast, show very high normative albite (45%-50%) particularly when compared with the Arran granites (30%-35%).

FIG. 11 MAJOR OXIDE VARIATION AGAINST SILICA FOR THE ROCKS FROM BOLTON HILL

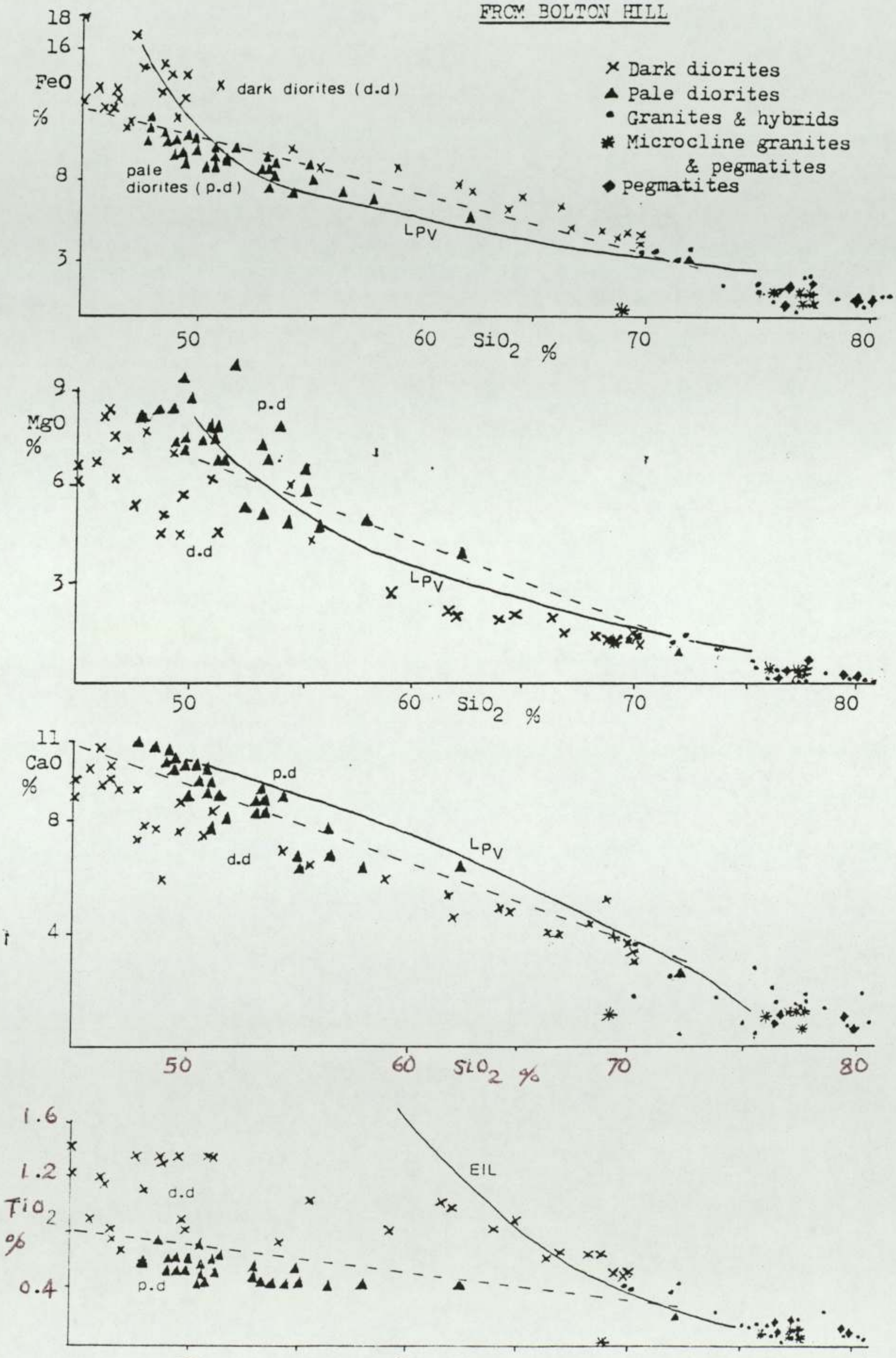
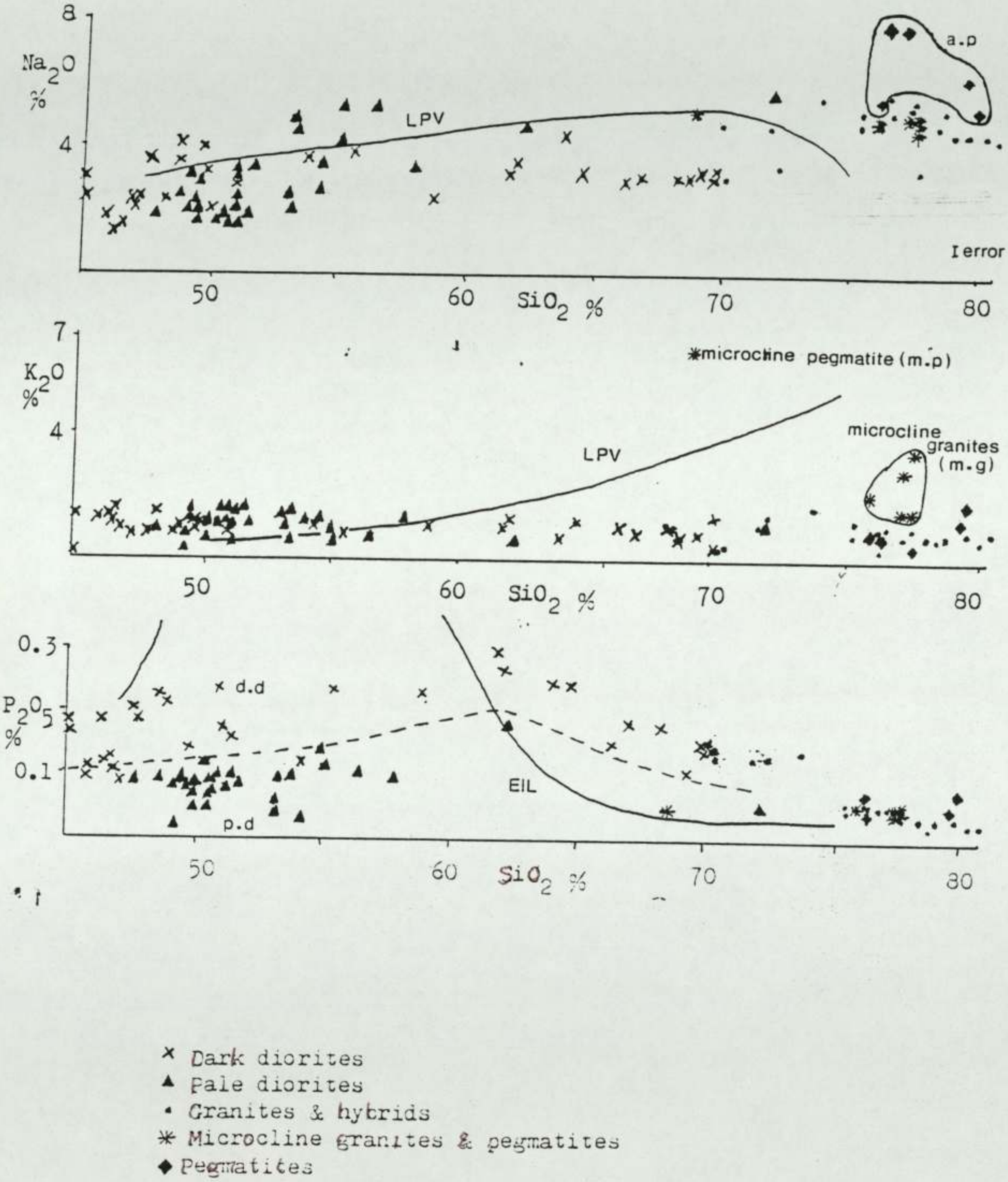


FIG. 12 MAJOR OXIDE VARIATION AGAINST SILICA FOR THE ROCKS FROM BOLTON HILL



Due to these differences in chemical composition, there are four potential endmember compositions. Both endmember diorites can be seen to form distinct linear hybridization trends with the albite granites, whilst the microcline granites play no apparent part in the process (Figs. 11 - 13).

The diagrams show inverse correlations of Al_20_3 , Mn0, Mg0, Fe0, Ca0 and $Ti0_2$ with $Si0_2$, and a positive correlation of Na_20. Potash forms a flat trend, with the diorites and albite granites showing similar contents, but concentrations in all the rocks involved in the assimilation process are extremely low.

The hybridization of the rocks has formed excellent linear trends with the following correlation coefficients:-

Table 2: Correlation coefficients of the Bolton Hill hybrids.

For the dark diorites:

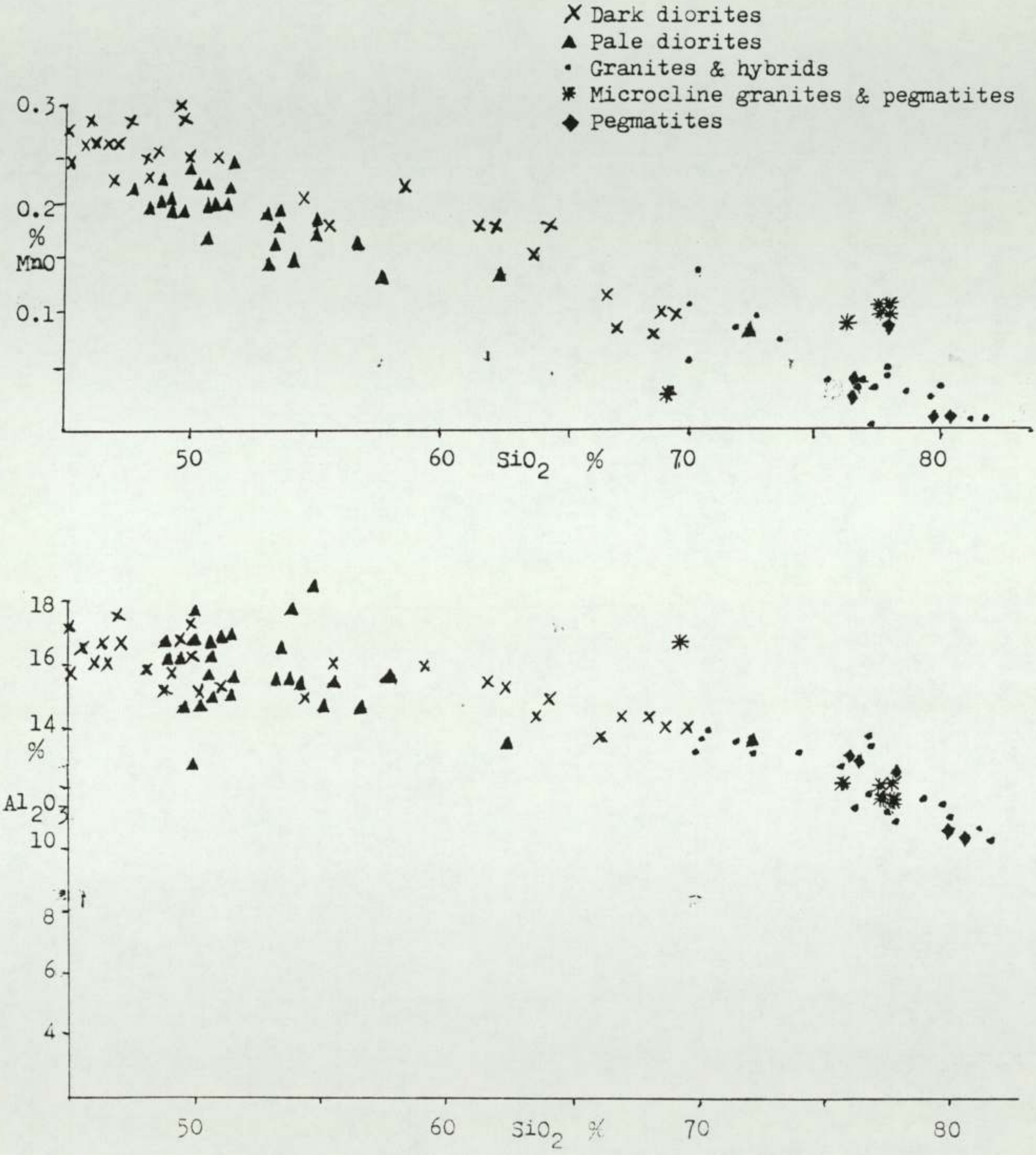
Fe0	$Ti0_2$	Mg0	Mn0	Ca0	Al_20_3	Na_20
0.986	0.975	0.950	0.962	0.964	0.924	0.708

For the pale diorites:

Fe0	$Ti0_2$	Mg0	Mn0	Ca0	Al_20_3	Na_20
0.980	0.938	0.969	0.966	0.972	0.828	0.708

The degree of scattering shown by Na_20 is undoubtedly caused by alteration, in particular the albite, calcite, prehnite alteration of the secondary veinlets. Due to the presence of these veinlets, some of this may be caused by input of Na although most of the scattering may be caused by re-distribution of existing Na.

FIG. 13 MAJOR OXIDE VARIATION AGAINST SILICA FOR THE ROCKS FROM BOLTON HILL



The high K_20 content of the microcline granites (frequently over 3%) is due exclusively to the presence of potash in the microcline. Potassium feldspar is absent from the albite granites which do not contain any primary K-bearing minerals. In the absence of potassic minerals, such as alkali feldspar or biotite ,in the albite granite, the small amount of K_20 actually present (1%) is likely to occur as a result of the late stage sericitic alteration, as implied by Thorpe (1970). This indicates that K is mobilized during hydrothermal alteration and hence K_20 values would not be expected to reflect the assimilation process. Further evidence of the mobility of alkalis during hydrothermal alteration would be the corundum normative nature of the granites, which is often a characteristic feature of altered rocks.

In a similar fashion to the Arran rock suite, the intermediate rock types show an increased P_20_5 content relative to both the basic diorites and granites (Fig. 12). It seems likely that this is due to the mobilization of P^{5+} by metasomatic fluids. Although these intermediate rocks contain the greatest concentration of P_20_5, consistent with petrographic evidence, the dark and pale endmember diorites themselves also have slightly differing contents of P_20_5. The concentrations of P_20_5 in the dark diorites are higher than those in the pale diorites, this feature demonstrates that it cannot be argued that the pale diorites are merely a slightly hybridized dark diorite.

A surprising feature of many of the diorites is their normative plagioclase values (Tables 30a-f) which can approach An_{78}. This labradorite composition is evidence that the diorites represent altered, original, gabbroic rocks. Some diorites do show more sodic plagioclase compositions within the andesine-oligoclase range. As they show no evidence of mixing at this stage, this suggests extensive sodic metasomatism rather than re-equilibration with the granitic magma, i.e. complete metasomatism of the rocks occurred prior to hybridization. A number of pegmatites are associated with the granites but play no obvious part in the hybridization process. Albite pegmatites are distinguished from the albite granites by virtue of their higher Na_20 (5%-8% compared with 4.5%-5%) and normative albite (up to 66%).

The microcline pegmatite shows low totals of Fe0, Ca0 and $Ti0_2$, relatively low $Si0_2$, but a very high K_20 content up to 6.5%. It also shows high normative orthoclase feldspar (38%).

Some quartz pegmatites are also present.

The microcline granite analyses are shown in Table 30b, nos. 222-224b. The microcline pegmatite is shown in Table 30a, no. 204 and the albite pegmatites in Table 30a, nos. 131-218.

An average composition was taken of the dark diorites, and an average albite granite composition, to be used as endmembers in the mixing process. The results obtained were tested against the dark-coloured intermediate rocks found at Bolton Hill. The sums of squares of residuals obtained ranged between 0.39 - 1.87 indicating a very close fit between expected and actual compositions (Tables 36a-d).

A similar procedure was carried out for the pale diorite endmember and the albite granite. These also produced a good correlation between expected and actual compositions of the pale intermediate rocks, the sums of squares of residuals ranging between 0.63-1.84 (Tables 36e-h). Soda contents were left out of the calculations due to the often intense albite veining and alteration seen in the complex.

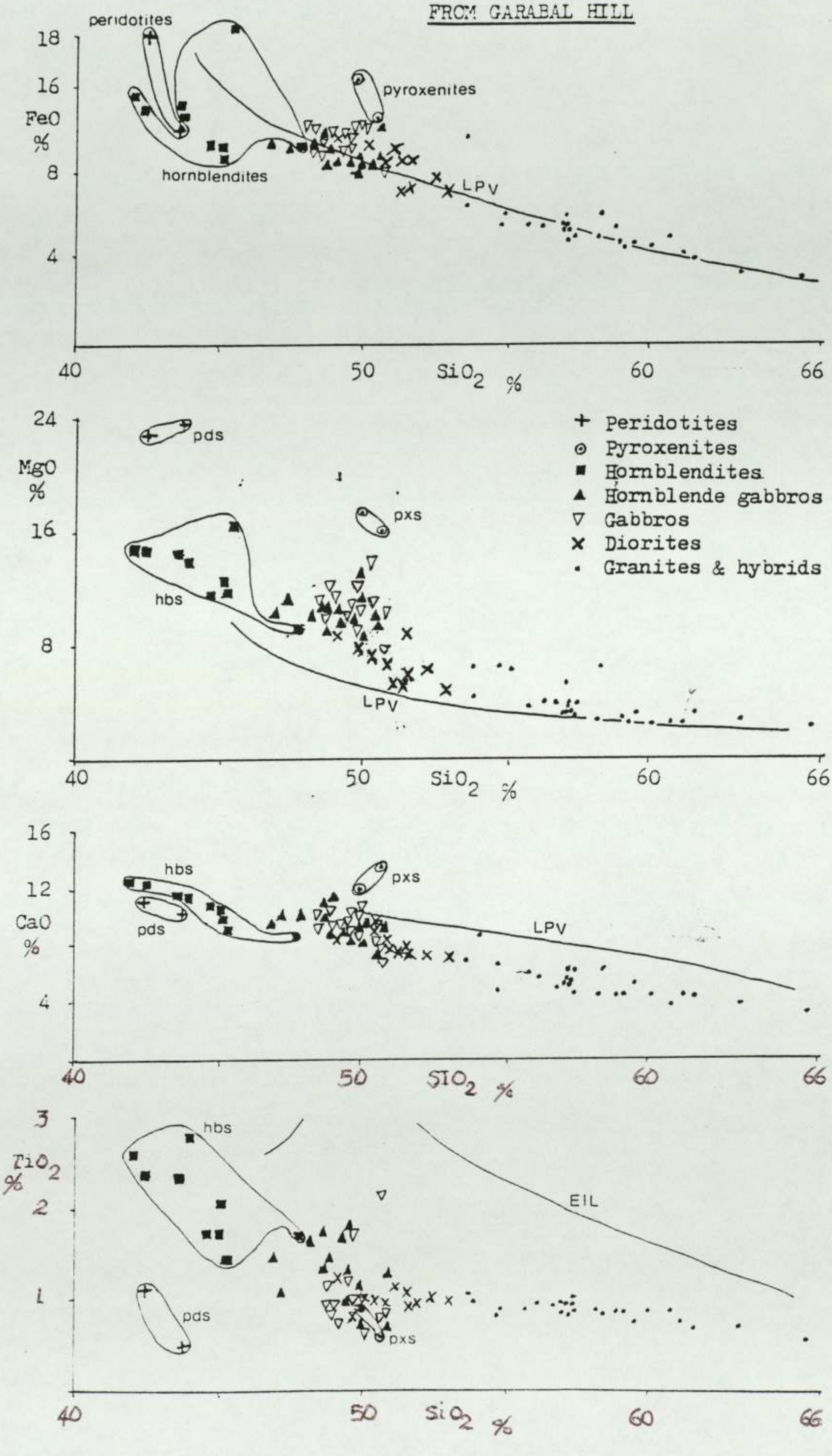
The residuals obtained from the intermediate rocks are strongly suggestive of extensive reaction between the albite granite and pale or dark diorite wallrocks. This results in the formation of two distinct pale and dark intermediate rock suites.

7.4.3 Garabal Hill

Major element contents of the Garabal Hill rocks are tabulated in Tables 31a-g, together with their respective normative values.

The SiO_2 content of the rock series varies from 62% in the granodiorites to 42% in the ultrabasic rocks, and forms a negative correlation with MgO, FeO, CaO, MnO, TiO_2 and a positive correlation with Na_2O and K_2O (Figs. 14-16).

FIG. 14 MAJOR OXIDE VARIATION AGAINST SILICA FOR THE ROCKS FROM GARABAL HILL



The rocks form linear trends for Mg0, Fe0, Mn0, Ca0 and $Ti0_2$ with $Si0_2$ down to values of 51% $Si0_2$. Below this there is a marked scatter of points on variation diagrams caused by the presence of a wide range of basic and ultrabasic rock types - peridotites, pyroxenites, hornblendites, gabbros, hornblende gabbros, hypersthene gabbros and norites. One of the major problems is to attempt to establish which of these basic rock types have played a part in the mixing process, and are potential endmembers.

The ultrabasic rocks show highest Fe0 and Mg0 values due to the abundance of mafic minerals, particularly olivine and pyroxene. Peridotites and hornblendites contain lowest $Si0_2$ and are strongly olivine normative, whilst the pyroxenites are quartz normative. The hornblendes are also normative in nepheline, and the gabbros range from olivine to quartz normative.

Alkalis increase towards the granitic rocks, being present in sodic plagioclase, alkali feldspar and biotite, but exhibit a great deal of scatter on variation diagrams. This is in part due to hydrothermal alteration, but also to metasomatism which alters the alkali content of many of the basic rocks.

Metasomatism is seen to have a great effect on the chemistry of the basic and ultrabasic rock types, particularly in terms of alkali content.

The replacement of pyroxenite by hornblendite has previously been proposed as being a result of the percolation of fluids (Wyllie & Scott, 1913; Nockolds, 1941). They proposed that these fluids originated from the gabbros rather than the granodiorite. This was due to the presence of brown hornblendes in the gabbros similar to that of the hornblendites. They argued that as the granodiorites contain green hornblendes, the ultrabasics would also be composed of green hornblendes had the metasomatic fluids originated from the granodiorite.

This colour featue is now known to be merely a result of the Ti content of the amphiboles, the brown metasomatic hornblende being more Ti-rich by forming in the Ti-rich basic rocks from Ti-rich augite, rather than in a Ti-poor acidic magma.

Alteration of pyroxenite to hornblendite results in a decrease in

SiO_2, with an increase in alkalis, Al_2O_3 and volatiles (3% in comparison with 0.5%). Although the change in SiO_2 and Al_2O_3 is probably accounted for by conversion of Ca-plagioclase to Na-plagioclase, alkalis and volatiles would seem to have been introduced into the rock.

The conversion of pyroxene to hornblende also results in the transformation of gabbros to hornblende gabbros. The alkali metasomatism in turn converts some of the gabbros into diorites by replacement of labradorite by andesine. This is seen in the increased Na_2O content (Fig. 15) of rocks at the margins of the basic mass. The metasomatic diorite analyses are presented in Table 31c (nos. 115-101) and their dioritic nature is confirmed by their normative albite:anorthite ratio which is indicative of andesine composition.

The variation diagrams of Na_2O and K_2O against SiO_2 (correlation coefficients 0.789, 0.779) indicate that the hybridization takes place between the granitic magma, and the hornblende gabbros and metasomatic diorites, i.e. metasomatism of the rocks preceded assimilation. The ultrabasic rocks and normal gabbros plot away from the main hybridization trend on the variation diagrams for these elements. This is consistent with the position of these rocks towards the centre of the basic mass where metasomatism and reaction with the granitic magma have not taken place.

Correlation coefficients for FeO, MgO, CaO between these granodiorite and diorite endmembers are 0,878, 0.900 and 0.950.

Phosphorus occurs at its highest concentrations in the intermediate hybrids (0.45%), a similar situation to that seen at Arran and Bolton Hill. It also occurs in high concentrations in the metasomatic diorites. This would strengthen the theory of P^{5+} migrating with metasomatic fluids into wallrocks. However, its presence in highest concentrations in the hybrid rocks may suggest it more easily combines with Ca in the fluid magma, during alteration of xenoliths and xenocrysts, than during modification of the bulk wallrock. This is possibly due to more efficient reaction of Ca-bearing mafic minerals.

Silica does not appear to significantly change during replacement of gabbros by hornblende

FIG. 15 MAJOR OXIDE VARIATION AGAINST SILICA FOR THE ROCKS FROM GARABAL HILL

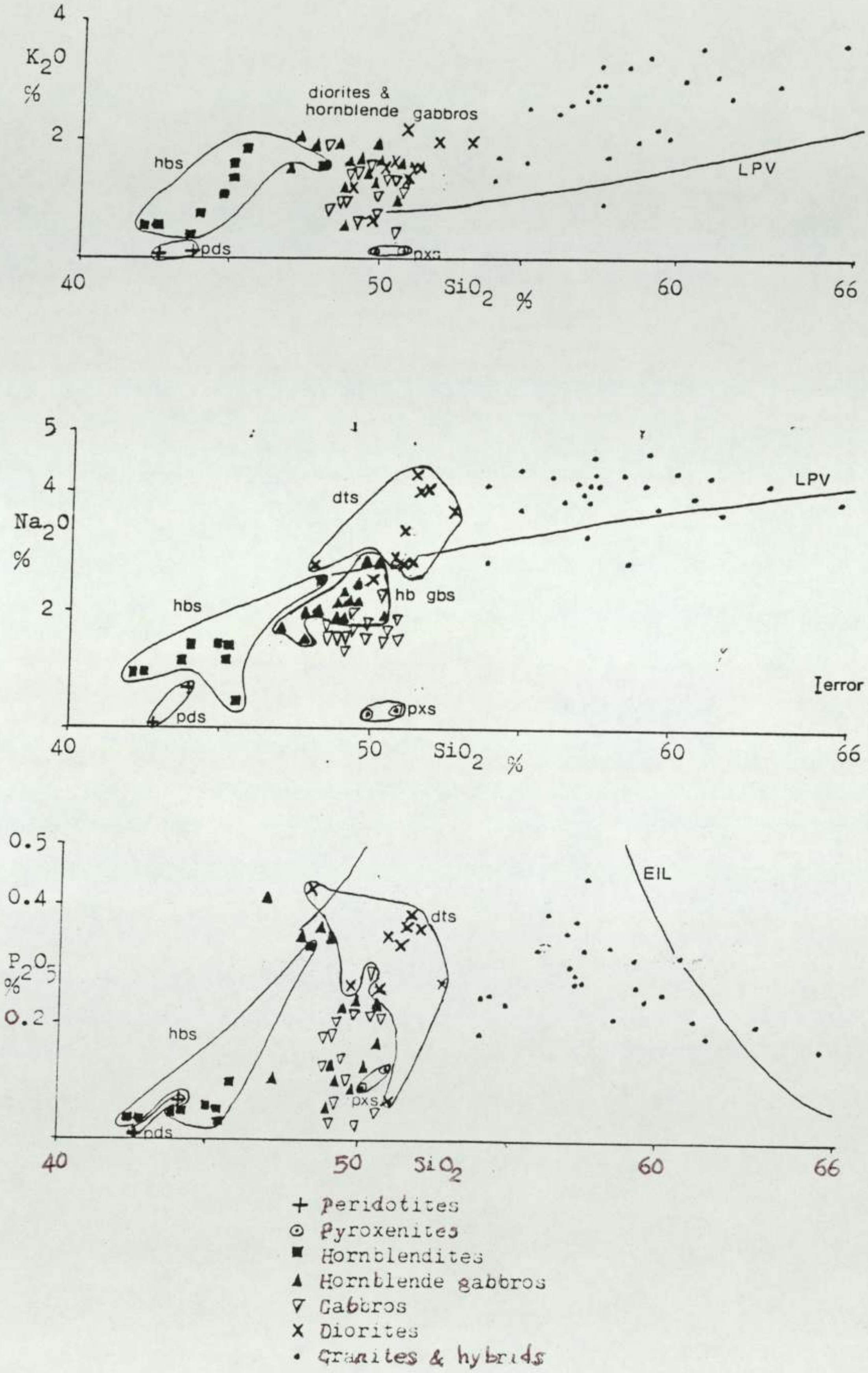
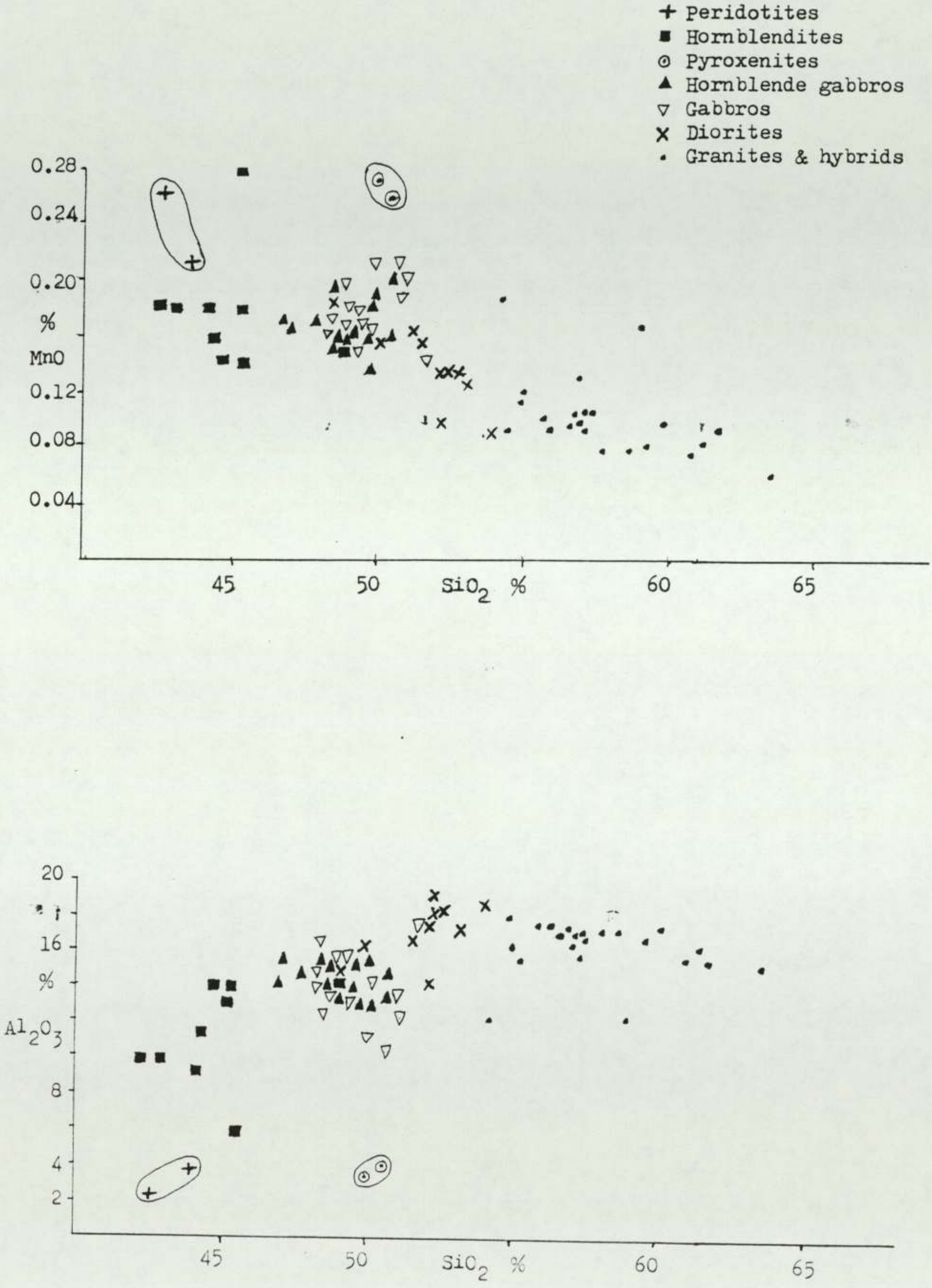


FIG. 16 MAJOR OXIDE VARIATION AGAINST SILICA FOR THE ROCKS FROM GARABAL HILL



gabbro/diorite suggesting that Si^{4+} in the main plays a passive role in metasomatism as indicated by Vernon (1976). Silica content of the basic rocks only increases significantly during direct contact and reaction with the acidic magma. Other elements appear to be slightly mobilized by fluids, e.g. Mg0, which plots slightly lower for the diorites than the more basic rocks, whereas other constituents, e.g. $Ti0_2$, Fe0 do not seem to be affected by the aqueous phase.

Aluminium does, however, appear to be mobilized by metasomatism, occurring in higher concentrations in the "metasomatic diorites" than the more gabbroic varieties. The Al_20_3 variation diagram (Fig. 16) clearly indicates a hybrid trend between these endmembers and the granite, whilst the basic rocks show lower Al contents. The Al does not appear to have been mobilized during alteration of gabbros to hornblende gabbros, possibly due to alteration being of a lesser degree.

Exact modelling of the hybridization process at Garabal Hill is difficult due to the enormous variation in composition of the basic and ultrabasic rocks. Of these, the "metasomatic" diorites appear, on field and geochemical grounds, to be the most likely basic endmembers. An average composition of these diorites was taken, and run in the least squares mixing program, with an average endmember granodiorite composition. The expected hybrid compositions were then compared with the actual values of some of the intermediate rocks present in the complex. The sums of squares of the residuals produced plots between 1.58-2.52 (Tables 37a-c) which are reasonable considering their mineralogical variability.

The only other likely candidates to be the basic endmembers are the gabbros, from which an average composition was taken and used in the mixing calculation. However, the sums of squares of the residuals produced were generally found to be higher than those obtained when using the diorites (0.83-7.76, Table 37d). These results indicate that formation of the intermediate rocks by hybridization of the diorites by granodioritic magma is more likely than by assimilation of the gabbros. This tends to reinforce the conclusions obtained from field and geochemical evidence.

7.5 Trace Element geochemistry

Trace element analyses are tabulated in Tables 32-34 for Arran, Bolton Hill and Garabal Hill respectively. All tabulated analyses were performed by X-ray Fluorescence spectrometry on powder briquettes, with the exception of REE analyses for Garabal Hill rocks and Sc analyses for Bolton Hill rocks, performed by Instrumental Neutron Activation Analysis. U and Th analyses for Garabal Hill were also determined by INAA.

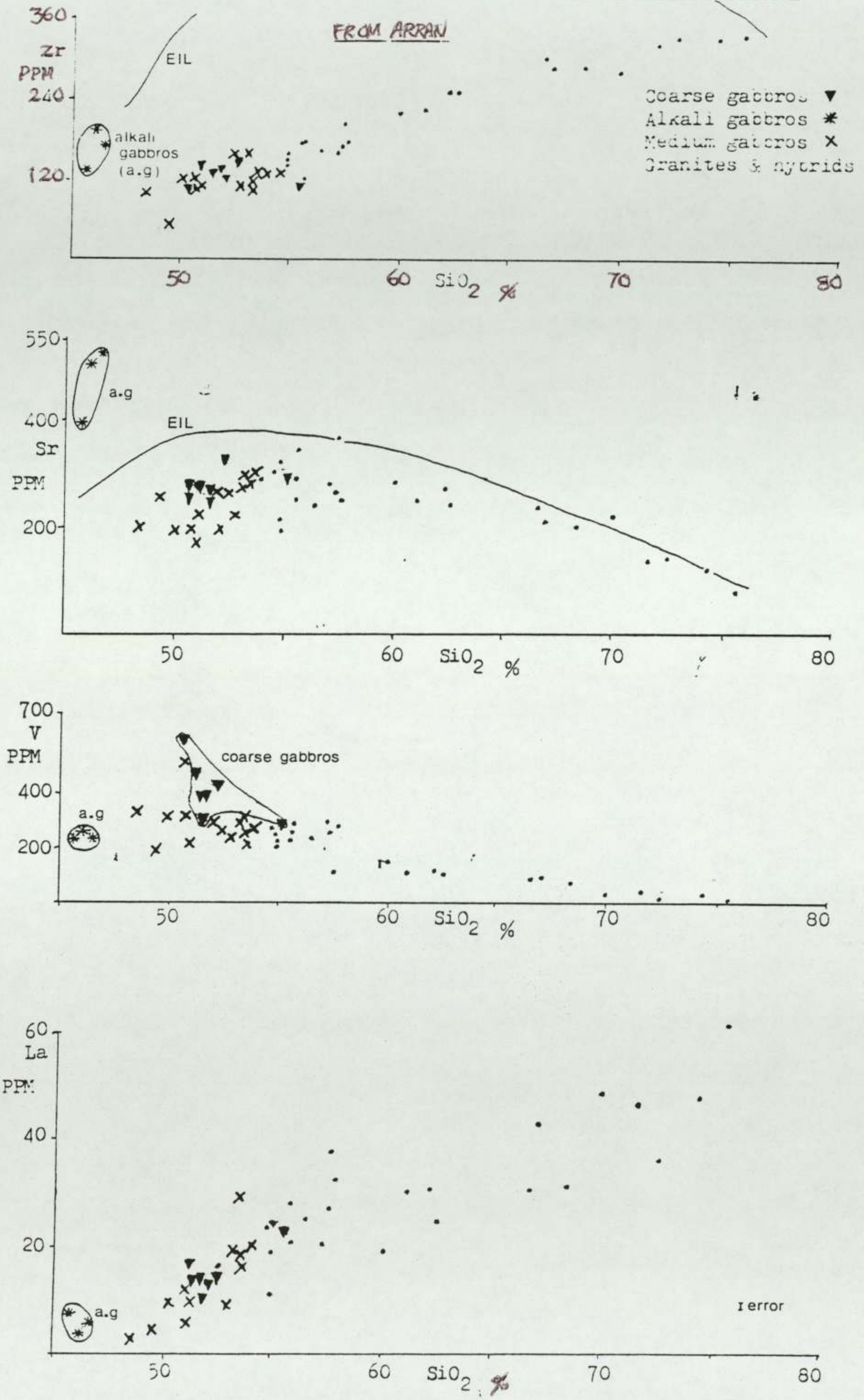
7.5.1 Glen Dubh, Arran

Variation diagrams illustrating the behaviour of trace elements in the Arran rocks are shown in Figs. 17-19. Following the approach used for major elements they are plotted against SiO_2. As with the major alkali elements, Rb and Ba increase in concentration in the granites. Both substitute for K in feldspars and micas. They also show some degree of scatter of points due to alteration although this is more apparent for Rb, with Ba showing a good linear trend with a correlation coefficient of 0.923 between granites and the proposed medium gabbro basic endmember.

Zirconium occurs in zircon which, being a stable mineral, is unaffected by hydrothermal alteration and other post magmatic processes. It is most numerous in the acidic endmembers and shows a correlation coefficient with SiO_2 of 0.979. Vanadium also forms a good linear hybridization trend between the granite and medium gabbros (correlation coefficient 0.942) and substitutes for Ti in oxides. The coarse gabbros contain higher concentrations of V than the other gabbroic rocks due to the abundance of Fe-Ti oxides in these rocks and can be shown to be innappropriate as basic endmembers on this criterion.

Similarly the alkali gabbros contain concentrations of Zr and Sr
which are higher than those in the medium gabbros and clearly place them off the mixing line. As with major element criteria this prohibits the alkali gabbros from being realistic endmembers in the hybridization process. The elements Nb and Y both increase in concentration in the granites. Nb^{5+} is known to substitute for Ti^{4+} and presumably occurs in sphene which is present in the granites (Vlasov, 1966a). Yttrium may occur in small concentrations in apatite or allanite. Both elements are regarded as immobile, except in the presence of F^- (Parker & Fleischer, 1968; Muecke & Clarke, 1981). The scattered plots for these elements against SiO_2 (particularly Y) are believed to be caused by the circulation of F-rich aqueous solutions during post magmatic alteration. This is further indicated by the presence of fluorite in alteration patches and veinlets in a number of the rock samples, and suggests that Nb and Y are not to be regarded as reliable indicators of hybridization in the Arran Central Ring Complex.

FIG. 17 TRACE ELEMENT VARIATION AGAINST SILICA FOR THE ROCKS FROM ARRAN



Chromium and Ni decrease in concentration in the granitic rocks and appear to show a tapering of concentrations from the basic to acidic rocks rather than the straightforward linear trends produce by other elements. This is believed to be due to the wide variation in concentration of these elements in gabbros showing similar values of SiO_2, rather than a restricted concentration range (e.g. Ni varies between 10-100 PPM in the gabbroic endmembers, whilst

Cr varies between 0-100 PPM in the same rocks). Any intermediate hybrid rocks formed between such endmembers and another, with a low content of these elements such as a granite, would also be expected to show a wide range of contents.

The trend formed by Ni in particular, on the variation diagram appears to be relatively more linear when compared with a compositional curve of this element produced by fractional crystallization (Fig. 19).

Strontium increases significantly in concentration in the intermediate hybrid rocks, showing contents up to 350 PPM in relation to the gabbros (250 PPM) and granites (100 PPM). Although Sr is suggested as being easily mobilized during hydrothermal alteration, this is probably not the cause of the "humped" pattern seen. This pattern has been noted in other complexes, many also with a proposed hybrid origin (Gunn & Watkins, 1969; Rock, 1974; Pankhurst *et al.*, 1976; Brown *et al.*, 1978; McBirney, 1979; Dickin *et al.*, 1981).

There have been conflicting arguments as to the reason for this Sr concentration in the intermediate members of the hybrid series. A number of workers have proposed that Sr^{2+} occurs preferentially in low temperature calcic plagioclase, substituting for Ca^{2+} (Anderson & Gottfried, 1971; Drake & Weill, 1975; Wood, 1978; Dickin et al., 1981), whilst Pankhurst *et al.*, (1976) interpreted the high Sr content of some basic xenoliths in Greenland, at Kangerdlugssuaq, as resulting from the incorporation into a magma of Sr-rich alkaline roof rock. The high Sr content of intermediate rocks has also been ascribed to selective diffusion (Rock, 1974) or to the presence of easily-mobilized Sr-bearing zeolites and carbonates (Gunn & Watkins, 1969).

At Glen Dubh it is significant that the increase in Sr corresponds closely to an increase in P_2O_5 content, reaching a maximum in the rocks of about 57.5% SiO_2. This would tend to

FIG. 18 TRACE ELEMENT VARIATION AGAINST SILICA FOR THE ROCKS FROM ARRAN

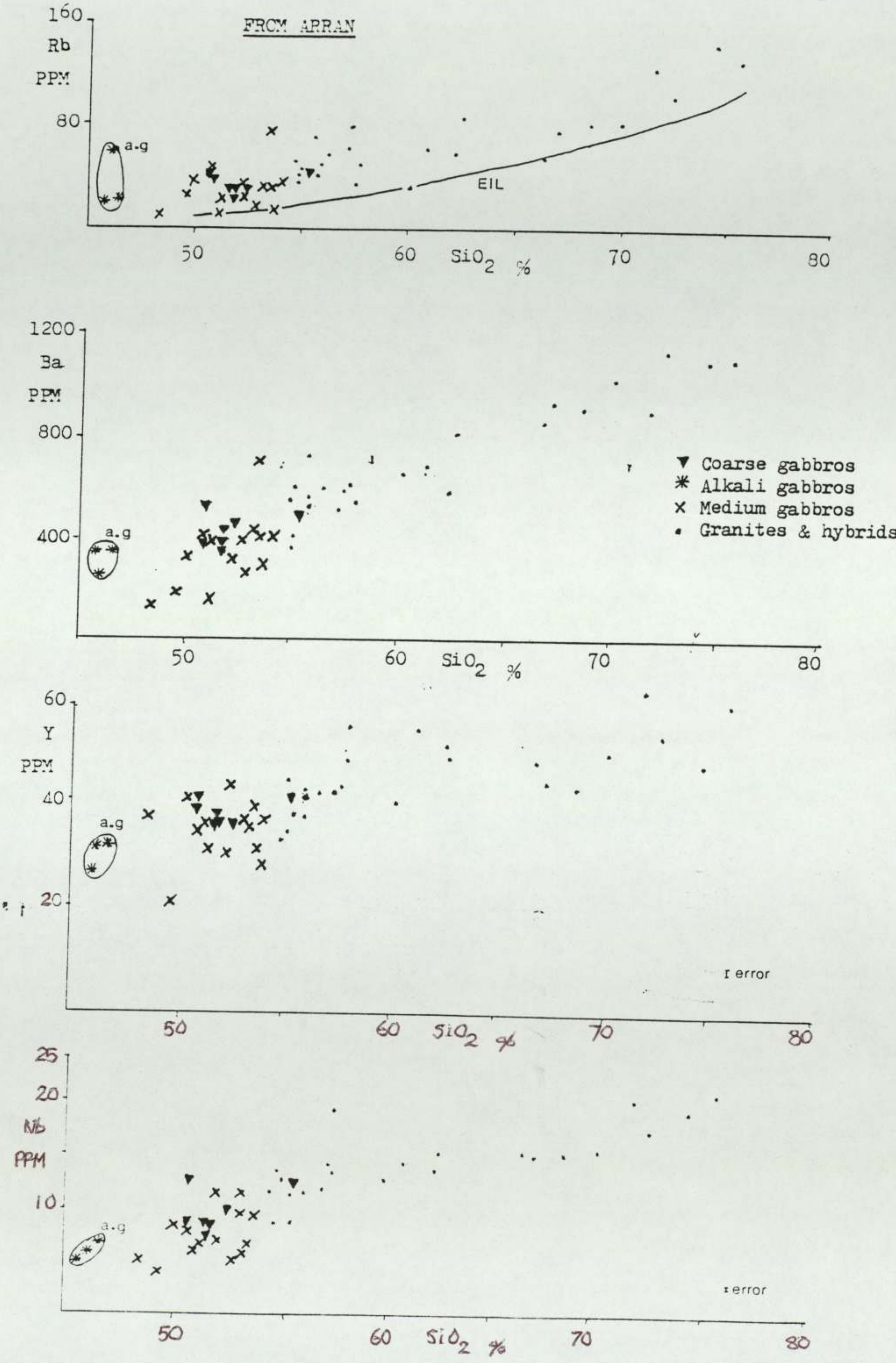
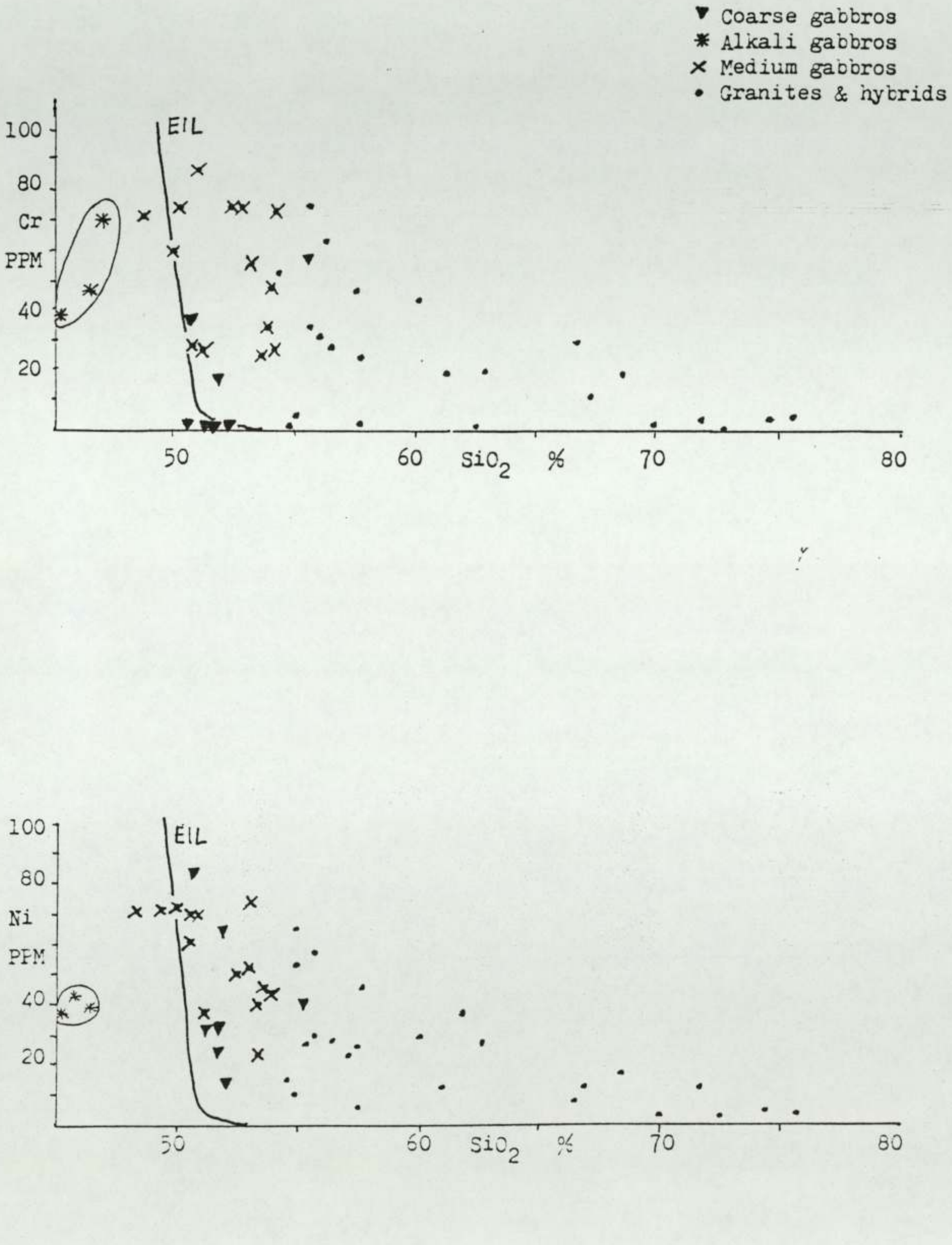


FIG. 19 TRACE ELEMENT VARIATION AGAINST SILICA FOR THE ROCKS FROM ARRAN



indicate the presence of much of the Sr in apatite, substituting for Ca. Some Strontium is also likely to be in feldspar in the basic rocks as it forms greater concentrations in these than in the granites.

Strontium may be one of the elements indicated by Burnham (1967) which are transported to higher temperature regions, in aqueous systems, when felsic magmas are in contact with basic wallrocks. This was proposed as the origin of the high Sr concentrations of the hybrid rocks at the Borgtinderne intrusion, Greenland (Brown *et al.*, 1978). Here the Sr was believed to have been mobilized from zeolites and carbonates in the country rock, before subsequently migrating through aqueous fluids towards the magma-wallrock contact and "draining" a large area of Sr.

At Glen Dubh a similar process is believed to have occurred. Here the Sr was released from other Ca-bearing minerals during metasomatism of the wallrocks. The Sr then migrated along with Ca before becoming fixed with some of the Ca in apatite by combining with P^{5+} in the fluids. This theory is particularly likely when the concentrations and distribution coefficients of Sr between apatite, plagioclase and silicate liquids are compared, using values taken from the literature (Vlasov, 1966a; Deer et al., 1962~~b~~c, 1963~~c~~b). The concentration is higher in apatite generally, and the distribution coefficient is approximately 10 orders of magnitude higher in apatite than other possible Sr-bearing magmatic minerals such as plagioclase. Consequently it is extremely likely that Sr has been preferentially concentrated in the apatite.

Thorium also increases in concentration in the granitic rocks but shows marked scattering of analyses. It tends to occur along with the rare earth elements (see Chapter 7.6.1.) and possibly Nb and Y. These elements are affected by the fluoride alteration.

7.5.2. Johnston Diorites

Variation diagrams for the Bolton Hill rocks are displayed in Figs. 20-23.

Rubidium and Ba substitute for K in certain minerals and produce identical "flat-lying" patterns. The potash-poor nature of the hybridizing albite granite results in very low concentrations of these elements in all the hybrid spectrum (0-30 PPM and 0-20 PPM respectively.

The microcline granites show higher contents of Rb and Ba than the albite granites, with these elements being sited in microcline (30-50 PPM and 250-430 PPM respectively). Concentrations are yet higher in the microcline pegmatites (80 PPM and 465 PPM respectively). These high concentrations compared to those in all the other rocks present at Bolton Hill once again indicate that the microcline-bearing granites and pegmatites play no part in the assimilation process.

Zirconium is generally accepted as an immobile element occuring almost entirely in zircon. Although it increases in concentration as compositions get more granitic, it shows a significant degree of scatter. This scatter is attributed to the presence of sporadic, very large zircon crystals (Plate 4.10) of up to 0.5 mm diameter, contrasting with the vast majority of the much smaller zircons. This presence of few, very large, grains results in difficulty in obtaining sample homogeneity.

The Sr content of the rock suite reaches its peak in the intermediate rocks, as at Arran. Once again the rocks of highest Sr are comparable to those of highest P_20_5 . In Bolton Hill rocks this is at approximately 63% $Si0_2$. As suggested for Arran therefore, the Sr is believed to be accommodated in apatite. Further evidence for the presence of Sr in apatites is the slightly higher Sr content of the dark diorites when compared to the pale diorites (Fig. 20). This correlates closely with their slightly higher P_20_5 (Fig. 12) and apatite content. As with the Arran hybrids, despite the bulk of the Sr occurring in apatite, in the more calcic basic rocks some Sr is inevitably present in minerals such as plagioclase.

FIG. 20 TRACE ELEMENT VARIATION AGAINST SILICA FOR THE ROCKS FROM BOLTON HILL

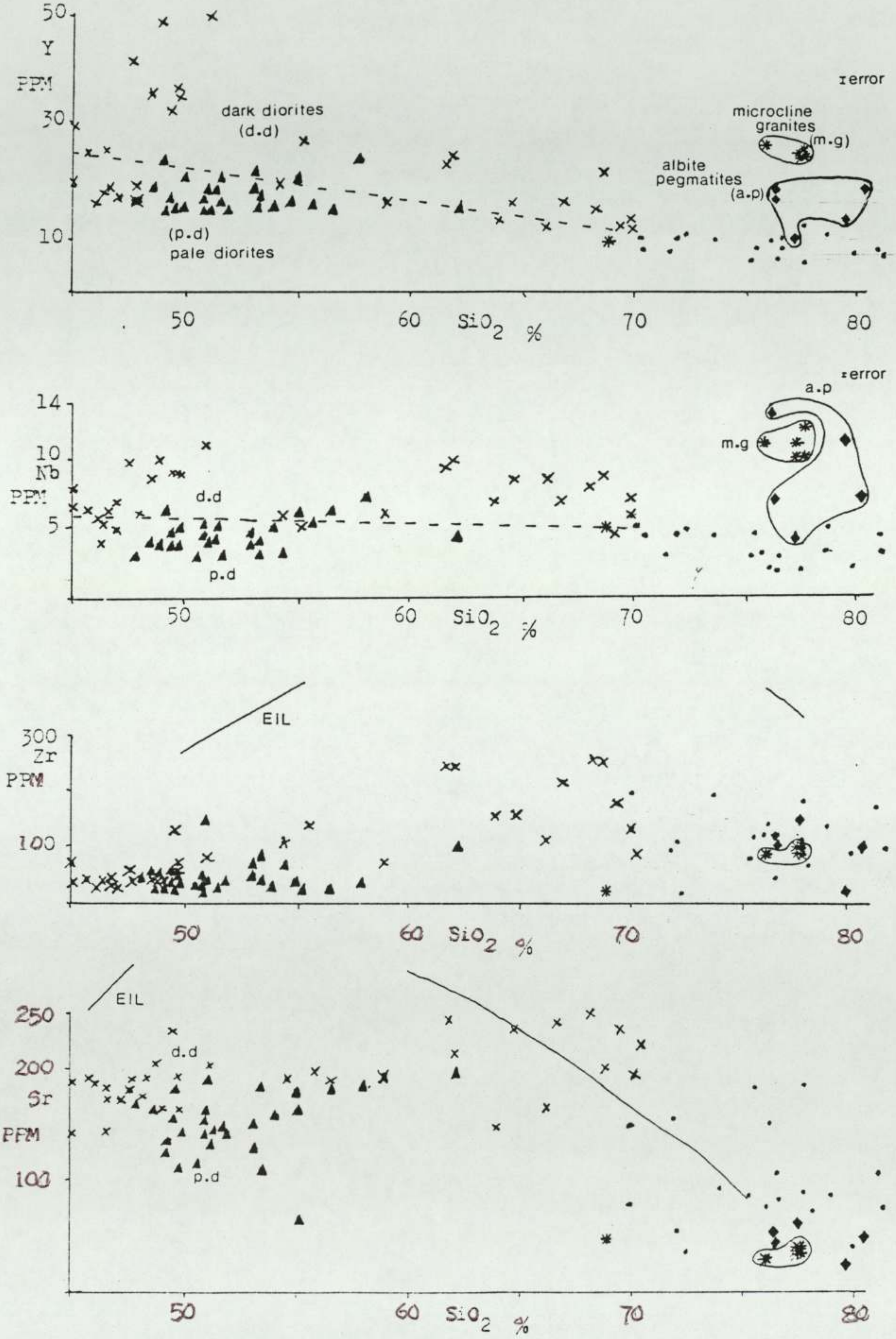
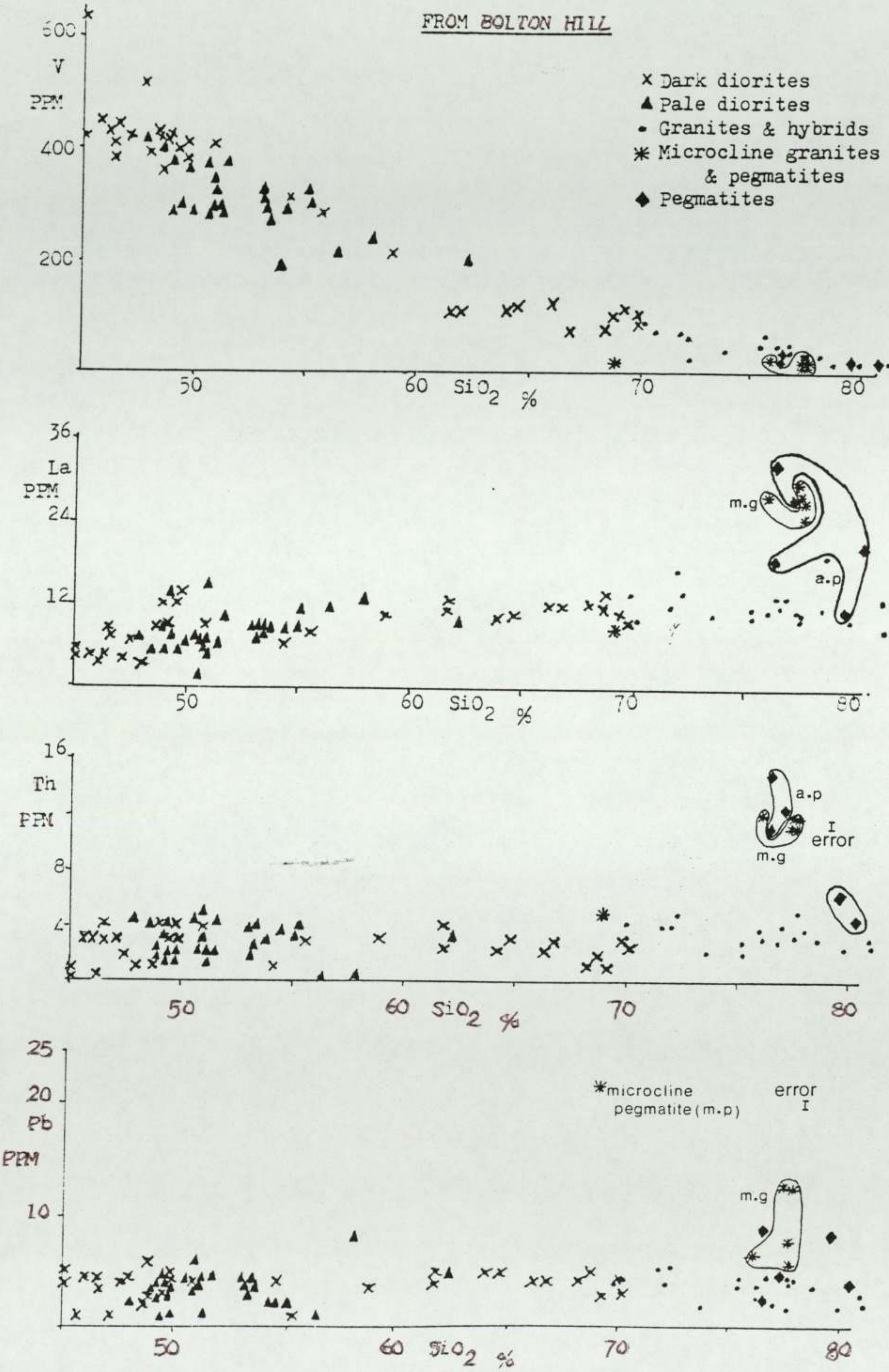


FIG. 21 TRACE ELEMENT VARIATION AGAINST SILICA FOR THE ROCKS FROM BOLTON HILL



Scandium, analyzed by INAA at Aldermaston, forms an excellent linear trend of hybridization with a correlation coefficient with SiO_2 of 0.964. It increases in concentration in the endmember diorites. The pale and dark diorites are not distinguishable using Sc, and it presumably occurs substituting for Ca (Vlasov, 1966a) in plagioclase and hornblende. The correlation coefficients of Sc with SiO_2 are very similar to those of Ca, being 0.964 for the dark diorites and 0.972 for the pale diorites.

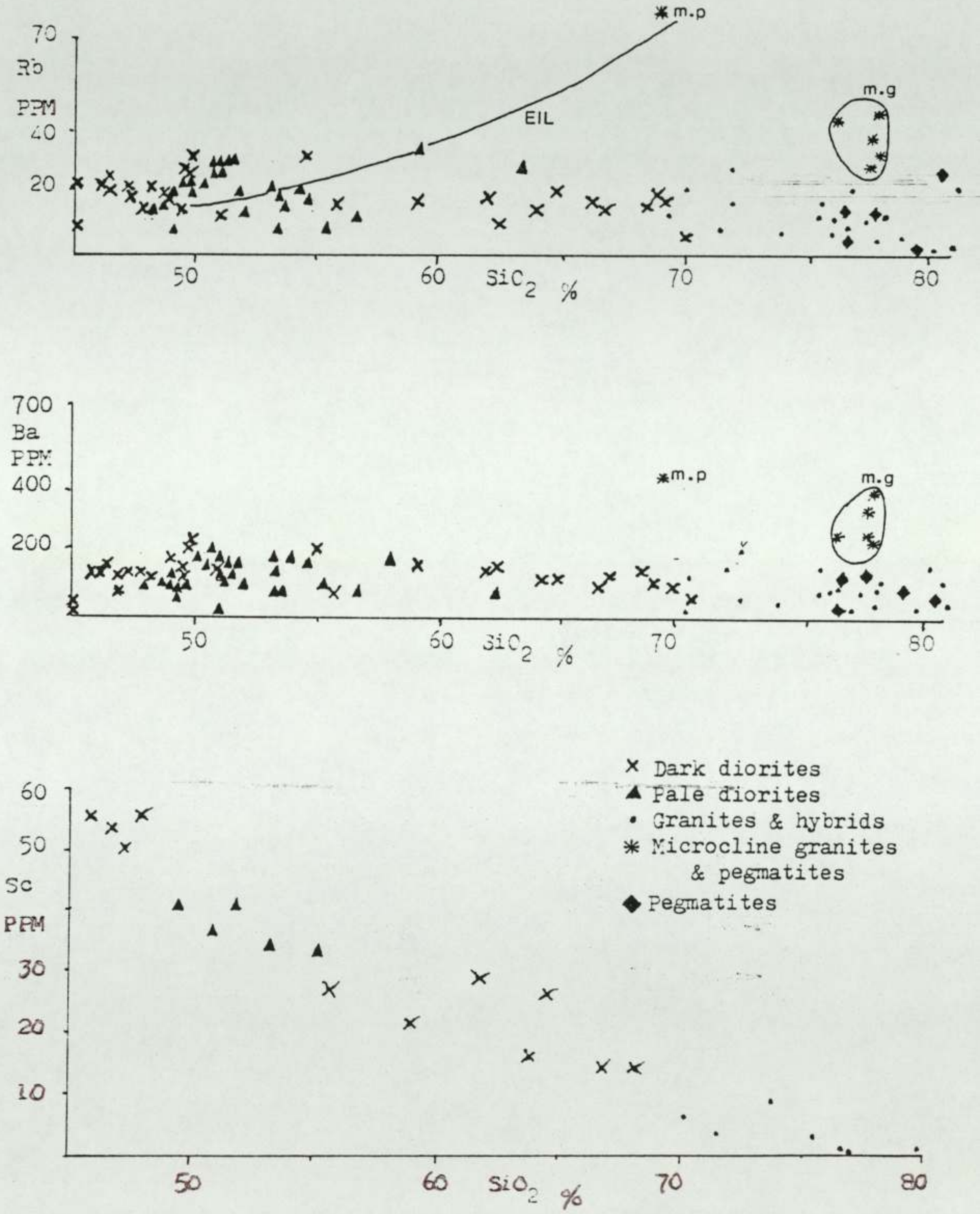
The endmember diorites can be distinguished on their contrasting contents of various other trace elements. Yttrium is present in concentrations of between 30-50 PMM in the dark diorites but only around 15-25 PPM in the pale variety. Both diorites show clearly defined separate hybrid assimilation trends with the albite granite. Vlasov (1966a) suggests that Y commonly occurs in apatite. This mineral is likely to be the mineral accommodating Y in the rock series, particularly in the apparent absence of any other possible Y-bearing minerals such as allanite. The higher Y content of the dark diorites compared with the pale diorites would tend to be in accordance with their higher P_2O_5 and Sr contents possibly reinforcing this theory.

The highest values of P_2O_5 and Sr in the Bolton Hill rocks occur in the intermediate rocks, whilst the highest values of Y occur in the diorites. This can be explained by the diorite apatites containing higher concentrations of Y. The intermediate rock apatites were formed by components transported in an aqueous phase whilst Y is likely not to be transported by such a phase unless rich in F^-. Therefore unlike P and Sr it does not form its highest concentrations in these intermediate rocks.

The microcline granites contain higher Y contents than the albite granites due to the presence of Y-bearing allanite in the potassic granites (Appendix 1, Table 16). This again allows the microcline granite to be excluded as a component in the mixing process.

The dark diorites are characterized by their higher Nb contents when compared to those of the paler diorites. Niobium largely occurs in substitution for Ti^{4+} (Vlasov, 1966a; Parker & Fleischer, 1968), most commonly in Fe-Ti oxides and possibly in some Ti-bearing silicates. This would account for the high Nb content of the dark diorites which contain a higher TiO_2 concentration, and higher modal Fe-Ti oxides, than the pale diorites.

FIG. 22 TRACE ELEMENT VARIATION AGAINST SILICA FOR THE ROCKS FROM BOLTON HILL



The difference in Nb concentrations, as with Y, has resulted in the clearly defined presence of two separate hybridization trends with the albite granite. In the more granitic rocks the Nb is increasingly present in sphene, probably formed from pre-existing ilmenite. There is a high Nb content in the microcline granites which are much richer in sphene than the Nb-poor albite granites. This high Nb of the microcline granites causes them to plot separately from the albite granites on variation diagrams of Nb against SiO_2 and, as with Y, precludes these granites from being endmembers in the mixing process.
Vanadium decreases linearly in the granites, with the dark diorites being richer in this element than the pale diorites, reflecting the substitution of V^{5+} for Ti^{4+} in Fe-Ti oxides such as ilmenite. The separate chemical mixing trends of the diorites with albite granite give correlation coefficients of 0.946 (dark diorite) and 0.965 (pale diorite).

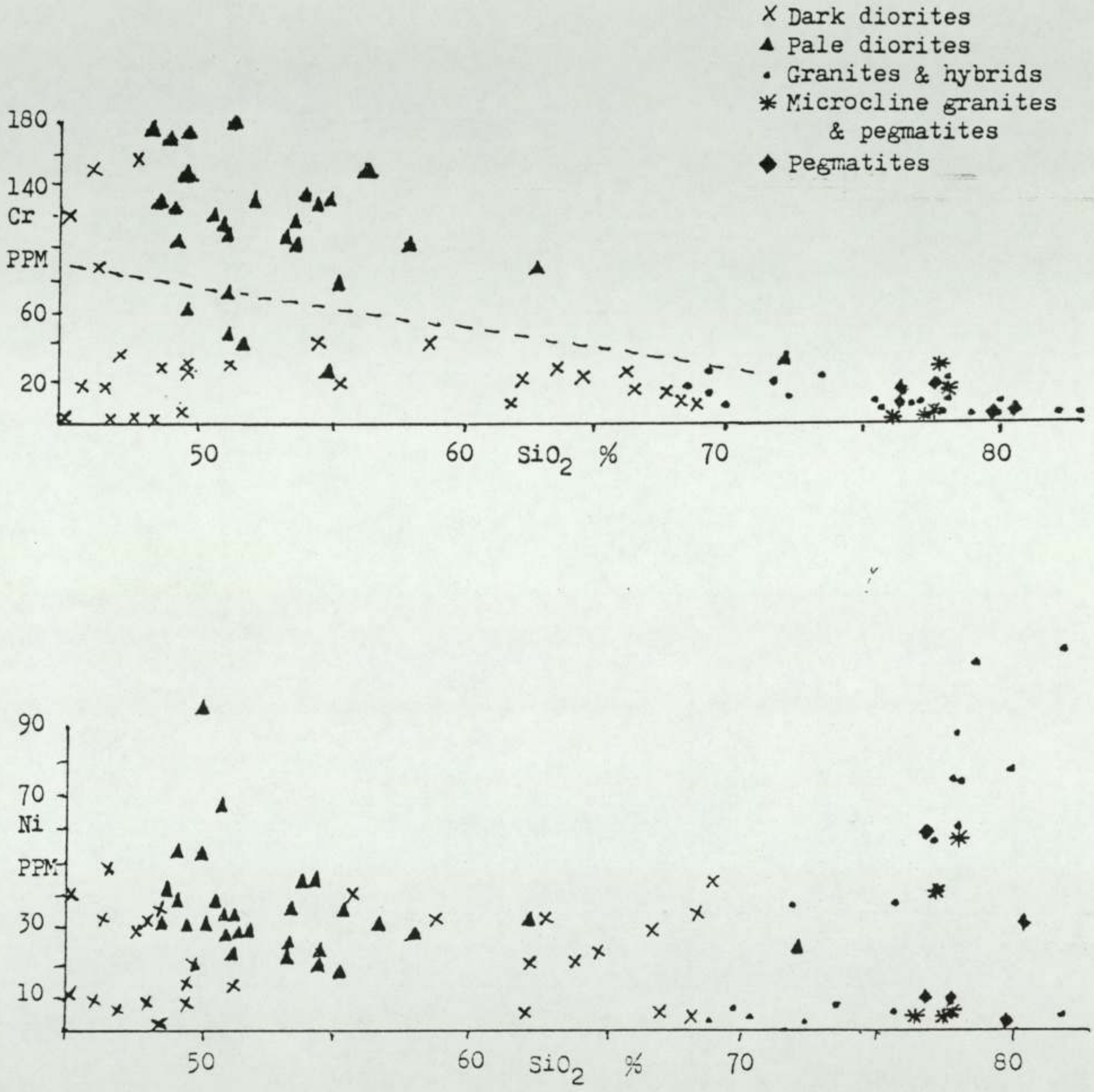
Zinc concentrations form a similar pattern being higher in the dark diorites. Correlation coefficients for Zn with SiO_2 for dark diorites is 0.926, and for the pale diorites 0.913.

Chromium forms two linear trends on the variation diagram against SiO_2 (Fig. 22). This is caused by the pale diorites showing generally higher concentrations of this element than the dark diorites, although the Cr contents of the rocks vary widely (0-180 PMM).

Nickel occurs in remarkably low concentrations in the rock series (Fig. 22), particularly in comparison with Ni values of the Garabal Hill rocks, and it occurs in equal amounts in the diorites and granites. This has produced a flat-lying, poorly defined, hybrid trend of similar appearance to that formed by K_2O. Despite the low concentrations of this element, the endmember diorites may be distinguished on Ni content, the pale diorites showing slightly higher values.

The Th and Pb analyses of the albite granites are very low, forming a flat-lying trend of variation with the diorites. In contrast, the microcline granites contain greater concentrations of these elements (12 PPM and 6-14 PPM, compared with 0-7 PPM and 0-8 PPM for the albite granites). They are present in Th-bearing allanite, a mineral absent from the albite granites and hybrids. The Pb occurs as a disintegration produce of Th and U

FIG. 23 TRACE ELEMENT VARIATION AGAINST SILICA FOR THE ROCKS FROM BOLTON HILL



from the allanite. The microcline pegmatite contains particularly high concentrations of Pb (22 PPM), and some albite pegmatites are very rich in Th, Nb and Y. None of these rocks are involved in the assimilation process.

7.5.3 Garabal Hill

Variation diagrams are shown in Figs. 24 - 26.

The alkali and alkali-earth elements Rb and Ba follow K into alkali feldspar and biotite, and increase in abundance in the granodiorites. They occur in greater concentrations in the hornblende gabbros and metasomatic diorites than in the relatively unmetasomatized gabbros. They are also richer in the hornblendites than the pre-existing pyroxenites, indicating that these elements were also introduced into the wallrocks by the metasomatic phase along with significant concentrations of the major alkalis. When metasomatic diorites or hornblende gabbros are chosen as the basic endmembers, reasonable correlation coefficients ensue for these elements against silica for a mixing trend with granodiorite. Coefficients are 0.678 for Rb/SiO_2 and 0.808 for Ba/SiO_2 and support the previous contention that, certainly for Garabal Hill rocks, metasomatism preceded assimilation. Some of the scattering of analyses in the more granitic rock types accounts for poorer correlation coefficients and may be caused by hydrothermal alteration, the lighter Rb being more affected than Ba by this alteration.

Niobium present in Fe-Ti oxides may have undergone very slight mobilization during metasomatism indicated by the slight increase in concentration in the hornblendites in relation to pyroxenites. The gabbros and hornblende gabbros however, are all similar indicating that any mobilization was trivial. The higher content of Nb in the granodiorites is due to the element substituting in sphene.

The elements Rb, Ba, Nb and Zr all suggest that hybridization involves granodioritic magma reacting with hornblende-gabbros and diorites with little, if any, involvement of the other basic or ultrabasic rocks. The very slight scatter of analyses of even immobile elements, which occasionally occurs, may be a direct result of variable mineralogy and composition in some of these original basic endmembers.

FIG. 24 TRACE ELEMENT VARIATION AGAINST SILICA FOR THE ROCKS FROM GARABAL HILL

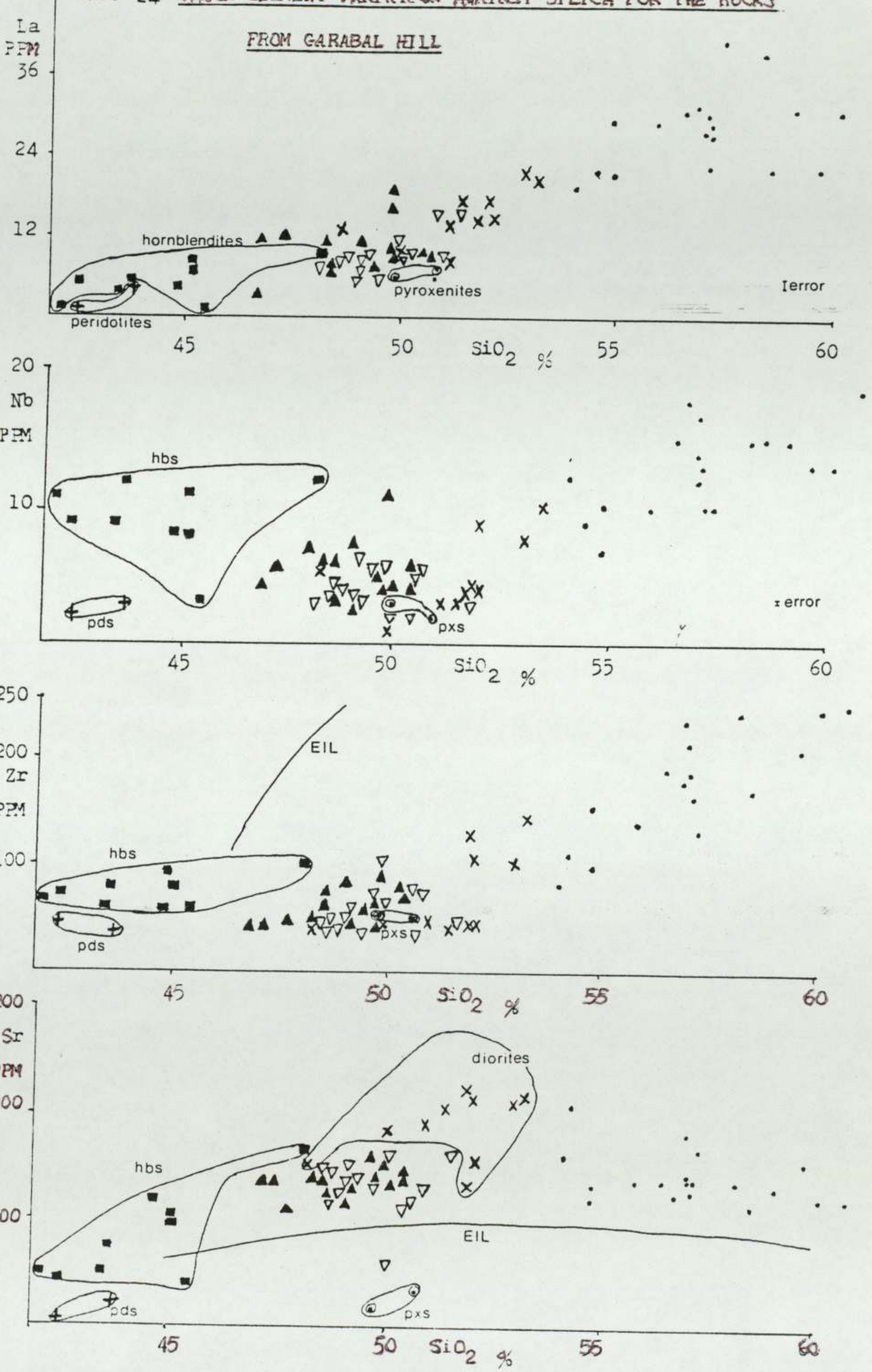
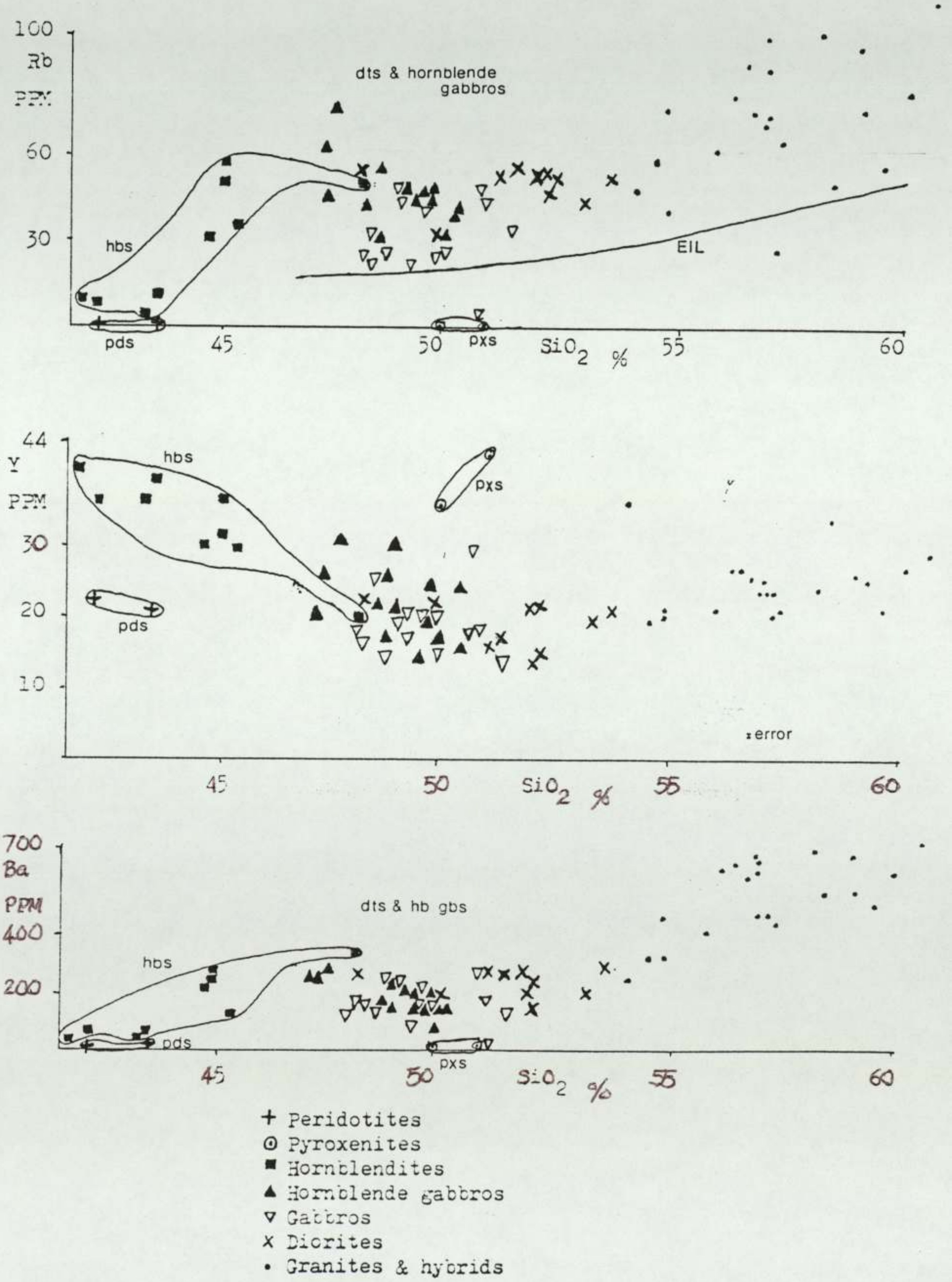


FIG. 25 TRACE ELEMENT VARIATION AGAINST SILICA FOR THE ROCKS FROM GARABAL HILL



Zirconium increases in the granitic rocks as zircon increases, whilst Y remains roughly constant in concentration throughout the basic rocks, indicating it to be immobile during the metasomatic phase. For both elements, their concentrations in pyroxenites and hornblendites respectively are similar, as are their contents in the gabbros and hornblende gabbros/diorites, which cannot therefore be separated. These features confirm their immobile nature during the phase of alkali metasomatism.

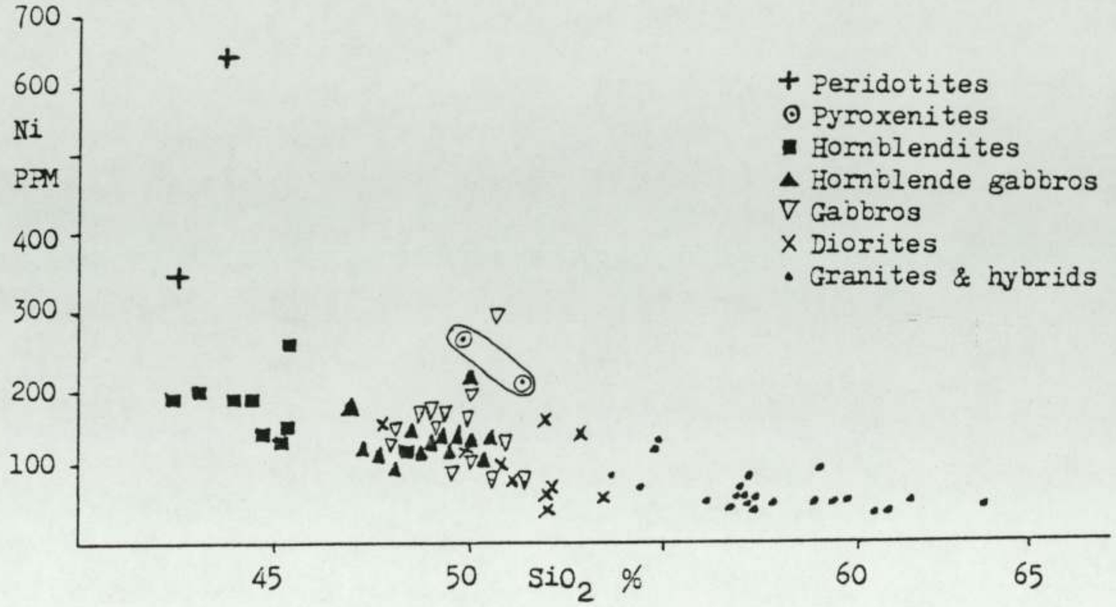
Analyses of Cr produce a relatively good linear trend for the Garabal Hill rocks between granodiorite and metasomatic diorite. The analyses in the diorites are very slightly lower than in the more basic rocks, indicating that some may be lost or locally redistributed during strong metasomatism. However, it appears to be unaffected by slight metasomatism, with concentrations in the gabbros and hornblende gabbros being similar (Fig. 26).

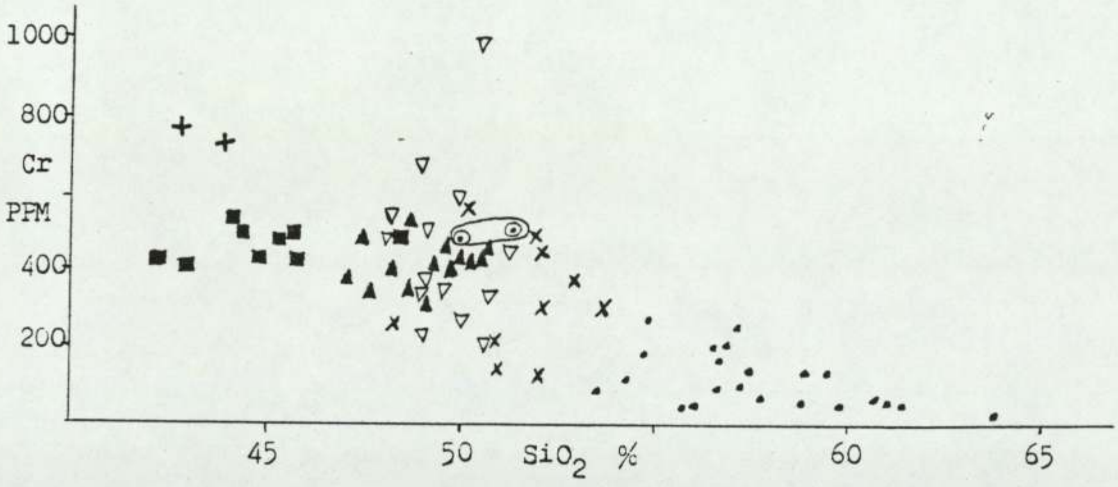
Nickel also gives a good linear variation between granodiorite and diorite. The diorites give roughly similar Ni values to the more gabbroic rocks indicating the element to be immobile during metasomatism (Fig. 26). Both Ni and Cr are thought to be strongly partitioned into olivine and indeed are abundant in the Garabal Hill peridotites. Vanadium forms an excellent linear trend with the diorites and appears to be immobile during the metasomatic phase.

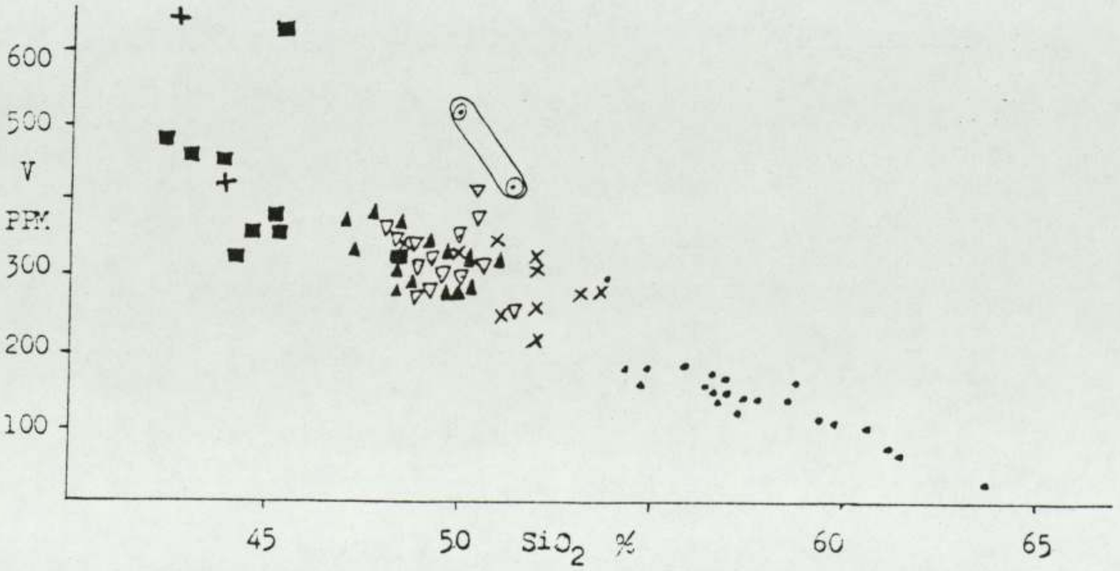
Strontium forms its characteristic humped pattern in the hybrids
(1100 PPM) with lower concentrations in the acidic and basic rocks (500 PPM). It also occurs in equally high concentrations in the metasomatic diorites with P_20_5, suggesting that these are the appropriate basic endmembers and that metasomatism of the wallrocks took place before hybridization. The great abundance of Sr in these metasomatic diorites is yet further evidence of its mobile nature during the metasomatic process. It also increases in content on replacement of pyroxenite by hornblendite. If Y occurs substituting for Ca in apatite, it would not be expected to form a humped pattern, such as that shown by P or Sr in the diorites and hybrids due to its immobile nature in metasomatic processes of this kind.

The elements U and Th decrease linearly from the granitic to the basic rocks to concentrations below detection limits. These elements are dominantly in allanite, the

FIG. 26 TRACE ELEMENT VARIATION AGAINST SILICA FOR THE ROCKS FROM GARABAL HILL







radioactive nature of which is shown by its metamict appearance, and form trends of hybridization with correlation coefficients of 0.938 (U) and
0.939 (Th). The high concentrations of Th in the Garabal Hill rocks in relation with those of Bolton Hill are a result of the greater abundance of Th-rich allanite, a phase also present at Glen Dubh. Variation diagrams for U and Th against $Si0_2$ are shown in Figs. 27 and 28.

The hybridization trends of these trace elements indicates that the metasomatized gabbros and diorites are the potential basic endmembers and preclude involvement of the ultrabasic rocks.

7.6 Rare Earth Element geochemistry

The analyses of the rare earths are shown with the trace element analyses in Tables 32-34. For all three complexes La was determined by X.R.F. Detailed REE analyses were obtained for the Garabal Hill Complex rocks by INAA. A similar attempt to perform INAA analyses for REE on the Johnston Diorite rocks proved unsuccessful because of the exceedingly low concentration of REE present.

7.6.1 Glen Dubh, Arran

The occurrence of aqueous phase F^- alteration in the Central Ring Complex has resulted in the mobilization of the rare earth elements. This is strongly suggested by the scattering shown for La on variation diagrams (Fig. 17). The alteration is also likely to have affected the behaviour of other rare earths, as it has with associated elements such as Nb and Y.

As a consequence, for the Arran complex, these elements have been judged to be of little use in demonstrating the mixing process and have not been analyzed for.

7.6.2. Johnston Diorites

Lanthanum analyses are very low throughout the Johnston Diorite rock series due to the absence of any independent rare earth-bearing minerals in the albite granite, and therefore their hybridization products. Despite the low concentrations of 12 PPM for the albite granite and 6-12 PPM for the diorites, a reasonably good linear trend is present between the endmembers established by previous geochemical criteria.

The occurrence of allanite accounts for the higher La content of the microcline granites (25-30 PPM), and some of the albite pegmatites are also rich in La.

The La in the diorites and albite granites is probably confined to the major silicate phases and is similar for both pale and dark diorites.

7.6.3 Garabal Hill

Detailed analytical work for REE has been carried out on the Garabal Hill rocks.

The granodiorites show higher light REE contents than the basic rocks but similar, low, heavy REE concentrations.

Allanite occurs commonly in the granodiorites and is known to strongly and preferentially accommodate the light REE's (Exley, 1980; Meighan *et al.*, 1984). These elements are partitioned into allanite whereas they are absent in other possible REE-bearing phases such as apatite, zircon or sphene (Nagasawa, 1970; Henderson, 1984; Jefferies, 1985). This would explain the high concentrations of these elements in the granodiorites.

Lanthanum, Ce and Nd show linear trends on variation diagrams, with correlation coefficients of 0.929, 0.909 and 0.830 respectively (Figs. 24 and 27). Allanites contain lesser amounts of Sm than La, Ce or Nd (Appendix 1, Table 16). Despite this, however, the element also shows a roughly linear variation with SiO_2 in the granite hybrids. The lower concentrations of Sm than the three lighter elements result in a greater spread of the analyses.

Europium and the heavy REE's Yb and Lu are very low in the granitic rocks as well as the gabbros due to their exclusion from the allanite structure (Fig. 28), an almost entirely light REE-bearing mineral (Vlasov, 1966a). All heavy REE's are likely to occur in very small amounts in other minerals such as apatite or possibly major silicates.

FIG. 27 TRACE ELEMENT VARIATION AGAINST SILICA FOR THE ROCKS FROM CARABAL HILL

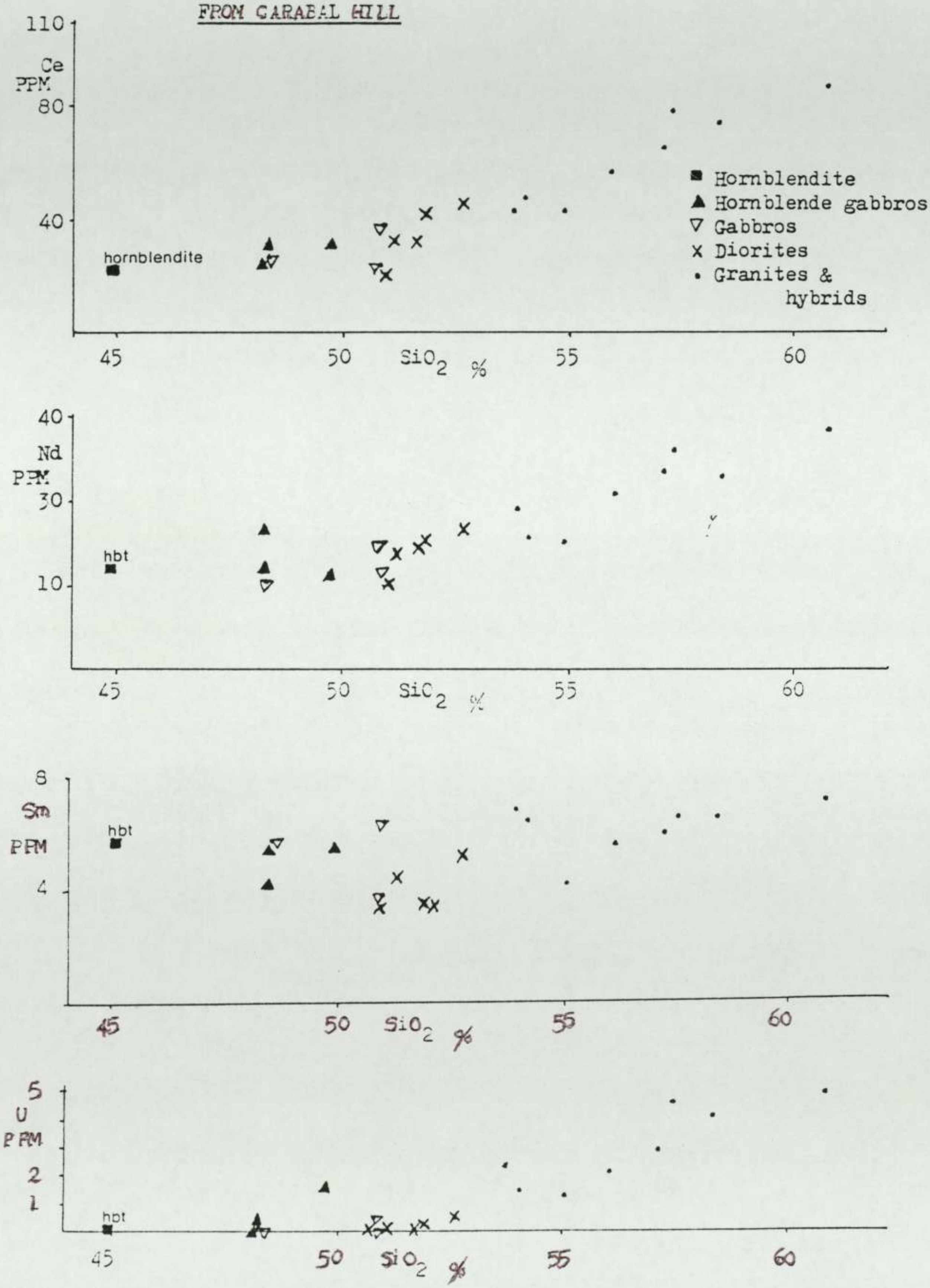
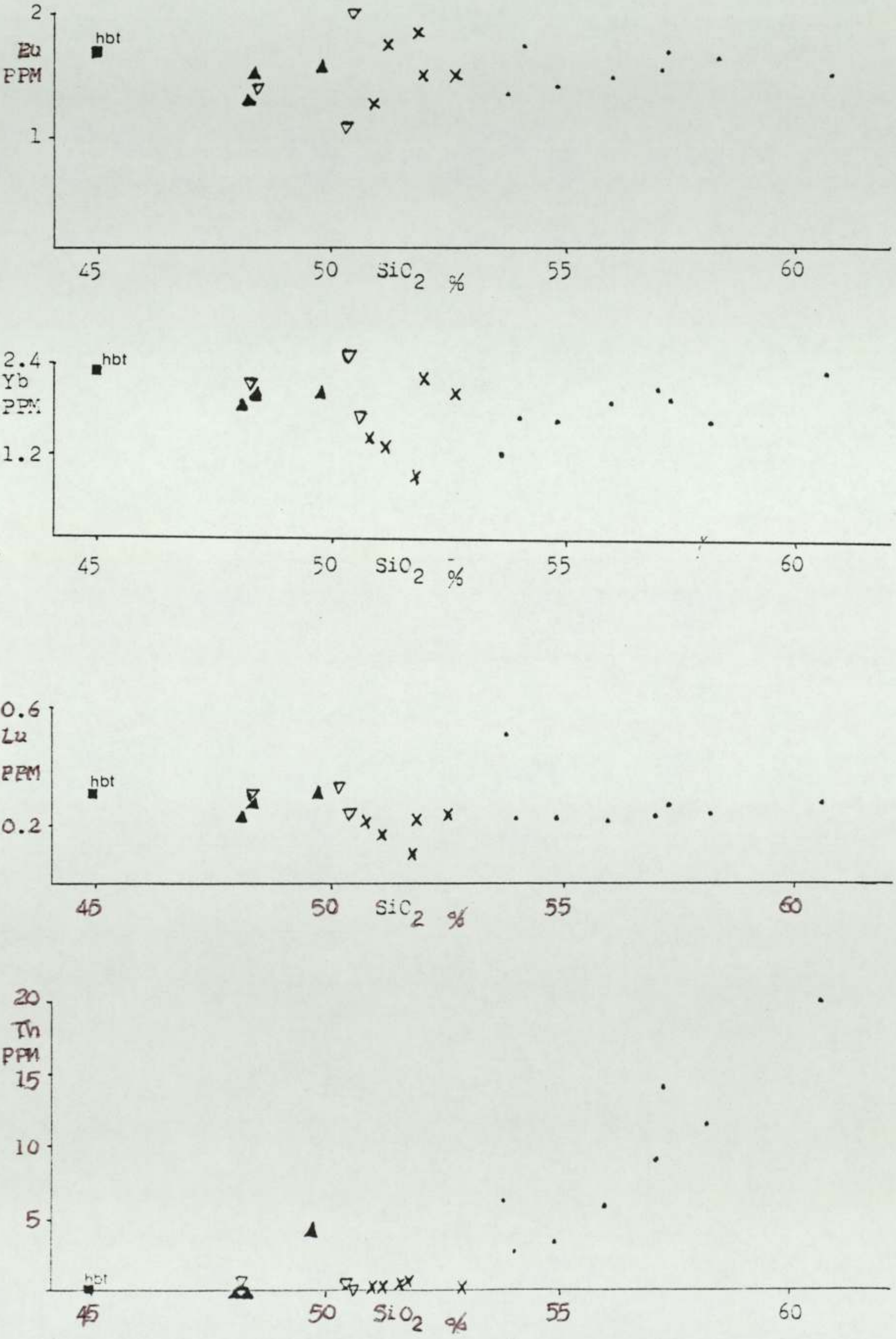


FIG. 28 TRACE ELEMENT VARIATION AGAINST SILICA FOR THE ROCKS FROM CARABAL HILL



The linear trends of variation of the light REE's are very marked. They appear to be in contrast to the pattern shown by the REE's in rocks with a supposed classical fractional crystallization origin such as the Skaergaard intrusion. Paster *et al.*, (1974) report that the crystallization of the major silicate minerals from basic magmas, has little affect on the REE concentrations of the magmas, due to their low distribution coefficients in these minerals. This results in a progressive increase in the magma until they become compatible, and hence much higher concentrations in the latest, most evolved, rocks of the series.

Haskin & Haskin (1968) found that at Skaergaard the light REE's increased by 15-fold in the last stages of solidification of the magma. This was a result of compatible behaviour and crystallization in distinct REE-bearing phases. Hasegawa (1960), Deer *et al.* (1962a) and Exley (1980) indicate that the mineral allanite has a very restricted composition (16%-25% REE) in igneous rocks, the REE's substituting for Ca and forming betwen 0.6-1.0 of the total number of 2.0 cations per unit cell. This strongly suggests that it is necessary for a build up of the REE's in a magma before the crystallization of a mineral, such as allanite, would occur. This conclusion is also supported by the work of Vlasov (1966b).

A REE pattern in a rock suite produced by fractional crystallization would therefore be expected to follow a markedly curved trend, with a gradual build up of the REE's, until these elements were in sufficient concentrations to allow the crystallization of allanite. The pattern would consequently be very similar to those described by Paster *et al.* (1974), and Haskin & Haskin (1968), and contrast markedly with a linear one formed by hybridization.

The trends of the REE's, as with many other elements, confirm hybridization between granodiorite and gabbro/diorite as the active fractionation mechanism, and preclude any involvement of the ultrabasic rocks of the complex.

Metasomatism of the basic rocks appears not to have changed the REE values. Pyroxenites show similar La concentrations to the hornblendites, whilst the gabbros; hornblende gabbros and metasomatic diorites all show similar La contents despite having undergone varying degrees of alkali metasomatism. This indicates that the REE's are a suitable group of elements to use at Garabal Hill to demonstrate the operation of the hybridization process. They are clearly immobile during both metasomatism and hydrothermal alteration in the igneous environment.

7.7 Discussion

Despite each of the three complexes showing assimilation of basic material by invading acid material, subtle differences in the endmember compositions are reflected in the geochemical concentrations and trends displayed by the hybrid rocks. In addition, however, each of the complexes show certain similarities, geochemically.

Major element variation for all three complexes clearly identifies the basic and acidic endmembers in each complex where a number of potential endmembers are present. Other acidic and basic rocks in the complexes can also be ruled out as possible endmembers using the same features. Selected major elements for all three complexes show good correlations with silica, and when computed in mixing calculations show good low sums of squares of residuals. This is exactly what would be expected for a process of assimilation.

Alkalis, and particularly Na, show greater scatter suggesting mobilization in some sort of aqueous phase (metasomatic or hydrothermal). However, correlation coefficients for these elements are still reasonable and perhaps suggest local readjustments rather than either input or removal.

Maximums for P_20_5 clearly indicate transport (in a fluid phase) and probably combination with Ca released from the pyroxene- amphibole-biotite or Ca plagioclase-Na plagioclase reactions, so forming apatite.

Slight differences in mineral chemistry between the complexes are reflected in their geochemical differences. An example is the low TiO_2 content of the Johnston diorites (maximums of 0.8% and 1.4% for the pale and dark diorites respectively) which are due to the Ti-poor nature of their hornblendes. The hornblendes of Arran are more Ti-rich, with the Garabal Hill amphiboles richer still, shown by the consequently higher TiO_2 contents of their gabbros (1.9% and 2% respectively).

The FeO and MgO contents of the basic rocks in the complexes are also a reflection of their contrasting concentrations in the
pyroxenes and amphiboles. The Garabal Hill rocks contain low FeO (10%) but high MgO (15%). Those of Arran have FeO of up to 14% and MgO of 7%, whilst the dark diorites of Bolton Hill, containing Fe-rich amphiboles, show FeO contents ranging up to 18% with MgO a maximum of 8%.

Turning to the acidic endmembers, variations in alkali content are also seen. Garabal Hill and Arran show Na_2O ranging up to 4.5% whereas the albite granites of Bolton Hill contain up to 6% Na_2O (8% in the case of some pegmatites). The K_2O content of Garabal Hill and Arran hybrid rocks show maximums of 4.5%, whereas the albite granites at Bolton Hill are of a concentration below 2% due to their highly sodic nature. Microcline granites from the same complex show 4% K_2O, with 7% for the microcline pegmatite. The minor alkalis also show similar concentration patterns.

Trace element geochemistry also shows a number of consistent features between the complexes. Supposedly immobile elements such as Zr, Nb, Y, Sc, V, (U,Th) and particularly light REE's, normally show good linear trends on variation diagrams against SiO_2. Exceptions do occur, however, with the scatter of Nb, Y and La in the Arran rocks showing operation of a F^--rich aqueous phase at this locality - mobilizing these elements. Also in the Johnston Diorites; scattering of few large zircon crystals (i.e. a sampling problem).

Trace elements such as Ba, and particularly Rb, follow K and show a degree of mobility, and hence scatter, at all three complexes. Behaviour of these elements at Garabal Hill may suggest that metasomatism preceded assimilation. Strontium shows a similar peaked distribution to P_2O_5 at each complex, suggesting it is present in apatite, substituting for

Ca.

Yttrium and REE linear trends suggest that these elements are not high in apatites (mainly being in allanite), or if they occur in apatites, concentration differs from basic to hybrid rocks (i.e. lower in hybrid rocks).

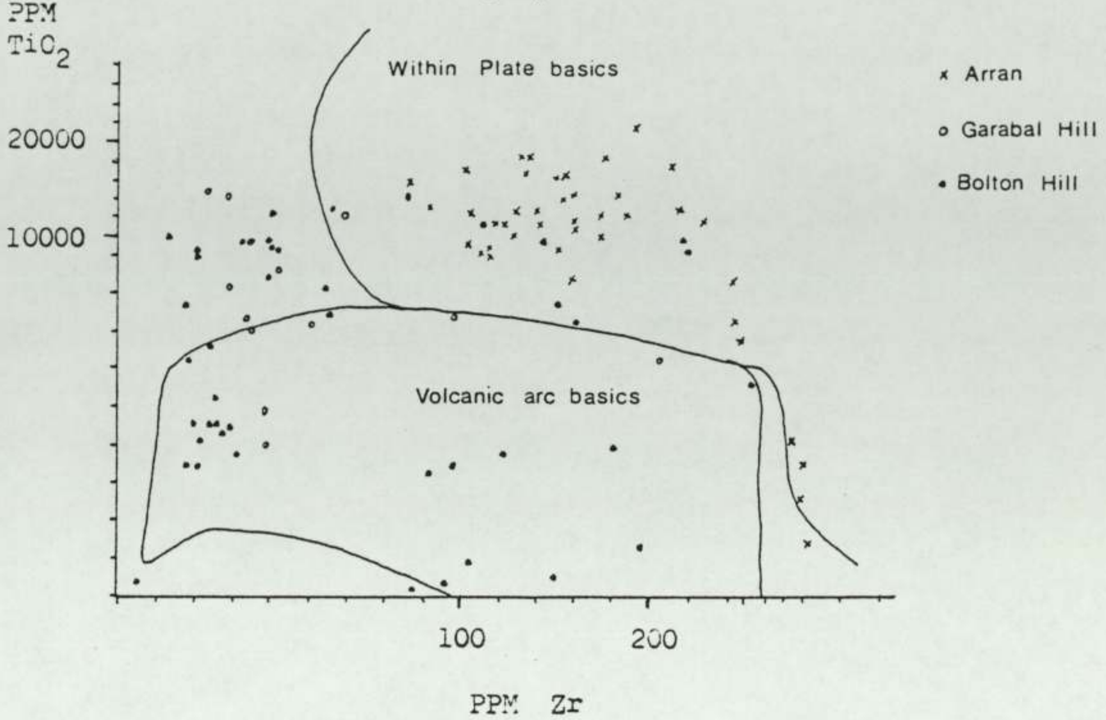
Trace element differences between the complexes may be a reflection of differing tectonic settings rather than reflecting processes occurring during assimilation. The Arran suite generally shows higher incompatible trace element contents than Garabal Hill or Bolton Hill, having formed in a rifting environment whilst the latter are believed to originate in a subduction setting (see Tables 32-34 for the element analyses). In these complexes, the elements Zr, Nb, Y, Ba, Rb and La are seen to be in higher concentrations at Arran. Strontium however, does not follow this pattern. Although all the above mentioned elements would be enriched in last stage liquids, Sr would occur substituting for Ca in plagioclase and shows a more compatible behaviour. Also Sr has already been shown to be mobile in aqueous phase and its concentration in various rocks may be a reflection of this.

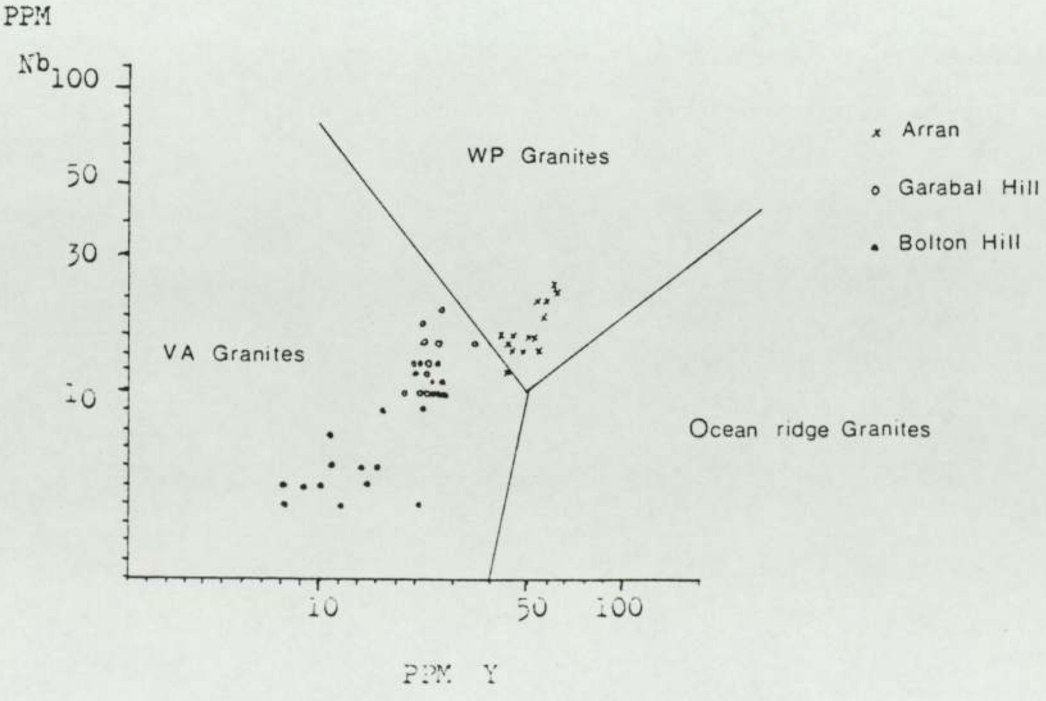
Tectonic settings for the Arran Central Ring Complex and the Garabal Hill Complex are relatively straightforward to determine due to their well established relationships with surrounding rock types, stratigraphic locations and tectonic settings. The Johnston Diorite intrusive complex presents more problems, as its contacts with the surrounding rocks are entirely faulted. Also its Precambrian age causes problems as there is conflicting evidence as to the position of orogenic zones and associated plate boundaries at this time.

The Johnston Diorite analyses have therefore been plotted on Tectonic Discrimination Diagrams of Pearce & Cann (1973) and Pearce *et al.*, (1984). Titanium oxide against Zr has been used for the endmember diorites, and Nb against Y for the granites (Fig. 29). Here, both granites and diorites fall into the fields representative of volcanic arc rocks, and are compared with those of Garabal Hill and Arran which plot respectively into the volcanic arc and within plate environments suggested above.

The Johnston Diorite Series is therefore believed to originate in a subduction zone environment. Such an environment is also proposed by Thorpe (1972, 1974), and is very

FIG. 29 TECTONIC DISCRIMINATION DIAGRAMS FOR BASIC ROCKS AND GRANITES (after Pearce & Cann, 1973 and Pearce et al. 1984)





similar structurally and petrographically to the igneous complex of the Malvern Hills, described by Lambert & Holland (1971). These similarities were also noticed by Wright (1968), and Thorpe (1972, 1974) who has suggested that both complexes once formed part of a subduction zone in a late Precambrian orogenic episode. This is also in agreement with their respective ages, dated at 643^{+5}_{-28} Ma for the Johnston Diorites (Patchett & Jocelyn, 1979), whilst the Malvern Hills complex has been dated using whole-rock Rb/Sr at 681 ± 53 Ma (Beckinsale *et al.*, 1981). The Malvernian rocks have also previously been dated at 635 Ma (Lambert in discussion after Fitch *et al.*, 1969).

8. FLUID PHASE GEOCHEMISTRY

8.1 Introduction

Fluid inclusions are common in quartz grains in the granitic rocks in the three complexes, although apparently absent from all other minerals. The number and size of the inclusions varies in different rocks from the different complexes. The albite granite at Bolton Hill contains larger and more abundant inclusions than the other granites, including the microcline granite from the same complex (Plates 8.1 and 8.2). The Arran granite, however, shows fewest inclusions.

The inclusions also appear generally to be slightly larger and more numerous in the xenolithic rocks compared with the granites. This is particularly well shown by rocks from the Arran complex (Plates 8.3 and 8.4).

Due to the important effect of metasomatic fluids escaping from the magma and altering the wallrocks, and the likelihood that fluid inclusions trapped in the quartz are remnants of these fluids (Ferry & Burt, 1982), an attempt has been made to analyze the contents of these inclusions in order to gain some idea as to their composition.

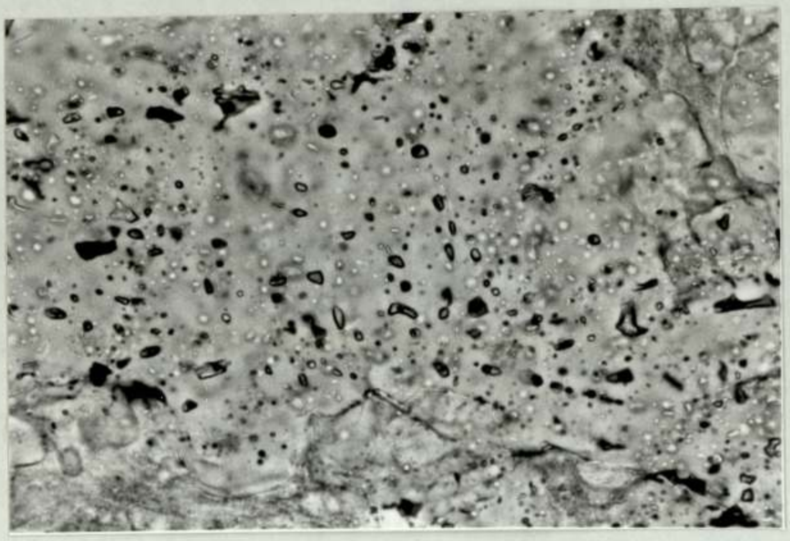
The procedure followed has been that of Shepherd *et al.*, (1985), whereby the rocks are crushed and washed with distilled water to dissolve any soluble constituents from the broken inclusions. These samples are then analyzed after removing suspended solids. A more detailed description of sample preparation, methods of analysis and drawbacks of the process are shown in Appendix 3, although it is important to stress that the results obtained are purely semi-quantitative.

8.2 Results

Analyses were carried out for the cations Na^+, K^+, Mg^{2+}, Ca^{2+} and Fe^{2+}, also for the anions Cl^- and F^-.

The alkalis were found to be in much greater concentrations than Mg^{2+}, Fe^{2+} and Ca^{2+} in the

PLATE 8.1 FLUID INCLUSIONS IN BOLTON HILL ALBITE GRANITE



Inclusions are very abundant and contained in quartz.

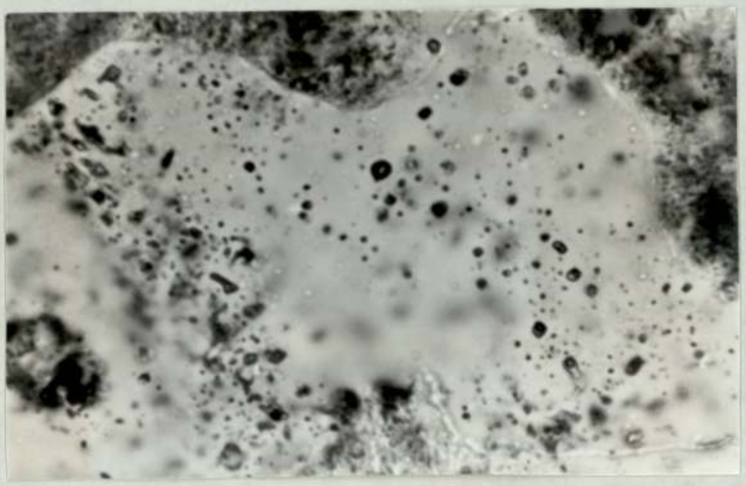
Field of view 0.225 mm (SPECIMEN BH5)

PLATE 8.2 FLUID INCLUSIONS IN BOLTON HILL MICROCLINE GRANITE

Inclusions are smaller and less abundant than those of the albite granite.

Field of view 0.225 mm (SPECIMEN BH222)

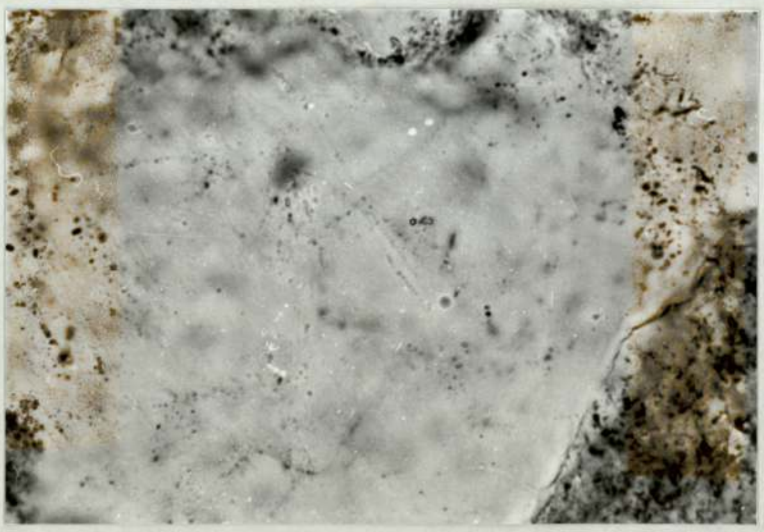
PLATE 8.3 FLUID INCLUSIONS IN ARRAN XENOLITHIC ROCK



Inclusions are abundant and contained in quartz.

Field of view 0.225 mm (SPECIMEN 43)

PLATE 8.4 FLUID INCLUSIONS IN UNCONTAMINATED ARRAN GRANITE



Quartz shows a marked absence of fluid inclusions in comparison with the quartz of the xenolithic rock.

Field of view 0.225 mm (SPECIMEN 20)

solutions from the more acidic rocks, due to their occurring in higher concentrations in the inclusions, which are in turn more numerous due to the greater abundance of quartz. Na, in turn, exceeds K in concentration between a ratio of 2 or 3 to 1.

The alkalis, however, decrease in the more basic rocks due to the paucity or absence of inclusion-bearing quartz, whereas Ca and Mg increase slightly. This increase, however, is likely to be a result of mineral breakdown and retention of ions in the solution - a problem described by Shepherd *et al.*, (1985), particularly as it coincides with a whole-rock increase in the concentration of these elements. This increase in these constituents is very low (a few PPM), so it is likely that any similar rise in alkalis in the more granitic rocks due to the same reason will also be low and consequently make little difference to their overall content (which range up to 50 PPM). Most of the alkalis are therefore believed to originate from the fluid inclusions rather than mineral breakdown. Similarly to the alkalis, Fe^{2+} also rises in abundance in the granitic rocks although to a much lesser extent.

The anions Cl^- and F^- are unlikely to be influenced by mineral breakdown due to their very low concentrations in magmatic silicate minerals, and are presumably almost entirely liberated from the inclusions. Cl^- greatly exceeds F^- in concentration in the aqueous phase in the samples from each complex. The ratios vary between 10 - 15:1 in the basic rocks to 100 - 150:1 in the acidic varieties, indicating the dominance of Cl^- over F^- in the metasomatic fluids. This feature is in accordance with Burnham (1967) who suggested that it preferentially occurs in magmatic vapour phases due to its low solubility in the melt, whereas F^- becomes fixed into crystalline silicates.

This is further indicated by higher Cl^- contents in the granites, whilst F^- is of a similar concentration in both granites and basic rocks.

Other constituents may be present in the fluids, e.g. Li^+, Ba^{2+}, Sr^{2+}, HCO_3^- . Indeed, SO_4^{2-} has also been shown to be present using a $BaCl_2$ solution which, when added to the sample solutions, produced a white precipitate.

8.3 Conclusions

The analyses of crushed fluid inclusions in the rock samples from the three complexes show remarkably similar characteristics. Three general conclusions can be drawn:-

(1) The dominant elements in decreasing abundance are
Na > K > Ca > Fe > Mg (although most Ca, Fe and Mg may be from mineral breakdown.
(2) The Na/K ratio is consistently between 2 - 3:1.
(3) Cl^- is greatly dominant over F^-, between 10 - 150:1, the greater ratio being in the more acidic rocks. This ratio is also consistent with the work of Burnham (1967).

The higher concentrations of these ions is greatest in the acidic and intermediate rocks due to the presence of quartz. However, there is less quartz in the intermediate rocks, which may reflect a higher proportion of inclusions in the fewer quartz grains present - this would be consistent with petrographic observations.

The composition of the fluid inclusions would appear to be largely made up of Na and K whilst the dominant anion is Cl^-. This is in accordance with other studies on the composition of metasomatic fluids, e.g. Shepherd *et al.*, (1985), and it is probable that these cations are largely present as chlorides. Indeed, Burnham (1967) proposed that 80% of alkalis in such fluids occur as chlorides. Some cations, however, will form complexes with other anions, which have not been analyzed but are known to occur in various degrees of abundance in fluid inclusions, e.g. SO_4^{2-} (see above), HCO_3, Br^-, I^-, S and P. The fluids would also be rich in H_2O, which is not possible to determine, and HCl.

The analysis of constituents from the fluid inclusions would tend to indicate the operation of an aqueous phase during the hybridization process and, to a certain extent, give some idea as to its composition. Metasomatic fluids are commonly believed to be Cl-rich aqueous phases which cause the redistribution of alkalis whilst other elements of higher ionic charge, e.g. Ca, Mg are not mobilized to such an extent. The presence of alkali chloride-rich aqueous fluids leaving a magma would be expected to modify the mineralogy of wallrocks, producing a new mineral assemblage richer in alkalis and volatiles. This is apparently the case in the complexes studied here.

9. **DISCUSSION**

Mineralogical, chemical and petrographic evidence together with field observations indicate that the series of intermediate rocks in each of the respective complexes of Glen Dubh, Garabal Hill and Bolton Hill are formed by the incorporation of basic igneous wallrocks by granitic magmas.

The assimilation of wallrocks in each case has resulted in the production of a variety of rock types ranging from distinct basic xenoliths in granite to heterogeneous and mottled diorites, monzodiorites and granodiorites (Streckeisen, 1976), or quartz diorites and tonalites in the case of the sodic, K-poor, Bolton Hill rocks.

Some of the mafic minerals observed in the granites themselves appear to be wallrock xenocrysts, indicating that even the supposed granite endmembers may be slightly contaminated.

The observations made and analyses performed in this study allow specific conclusions to be reached concerning the nature and extent of the assimilation process, and related processes, in each of the three named areas. These conclusions have a wider application in the examination of hybrid complexes in general and have possible relevance to the many calc-alkali intermediate rock type occurrences.

9.1 Original ideas for origins in the three centres

In earlier work on these three hybrid complexes, a number of proposals have been put forward as to the origins of the series of rock types.

The Johnston Diorites have been described as "dominantly gabbroic" (Rast & Crimes, 1969) which is obviously incorrect in terms of their petrographic features. They have also been termed "ortho-amphibolites" (Baker *et al.*, 1968), and in this sense the endmember diorites could be regarded as amphibolites formed by metasomatism and metamorphism of gabbros to "amphibolite grade". Indeed, as already argued, they are not true diorites although the term "diorite" will remain for reasons of familiarity.

Thorpe (1970) interpreted the rocks at Bolton Hill as being produced by the fractional crystallization of an andesitic magma,
with the granitic rocks forming along a liquid line of descent. The accumulation of plagioclase and hornblende crystals causing the scatter in the plots at the basic (diorite) end of variation diagrams.

Evidence presented in the geochemistry chapter explains this scatter as the result of there being two distinct basic dioritic rock types present, and indeed Thorpe in later studies (1972, 1982) favoured a hybrid origin for the intermediate rocks. Such an origin was also advocated by Wright (1968, 1969) and Baker (1982).

In studies concerning the Garabal Hill complex, the wide range of rock types present have been said to be caused by various processes. "Differentiation during consolidation in a subterranean reservoir" was favoured by Dakyns & Teall (1892) and "intrusion of separate ultrabasic and acid magmas" by Wyllie & Scott (1913). Nockolds (1941) favoured "fractionation of a pyroxene-mica diorite" with crystal accumulation forming the basic and ultrabasic rocks, and a liquid line of descent producing the granites.

In Arran, both the series of rocks of intermediate composition at Glen Dubh and the lavas of similar compositions in the Central Ring Complex have been proposed as possible acid-basic hybrids (Tyrrell, 1928; King, 1953).

The main alternatives to a hybrid origin for the intermediate rocks would appear to involve processes of fractional crystallization or partial melting.

Fractional crystallization does not explain certain features of all the complexes, particularly the abundance of heterogeneous and xenolithic acid and intermediate rock types, which would not be expected to occur in a fractionation sequence.

The essentially linear chemical trends shown by many of the variation diagrams would appear to contrast markedly with the curved trends that would be predicted for many elements if a fractional crystallization model was invoked.

In the case of the Johnston Diorites it would seem highly improbable that two basic endmember magmas could both fractionate along different and converging chemical paths (for many elements) to form two chemically, and petrographically, identical granites.

The suggestion of Thorpe (1970) for the fractionation origin of the Bolton Hill sequence was based upon the supposed non-linearity of trends on variation diagrams. This present study, however, does not agree with this finding, with many major and trace elements exhibiting excellent linear trends for granite with both dark and pale diorites. The scattering shown by the basic endmember compositions is inevitable due to the slightly differing compositions of the two diorites.

The theories of the origin of the Garabal Hill complex by Dakyns & Teall (1892) and Nockolds (1941) both involve a fractional crystallization model, despite Nockolds' previously preferring one of hybridization (1934b).

The fractional crystallization theory of Nockolds can be discounted on a number of aspects. It is based largely on the existence of a parental pyroxene-mica diorite, suggested to be the first intrusion in the complex. This pyroxene-mica diorite was described as the first rock type intruded on the grounds that it was not seen to cut any of the other rock varieties, all the rocks being assumed to be distinct and separate intrusions. These separate intrusions are now known to be gradational between gabbro and granodiorite, rather than individual, with no intrusive boundaries between the various rock types. They cover a wide range of compositions and are due to reaction between these two endmembers. Nockolds himself described the boundaries between his proposed separate "intrusions" as being "hardly ever seen" despite persisting with this theory.

Fractional crystallization of a parental magma would also be expected to result in the first-formed basic rocks forming a chilled margin around the edges of the complex, with the more evolved acidic varieties occurring towards the core. This is directly the opposite of what is found, with the basic rocks at the core, surrounded by granodiorite.

Partial melting also appears to be unlikely as a mechanism for the formation of the intermediate rocks studied, again due to the linearity of variation diagram compositional trends. Yoder (1970, 1973) prefers this process as a mechanism for producing discrete endmember basic and acid parent magmas prior to intrusion to higher levels, without the production of rocks of intermediate composition.

It is unlikely that any of the series of rock types at Bolton Hill, Garabal Hill or Glen Dubh were formed by a partial melting process because of the abundance and great variety of rocks of intermediate composition.

In the Bolton Hill complex, as with fractional crystallization, it would be unlikely that a mechanism of partial melting would produce two chemically and petrographically distinct basic and intermediate rock series, but with two chemically and petrographically identical granites. These trends would imply that the source regions for these melts would have to be of specific and differing compositions and/or depths. Such specific conditions seem unlikely.

It appears, from all available evidence, that only hybridization of basic wallrocks by acid magmas could satisfactorily explain the features seen in all the complexes. The individual acid and basic endmembers were formed by other processes such as contrasted differentiation (King, 1963) or partial melting (Yoder, 1970, 1973) outside the scope of this study. Certain authors (Nockolds, 1934b; King, 1963; Yoder, 1970, 1973) have expressed doubts as to the ability of a process such as fractional crystallization or partial melting to form rocks of intermediate composition. Certainly significant quantities of intermediate rocks, when seen in environments like the three complexes studied, require alternative explanations as to their origins.

9.2 The assimilation process

9.2.1 Energy considerations

The amount of assimilation occurring in an igneous complex is dependent upon a number of factors. In particular the temperature of the surrounding wallrocks, and of the intrusive magma itself, may decide the degree of reaction. Also the effects of metasomatism may influence this process.

Xenoliths tend to occur at the margins of an intrusion where heat loss is greatest and insufficient heat and time are present to allow assimilation to go to completion. Consequently a magma intruding at a high level in relatively cooler country rocks may undergo less reaction with the surrounding wallrocks than a magma intruding at deeper levels into hotter wallrocks, the latter magma retaining more energy for hybridization due to it losing less energy on heating its surroundings. A complication of this, however, is that a high level granite may be poor in volatiles, and therefore be at a higher temperature than a low level granite, with the result that there may be a greater difference between its temperature during intrusion and the crystallization temperature. This may allow slightly more energy for assimilation.

Examples of high level and low level intrusions are believed to be represented by those of Glen Dubh and Bolton Hill. The Central Ring Complex of Arran is seen to have intruded through Mesozoic sediments and Tertiary lavas (Tyrrell, 1928; King, 1955), whilst the Johnston Diorite Series shows no intrusive contacts with surrounding rocks and has been thrust-faulted into its present position. In addition, the Central Arran granite is thought to have been "dry" allowing a higher level of emplacement, whilst the albite granite at Bolton Hill is believed to have been volatile-rich, and subsequently is likely to have crystallized at a deep level.

The volatile-rich nature of a magma may also play an important role in the extent of assimilation by metasomatizing the wallrocks, and converting wallrock phases into others more in equilibrium with the intruding magma. This has the result that less energy is required from the magma for equilibration. Consequently the magma is liquid for longer, allowing reaction and mixing between the two endmembers to be more extensive. This is clearly expressed by Eichelberger (1975) who states that "when a crystalline phase comes into contact with a liquid with which it is not in equilibrium, it will tend to react with that liquid and change to a composition more appropriate to the new system. This fulfills the equilibrium condition that the chemical potential of each component must be the same in all co-existing phases, the energy for this reaction being supplied by lowering the temperature of the system and by crystallization."

It seems reasonable therefore to assume that, with extreme metasomatism, the mineralogy of the wallrocks is stabilized, less heat energy is needed from the magma for equilibration, and hybridization can occur to a greater extent before crystallization takes place. This process is seen more clearly in the Bolton Hill diorites and Garabal Hill rocks than those of Glen Dubh which have suffered little basic wallrock alteration.

A final point regarding the metasomatic fluids would be their
tendency to partly heat up the country rocks on leaving the magma, again resulting in less heat energy being lost by the magma for this purpose.

9.2.2 The mechanical breakdown process

The mechanical breakdown of wallrocks may be aided by metasomatism and replacement of pre-existing minerals with ones of lower density.

In gabbroic wallrocks such as the ones described in this study, originally present pyroxenes with densities of 3350 kg/m^3 show replacement by hornblendes of density 3220 kg/m^3 (Arran) and 3130 - 3150 kg/m^3 (Garabal Hill), according to the data of Deer *et al.*, (1963a). These pyroxenes and hornblendes also show alteration to biotites of a density between 2700 - 3300 kg/m^3 (Deer *et al.*, 1962b).

Similarly, the Johnston Diorites are thought to represent metasomatized gabbros originally containing augite (3350 - 3400 kg/m^3) and ferrohypersthene (3600 - 3700 kg/m^3) which have been replaced by hornblende (3200 - 3250 kg/m^3) and cummingtonite (3300 kg/m^3) (Deer *et al.*, 1963a).

The replacement by lower density minerals has been suggested by Brown *et al.* (1978) to set up stresses in the rocks and causing fracturing as a response to volume increases. This would cause the opening of microcavities and allow further access for both metasomatizing solutions and for the intrusion of the acid magma to invade the rock and break off xenoliths.

The incorporation of xenoliths in the magma is also believed to be aided by the differential thermal expansion of the respective minerals during heating and recrystallization. This can cause the breaking off of xenoliths along pre-existing planes of weakness in rocks showing appropriate rheological properties. This may be the more dominant process in the Arran rocks where recrystallization of the wallrocks is common, whilst there is less intense metasomatism than in the rocks of Garabal Hill and Bolton Hill. In these latter complexes the breakdown may be largely caused by the metasomatically-induced stresses indicated earlier.

A further process which has been suggested to aid the mechanical breakdown of wallrock, the solution of interstitial zeolites (Eichelberger, 1974), is not appropriate in the plutonic rocks studied here, although it may be important in basalt lavas.

9.2.3 Endmember composition

In all three complexes a number of possible endmember rocks can be identified from field observations.

At Glen Dubh, Arran, there are four separate gabbros. The alkali gabbros and coarse gabbros can be eliminated from involvement in the hybridization process with granite, on chemical and petrographic grounds. In addition, the hypersthene gabbros are unlikely to have been involved on petrographic evidence due to the absence of hypersthene or cummingtonite in the hybrid rocks. On the available petrographic and geochemical evidence, the medium gabbro is proposed as the dominant basic endmember at Glen Dubh. This is consistent with it outcropping to a greater areal extent than the other gabbros.

It is also indicated by mixing calculations which show that, for various intermediate rock types, the sums of squares of residuals
are generally lower for reaction between granite and an average medium gabbro composition, than those for mixing between the granite and both coarse and alkali gabbros (Tables 35a - 35e). In the Bolton Hill complex both the pale and dark diorites can be shown both petrographically and geochemically to have reacted with granite. Mixing trends involving both these basic endmembers can clearly be seen on variation diagrams (Figs. 11 - 13 and 20 - 23). However, of the two granitic types present, only the albite granite has reacted with the diorites. The microcline granite is not, on petrographic and chemical evidence, involved in the hybridization process, the difference chemically being seen particularly well on variation diagrams involving K and related alkali elements.

On similar grounds the pegmatitic bodies may also be eliminated from the hybridization process. Mixing calculations show particularly excellent correlations. between actual and predicted compositions for the intermediate rocks, during mixing of an average albite granite composition and an average pale and dark diorite, the sums of squares of residuals ranging between 0.39 - 1.97 for the dark diorite hybrids, and 0.63 - 1.84 for the pale diorite hybrids (Tables 36a - 36h).

At the Garabal Hill complex, although there is only one acidic endmember, a number of potential basic and ultrabasic endmembers are present. The ultrabasic varieties tend to plot removed from the main hybridization trend for most elements on variation diagrams (Figs. 14 - 16 and 24 - 28) and are thought not to be involved in the mixing process. Much geochemical evidence points to the gabbroic rocks as the basic endmember. However certain elements point more specifically to the hornblende gabbros, and in particular the "metasomatic diorites". The straight line relationships with these rock types implies that at Garabal Hill, metasomatism involving the influx of alkalis and certain other mobile constituents into the wallrocks, preceded assimilation and mixing.

The mixing calculations carried out tend to agree with the diorites being the basic endmember at Garabal Hill. Sums of squares of residuals, between predicted and observed compositions, for mixing between granodiorite and an "average" diorite varied between 1.58 - 2.54 (Tables 37a - 37c), whilst similar values for mixing of granodiorite and gabbro ranged from 0.83 - 12.63 (Table 37d).

These findings are completely consistent with field evidence in the complex. Here the granodiorite is seen to be in contact with the marginal diorites and possibly hornblende gabbros, whereas the unmetasomatized gabbros and ultrabasic rocks occur towards the centre of the basic core and away from contact with the acidic magma. This zonal relationship prevents any reaction between these rock types and acid magma.

9.2.4 Chemical evidence for mixing

The complexes studied all show localized reaction between granitic magma and basic wallrock, which involves no melting of the wallrock. This relatively simple system reduces or eliminates the possible complications which would be caused if large scale melting were involved. The linear compositional variations produced during hybridization would be modified if a basic magma were assimilating an acidic wallrock, due to the possible effects of fractional crystallization occurring at the same time (O'Hara, 1977; Taylor 1980; De Paolo, 1981; Best 1982). However this combination of processes is perhaps more appropriate at deep levels in the crust, as opposed to the shallower levels in which these complexes are believed to have intruded.

Other complications, such as the bulk-rock selective contamination of the magma by certain constituents (Fratta & Shaw, 1974; Dostal & Fratta, 1977; Watson, 1982), and the selective enrichment of particular minerals in a magma due to differential dissolution rates of phenocrysts (Donaldson, 1984a), are also avoided due to the absence of any melting. The only likely processes which may alter the linear variation expected from an acidic liquid/basic rock reaction would be volatile transfer (Hart & Allegre, 1980), however only certain constituents are believed to be affected by aqueous fluids (e.g. Na, K). Indeed, metasomatism is thought to alter the wallrocks prior to assimilation and would therefore not change the linear trend, though late stage alteration would.

Any other explanation of linear trends would require combinations of processes too fortuitous to be realistic. Fractional crystallization in particular would be expected to produce a curved trend (Middlemost, 1985) for most elements (especially REE's) due to the partitioning of elements into certain minerals. Even a combination of fractional crystallization and assimilation would modify the linear trends (Best, 1982).

In the Arran rocks, most elements show linear variation with SiO_2 between granite and medium gabbro with slight scattering of Na, K, La and Y due to alteration. Good correlation coefficients and low sums of squares of residuals are also apparent (Chapter 9.4.1. and Tables 35a - 35c) for these rock types, although correlation coefficients are best for the more "immobile" elements.

At Bolton Hill many good linear trends are shown due to hybridization of both types of diorite with the albite granite. The separate trends are clearly seen on the diagrams for elements such as TiO_2, FeO, MgO, Nb and Y where the diorites show markedly differing concentrations, whereas on other diagrams (e.g. CaO, Na_2O, etc.) the trends merge due to both diorites showing similar concentrations. The correlation coefficients for major elements against SiO_2 are very good (Chapter 9.4.2.), with the exception of Na_2O and K_2O which are believed to have been affected by the intense alteration and metamorphism. The sums of squares of residuals from the mixing calculations show excellent values between the observed and predicted trends (Tables 36a - 36h).

The hybridization trends on variation diagrams for the Garabal Hill rocks are not as well defined compared to the previous complexes due to the very variable nature and composition of the rock types. Nevertheless good correlation coefficients are found between SiO_2 and other major elements, again with the exception of alkalis which are susceptible to alteration (Chapter 9.4.3.). Mixing calculations carried out for reaction between granite and "diorite" show reasonable sums of squares of residuals when taking into account the widely variable nature of the rock series, the results being generally somewhat lower than those obtained using other potential endmembers (Tables 37a - 37c).

9.3 Recognition of assimilation

Complete equilibration between a granitic magma and a basic wallrock would be expected to form an apparently normal rock of intermediate composition, showing no visible evidence of hybridization having occurred (Harker, 1904). Indeed, the homogeneous hornblendic rocks of uncontaminated aspect at Glen Dubh, Arran, described by Tyrrell (1928), and seen during this study, were suggested as being caused by "complete equilibration between granite and gabbro."

Assimilation of country rock by a magma may only be recognized if incomplete equilibration has occurred. This is the normal circumstance in high level intrusions and may be identified by a combination of features:-

(1) The wallrocks may show net veining by the acidic rock, whilst the acidic material contains xenoliths showing varying degrees of breakdown to xenocrysts. The xenoliths may have a sharp, angular or diffuse, rounded appearance dependent upon their degree of reaction with the granite, which may in turn become a more heterogeneous dark granite.

All the above features are well developed in the complexes of Glen Dubh, Bolton Hill and Garabal Hill.

Some xenoliths may show recrystallization textures with the formation of radiating aggregates of minerals. This is seen at Glen Dubh, but not at Bolton Hill or Garabal Hill, and is not a universal occurrence in hybrid intrusions, being caused by dry metamorphism. Xenoliths showing similar radiating textures have been described by authors in other complexes as being caused by chilling of basic pillows in acidic magma, and have been used as evidence for mixing of magmas. Similarly, the rounded outlines of many xenoliths in acidic rocks have also been attributed to their having formed by rapid crystallization of basic magma in acid (Vernon, 1984). However, the interpretation of similar features in this study indicates a different origin.

(2) Xenocrysts in the hybrid rocks show clear disequilibrium textures, in particular the zoning of plagioclase and hornblende, and the rimming of pyroxene cores by amphibole and biotite.

The zoning of hornblende is usually from brown cores to green/brown or green margins. The presence of brown or green/brown hornblendes in intermediate or granitic rocks has been proposed as being evidence of their hybrid origin. Didier (1973) has indicated that "hybrid granitic rocks often contain brown or green/brown amphiboles which have unusually high Fe and Ti contents, such colours never being found in non-hybridized granitic rocks." This would be in accordance with the higher whole-rock contents of these elements.

The absence of brown hornblendes in the granitic rocks however, does not necessarily indicate a non-hybrid origin, the original colour of the hornblendes being dependent upon the abundance of Fe-Ti oxides in the pre-existing pyroxene. Whereas the Garabal Hill and Glen Dubh rocks contain brown hornblendes, those of Bolton Hill are green due to their Ti-poor nature.

The replacement of pyroxene in hybrid rocks by brown to green-zoned hornblende has previously been recognized in hybrid complexes (Deer, 1935; Read, 1935; Anderson, 1935; Nicholls, 1951; Brown *et al.*, 1978).

The presence of cummingtonite may also be a feature in hybrid rocks where a hypersthene-bearing rock has been assimilated. This has been seen at Bolton Hill and in work by previous authors (e.g. Kuno, 1938).

Mineral textures indicative of magma mixing, as outlined by Donaldson (1984b), are not found in this study.

(3) Hybrid rocks show linear compositional trends on variation diagrams for most elements, between the basic wallrock composition and that of the assimilating magma, particularly if the endmembers are of fixed compositions. The linearity is less well defined if one endmember is of variable composition, e.g. the Garabal Hill basic endmember in this study.

On the variation diagrams the intermediate rocks show "abnormal" compositions to equivalent rocks which would have formed by such a process as fractional crystallization. Certain constituents would show higher contents (e.g. Fe, Ti) whilst others would appear lower (e.g. Na).

The main alternatives to assimilation in the formation of the intermediate rocks are those of magma-mixing and restite separation. These processes may be discounted in the three complexes studied here.

(A) Magma-mixing is ruled out as it would be expected to produce rounded, "chilled" pillows showing a decrease in grainsize of the pillows towards the contact with the felsic material rather than the angular, sometimes recrystallized xenoliths actually seen. The inclusions may be expected to form parallel elongated swarms (Frost & Mahood, 1987) and some mineral melting (felsic minerals) may be expected.

In addition, many xenoliths in these complexes show both sharp and gradational margins which would not be expected, according to the previous authors, in magma-mixed rocks.

(B) Restite separation may also be dismissed in these complexes due to the presence of wallrock and xenoliths of the same composition (not expected where xenoliths have been derived from great depth).

Restite xenoliths, if derived from great depth would be expected to occur uniformly distributed throughout an intrusion, whereas xenoliths in these complexes increase in abundance towards the granite-wallrock contact.

The xenoliths would, in addition, be expected to be of a rounded appearance due to breakdown and disintegration during transport by the felsic magma, whereas those studied here are often angular. In their study, Chappell *et al.*, (1987) stress how restite is carried by a magma as individual crystals or small aggregates; this would appear to be further evidence against restite-separation in these complexes where xenoliths may be quite large (up to 1 metre).

Finally, where a liquid is formed by partial melting of a solid, if some crystals remain they must have been just in equilibrium with the liquid at some stage, and may be expected to show slight evidence of marginal melting themselves. This feature is not seen in the complexes in this study.

9.4 Metasomatism

9.4.1 Metasomatism as an aid to assimilation

Metasomatism is generally associated more strongly with alkaline rocks, where its effects can be seen hundreds of metres from the contact zones (Kogarko, 1974; Brown *et al.*, 1978). It is known, however, to occur to a much lesser extent around "calc-alkaline" plutons

(Anderson, 1963) and has been described in each of the complexes studied here, none of which are of an alkaline nature.

This metasomatic alteration of wallrocks is caused by aqueous fluids boiling off the magma during its intrusion at high levels of emplacement where P_V exceeds total P, subsequently allowing the release of these volatiles. These fluids, depending on their composition, can carry large concentrations of alkalis and other elements which help to modify the wallrock before its reaction with the granite. They migrate through the country rock by diffusion and/or infiltration; the bimetasomatism of Korzhinskii (1970). The metasomatism of the wallrocks may precede, or occur at the same time as assimilation, presumably according to their distance from the magma/wallrock contact.

The importance of volatiles in the alteration and breakdown of country rocks has been noted by numerous authors. It is shown in the areas of study by the great abundance of hydrous minerals (e.g. hornblende, biotite) in xenoliths forming at the expense of anhydrous ones (e.g. augite, hypersthene). Nockolds (1933) even reported the presence of hydrous phases replacing augite in xenoliths in Mull granophyres, although the granophyres themselves did not contain primary hydrous minerals. This indicates preferential concentration of volatiles in the xenolith presumably as a consequence of the xenolith chemistry favouring the formation of hydrous phases. This occurs to an extent in some of the Arran xenoliths where biotite can occur far more abundantly than in the granites.

Volatiles are important as they allow increased rates of diffusion for various elements (Kogarko, 1974) and act as a medium of low viscosity for transfer of these elements. In particular, metasomatism is seen to cause an increase in alkali content of the wallrocks by diffusion from the granite in response to a concentration gradient. Brown & Becker (1986) describe basic inclusions in a net-veined complex at Kialineq, Greenland as being richer in alkalis than the normal basic rocks of the area (in agreement with the experimental diffusion work of Watson (1982)). This may produce selective enrichment in certain constituents whereas others are slower to be introduced due to their slow diffusion rates.

The cooling of a volatile-rich magma, precipitating anhydrous phases, may also result in the escaping gases fracturing the wallrocks and breaking off xenoliths, thereby allowing the possibility of further reaction.

9.4.2 Mineralogical effects of metasomatism

The metasomatic fluids can have the effect of extensive changes in wallrock mineralogy, causing the replacement of anhydrous pyroxene by hydrous minerals such as hornblende and biotite, and of calcic plagioclase by more sodic plagioclase. In the Bolton Hill granitic rocks, the presence of a volatile-rich magma is indicated by the occurrence of brunsvigite replacing hornblende. This mineral was mistakenly identified as biotite in descriptions of the rocks by previous authors (Cantrill *et al.*, 1916) as it is often seen replacing hornblende in other complexes.

Also in the Bolton Hill rocks, hornblende may be seen replacing cummingtonite, which in turn is believed to have been formed metasomatically from previously-existing orthopyroxene. The volatile-rich nature of the granite and the presence of cummingtonite in the dark diorites at Bolton Hill offers evidence for the original presence of two types of gabbroic wallrock, now completely metasomatized to diorite.

Another mineralogical feature associated with metasomatized rocks is the abundance of apatite needles, often contained in zoned hornblende or feldspar. In addition, minerals such as epidote, particularly common in the Arran and Bolton Hill hybrids, and sphene (common in the Garabal Hill hybrids) are also abundant in metasomatic rocks.

The chemical compositions of the Johnston Diorites are very much in the region of that expected for gabbros, being low in SiO_2 (45%), well below that of normal diorites. These rocks are also highly olivine normative which would not be expected in typical diorites. This is a further indication of the diorites previously being gabbros, the dark cummingtonite-bearing diorite having been a hypersthene gabbro, whilst the pale diorite is believed to have formed from a "normal" gabbro containing no orthopyroxene.

Cummingtonite, although present at Bolton Hill, is absent from the Arran rocks suggesting that the hypersthene gabbros were not involved in the hybridization process at Glen Dubh.

Cummingtonite was also not seen in Garabal Hill rocks during this study although it was reported as being present in the complex by Nockolds (1941). This reported presence suggests that hypersthene-bearing rocks may also have been involved in the hybridization process at Garabal Hill.

9.4.3 Chemical effects of metasomatism

The main effect of metasomatism is the introduction of certain constitutents to an existing wallrock, in particular the introduction of volatiles and alkalis.

The addition of these constituents may result in a reciprocal reaction of elements, by diffusion, out of the wallrock, e.g. Ca^{2+} released by pyroxene altering to hornblende and biotite (see Chapter 6.8) (diffusion of consitituents via an aqueous phase has been shown experimentally by Yoder (1973), even where little change is seen petrographically).

Korzhinskii (1970) described how metasomatic fluids may form what he termed "aureoles of reflected alkalinity" when percolating through rocks of ultrabasic composition. Such a process would appear to have occurred at Garabal Hill where Na-metasomatism appears more pronounced than K near the contact between basic and acidic rocks (Fig. 15). Differential behaviour of alkalis is also described. Vernon (1976) and Burnham (1979a) have shown evidence that the smaller Na^+ ion diffuses faster than K^+ through an aqueous phase. This may be an explanation for the apparently greater degree of Na-metasomatism seen in the Garabal Hill wallrocks. This lack of build-up of K in the wallrocks would also explain the low abundance of "metasomatic" biotite, whilst similarly-formed hornblende is common.

The Bolton Hill complex differs from those of Arran and Garabal Hill in undergoing merely Na-metasomatism due to the K-poor nature of the system. This causes the formation of brunsvigite in place of biotite.

Increased concentration of P_20_5 is a common feature of hybrid, xenolithic and metasomatically altered rocks. It corresponds with an increase in apatite content of the rocks in relation to the endmembers (Nockolds, 1933). This feature suggests that P^{5+} is transported in aqueous fluids as a complex, or as a volatile in its own right (Burnham, 1979b). Indeed, this argument is strengthened by the findings of White & Waring (1963) who detected the presence of P in volcanic gases, indicating that it can be mobile in the igneous environment.

The high P_20_5 concentration in rocks at other localities, e.g. the hybrid rocks at Kialineq (Brown & Becker, 1986) attributed to fractional crystallization may have a similar origin.

Metasomatic alteration of wallrocks results in the release of Ca^+ by Ca-bearing minerals, e.g. Ca-plagioclase and pyroxene on their replacement by Na-plagioclase, hornblende and mica. Some of this Ca combines with influxing P to form apatite. It may also combine with other components in the aqueous phase to form epidote (e.g. Arran and Bolton Hill). Also Ti, released from alteration of ilmenite or during zoning of Ti-rich hornblende, may also react with the Ca^{2+} to form sphene. This is particularly evident at Garabal Hill.

Despite much of this excess Ca^{2+} forming these minerals, it would appear that some Ca^{2+} is lost from the wallrocks or xenoliths by way of reciprocal reaction.

The increase in P_20_5 content of the hybrids, xenoliths and metasomatized wallrocks is matched by an almost directly comparable rise in Sr in all three complexes studied. This is suggestive of its occurrence in apatite, rather than other possible phases such as low temperature calcic plagioclase, as proposed by Drake & Weill (1975) and Wood (1978), or zeolites as proposed by Gunn & Watkins (1969). It is interesting to notice that similar increases in both P_20_5 and Sr have been reported in rocks from a number of hybrid localities including that of marscoite (Wager *et al.*, 1965; Rock, 1974).

The close correlation of P and Sr is particularly well seen in the dioritic members of the Johnston Diorites, with the dark varieties being richer in both P_20_5 and Sr than the pale diorites and containing visibly more apatite. The difference in apatite content may reflect differences in the Ca content of the original gabbros, with more Ca^{2+} being released during formation of the dark diorite to combine with the P.

Sr is known to be a mobile element (Cann, 1970; Wood *et al.*, 1976; Condie *et al.*, 1977; Humphris & Thompson, 1978; Dickin & Jones, 1983) and is believed to migrate along temperature gradients, through the medium of an aqueous fluid, to higher temperature regions when felsic rocks are in contact with basic rocks (Burnham, 1967). This would have the result of the wallrock being slightly depleted in this element over a large area during metasomatism (Brown *et al.*, 1978) after being released by the alteration and replacement of original Ca-bearing minerals.

In other complexes the Sr has been suggested to originate by breakdown of country rock zeolites, followed by mobilization through an aqueous phase into the hybrid rocks. Pankhurst *et al.*, (1976) proposed that the very high Sr contents of xenoliths in the Kangerdlugssvaq intrusion, East Greenland, were due to the incorporation into the magma of original alkali-rich gabbros, no longer seen in the area. However, in view of the observations made in the complexes studied, a metasomatic origin appears more appropriate for their high Sr content.

This observation is in close agreement with the work of Vlasov (1966a) who proposed that "strontium is incorporated in apatite
during gaseous stages of mineralization", and also that it "accompanies volatiles during magmatism."

The concentrations of P and Sr are higher in the "metasomatic diorites" than the unmetasomatized basic rocks at Garabal Hill indicating that these constituents move through the wallrocks via the aqueous fluids, indeed the Johnston diorites at Bolton Hill probably also contain higher contents of these elements than their original gabbros which are not longer represented. However, the concentrations of these elements are usually still higher in the xenolithic and hybrid intermediate rocks in the complexes. This is presumably due to the presence of the acidic magma allowing the faster, and more efficient, transfer of constituents to and from the crystalline material via the aqueous phase, whereas in the wallrocks the same constituents would have to travel between grain boundaries or along fractures, the reactions subsequently being slower. The lower concentrations in the more acidic hybrids is due to the lesser abundance of basic material reacting with the magma and releasing Ca, with which they can combine.

9.4..4 The evolution and nature of the fluid phase

The volatile fluids evolved from the granites are likely to have been dominantly hydrous but also rich in chlorides. Chloride does not tend to form stable magmatic minerals or complexes in silicic systems (Burnham, 1979a) and is only stabilized in sodalite in undersaturated systems. Unlike fluoride, which is more readily fixed in crystallizing phases, it has a very large partition coefficient in favour of the aqueous phase. This is borne out by analysis of fluid inclusions in the rocks of the complexes studied. In all cases Cl^- greatly exceeds F^- in concentration by a ratio between 10 and 150:1 (consistent with the work of Burnham, 1967), the ratios being greatest in the more acidic rocks. These are the dominant anions although others may also occur, e.g. SO_4^{2-} (confirmed as present in this study), Br^-, I^-, S and P (Shepherd *et al.*, 1985).

Although Cl^- can occur in very small amounts in the minerals apatite and biotite, again the F/Cl ratios are usually high, indicating preferential fixation of the F^-.

As suggested earlier (see Chapter 9.4.3.) and confirmed by fluid inclusion analysis, Na and K are the dominant cations, with the probable exception of H^+ which cannot be analyzed. Na is seen to be itself dominant over K by a consistent ratio of 2 or 3:1. This is presumably due to its smaller size causing Na to diffuse more quickly into, and through, aqueous fluids (Vernon, 1976; Burnham, 1979a).

The solubility of alkalis in the aqueous phase is greatly increased by the presence of Cl^- and enhances the effects of metasomatism at low pressures. This causes marked redistribution of alkalis with extensive changes in basic wallrocks (Burnham, 1967, 1979a; Korzhinskii, 1970; Wyllie, 1979).

Much work has been carried out suggesting how metamorphic and metasomatic fluids are Cl^--rich, dominantly of Na, K and H (Ferry & Burt, 1982). Indeed Burnham (1967) suggested that 80% of alkalis are carried as chlorides. This also appears to be the case for the complexes studied here, and would explain the extensive modification shown by some of the basic rocks. The presence of Cl^- has been indicated, in addition, to greatly increase the mobility of Sr (Vlasov, 1966a; Kogarko, 1974) in aqueous systems. The marked rise in concentration of Sr, shown by metasomatized and hybrid rocks in this study, has indicated the mobile nature of this element which may have been further increased by the presence of large amounts of Cl^-.

It is interesting to note that the Arran rocks show the highest F/Cl ratios of the three complexes in fluid inclusion analysis, which may indicate more F^- was in this system generally, as indicated petrographically by the occurrence of fluorite and the lack of uniformity of rare earth element analysis.

The importance of volatiles in the breakdown of wallrock xenoliths and in metasomatic processes, may be indicated by numbers of inclusions and their size. These can be compared in quartz crystals in both the xenolithic rocks and hybrids, and in the normal uncontaminated granites. Of the rocks studied, the albite granite of Bolton Hill is richest in fluid inclusions possibly indicating its originally hydrous nature in relation to the other granites, including the microcline granite from the same complex. In contrast, the Arran granite contains apparently few inclusions in their quartz crystals, particularly in comparison with the quartz crystals in the xenolithic rocks where the inclusions are larger and more abundant. Although they are larger and more numerous in the quartzes in xenolithic rocks, the concentration of alkalis detected from the inclusions is slightly lower than the concentrations in the granites. As these analyses were performed on bulk-rock material, this is likely to be due to the presence of a greater abundance of quartz in the granitic rocks when compared to the xenolithic hybrid rocks. In the xenolithic hybrid rocks there is an increased abundance of inclusions in relation to the total quartz content of the rocks. This provides further evidence for the migration of volatiles towards the "drier" basic rocks.

The relative abundance of fluid inclusions in the different granites from the three areas may be related to the original water content of the magmas and consequently to the extent of metasomatic alteration associated with them. This alteration is more extensive in the Johnston diorites than at Garabal Hill and is even less pronounced in the gabbroic rocks at Glen Dubh, Arran, where it is mainly restricted to xenoliths. The extent of metasomatic alteration, together with quartz fluid inclusion evidence, would tend to point to the apparent dryness of the Central Arran granite in comparison with the other complexes. Indeed, Tyrrell (1928) noted that the alteration of rocks surrounding the Arran Northern Granite was "much less than might have been expected" often amounting to "little more than mere induration." Dickin *et al.*, (1981) have also remarked upon the apparent dryness of most intrusions at Arran.

As observed at Garabal Hill, extensive metasomatism can result in complete replacement of pyroxene by hydrous minerals, and labradorite plagioclase by andesine, ultimately forming diorites from original gabbros. In this way the Johnston diorites are believed to have formed by alteration of gabbros during intrusion of a volatile-rich granite magma. This is likely to have been the albite granite due to the abundance of fluid inclusions which it contains within quartz. Evidence for the volatile-rich nature of the albite granite lies also in the occurrence of the brown and green, iron-rich, brunsvigite variety of chlorite seen in many of the granitic rocks from the Bolton Hill complex. This was mistakenly identified as biotite in descriptions of the rocks by other authors (e.g. Strahan *et al.*, 1914). This mineral is often seen replacing hornblende in a similar fashion to the way in which biotite replaces hornblende in other complexes.

Brunsvigite has been described elsewhere occurring as a supposedly primary magmatic mineral, although almost entirely in spilite volcanics (Battey, 1956; Nicholls, 1958). These occurences are controversial, occurring in veinlets and amygdales, often as aggregates associated with calcite rather than individual magmatic crystals as seen at Bolton Hill. These previous descriptions would appear to be more obviously formed by a late stage hydrothermal event, the more normal cause of chlorites in igneous rocks. This is particularly the case when found in association with minerals such as epidote, calcite, prehnite and pumpellyite (Battey, 1956; Bevins & Rowbotham, 1983) and when occurring as groundmass replacement products. Fe-rich chlorites of brunsvigite composition have also been described by Nockolds & Richey (1939) as occurring in replacement veins in granites (greisens).

The obvious similarity of the spilitic occurrences of brunsvigite with the albite granite of Bolton Hill as the Na-rich, K-poor nature of both environments.

In earlier work on brunsvigite, Battey (1956) stressed the difficulty in obtaining the precipitation of albite and chlorite from a granitic melt, but that it can be greatly reduced under hydrous conditions. The experimental work of Tuttle & Bowen (1958) has shown how excess H_20 can lower the melting temperature of the system Na Al Si_3 0_8 - K Al Si_3 0_8 - Si 0_2 - H_20 to below 700° C at up to 5k bar PH_20 (implying PH_20 = P total, i.e. water saturated). This would indicate that the granite originated, and crystallized at depths as implied in Chapter 9.2.1.

Work on the system Na Al Si_30_8 - Ca Al_2 Si_2 0_8 - Si 0_2 - H_20 by Yoder (1967) also indicates a decreased melting temperature of sodic-calcic granite down into the stability field of chlorite (approximately 680° C) and low albite at 5k bar PH_20.

Amphibole is unstable under such conditions, which accounts for its absence in the more granitic rocks of the Johnston diorite series. Whereas in potassic magmas hornblende is replaced by biotite, in the Na-rich, K-poor magmas at Bolton Hill, chlorite is the stable phase (Battey, 1956). The absence of biotite at Bolton Hill, due to the K-poor nature of the albite granite, would suggest that the fluids emanating from the granites were also K-poor and largely sodic in composition. Although aqueous fluids leaving a normal granite are typically richer in Na than K, it is interesting to note that the "average" Na/K ratios of the fluid inclusion analyses are 1.7 - 2.0 for Arran and Garabal Hill, but 2.8 for Bolton Hill. This finding is in accordance with the fluids at Bolton Hill being dominantly sodic, as suggested above.

Burnham (1979a) has proposed that highly Na Cl-rich aqueous phases can separate from granite magmas at temperatures of around 700° C which, assuming a PH_20 of 5k bar, is closely comparable to the possible temperature of the albite granites during intrusion, from the experimental work of Tuttle & Bowen (1958) and Yoder (1967).

The presence of chlorite, together with metasomatism and fluid inclusion evidence would tend to testify to the albite granites originally hydrous nature. Tuttle & Bowen (1958) stated that "hydrous granites have a greater effect on the surrounding wallrocks, much more so than anhydrous ones". Consequently the albite granites would be expected to have extensively metasomatized the wallrocks during intrusion. On this basis it is suggested that the diorites are intensely metasomatized gabbros, having been effectively altered to amphibolite-grade rocks by the intruding granitic magma and its associated magmatic aqueous fluids.

A further feature indicating the volatile-rich nature of the Bolton Hill and also the Garabal Hill complexes, in comparison with the Glen Dubh rocks at Arran, is in the recrystallization texture of the xenoliths at Glen Dubh. This is not seen in the xenoliths from the other complexes. It is believed to be due to the Arran xenoliths undergoing dry metamorphic recrystallization and forming pyroxene- hornfels facies rocks with contrasting textures to those at Bolton Hill and Garabal Hill. At the latter complexes, the xenoliths and wallrocks suffered wet metamorphism and metasomatism to amphibolite hornfels facies. A similar feature has been shown to have occurred at the Lilloise intrusion (East Greenland) where wallrocks show different textures and mineralogies depending upon where water escaped from the intruding magma (a magmatic aqueous phase being proved by stable isotope studies). Where this phase escaped, the wallrocks were amphibolitized whilst where water was not channeled a two-pyroxene hornfels was produced with a mosaic texture (A. Chambers pers. comm.). The features of this intrusion appear markedly similar to the features seen between the complexes described in this study.

9.5 Additional processes

All three complexes have been affected by hydrothermal alteration after final crystallization. The evidence is seen in the form of veinlets, and in the replacement of primary minerals by yellowish-green penninitic chlorite, epidote, uralite and sericite.

The absence of uralite at Bolton Hill is due to prior metasomatic alteration to hornblende of all the original pyroxenes, so leaving no remnant pyroxenes to be uralitized. This is in contrast to the similar complex of the Malverns where pyroxene cores remain surrounded by hornblende (Lambert & Holland, 1971). These pyroxenes are also uralitized.

The veinlets and scarce alteration patches of calcite, albite and prehnite, which post-date these earlier ones in the Johnston Diorites, are believed to have been caused by the phase of low grade metamorphism associated with the thrusting of the whole complex over younger sedimentary rocks during the Hercynian Orogeny. This thrusting also caused a degree of shearing and deformation shown by minerals in the complex, and the larger scale faulting present in Bolton Hill quarry. This is in contrast to similar metamorphic alteration occurring elsewhere in South Wales which has also been designated low grade prehnite-pumpellyite burial metamorphism, but of Caledonian age (Bevins, 1978; Bevins *et al.*, 1981; Roberts, 1981; Bevins & Rowbotham, 1983).

This hydrothermal and metamorphic alteration has had a minimal geochemical effect on the rocks in the complexes with only certain mobile elements believed to have been affected to any great extent. Most elements are thought to have been merely locally re-distributed within the rocks or unaffected completely. This allows the original assimilation and metasomatic processes to be more clearly unravelled.

9.6 General implications for the formation of intermediate rocks assimilation and mixing

The presence of xenoliths and xenocrysts of basic rock within granitic or syenitic rocks is a common occurrence in many igneous complexes intruded at high crustal levels (Brown *et al.*, 1978), and also in many acid and intermediate volcanic rocks (Eichelberger, 1975).

The great abundance of intrusions and complexes showing the various characteristics of hybridization, and the marked absence of rocks of intermediate composition in many large gabbro-granite plutonic complexes, except for those obviously formed in this way (King, 1963, 1982), may be a good indication as to the importance of assimilation as a process in the formation of intermediate igneous rocks.

Bowen (1928) indicated that significant contamination of a magma by large scale assimilation of crystalline material was unlikely as the heat required would result in crystallization of the magma. Eichelberger (1974, 1975) has since shown that mechanical disintegration can play an important role in the breakdown of wallrocks and suggests that contamination is largely a mechanical process with neither superheat nor latent heats, generated by crystallization, being necessary. Bowen also did not evaluate the possible effects of metasomatism on the wallrocks where alteration to give compositions in equilibrium with the magma might precede reaction with the magma (Brown *et al.*, 1978).

Eichelberger (1975) has stressed that there are numerous localities where contamination is indicated by field evidence, and
where the formation of intermediate rocks by assimilation is more consistent with chemical and petrological data than processes such as fractional crystallization or partial melting. The presence of so many volcanic regions where repeated intrusion and extrusion take place over long periods suggests that contamination will be a widespread phenomenon. Eichelberger suggests that the reason for the prevalence of andesitic rocks in volcanic activity associated with subduction zones relates to the stationary nature of the volcanism. This allows magma to periodically or continually rise through a thick, hot, volcanic pile with extensive opportunity for contamination. In comparison, other environments such as rift environments, are characterised by continual migration of the volcanic focus relative

to the volcanic products, with the result that the lava pile is thinner and there is less opportunity for contamination. Both extrusive and intrusive material tend to be bimodal in composition with very limited occurrences of intermediate rocks. The British Tertiary is an example.

King (1963) also implies that it is difficult to account for the bulk of intermediate rocks in calc-alkali arcs and assimilation is a possible mechanism for their production, particularly with so little intermediate material found in rift settings.

Eichelberger (1975) concludes that fractional crystallization and partial melting may be "of little importance for most intermediate rocks" particularly for those of calc-alkaline affinity. With so much evidence in favour of assimilation as a major process, the author would tend, to an extent, to agree with this conclusion. These ideas have been strengthened in recent years by the resurgence of interest in the production of some calc-alkaline intermediate rocks by hybridization. Walker (1983) aptly described this as being "a long neglected process".
Anderson (1976) proposed that the hybridization mechanism of magma mixing is a common method of contamination in Circum-Pacific belts and he suggests that it is probably the dominant process in the formation of andesites, rather than fractional crystallization. In addition, Eichelberger himself has more recently indicated that magma mixing may be of similar importance to assimilation (Eichelberger, 1978, 1980). He cites "mixture-lavas" as being the dominant type in volcanic arcs, with rhyolitic lavas few in comparison, but notes that, in contrast, granitic intrusions are abundant with few true diorite plutons. His explanation is that the intermediate lavas form by mixing of acid and basic magmas at high level and are erupted without the formation of intermediate plutons. He states that the high level diapiric rise of viscous acid magma through less viscous basic magma promotes mixing and results in few rhyolitic magmas reaching the surface unmodified. In contrast, completely unmodified granite plutons exist in abundance at depth, below the level of mixing. This process could occur equally well between acidic magmas and solidified basic material by mechanisms considered in this study. The possibility of this occurring on a very large scale has been suggested recently by a number of authors who favour a combined crystallization/assimilation model.

On all available evidence there seems little doubt that assimilation and/or magma mixing occurs, particularly at Destructive Plate Margins, although it is uncertain which is dominant.

Assimilation, however, may only produce significant amounts of intermediate material where felsic magma rises through thick piles of mechanically weak basalt lavas, whereas in the plutonic environment they would have to assimilate tough plutonic rocks which would require more energy.

A liquid basalt would allow faster and easier ascent for a felsic melt through the crust than solid country rocks, allowing mixing to occur, and may be more likely when considering the length of time required for complete crystallization of a magma.

However, due to the complex nature of igneous systems in the crust and mantle, it appears unlikely that a single process would produce all intermediate rocks. It is more likely that both assimilation and magma mixing take place, possibly with minor involvement of other processes.

Although the end products of assimilation and magma mixing are difficult to distinguish, there is no escaping the great volumes of evidence for hybridization in general being far more common, and important, in the formation of a wide range of rock types than has previously been thought.

The totally different ages of the complexes studied here, and elsewhere, indicates that the hybridization process is widespread, not only in different tectonic settings but also throughout geological time.

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APPENDIX 1 - MINERAL ANALYSIS

1.1: Electron Probe Microanalysis

Mineralogical analyses were performed by Wavelength Dispersive techniques using a Cambridge Microscan 5 electron microprobe, operated under high vacuum with an accelerating voltage of 15 kV. Results were corrected for counter dead time and mass absorption effects and recalculated on the basis of a number of oxygen atoms. This was done with a MACZAF correction program on a BBC microcomputer.

Minerals were analyzed using polished thin sections coated with carbon to a thickness of 250 Angströms. Analyses were carried out with a focussed beam, and analyses for all elements were performed on the same spot. Throughout the analyses, two spectrometers were available allowing simultaneous determination of two elements.

Peak values were determined and compared with background values, which were obtained by analyzing the material at 2° on either side of the relevant peak. Counts were taken over a time interval of 10 seconds for both peak and background. The counts were averaged over 4 runs and 2 runs for peak and background respectively. The standards used, and the optimum operating conditions for the elements analyzed are shown below.

Table 3: Operating conditions and standards for EPMA

Element	Detection limits (oxide wt %)	Analyzing crystal	Standard
Na	0.01	RAP	Jadeite
Mg	0.01	RAP	MgO
Al	0.01	RAP	Al_2O_3
Si	0.03	RAP	Wollastonite
K	0.02	PET	Orthoclase
Ca	0.06	LiF	Wollastonite
Ti	0.03	LiF	Ti
Mn	0.02	LiF	Mn_3O_4
Fe	0.02	LiF	Fe_3O_4
Y	0.02	PET	Y
La	0.11	LiF	LaB_6
Ce	0.09	LiF	$CeAl_2$
Pr	0.10	LiF	PrF_3
Nd	0.09	LiF	NdF_3
Sm	0.09	LiF	SmF_3
Gd	0.09	LiF	GdF_3
Dy	0.09	LiF	DyF_3
Th	0.03	PET	Th

Detection limits for the individual elements were calculated according to the equation:

$$d.L. = \left(\frac{2.8\sqrt{Bg}}{\sqrt{t} \times \text{Std Peak}} \right) \times 100$$

where Bg = Standard background counts
t = length of time taken for counting
Std Peak = Standard peak counts.

This gives a detection limit at a 99% confidence level.

1:2 Mineral recalculations

The electron microprobe does not distinguish between ferric and ferrous Fe, which can be a problem when working out structural formulae. It is presented in Tables 1 - 12 as Fe0.

Pyroxenes

There have been various suggestions to alleviate the problem of ferric iron in pyroxenes.

Essene & Fyfe (1967) and Mysen & Heier (1972) estimated the Fe^{3+}/Fe^{2+} ratio from analysis totals.

The method adopted by Cawthorn & Collerson (1974) involved the manipulation of the oxidation ratio such that the sum of the cations is equal to 4.000 (calculated to 6 oxygens). They indicate that it produced comparable results to those obtained by classical analytical methods but that the results should be treated as approximate.

Larsen (1976) also uses cation-based stoichiometric calculations to evaluate Fe_20_3 , but emphasizes the problem that the method demands a complete and accurate analysis of all other elements. The disadvantages of using stoichiometry are that some varieties of pyroxene have been shown to have cation site deficiencies, i.e. less than 4.000 (Cawthorn & Collerson, 1974), so that the recalculation would give false totals.

Another method is that proposed by Carmichael (1962) where, in fully analyzed pyroxenes, (Na + K) is almost matched by equal amounts of Fe^{3+} on an atomic basis, thereby balancing the charge. He suggests that there is a small deficiency of Fe^{3+} in relation to alkalis, which is compensated for by Al to balance the structure. This procedure has been followed by other authors (Stephenson, 1972; Brown *et al.*, 1978) but may only be accurate for alkali pyroxenes with high alkali contents.

A disadvantage with this method was described by Cawthorn & Collerson (1974) who prefer the combination of (Na + K) primarily with octahedral Al with any excess alkalis subsequently combining with Fe^{3+}, i.e. the jadeite molecule is formed before the acmite molecule.

As indicated earlier, this procedure may give similar results to the method of Carmichael (1962) for alkali pyroxenes, but for normal pyroxenes with very low alkali contents the results would be completely different particularly if octahedral Al exceeded (Na + K). All Fe in this work has consequently been expressed as Fe0, with any Fe_20_3 present in the pyroxenes assumed to be of only minor proportions.

Amphiboles

Due to the complexity of the amphibole structure and composition, the determination of ferric iron content is exceedingly difficult.

Larsen (1976) suggested the calculation of Fe^{3+} on the basis of 16 cations and 46 negative charges per formula unit in an analogous fashion to pyroxenes. However, because of the complex nature of amphiboles, any slight analytical errors are compounded through a calculation (more so than in pyroxenes) as elements are assigned to their various sites. This would mean that when ferric iron is finally calculated, the result could show little relation to the true figure. The presence or absence of F^- in the amphibole structure also complicates matters.

Leake (1978), in an I.M.A. Subcommittee on Amphiboles report, put forward a scheme whereby the formula is calculated on the basis of 23 oxygens, with the adjustment of total cations excluding (Ca + Na + K) to 5 + 8 by varying the Fe^{2+}/Fe^{3+} ratio.

In an addendum to the same report, Leake & Hey recommend an alternative of calculating the formula on the basis of 13 cations (exclusive of Ca + Na + K) before adjusting the Fe^{2+}/Fe^{3+} ratio to bring oxygens to total 23 (or if water has been determined, 0 + OH to 24).

Brown *et al.*, (1982) found that neither procedure gave values sufficiently consistent with those obtained wet chemically, and calculated their formulae on the basis of zero Fe^{3+}, this representing the least departure from the data.

Helz (1973) describes a number of methods of estimating the Fe^{3+} content of amphiboles, but describes the results as being excessive and not particularly accurate, before ultimately expressing total Fe as Fe0.

Mezger *et al.*, (1985) used a fixed $Fe0/(Fe0 + Fe_20_3)$ ratio of 0.7, but this would seem too generalized and unlikely for hornblendes from different environments. Hawthorne (1983) showed that a whole range of possible amphibole recalculation schemes exist, all based on adjusting the Fe^{3+}/Fe^{2+} ratio to obtain electroneutrality, but found that no significant correlation exists between observed and calculated values in published literature. In view of these conclusions, it has been decided to express all the Fe present in the amphiboles studied as FeO. This may result in slight innaccuracies with the more complex amphiboles such as hornblende, where Fe^{3+} may be present. In contrast, the monoclinic Fe-Mg-Mn amphiboles, e.g. cummingtonite have been proposed by Hawthorne (1983) as having Fe^{3+}/Fe^{2+} ratios equal to zero.

Micas

The Fe_2O_3 content of micas, as with the amphiboles, is difficult to determine due to their complex nature. Consequently the total Fe content has again been reported as FeO.

Mezger et al., (1985) used an average $FeO/(FeO + Fe_2O_3)$ ratio of 0.87 for biotites, but the data of Nockolds (1947) clearly indicates that the ratio can range much more widely than this.

1.3 Amphibole classification

In the absence of water and F^- determinations, the analyses of amphiboles are computer reduced on the basis of 23 oxygen atoms and the formula calculated following the recommendations of the I.M.A. Subcommittee on Amphiboles (Leake, 1978) to the standard formula:

$$A_{0-1}\ B_2\ C_5^{VI}\ T_8^{IV}\ O_{22}\ (OH)_2$$

The method used is:-

(a) Sum T to 8 using Si then Al, Fe^{3+}, Ti^{4+}

(b) Sum C to 5 using excess Al, Ti, (Fe^{3+}) from (a) then Mg, Fe^{2+}, Mn.

(c) Sum B to 2 using excess Fe^{2+}, Mn, Mg from (b), then Ca, Na.

(d) Excess Na from (c) is assigned to A, then all of K.

Total of A should be between 0.00 and 1.00 inclusive.

1.4 X-ray diffraction analysis of an olivine-replacement product

An X.R.D. trace was made of the unknown orange-green pleochroic Fe-Mg silicate, seen replacing olivine in some peridotites from Garabal Hill, in an attempt to determine its nature and identification.

This was carried out by grinding the mineral out of the thin section very carefully, avoiding contamination from all other minerals, subsequently mounting the powder using araldite in the Powder Camera.

Araldite is used to bind the powder due to its amorphous nature which does not produce a diffraction pattern on the X-ray film inside the camera.

The powder was bombarded with X-rays, produced using a copper tube, for one and a half hours before developing the film. The diffraction pattern formed however, was very similar to the pattern chacteristic of calcite for many of the major latttice "d" spacings. This result was obtained twice using different powder mounts from separate thin sections over separate diffraction runs. This would tend to confirm that the patterns were not caused by any contamination.

Unfortunately it must be assumed that the particular mineral is possibly unstable under the x-ray beam, resulting in its almost complete breakdown so that even its atomic "d" spacing cannot be used in its identification.

The mineral has, for this reason, remained unidentifiable and has continued to be referred to as an olivine-replacement product.

The most strongly developed "d" spacings of the mineral, evident from the X.R.D. analysis are shown below:

3.036 Angströms
2.839 Angströms
2.500 Angströms
2.284 Angströms
2.093 Angströms
1.911 Angströms
1.871 Angströms
1.621 Angströms
3.466 Angstrøms
1.604 Angströms

Tables of mineral analyses

Tables 4 - 17 inclusive give mineral analyses of phases from the three complexes investigated. Most analyses have been calculated to numbers of ions on the basis of the appropriate number of oxygens.

It should be noted that Fe is expressed as Fe0 (see Appendix 1:2).

Table 4: <u>Olivines, Garabal Hill</u> (SPECIMEN GH 111)

%			
$Si0_2$	38.89	41.13	39.22
$Ti0_2$	0.06	0.04	0.3
Al_20_3	0.02	0.02	0.11
Fe0	21.32	18.89	19.41
Mn0	0.47	0.45	0.51
Mg0	38.18	36.01	38.65
Ca0	0.07	0.17	0.65
	99.01	96.71	98.58
Si	1.02	1.08	1.02
Fe	0.47	0.41	0.42
Mg	1.49	1.41	1.50
Ca	-	-	0.02
Mn	0.01	0.01	0.01
0	4	4	4

Table 5: Garabal Hill Fe-Mg Silicates (Olivine-alteration product) (SPECIMEN GH 111)

%					
SiO_2	46.51	45.46	41.91	49.69	46.17
TiO_2	0.02	0.02	0.01	0.01	-
Al_2O_3	1.65	0.53	4.56	0.03	1.52
FeO	19.03	19.94	19.14	16.12	17.57
MgO	21.79	20.50	21.11	20.93	22.24
Cao	0.30	0.40	0.33	0.51	0.47
MnO	0.05	0.07	0.07	0.06	0.06
Na_2O	0.07	0.06	0.08	0.07	0.07
K_2O	0.15	0.11	0.15	0.23	0.13
Total:	89.57	87.10	87.36	87.65	88.23

Table 5. contd: Garabal Hill Fe-Mg Silicates (Olivine-alteration product)

%						
SiO_2	48.79	42.02	38.65	37.60	35.74	37.17
TiO_2	0.01	-	0.04	0.05	0.02	-
Al_2O_3	1.49	4.75	0.52	0.07	0.17	-
FeO	16.32	19.09	27.23	28.05	26.17	26.66
MgO	21.91	10.46	18.52	19.95	21.50	19.81
Cao	0.44	0.28	0.56	0.67	0.91	0.55
MnO	0.05	0.08	0.13	0.11	0.14	0.10
Na_2O	0.09	0.08	0.20	0.07	0.09	0.08
K_2O	0.11	0.09	0.25	0.10	0.01	0.07
Total:	89.21	88.85	86.10	86.67	84.75	84.44

Table 6: Clinopyroxenes (and orthopyroxene) - Arran

% SPECIMEN	53	53	53	43	53
$Si0_2$	52.84	51.94	52.75	52.69	53.71
$Ti0_2$	0.12	0.10	0.16	0.14	0.21
Al_20_3	1.14	0.39	0.61	0.48	0.60
Fe0	12.99	13.91	11.07	13.59	11.08
Mg0	11.70	10.35	13.31	11.00	13.29
Ca0	20.85	21.49	21.02	20.74	21.01
Mn0	0.51	0.58	0.53	0.68	0.50
Na_20	-	-	-	0.25	0.22
K_20	0.05	0.02	0.03	0.02	-
Total:	100.19	98.77	99.47	99.59	100.62
Si	1.99	2.00	1.99	1.99	2.03
Al	0.01	-	0.01	0.01	-
Al	0.04	0.02	0.02	0.01	0.03
Ti	-	-	-	-	0.01
Fe	0.41	0.45	0.35	0.43	0.35
Mg	0.66	0.60	0.75	0.62	0.75
Ca	0.84	0.89	0.85	0.84	0.85
Mn	0.01	0.02	0.01	0.02	0.01
0	6	6	6	6	6

Table 6. contd: Clinopyroxenes (and orthopyroxene) - Arran

% SPECIMEN	53	45	45	53	53
$Si0_2$	53.65	54.40	53.50	50.45	51.09
$Ti0_2$	0.21	0.13	0.22	0.10	0.37
Al_20_3	0.69	0.82	2.34	0.25	0.75
Fe0	10.85	12.36	12.34	19.83	26.88
Mg0	12.33	11.82	12.70	6.79	16.13
Ca0	21.52	20.18	19.47	20.54	1.72
Mn0	0.47	0.59	0.51	0.70	0.96
Na_20	0.06	-	-	-	0.14
K_20	-	-	-	0.01	0.01
Total:	99.76	100.30	100.08	98.67	98.05
Si	2.00	2.03	1.98	2.00	1.90
Al	-	-	0.02	-	0.03
Al0	0.03	0.04	0.08	0.01	-
Ti	0.01	-	0.01	-	0.01
Fe	0.34	0.39	0.38	0.66	0.34
Mg	0.69	0.66	0.70	0.40	0.89
Ca	0.86	0.81	0.77	0.87	0.07
Mn	0.01	0.02	0.01	0.02	0.03
0	6	6	6	6	6

Table 7: <u>Orthopyroxenes - Garabal Hill</u>

% SPECIMEN	GH7	GH7	GH7	GH14
$Si0_2$	58.86	55.98	58.60	55.21
$Ti0_2$	0.14	0.31	0.01	0.24
Al_20_3	1.24	1.62	1.20	1.25
Fe0	16.67	15.85	14.20	17.90
Mg0	24.28	22.05	25.27	24.21
Ca0	1.19	3.14	0.63	1.24
Mn0	0.46	0.44	0.36	0.53
Na_20	0.02	0.01	-	0.01
Total:	100.86	99.40	100.28	100.58
Si	2.07	2.00	2.08	2.04
Al	0.05	0.07	0.05	0.06
Ti	-	0.01	-	0.01
Fe	0.51	0.48	0.42	0.54
Mg	1.32	1.18	1.34	1.34
Ca	0.05	0.12	0.02	0.05
Mn	0.01	0.01	0.01	0.01
0	6	6	6	6

Table 8: <u>Clinopyroxenes - Garabal Hill</u>

% SPECIMEN	GH7	GH7	GH7	GH14	GH14
SiO_2	52.56	53.74	54.07	53.66	51.75
TiO_2	0.86	0.63	0.41	0.71	0.74
Al_2O_3	3.11	2.61	2.11	2.11	1.90
FeO	7.76	8.19	8.15	8.76	10.38
MgO	13.76	13.37	13.88	15.02	14.32
CaO	21.24	21.43	21.54	18.37	20.00
MnO	0.31	0.27	0.27	0.27	0.31
Na_2O	0.49	0.43	0.44	0.27	0.35
Total:	100.09	100.66	100.73	99.27	99.75
Si	2.00	2.04	2.04	1.95	1.9-
Al	-	-	-	0.05	0.01
Al	0.14	0.12	0.09	0.04	0.08
Ti	0.03	0.02	0.01	0.02	0.02
Fe	0.25	0.25	0.25	0.27	0.32
Mg	0.77	0.76	0.78	0.81	0.79
Ca	0.85	0.87	0.87	0.72	0.80
Mn	0.01	0.01	0.01	0.01	0.01
Na	0.04	0.03	0.03	0.02	0.02
O	6	6	6	6	6

Table 9a: <u>Hornblendes - Arran</u>

% Specimen	BA1	BA1	BA1	BA1	58
$Si0_2$	48.72	47.36	47.07	47.59	47.55
$Ti0_2$	1.43	1.04	1.08	0.98	1.33
Al_20_3	5.73	5.44	5.31	5.09	5.22
Fe0	16.45	16.44	16.31	16.85	19.26
Mg0	12.30	12.90	12.82	11.64	10.42
Ca0	11.04	10.85	10.86	10.95	11.09
Mn0	0.32	0.39	0.42	0.45	0.39
Na_20	0.78	0.69	0.94	1.19	1.27
K_20	0.44	0.36	0.35	0.33	0.52
Total:	97.23	95.46	95.16	95.07	97.03
Si	7.23	7.18	7.25	7.27	7.21
Al	0.77	0.82	0.75	0.73	0.79
Al	0.23	0.15	0.20	0.19	0.14
Ti	0.16	0.12	0.12	0.11	0.15
Fe	2.04	2.08	2.08	2.15	2.44
Mg	2.72	2.91	2.91	2.65	2.35
Mn	0.04	0.05	0.05	0.06	0.05
Ca	1.76	1.76	1.77	1.79	1.80
Na	0.23	0.20	0.28	0.35	0.37
K	0.08	0.07	0.07	0.06	0.10
0	23	23	23	23	23

Table 9a. contd: <u>Hornblendes - Arran</u>

% Specimen	58	BA1	43	58	58	58
$Si0_2$	47.31	47.88	45.18	47.31	48.10	47.45
$Ti0_2$	1.44	1.62	1.53	1.61	1.51	1.85
Al_20_3	5.43	5.81	6.46	6.16	5.72	6.91
Fe0	19.51	16.01	16.73	17.16	16.59	16.50
Mg0	9.91	11.82	10.77	12.13	12.70	10.73
Ca0	11.40	10.69	11.55	10.84	11.12	10.71
Mn0	0.35	0.31	0.46	0.28	0.31	0.27
Na_20	1.08	0.93	2.61	1.48	1.49	1.33
K_20	0.54	0.50	0.59	0.55	0.49	0.62
Total:	96.97	95.56	95.88	97.52	98.02	96.36
Si	7.19	7.30	6.94	7.07	7.12	7.13
Al	0.81	0.70	1.06	0.93	0.88	0.87
Al	0.16	0.34	0.11	0.16	0.12	0.35
Ti	0.16	0.19	0.18	0.18	0.17	0.21
Fe	2.48	2.04	2.15	2.14	2.05	2.07
Mg	2.24	2.66	2.47	2.70	2.80	2.40
Mn	0.04	0.04	0.06	0.03	0.04	0.03
Ca	1.86	1.74	1.90	1.74	1.76	1.72
Na	0.32	0.28	0.78	0.43	0.43	0.39
K	0.10	0.10	0.12	0.10	0.09	0.12
0	23	23	23	23	23	23

Table 9b: Hornblendes - Arran

% Specimen	58	BA1	53	53	43
$Si0_2$	46.90	46.32	46.26	46.25	46.43
$Ti0_2$	1.90	1.75	1.93	2.02	2.05
Al_20_3	6.22	7.18	6.70	7.02	9.38
Fe0	15.06	15.44	17.58	15.93	15.10
Mg0	12.96	11.59	10.68	11.82	12.25
Ca0	11.36	11.16	11.18	11.08	11.72
Mn0	0.27	0.27	0.32	0.25	0.27
Na_20	1.32	1.60	1.51	1.73	1.83
K_20	0.54	0.58	0.58	0.60	0.67
Total:	96.54	95.89	96.76	96.69	99.71
Si	7.09	7.00	7.00	6.95	6.74
Al	0.91	1.00	1.00	1.05	1.26
Al	0.20	0.28	0.20	0.19	0.34
Ti	0.22	0.20	0.22	0.23	0.22
Fe	1.90	1.95	2.23	2.00	1.83
Mg	2.70	2.61	2.41	2.65	2.65
Mn	0.04	0.03	0.04	0.03	0.03
Ca	1.84	1.81	1.81	1.78	1.82
Na	0.39	0.47	0.44	0.50	0.52
K	0.10	0.11	0.11	0.11	0.12
0	23	23	23	23	23

Table 9b. contd: Hornblendes - Arran

% Specimen	43	45	58	10	18	10
$Si0_2$	45.10	44.94	46.35	47.56	48.56	49.18
$Ti0_2$	2.10	1.68	2.11	1.93	1.62	1.37
Al_20_3	7.46	7.59	7.23	6.36	6.12	5.51
Fe0	14.86	15.47	15.66	15.45	16.22	17.54
Mg0	11.74	12.45	12.77	11.40	11.46	12.42
Ca0	11.81	11.02	11.14	11.86	11.41	10.89
Mn0	0.27	0.29	0.26	0.34	0.40	0.37
Na_20	2.03	2.09	1.71	1.19	0.66	1.61
K_20	0.66	0.55	0.60	0.63	0.53	0.51
Total:	96.02	96.08	97.83	96.71	96.97	99.39
Si	6.90	6.85	6.88	7.18	7.21	7.19
Al	1.10	1.15	1.12	0.82	0.79	0.81
Al	0.25	0.22	0.14	0.31	0.29	0.14
Ti	0.24	0.19	0.24	0.22	0.18	0.15
Fe	1.90	1.99	1.94	1.95	2.02	2.14
Mg	2.65	2.85	2.82	2.54	2.54	2.71
Mn	0.03	0.04	0.03	0.04	0.04	0.04
Ca	1.94	1.81	1.77	1.92	1.82	1.71
Na	0.60	0.62	0.49	0.35	0.23	0.46
K	0.13	0.11	0.11	0.12	0.10	0.10
0	23	23	23	23	23	23

Table 9c. contd: Hornblendes - Arran

% Specimen	10	10	10	18	10	BA1
$Si0_2$	47.32	48.32	47.85	48.24	47.90	45.94
$Ti0_2$	1.50	1.52	1.37	1.44	1.57	1.68
Al_20_3	5.72	6.50	5.85	5.89	6.55	7.59
Fe0	16.69	17.21	17.15	16.91	16.66	15.47
Mg0	11.91	10.34	10.39	10.59	10.83	12.45
Ca0	10.45	10.50	10.79	10.33	10.69	11.02
Mn0	0.32	0.35	0.36	0.33	0.36	0.29
Na_20	1.62	1.22	1.61	1.45	1.21	2.09
K_20	0.74	0.72	0.78	0.69	0.76	0.55
Total:	96.81	96.69	96.15	95.88	96.52	97.08
Si	7.06	7.22	7.13	7.18	7.23	6.75
Al	0.94	0.78	0.87	0.82	0.77	1.25
Al	0.10	0.23	0.20	0.26	0.26	0.12
Ti	0.17	0.18	0.16	0.17	0.19	0.19
Fe	2.15	2.24	2.23	2.19	2.19	1.99
Mg	2.74	2.40	2.41	2.45	2.31	2.85
Mn	0.04	0.04	0.05	0.04	0.05	0.04
Ca	1.72	1.75	1.80	1.72	1.80	1.81
Na	0.48	0.37	0.49	0.44	0.37	0.62
K	0.15	0.14	0.16	0.14	0.15	0.11
0	23	23	23	23	23	23

Table 9c: Hornblendes - Arran

% Specimen	43	43	43	43	43
$Si0_2$	47.98	46.49	46.52	47.01	48.14
$Ti0_2$	1.19	2.03	1.69	1.96	1.34
Al_20_3	6.17	6.93	6.83	6.98	6.57
Fe0	16.11	15.05	15.63	15.45	16.71
Mg0	12.07	11.75	10.87	10.89	10.81
Ca0	11.26	11.74	11.71	11.40	11.53
Mn0	0.39	9.28	0.32	0.29	0.32
Na_20	1.36	1.95	2.18	2.23	0.84
K_20	0.45	0.66	0.60	0.67	0.53
Total:	96.97	96.89	96.36	96.87	96.80
Si	7.20	6.85	6.91	6.86	7.27
Al	0.80	1.15	1.09	1.14	0.73
Al	0.15	0.14	0.16	0.14	0.28
Ti	0.14	0.24	0.20	0.23	0.16
Fe	2.11	1.98	2.03	2.01	2.03
Mg	2.58	2.52	2.51	2.53	2.48
Mn	0.05	0.04	0.04	0.04	0.04
Ca	1.89	1.98	1.95	1.90	1.91
Na	0.41	0.60	0.66	0.67	0.25
K	0.09	0.13	0.12	0.13	0.10
0	23	23	23	23	23

Table 9 d: Hornblendes - Arran

% SPECIMEN	BA1	10	10	58	10	58
SiO_2	45.52	49.06	48.86	48.18	48.86	48.37
$Ti0_2$	1.91	1.22	1.45	1.66	1.53	1.35
Al_20_3	7.70	6.57	6.40	6.26	5.82	5.30
Fe0	15.52	16.27	17.15	17.19	16.61	16.31
Mg0	12.37	9.99	9.59	12.29	12.76	13.53
Ca0	10.56	11.24	11.49	11.17	11.30	11.10
Mn0	0.26	0.51	0.46	0.36	0.38	0.46
Na_20	2.78	0.53	0.27	1.45	1.47	1.23
K_20	0.60	0.53	0.56	0.56	0.50	0.53
Total:	97.23	95.91	96.21	99.11	99.22	98.17
Si	6.69	7.43	7.45	6.92	7.10	7.01
Al	1.31	0.57	0.55	1.08	0.90	0.99
Al	0.09	0.42	0.42	0.14	0.10	0.16
Ti	0.22	0.14	0.17	0.18	0.17	0.18
Fe	2.00	2.06	2.06	2.06	1.99	2.15
Mg	2.83	2.26	2.18	2.63	2.73	2.40
Mn	0.03	0.05	0.05	0.04	0.04	0.04
Ca	1.74	1.82	1.88	1.72	1.74	1.85
Na	0.83	0.16	0.08	0.40	0.41	0.22
K	0.12	0.10	0.11	0.10	0.09	0.09
0	23	23	23	23	23	23

Table 10a: Hornblendes (Pale) - Bolton Hill

% Specimen	BH100	BH100	BH100	BH100	BH100
SiO_2	48.67	48.51	48.02	49.44	48.23
TiO_2	1.00	0.83	0.98	0.87	0.89
Al_2O_3	7.89	8.29	7.49	8.06	7.65
FeO	15.40	15.56	15.51	16.06	14.97
MgO	13.56	13.13	13.76	12.84	13.32
CaO	10.72	10.65	10.00	10.59	10.65
MnO	0.47	0.42	0.49	0.51	0.42
Na_2O	1.08	1.05	1.06	0.95	1.09
K_2O	0.31	0.35	0.27	0.32	0.24
Total:	99.10	98.79	97.58	98.64	97.56
Si	6.85	6.81	6.76	6.80	6.83
Al	1.15	1.19	1.20	1.20	1.17
Al	0.16	0.14	-	0.09	0.05
Ti	0.11	0.08	0.10	0.09	0.09
Fe	1.81	1.77	1.76	1.93	1.69
Mg	2.84	2.81	2.88	2.73	2.92
Mn	0.05	0.04	0.05	0.05	0.04
Ca	1.62	1.60	1.55	1.60	1.54
Na	0.28	0.28	0.28	0.25	0.29
K	0.05	0.06	0.05	0.06	0.04
0	23	23	23	23	23

Table 10a. contd: Hornblendes (Pale) - Bolton Hill

% Specimen	BH100	BH100	BH103	BH103	BH103	BH103
SiO_2	48.26	48.11	48.11	50.22	48.31	48.26
TiO_2	0.90	0.71	0.67	0.61	0.89	0.77
Al_2O_3	8.88	7.71	8.30	6.40	8.08	7.69
FeO	14.98	15.19	17.26	16.88	16.98	17.40
MgO	13.63	13.26	10.57	11.95	11.56	11.66
CaO	10.92	10.81	10.97	10.55	11.46	11.32
MnO	0.42	0.44	1.18	1.08	1.07	1.10
Na_2O	0.84	0.95	1.06	0.67	0.94	1.11
K_2O	0.28	0.33	0.25	0.18	0.30	0.25
Total:	99.11	97.51	98.37	98.54	99.59	99.56
Si	6.84	6.80	6.80	7.06	6.94	6.95
Al	1.16	1.20	1.20	0.94	1.06	1.05
Al	0.25	0.03	0.18	0.12	0.31	0.25
Ti	0.09	0.07	0.07	0.06	0.10	0.08
Fe	1.70	1.74	2.04	1.98	2.04	2.10
Mg	2.95	2.98	2.23	2.50	2.48	2.50
Mn	0.04	0.04	0.12	0.11	0.11	0.11
Ca	1.72	1.66	1.66	1.59	1.76	1.75
Na	0.22	0.25	0.29	0.18	0.26	0.31
K	0.05	0.06	0.05	0.03	0.05	0.05
0	23	23	23	23	23	23

Table 10b: Hornblendes (Pale) - Bolton Hill

% Specimen	BH136	BH136	BH136	BH136	BH136
SiO_2	48.33	48.74	48.08	48.21	47.85
TiO_2	1.02	0.51	1.13	1.16	1.13
Al_2O_3	8.10	7.54	7.90	8.03	7.94
FeO	17.63	18.57	18.76	18.31	18.03
MgO	11.85	11.98	11.88	11.13	11.53
CaO	10.51	11.01	10.50	10.69	10.65
MnO	0.44	0.39	0.46	0.44	0.44
Na_2O	1.07	0.57	1.22	1.15	1.24
K_2O	0.22	0.17	0.16	0.18	0.16
Total:	99.17	99.48	100.09	99.30	98.97
Si	6.90	7.13	7.00	6.92	6.84
Al	1.10	0.87	1.00	1.08	1.16
Al	0.26	0.43	0.35	0.26	0.18
Ti	0.11	0.06	0.12	0.13	0.12
Fe	2.11	2.27	2.28	2.20	2.16
Mg	2.52	2.61	2.58	2.38	2.46
Mn	0.04	0.04	0.05	0.04	0.04
Ca	1.61	1.68	1.64	1.65	1.63
Na	0.30	0.16	0.34	0.32	0.34
K	0.04	0.03	0.03	0.03	0.03
0	23	23	23	23	23

Table 10b. contd: Hornblendes (Pale) - Bolton Hill

% Specimen	BH136	BH136	BH102	BH102	BH102	BH102
SiO_2	48.94	49.34	47.87	47.42	48.02	47.36
TiO_2	0.96	0.97	0.75	1.02	0.99	0.94
Al_2O_3	7.13	7.66	6.81	7.83	7.18	8.46
FeO	17.82	16.58	18.30	18.42	17.35	18.25
MgO	11.36	11.77	11.51	10.83	10.39	10.47
CaO	10.48	10.14	10.14	9.96	11.05	11.26
MnO	0.43	0.39	0.44	0.45	0.40	0.47
Na_2O	1.04	1.33	0.55	0.40	0.33	0.33
K_2O	0.17	0.17	0.24	0.28	0.18	0.32
Total:	98.33	98.35	96.61	96.71	95.89	97.86
Si	7.11	7.11	6.62	6.51	6.55	6.67
Al	0.89	0.89	1.11	1.27	1.16	1.33
Al	0.33	0.41	-	-	-	0.08
Ti	0.11	0.11	0.08	0.11	0.10	0.10
Fe	2.16	2.20	2.12	2.12	1.98	2.15
Mg	2.42	2.53	2.37	2.22	2.11	2.20
Mn	0.04	0.04	0.04	0.04	0.04	0.05
Ca	1.63	1.57	1.50	1.47	1.62	1.70
Na	0.29	9.37	0.15	0.15	0.09	0.09
K	0.03	0.03	0.04	0.05	0.03	0.06
0	23	23	23	23	23	23

Table 10c: Hornblendes (Dark) - Bolton Hill

% Specimen	BH126	BH126	BH126	BH126	BH126
SiO_2	46.04	47.96	48.27	46.95	46.63
TiO_2	1.03	1.01	1.15	1.06	1.04
Al_2O_3	8.64	7.74	7.91	8.31	7.81
FeO	21.49	20.91	20.38	20.44	22.45
MgO	8.11	9.00	8.82	8.44	9.30
CaO	11.08	10.80	9.81	12.37	9.20
MnO	0.78	0.81	0.78	0.72	0.94
Na_2O	1.08	1.13	1.05	0.94	0.95
K_2O	0.33	0.32	0.28	0.30	0.25
Total:	98.58	99.68	98.45	99.53	98.57
Si	6.68	7.05	7.12	6.85	6.70
Al	1.32	0.95	0.88	1.15	1.30
Al	0.16	0.36	0.42	0.25	0.02
Ti	0.11	0.11	0.12	0.11	0.11
Fe	2.61	2.51	2.48	2.55	2.70
Mg	1.85	1.91	1.84	1.80	1.99
Mn	0.08	0.08	0.08	0.07	0.09
Ca	1.72	1.66	1.47	1.90	1.42
Na	0.30	0.31	0.29	9.26	0.26
K	0.06	0.06	0.05	0.06	0.05
O	23	23	23	23	23

Table 10c. contd: Hornblendes (Dark) - Bolton Hill

% Specimen	BH126	BH113	BH113	BH113	BH128	BH128
SiO_2	46.24	47.73	46.78	46.68	46.26	46.40
TiO_2	1.00	1.40	1.06	1.01	1.08	1.15
Al_2O_3	8.36	7.02	7.12	7.13	7.41	3.61
FeO	21.51	18.52	18.92	18.86	21.00	20.88
MgO	8.35	11.50	10.30	10.32	9.63	8.73
CaO	10.02	10.35	10.35	10.39	9.75	10.69
MnO	0.94	0.48	0.35	0.48	0.83	0.70
Na_2O	0.87	1.91	1.15	1.15	0.98	1.24
K_2O	0.33	0.11	0.12	0.11	0.22	0.39
Total:	97.62	99.02	96.15	96.13	97.16	98.79
Si	6.60	7.04	7.10	7.09	6.85	6.83
Al	1.40	0.96	0.90	0.91	1.15	1.17
Al	-	0.26	0.37	0.37	0.09	0.30
Ti	0.11	0.16	0.12	0.12	0.12	0.13
Fe	2.57	2.28	2.40	2.40	2.59	2.53
Mg	1.97	2.53	2.33	2.34	2.13	1.89
Mn	0.09	0.09	0.07	0.06	0.08	0.07
Ca	1.53	1.63	1.68	1.69	1.48	1.66
Na	0.24	0.55	0.34	0.34	0.27	0.43
K	0.06	0.02	0.02	0.02	0.04	0.07
O	23	23	23	23	23	23

Table 10d: Hornblendes (Dark) - Bolton Hill

% Specimen	BH128	BH128	BH128	BH128	BH128
SiO_2	46.04	46.24	46.17	46.56	46.57
TiO_2	0.94	0.92	0.96	1.30	1.32
Al_2O_3	8.30	8.39	8.01	7.27	7.21
FeO	21.14	21.04	20.96	19.61	21.01
MgO	9.09	8.99	9.11	10.76	10.16
CaO	10.44	10.56	10.93	10.45	10.04
MnO	0.82	0.81	0.79	0.64	0.84
Na_2O	1.16	1.18	1.06	1.14	0.93
K_2O	0.40	0.41	0.39	0.22	0.22
Total:	98.32	98.54	98.38	97.95	98.30
Si	6.75	6.79	6.77	6.79	6.80
Al	1.25	1.21	1.23	1.21	1.20
Al	0.16	0.22	0.13	0.01	0.02
Ti	0.10	0.10	0.10	0.14	0.14
Fe	2.65	2.60	2.63	2.44	2.53
Mg	1.96	1.94	1.96	2.29	2.18
Mn	0.08	0.08	0.08	0.06	0.08
Ca	1.62	1.64	1.69	1.60	1.55
Na	0.32	0.33	0.30	0.31	0.26
K	0.07	0.08	0.07	0.04	0.04
0	23	23	23	23	23

Table 10d. contd: Hornblendes (Dark) - Bolton Hill

% Specimen	BH128	BH126	BH126	BH128	BH128
SiO_2	46.73	48.17	47.93	45.58	46.08
TiO_2	0.93	1.00	1.07	0.80	0.92
Al_2O_3	7.40	8.65	8.07	8.25	7.11
FeO	21.23	20.83	20.93	20.21	20.67
MgO	9.01	8.69	9.06	9.29	9.30
CaO	10.86	11.41	10.29	10.72	10.08
MnO	0.84	0.70	0.81	0.95	0.90
Na_2O	0.99	0.20	0.59	0.95	0.90
K_2O	0.35	0.24	0.22	0.31	0.32
Total:	98.34	99.89	98.97	96.85	96.16
Si	6.73	7.05	7.09	6.72	6.75
Al	1.27	0.95	0.91	1.28	1.24
Al	0.05	0.55	0.54	0.09	0.03
Ti	0.12	0.11	0.12	0.09	0.10
Fe	2.65	2.55	2.59	2.58	2.62
Mg	1.99	1.90	2.00	2.15	2.14
Mn	0.09	0.07	0.08	0.07	0.08
Ca	1.69	1.89	1.63	1.62	1.59
Na	0.28	0.06	0.17	0.26	0.24
K	0.06	0.05	0.04	0.06	0.06
0	23	23	23	23	23

Table 11: <u>Cummingtonites - Bolton Hill</u>

% SPECIMEN	BH126	BH126	BH128	BH128
$Si0_2$	53.89	54.58	51.93	50.12
$Ti0_2$	0.29	0.29	0.38	0.33
Al_20_3	1.92	1.70	2.77	3.76
Fe0	28.03	27.88	26.32	25.91
Mg0	12.99	13.24	13.18	13.32
Ca0	1.59	1.12	2.91	2.76
Mn0	1.73	1.73	1.11	1.54
Na_20	-	-	0.40	0.02
K_20	0.02	-	0.04	0.02
Total:	100.46	100.54	99.04	98.22
Si	7.82	7.88	7.68	7.50
Al	0.18	0.12	0.32	0.50
Al	0.15	0.17	0.16	0.16
Ti	0.03	0.03	0.04	0.04
Fe	3.40	3.37	3.26	3.24
Mg	2.81	2.85	2.91	2.97
Mn	0.17	0.17	0.14	0.20
Ca	0.25	0.17	0.46	0.44
Na	-	-	0.11	0.13
K	-	-	0.01	-
0	23	23	23	23

Table12a: Hornblendes - Garabal Hill

% Specimen	GH3	GH3	GH3	GH3	GHi4
$Si0_2$	55.34	54.06	51.37	51.18	51.10
$Ti0_2$	0.96	0.98	1.06	1.07	0.34
Al_20_3	5.59	5.72	6.03	5.95	5.92
Fe0	15.03	13.12	15.43	13.44	11.07
Mg0	10.70	11.49	11.74	11.45	16.00
Ca0	10.34	10.81	10.95	11.83	11.57
Mn0	0.40	0.34	0.38	0.36	0.16
Na_20	1.04	1.01	1.08	1.11	0.40
K_20	0.55	0.57	0.58	0.60	0.36
Total:	99.95	98.10	98.62	96.99	96.92
Si	7.79	7.72	7.44	7.49	7.37
Al	0.21	0.28	0.56	0.51	0.63
Al	0.72	0.68	0.47	0.52	0.38
Ti	0.10	0.11	0.12	0.12	0.04
Fe	1.77	1.57	1.87	1.64	1.34
Mg	2.25	2.45	2.53	2.50	3.44
Mn	0.05	0.04	0.05	0.04	0.02
Ca	1.56	1.65	1.70	1.85	1.79
Na	0.28	0.28	0.30	0.32	0.11
K	0.10	0.10	0.11	0.11	0.07
0	23	23	23	23	23

Table 12a. contd: Hornblendes -Garabal Hill

% Specimen	GH3	GH3	GH3	GHi4	GH21	GH21
$Si0_2$	53.32	51.33	51.29	50.48	49.58	49.30
$Ti0_2$	0.40	0.29	0.43	0.75	1.01	0.65
Al_20_3	4.04	6.57	6.85	6.38	6.26	5.44
Fe0	12.76	12.56	13.07	10.94	14.09	15.12
Mg0	16.15	13.75	12.90	14.77	14.12	12.21
Ca0	10.87	10.93	10.97	11.98	11.62	11.96
Mn0	0.38	0.33	0.39	0.19	0.28	0.50
Na_20	0.91	1.01	0.53	0.28	0.96	0.66
K_20	0.22	0.20	0.25	0.39	0.50	0.44
Total:	99.05	96.97	96.68	96.16	98.42	96.28
Si	7.56	7.49	7.41	7.35	7.19	7.35
Al	0.44	0.51	0.59	0.65	0.81	0.65
Al	0.24	0.63	0.65	0.44	0.26	0.31
Ti	0.04	0.03	0.05	0.08	0.11	0.07
Fe	1.51	1.57	1.64	1.33	1.71	1.89
Mg	3.42	3.07	2.89	3.20	3.05	2.71
Mn	0.05	0.04	0.05	0.02	0.03	0.06
Ca	1.65	1.76	1.77	1.87	1.81	1.91
Na	0.25	0.29	0.15	0.08	0.27	0.19
K	0.04	0.04	0.05	0.07	0.09	0.08
0	23	23	23	23	23	23

Table 12b: Hornblendes - Garabal Hill

% Specimen	GH21	GH3	GH3	GH14	GH14
$Si0_2$	49.53	49.96	48.86	49.63	48.57
$Ti0_2$	0.70	0.78	0.68	0.81	1.20
Al_20_3	5.56	5.33	5.75	7.05	8.15
Fe0	15.54	14.34	14.09	11.04	11.47
Mg0	12.42	12.66	14.45	15.02	14.42
Ca0	11.28	10.50	10.65	11.88	12.05
Mn0	0.55	0.38	0.39	0.16	0.18
Na_20	1.00	1.33	1.58	0.41	0.59
K_20	0.40	0.47	0.41	0.40	0.55
Total:	96.98	95.75	96.86	96.40	97.18
Si	7.34	7.44	7.22	7.22	7.05
Al	0.66	0.56	0.78	0.78	0.95
Al	0.31	0.37	0.22	0.43	0.44
Ti	0.08	0.09	0.08	0.09	0.13
Fe	1.93	1.78	1.74	1.34	1.39
Mg	2.74	2.81	3.18	3.26	3.12
Mn	0.07	0.05	0.05	0.02	0.02
Ca	1.79	1.67	1.69	1.85	1.87
Na	0.29	0.38	0.45	0.12	0.17
K	0.08	0.09	0.08	0.07	0.11
0	23	23	23	23	23

Table 12b. contd: Hornblendes - Garabal Hill

% Specimen	GH21	GH21	GH3	GH21	GH3	GH3
$Si0_2$	48.73	48.63	48.61	48.02	47.15	47.71
$Ti0_2$	0.97	0.70	0.68	1.03	1.12	1.14
Al_20_3	6.35	6.15	6.46	6.75	8.09	7.79
Fe0	13.81	16.04	13.88	14.11	15.15	15.49
Mg0	13.81	12.57	14.38	14.58	13.65	13.13
Ca0	11.67	11.35	10.86	11.59	10.28	10.63
Mn0	0.26	0.45	0.33	0.19	0.40	0.39
Na_20	0.90	1.11	1.2	0.94	1.59	1.05
K_20	0.56	0.48	0.41	0.43	0.59	0.58
Total:	97.06	97 48	96.83	97.64	98.02	97.01
Si	7.17	7.20	7.16	7.04	6.93	7.01
Al	0.83	0.80	0.84	0.96	1.07	0.99
Al	0.27	0.27	0.28	0.21	0.33	0.36
Ti	0.11	0.08	0.08	0.11	0.12	0.13
Fe	1.70	1.99	1.71	1.73	1.86	1.90
Mg	3.03	2.78	3.16	3.19	2.99	2.87
Mn	0.03	0.06	0.04	0.02	0.05	0.05
Ca	1.84	1.80	1.72	1.82	1.62	1.67
Na	0.26	0.32	0.35	0.27	0.45	0.30
K	0.10	0.09	0.08	0.08	0.11	0.11
0	23	23	23	23	23	23

Table 12c: Hornblendes - Garabal Hill

% Specimen	GH3	GH14	GH14	GH3	GH3
SiO_2	47.20	46.62	49.97	46.22	46.21
TiO_2	1.31	2.02	0.35	1.65	1.39
Al_2O_3	6.57	9.14	5.84	9.27	7.14
FeO	14.35	11.46	10.03	15.54	14.98
MgO	12.68	13.63	17.03	12.08	11.86
CaO	12.07	11.59	11.49	10.51	11.97
MnO	0.39	0.13	0.19	0.42	0.42
Na_2O	1.12	0.81	0.94	1.41	1.28
K_2O	0.72	0.77	0.34	0.74	0.73
Total:	96.41	96.71	96.18	97.84	95.98
Si	7.06	6.87	7.27	6.83	6.98
Al	0.94	1.13	0.73	1.17	1.02
Al	0.22	0.46	0.27	0.44	0.25
Ti	0.15	0.22	0.04	0.18	0.16
Fe	1.80	1.41	1.22	1.92	1.89
Mg	2.83	2.99	3.69	2.66	2.67
Mn	0.05	0.02	0.02	0.05	0.05
Ca	1.93	1.83	1.79	1.66	1.94
Na	0.32	0.23	0.27	0.40	0.37
K	0.14	0.15	0.06	0.14	0.14
O	23	23	23	23	23

Table12c. contd: Hornblendes - Garabal Hill

% Specimen	GH3	GH3	GH3	GH3	GH3	GH3
SiO_2	46.48	45.73	45.41	45.42	45.09	44.74
TiO_2	1.27	1.45	1.41	1.40	2.06	2.01
Al_2O_3	6.28	7.67	7.27	7.54	9.73	10.23
FeO	15.27	15.45	15.03	14.88	15.03	15.73
MgO	11.90	11.67	12.38	12.19	13.14	12.02
CaO	11.79	11.82	12.10	12.18	10.44	10.49
MnO	0.38	0.40	0.43	0.45	0.44	0.45
Na_2O	1.32	1.25	1.23	1.32	1.50	1.32
K_2O	0.79	0.72	0.73	0.73	0.62	0.85
Total:	96.12	96.23	95.98	96.11	98.05	97.84
Si	7.01	6.91	6.88	6.87	6.65	6.64
Al	0.99	1.09	1.12	1.13	1.35	1.36
Al	0.25	0.27	0.18	0.21	0.34	0.43
Ti	0.15	0.17	0.16	0.16	0.23	0.22
Fe	1.93	1.95	1.90	1.88	1.85	1.95
Mg	2.68	2.63	2.80	2.75	2.89	2.66
Mn	0.05	0.05	0.05	0.06	0.06	0.06
Ca	1.91	1.91	1.96	1.97	1.65	1.67
Na	0.39	0.37	0.36	0.39	0.43	0.38
K	0.14	0.15	0.14	0.14	0.12	0.16
O	23	23	23	23	23	23

Table 12d: Hornblendes - Garabal Hill

% Specimen	GH7	GH3	GH3	GH3	GH3
SiO_2	44.51	44.22	44.49	43.55	43.94
TiO_2	2.89	1.50	1.92	1.85	1.92
Al_2O_3	9.22	9.08	8.49	9.55	8.43
FeO	12.90	15.62	15.15	15.65	15.43
MgO	12.55	11.73	11.67	11.06	11.26
CaO	11.72	12.13	12.02	12.03	11.98
MnO	0.18	0.47	0.51	0.53	0.53
Na_2O	2.18	1.33	1.47	1.47	1.58
K_2O	0.71	0.83	0.89	0.88	0.94
Total:	96.86	96.91	96.61	96.57	96.01
Si	6.63	6.65	6.72	6.68	6.70
Al	1.37	1.35	1.28	1.32	1.30
Al	0.25	0.26	0.23	0.31	0.22
Ti	0.32	0.17	0.22	0.21	0.22
Fe	1.61	1.99	1.91	2.01	1.97
Mg	2.79	2.67	2.63	2.53	2.56
Mn	0.02	0.06	0.06	0.07	0.07
Ca	1.87	1.98	1.95	1.98	1.96
Na	0.63	0.39	0.43	0.44	0.47
K	0.09	0.13	0.12	0.13	0.10
0	23	23	23	23	23

Table12d. contd: Hornblendes - Garabal Hill

% Specimen	GH7	GH3	GH3	GH3	GH7	GH7
SiO_2	43.01	43.24	45.82	42.80	42.27	42.13
TiO_2	2.29	1.85	1.20	1.89	4.31	3.91
Al_2O_3	12.14	9.41	7.99	9.81	11.77	11.71
FeO	14.45	16.47	14.91	15.73	11.66	11.77
MgO	11.49	10.88	12.31	12.49	12.58	12.56
CaO	11.99	12.14	12.11	10.47	12.15	11.92
MnO	0.18	0.43	0.48	0.43	0.13	0.14
Na_2O	2.26	1.46	1.11	1.55	2.02	2.02
K_2O	0.18	1.04	0.71	0.84	0.78	0.83
Total:	97.98	96.92	96.64	96.01	97.67	96.99
Si	6.49	6.57	6.95	6.51	6.24	6.26
Al	1.51	1.43	1.05	1.49	1.76	1.74
Al	0.65	0.26	0.30	0.27	0.29	0.31
Ti	0.23	0.21	0.14	0.22	0.48	0.44
Fe	1.82	2.09	1.89	2.00	1.44	1.46
Mg	2.58	2.47	2.78	2.83	2.77	2.78
Mn	0.02	0.05	0.06	0.06	0.02	0.02
Ca	1.94	1.98	1.97	1.81	1.92	1.90
Na	0.66	0.43	0.33	0.46	0.58	0.58
K	0.04	0.20	0.14	0.16	0.15	0.16
0	23	23	23	23	23	23

Table12e: Hornblendes - Garabal Hill

% Specimen	GH14	GH14	GH14	GH7	GH14
SiO_2	42.94	42.38	42.79	41.84	41.76
TiO_2	3.96	3.64	4.40	4.29	3.86
Al_2O_3	11.35	11.50	10.65	11.85	11.35
FeO	12.09	12.71	12.17	11.65	13.99
MgO	11.41	10.98	11.36	12.39	11.99
CaO	11.85	11.99	11.58	12.15	11.81
MnO	0.14	0.15	0.14	0.13	0.17
Na_2O	1.58	1.86	1.80	2.01	1.52
K_2O	1.09	1.14	1.17	0.77	1.20
Total:	96.41	96.35	96.06	97.08	97.65
Si	6.45	6.41	6.47	6.21	6.24
Al	1.55	1.59	1.53	1.79	1.76
Al	0.46	0.46	0.37	0.28	0.24
Ti	0.45	0.41	0.50	0.48	0.43
Fe	1.52	1.61	1.54	1.45	1.75
Mg	2.56	2.48	2.56	2.74	2.67
Mn	0.02	0.02	0.02	0.02	0.02
Ca	1.91	1.94	1.88	1.93	1.89
Na	0.47	0.54	0.53	0.58	0.44
K	0.21	0.22	0.23	0.15	0.23
O	23	23	23	23	23

Table 12e. contd: Hornblendes - Garabal Hill

% Specimen	GH14	GH14	GH3	GH3	GH14
SiO_2	40.98	47.06	43.45	53.54	46.86
TiO_2	4.59	1.48	1.96	1.98	0.79
Al_2O_3	10.98	8.46	9.81	9.40	7.62
FeO	13.05	11.69	15.82	15.45	14.95
MgO	11.91	13.90	11.27	11.15	13.67
CaO	11.52	12.21	11.47	11.74	10.75
MnO	0.17	0.17	0.49	0.53	0.38
Na_2O	1.63	0.55	1.66	1.56	1.10
K_2O	1.22	0.67	0.92	0.89	0.51
Total:	96.05	96.19	96.85	96.24	96.63
Si	6.21	7.01	6.65	6.70	6.96
Al	1.79	0.99	1.35	1.30	1.04
Al	0.17	0.49	0.24	0.22	0.31
Ti	0.52	0.17	0.23	0.23	0.09
Fe	1.65	1.46	2.02	1.99	1.88
Mg	2.69	3.01	2.57	2.55	3.07
Mn	0.02	0.02	0.06	0.07	0.05
Ca	1.87	1.95	1.88	1.94	1.73
Na	0.48	0.16	0.49	0.46	0.32
K	0.24	0.13	0.18	0.17	0.10
O	23	23	23	23	23

Table 13: Biotites - Arran

% SPECIMEN	45	45	45	43	43
SiO_2	38.46	38.37	40.10	38.93	38.82
$Ti0_2$	5.20	4.83	5.00	4.72	4.91
Al_20_3	13.05	12.77	12.96	13.82	13.79
Fe0	19.09	21.26	17.31	11.92	11.98
Mg0	13.11	11.95	13.67	11.92	11.98
Ca0	0.15	0.09	0.03	0.04	0.01
Mn0	0.21	0.27	0.21	0.13	0.12
Na_20	0.53	0.48	0.54	0.36	0.31
K_20	8.55	8.65	8.94	8.97	8.82
Total:	98.35	98.67	98.76	96.80	96.71
Si	5.65	5.68	5.81	5.49	5.48
Al	2.26	2.23	2.21	2.42	2.42
Ti	0.58	0.54	0.54	0.49	0.53
Fe	2.35	2.63	2.10	2.29	2.35
Mg	2.87	2.64	2.95	2.46	2.54
Mn	0.03	0.03	0.03	0.02	0.02
Ca	0.02	0.01	0.01	-	-
Na	0.15	0.14	0.15	0.09	0.08
K	1.60	1.64	1.65	1.85	1.84
0	22	22	22	22	22

Table 14 a: Biotites - Garabal Hill

% SPECIMEN	GH3	GH21	GH21	GH1	GH1	GH1	GH21
SiO_2	36.25	38.00	37.62	37.91	37.98	36.98	37.57
$Ti0_2$	4.67	4.28	4.30	4.29	4.37	2.86	4.26
Al_20_3	11.78	13.78	13.68	13.82	13.95	13.87	14.32
Fe0	20.28	20.18	19.35	20.19	20.82	19.92	19.32
Mg0	10.41	11.00	11.10	11.31	11.18	11.98	11.26
Ca0	0.01	0.02	0.02	0.02	0.03	0.02	-
Mn0	0.23	0.29	0.31	0.30	0.37	0.17	0.26
Na_20	-	0.21	0.17	0.21	0.22	0.15	0.16
K_20	9.11	9.23	9.23	9.27	9.38	8.66	8.96
Total:	92.74	96.99	95.78	97.34	98.30	94.61	96.02
Si	5.74	5.59	5.64	5.54	5.62	5.55	5.64
Al	2.20	2.36	2.30	2.46	2.48	2.31	2.31
Ti	0.56	0.45	0.44	0.48	0.49	0.28	0.44
Fe	2.68	2.35	2.21	2.54	2.61	2.32	2.20
Mg	2.46	2.29	2.26	2.53	2.50	2.28	2.29
Ca	-	-	-	-	-	-	-
Na	-	0.06	0.05	0.08	0.09	0.04	0.04
K	1.84	1.64	1.61	1.83	9.85	1.61	1.66
0	22	22	22	22	22	22	22

Table 14b: <u>Biotites (Metasomatic) - Garabal Hill</u>

% Specimen	GH7	GH7	GH7	GH7	GH7
SiO_2	38.68	38.29	38.43	38.36	38.32
TiO_2	4.63	6.60	5.72	5.03	5.86
Al_2O_3	14.66	14.30	14.61	14.81	14.54
FeO	12.43	13.21	12.94	12.75	12.63
MgO	15.52	14.20	14.53	14.81	14.17
CaO	0.06	0.02	0.06	0.01	-
MnO	0.02	0.04	-	0.04	-
Na_2O	0.49	0.56	0.36	0.40	0.59
K_2O	8.47	8.73	8.84	8.93	8.71
Total:	94.96	95.95	95.49	95.14	94.82
Si	5.65	5.59	5.67	5.63	5.61
Al	2.35	2.24	2.37	2.32	2.34
Ti	0.48	0.66	0.57	0.50	0.60
Fe	1.46	1.67	1.63	1.60	1.68
Mg	3.02	2.82	2.86	3.00	3.06
Mn	-	-	-	-	-
Ca	0.01	-	0.01	-	-
Na	0.12	0.14	0.09	0.10	0.15
K	1.41	1.48	1.49	1.49	1.45
0	22	22	22	22	22

Table 14b. contd: <u>Biotites (Metasomatic) - Garabal Hill</u>

% Specimen	GH7	GH14	GH14	GH14
SiO_2	37.04	38.25	38.17	39.56
TiO_2	4.83	3.19	3.30	3.00
Al_2O_3	15.18	15.22	16.52	16.91
FeO	14.43	13.39	13.29	12.67
MgO	14.82	15.23	15.30	13.67
CaO	0.07	0.02	0.03	0.99
MnO	0.05	0.09	0.09	0.10
Na_2O	0.46	0.91	0.53	0.94
K_2O	9.39	8.70	8.46	7.85
Total:	96.27	95.00	95.42	95.69
Si	5.33	5.63	5.42	5.39
Al	2.58	2.36	2.56	2.61
Ti	0.49	9.32	0.30	0.30
Fe	1.81	1.87	1.76	1.69
Mg	3.29	2.98	3.00	2.87
Mn	-	0.01	0.01	0.01
Ca	0.01	-	-	0.14
Na	0.12	0.23	0.14	0.24
K	1.60	1.46	1.42	1.31
0	22	22	22	22

Table 15: <u>Chlorites - Bolton Hill</u>

% Specimen	BH128	BH128	BH128	BH128	BH128
$Si0_2$	28.36	28.31	28.20	29.23	27.56
$Ti0_2$	3.37	1.53	3.15	1.76	1.91
Al_20_3	14.99	16.55	15.61	15.57	16.77
Fe0	28.28	29.11	28.38	28.66	29.13
Mg0	10.60	10.83	10.51	10.62	10.83
Ca0	2.17	1.12	2.37	1.57	1.34
Mn0	0.42	0.44	0.39	0.46	0.42
Na_20	-	0.03	0.04	0.06	-
K_20	0.20	0.12	0.20	0.26	0.58
Total:	88.39	88.04	88.85	88.19	88.54
Si	6.08	6.08	6.02	6.26	5.92
Al	1.92	1.92	1.98	1.74	2.08
Al	1.87	2.17	1.95	2.19	2.17
Ti	0.54	0.25	0.51	0.28	0.31
Fe	5.07	5.23	5.07	5.13	5.24
Mg	3.39	3.47	3.35	3.39	3.47
Mn	0.08	0.08	0.07	0.08	0.08
Ca	0.50	0.26	0.54	0.36	0.31
Na	-	0.01	0.02	0.03	-
K	0.06	0.03	0.05	0.07	0.16
0	28	28	28	28	28

% Specimen	BH128	BH128	BH128	BH128	BH128	BH126
$Si0_2$	28.58	28.02	27.88	30.62	28.77	28.34
$Ti0_2$	1.72	1.84	2.14	2.50	3.51	3.12
Al_20_3	15.97	16.06	15.55	15.11	16.20	16.07
Fe0	28.17	28.33	27.15	28.17	28.78	28.47
Mg0	11.74	11.24	10.76	9.72	9.75	10.66
Ca0	1.23	1.32	3.42	1.73	1.97	2.08
Mn0	0.49	9.49	9.38	0.39	0.39	0.53
Na_20	-	-	-	0.06	-	-
K_20	0.16	0.17	0.17	0.69	0.12	0.24
Total:	88.06	87 47	87.45	88.99	88.49	89.51
Si	6.12	6.05	6.04	6.47	6.15	6.08
Al	1.88	1.95	1.96	1.53	1.85	1.92
Al	2.15	2.14	2.01	2.24	2.18	2.08
Ti	0.28	0.30	0.35	0.40	0.40	0.51
Fe	5.04	5.12	4.92	4.98	5.14	5.08
Mg	3.74	3.62	3.47	3.06	3.10	3.40
Mn	0.09	0.09	0.07	0.07	0.07	0.08
Ca	0.28	0.31	0.79	0.39	0.45	0.50
Na	-	-	-	0.02	-	-
K	0.04	0.05	0.05	0.19	0.03	0.03
0	28	28	28	28	28	28

Table 16: <u>Allanites</u>

	<u>Arran</u>		<u>Bolton Hill</u>		<u>Garabal Hill</u>	
% Specimen	20	20	BH 228	BH 228	GH 3	GH 3
SiO_2	29.51	29.27	30.34	30.14	31.33	29.68
$Ti0_2$	2.51	2.61	-	-	0.90	1.01
$Th0_2$	0.76	0.26	0.17	0.17	0.60	1.40
$Al_2 0_3$	11.91	11.44	16.16	15.93	11.58	11.69
Fe0	14.44	14.85	12.00	11.28	12.94	11.35
Mg0	0.90	0.99	-	-	1.09	0.98
Ca0	8.92	9.24	11.99	11.64	11.94	10.84
Mn0	0.29	0.34	0.71	0.72	0.37	0.58
Ce ~~Na~~$_20$	12.74	13.26	9.63	9.77	9.62	10.74
La ~~K~~$_20$	7.66	7.88	5.08	5.55	5.34	6.71
Pr$_20_5$	2.88	3.04	2.11	2.22	2.62	2.69
Nd_20_3	5.06	4.70	4.95	5.19	2.47	2.28
Sm_20_3	1.36	1.44	1.51	1.41	1.10	0.99
Gd_20_3	1.64	1.81	1.63	1.70	1.72	1.63
Dy_20_3	-	-	0.20	0.20	-	-
Y_20_3	-	-	0.43	0.46	-	-
Total:	100.58	101.13	96.91	96.39	93.62	92.57

Table 17: Prehnites - Bolton Hill

% SPECIMEN	BH 114	BH 114
SiO_2	46.12	42.86
TiO_2	0.08	0.05
Al_2O_3	20.67	23.63
FeO	3.17	1.70
MgO	0.34	-
CaO	24.90	25.40
MnO	0.04	-
K_2O	0.03	-
Total	95.38	93.64
Si	3.01	2.92
Al	-	0.08
Al	1.69	1.90
Ti	0.01	0.01
Fe	0.19	0.09
Ca	1.94	1.94
O	12	12

APPENDIX 2: WHOLE ROCK ANALYSIS

2:1 Major element analysis

2:1.1 Sample preparation

Samples were collected in order to be of sufficient size to produce a representative chemical analysis after grinding and homogenization, larger samples being necessary for coarser-grained material. Weathered surfaces of specimens were removed.

Rock specimens were reduced to fragments of diameter 6 cm. or less using a hammer or rock splitter. These fragments were then reduced to gravel-sized particles using a jaw crusher, and the total mass of rock was reduced to approximately 150 gm. by taking 1/2, 1/4 or 1/8 fractions for further grinding.

These fractions were ground for 3 minutes in a tungsten carbide-barrelled Tema Mill in order to obtain a flour-grade consistency. A few representative samples were withdrawn after 30 seconds grinding for possible FeO determinations.

Major elements were analyzed by the fusion technique, reducing inter-element effects and eliminating particle size and inhomogeneity effects.

Rock powders were dried at 110°C for one hour to evaporate any adsorbed H_2O^+ before being prepared into glass discs using a modified form of the technique by Norrish & Hutton (1969).

0.75 gm. powder was mixed with (0.75 x 5.33333 gm.) of Johnson Matthey Spectroflux 105 and fused in Pt/Au crucibles at 1100°C for 20 minutes.

After first making good any losses due to evaporation of volatiles by adding more spectroflux, the mixture was poured into graphite moulds and pressed into glass discs.

2:1.2 Standards

The standards used to calibrate for the analyses shown in this work are listed ~~above~~ below, complete with their relevant elemental concentrations (Table 18).

2:1.3 Analytical techniques

Major elements were determined by X-Ray Fluorescence using a Philips PW1400 X-Ray Fluorescence Spectrometer. The concentrations of the samples were averaged over 2 runs. Operating conditions for major elements are tabulated below.

Table 18: XRF Standard Concentrations - Majors

	$Fe_2O_3^T$	Fe_2O_3	FeO	MnO	TiO_2	CaO	K_2O	P_2O_5	SiO_2	Al_2O_3	MgO	Na_2O	H_2O^+	H_2O^-	CO_2
Granite NIM-G	2.02	0.58	1.30	0.021	0.09	0.78	4.99	0.01	75.70	12.09	0.06	3.36	0.49		0.10
Syenite NIM-S	1.40	1.07	0.30	0.01	0.04	0.68	15.35	0.12	63.63	17.34	0.46	0.43	0.22		0.09
Pyroxenite NIM-P	12.76	1.02	10.59	0.22	0.20	2.66	0.09	0.02	51.10	4.18	25.33	0.37	0.26		0.08
Lujavrite NIM-L	9.96	8.74	1.13	0.77	0.48	3,22	5,51	0.06	52.40	13.64	0.28	8.37	2.31		0.17
Dunite NIM-D	16.96	0.71	14.63	0.22	0.02	0.28	0.01	0.01	38.96	0.30	43.51	0.04	0.30		0.40
Norite NIM-N	8.91	0.80	7.30	0.18	0.20	11.50	0.25	0.03	52.64	16.50	7.50	2.46	0.33		0.10
Diabase DNC-1	9.93	1.79	7.32	0.148	0.484	11.49	0.23	0.07	47.15	18.34	10.13	1.89	0.73	0.29	
Shale SCO-1	5.22	4.26	0.86	0.05	0.62	2.64	2,82	0.22	63.39	13.70	2.76	0.95	3.90		2.75
Andesite AGV-1	6.76	4.47	2.06	0.096	1.06	4.94	2.90	0.48	59.25	17.15	1.53	4.25	0.80	1.02	
Granite GS-N	3.75	1.92	1.65	0.056	0.68	2.50	4.63	0.28	65.80	14.67	2.30	3.77	1.02	0.28	0.18
Diorite DR-N	9.70	3.70	5.40	0.22	1.09	7.05	1.70	0.25	52.85	17.52	4.40	2.99	2.22	0.25	0.10
Dunite DTS-1	8.73	1.01	6.95	0.121	0.00	0.14	0.001	0.002	40.47	0.32	49.65	0.018	0.43	0.06	0.07
Rhyolite RGM-1	1.89	0.50	1.24	0.04	0.27	1.15	4.35	0.05	73.47	13.80	0.28	4.12	0.50		0.01
Granite GH	1.34	0.41	0.84	0.05	0.08	0.69	4.76	0.01	75.80	12.50	0.03	3.85	0.46	0.14	0.30
Mica Schist SDC-2	6.85	2.46	3.98	0.12	1.00	1.39	3.24	0.18	66.15	15.75	1.70	2.10	1.70		0.09
Basalt BHVO-1	12.23	2.74	8.55	0.17	2.69	11.33	0.54	0.28	49.90	13.85	7.31	2.29	0.20		0.04
Anorthosite ANG	3.36	0.87	2.24	0.04	0.22	15.90	0.13	0.01	46.30	29.80	1.80	1.63	0.61	0.11	0.13
Phlogopite Mica Mg	9.46	1.98	6.73	0.26	1.63	0.08	10.00	0.01	38.30	15.20	20.40	0.12	2.09	0.31	0.15
Syenite STM-1	5.20	2.89	2.10	0.22	0.13	1.09	4.29	0.16	59.66	18.44	0.10	8.95	1.44		0.02
Basalt BR	12.88	5.58	6.57	0.20	2.60	13.80	1.40	1.04	38.20	10.20	13.28	3.05	2.30	0.50	0.86
Granite GA	2.83	1.36	1.32	0.09	0.38	2.45	4.03	0.12	69.90	14.50	0.95	3.55	0.87	0.09	0.11
Biotite Mica Fe	25.65	4.64	18.91	0.35	2.50	0.43	8.75	0.45	34.40	19.50	4.55	0.30	2.91	0.43	0.19
Basalt BE-N	12.84	5.34	6.74	0.20	2.61	13.87	1.39	1.05	38.20	10.07	13.15	3.18	2.24	0.50	0.74
Peridotite PCC-1	8.34	2.72	5.06	0.119	0.014	0.52	0.005	0.002	41.88	0.74	43.23	0.027	4.71	0.42	0.15
Granite MA-N	0.47	0.13	0.31	0.04	0.01	0.59	3.18	1,39	66.60	17.62	0.04	5.84	1.08	0.21	0.13
Grandiorite GSP-1	4.32	1.75	2.31	0.04	0.656	2.04	5.51	0.28	67.37	15.16	0.99	2.80	0.53	0.08	0.11
Basalt BCR-1	13.46	3.59	8.88	0.182	2.22	6.95	1.69	0.37	54.35	13.63	3.45	3.27	0.78	0.78	
Gabbro MRG-1	17.82	8.26	8.63	0.17	3.69	14.77	0.18	0.06	39.32	8.50	13.49	0.71	0.98		1.00

Table 18 contd:

XRF Standard Concentrations - Majors

	$Fe_2O_3^T$	Fe_2O_3	FeO	MnO	TiO_2	CaO	K_2O	P_2O_5	SiO_2	Al_2O_3	MgO	Na_2O	H_2O^+	H_2O^-	CO_2
Syenite SY2	6.28	2.28	6.62	0.32	0.14	7.98	4.48	0.43	60.10	12.12	2.70	4.34	0.43		0.46
Synth. Glass VS-N	4.14			0.10	1.08	4.35	8.12	0.09	36.45	59.20	0.04	0.04	0.90	0.15	0.62
Kyanite DT-N	0.66	0.55	0.10	0.008	1.40	0.04	0.12	0.09	36.45	59.20	0.04	0.04	0.90	0.15	0.62
Diabase W2	10.80	1.53	8.34	0.167	1.062	10.86	0.63	0.141	52.68	15.45	6.37	2.20	0.55	0.25	
Granite G2	2.68	1.07	1.45	0.034	0.492	1.97	4.49	0.14	69.04	15.14	0.76	4.07	0.51	0.10	0.08
Serpentine UB-N	8.34	5.36	2.68	0.12	0.11	1.20	0.02	0.04	39.43	2.90	35.21	0.10	10.84	1.26	0.39
Basalt BIR-1	11.33	2.06	8.34	0.175	1.062	10.86	0.63	0.021	47.96	15.53	9.70	1.82	0.09	0.08	
Bauxite BX-N	23.17	22.88	0.26	0.05	2.37	0.17	0.05	0.13	7.40	54.21	0.11	0.04	11.48	0.44	0.44
Feldspar FK-N	0.09	0.02	0.06	0.005	0.02	0.11	12.81	0.024	65.02	18.61	0.01	2.58	0.32	0.14	0.09
K-Feldspar NBS70a	0.075				0.01	0.11	11.80		67.10	17.90		2.55			
Na-Feldspar NBS99a	0.065				0.007	2.14	15.20	0.02	65.20	20.50	0.02	6.20			
QMC Aplite 11	0.54	0.33	0.20	0.03	0.05	0.80	4.28	0.02	75.36	13.92	0.11	4.59	0.13		
QMC Dolerite 13	16.22	5.09	10.04	0.22	2.60	8.20	1.43	0.40	49.75	13.07	4.18	2.92	1.71		
QMC Pelite M2	9.25	2.31	6.30	0.26	0.72	1.75	7.90	0.50	48.88	23,97	2.45	1.40	3.21		
QMC Calc. Sil. M3	4.55	0.91	3.33	0.28	0.83	12.01	0.71	0.36	55.59	17.62	1.21	2.98	0.78		2.98

Table 19: Operating conditions for major elements

Ele-ment	Line	Colli-mator	Energy Window Upper	Lower	kV	Ma	Angle	Back-ground +	-
Na	KA	Coarse	74	25	40	70	55.170	2.5	2.5
Mg	KA	Coarse	72	30	40	70	45.260	2.3	2.3
Al	KA	Coarse	70	32	50	55	145.045	1.5	1.5
Si	KA	Coarse	72	32	50	55	109.200	2.0	2.0
P	KA	Coarse	68	34	40	70	141.120	2.2	0.0
K	KA	Coarse	66	34	50	55	136.800	3.5	0.0
Ca	KA	Coarse	66	34	50	55	113.240	2.0	2.0
Ti	KA	Fine	64	10	50	55	86.185	2.0	1.1
Mn	KA	Fine	64	16	50	55	95.190	0.8	0.6
Fe	KA	Fine	66	18	50	55	57.535	1.5	1.5

Analytical errors for the elements , using the techniques established, by XRF have been determined by multiple runs of a number of samples. The errors on the major elements appear to be insignificant when compared with their overall totals and are tabulated below.

Table 20: Analytical errors for major elements

	Na_20	Mg0	Al_20_3	$Si0_2$	K_20
%	0.26	0.01	0.14	0.12	0.001

	Ca0	$Ti0_2$	Mn0	Fe0	P_20_5
%	0.02	0.015	0.002	0.01	0.013

Error bars have been included in the variation diagrams where significant.

The whole-rock analyses of the samples are displayed in percentage terms in Tables 29 - 31.

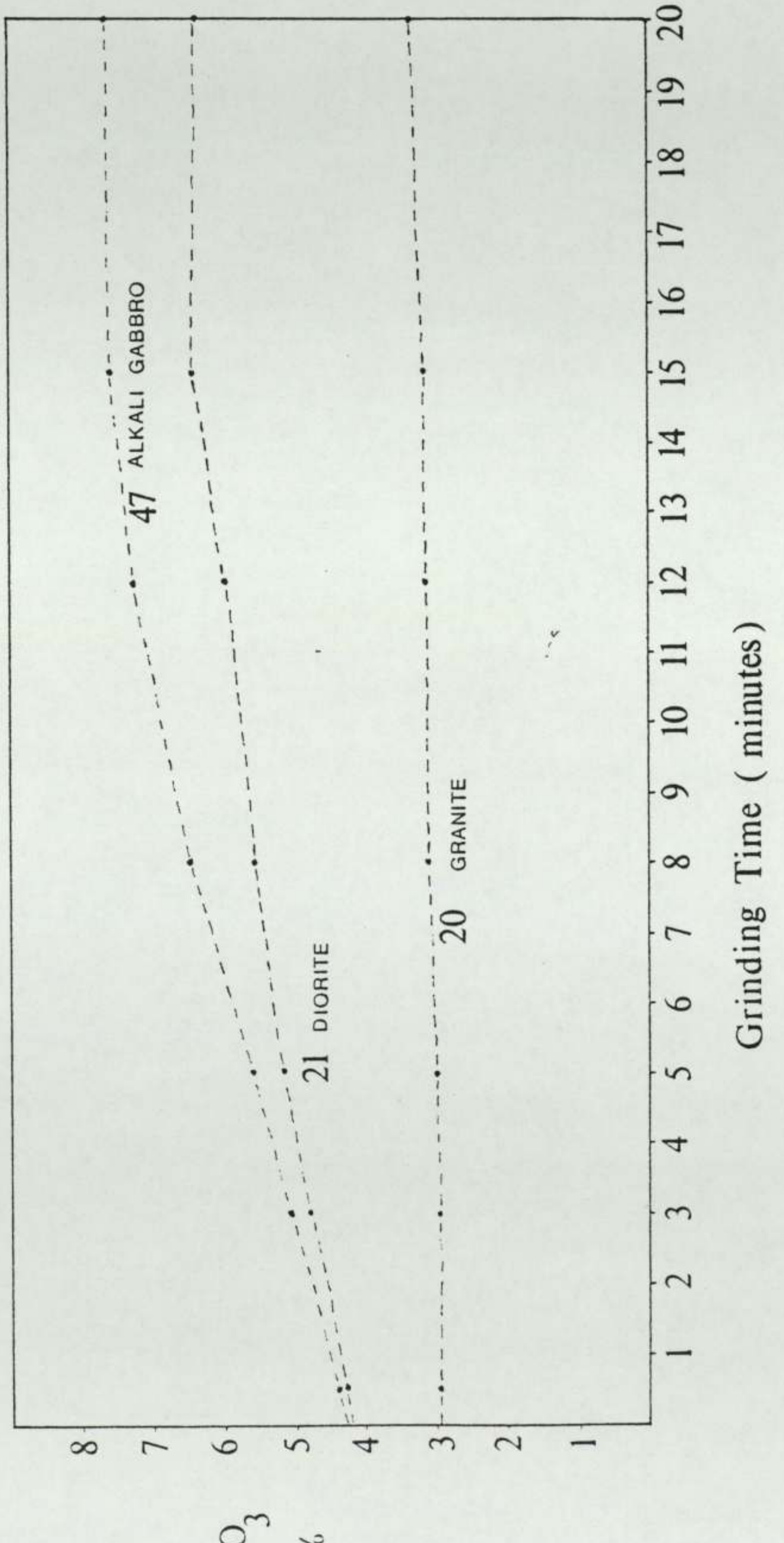
2:1.4 Ferrous/ferric ratios

All whole rock Fe contents are expressed as Fe0 as Fe^{3+}/Fe^{2+} ratios cannot be determined by XRF. Ferric iron can be determined using the oxidation-decomposition method of Wilson (1955) on rock powders of known total iron contents. Original ferric/ferrous ratios of rocks however, are known to be affected by the grinding procedure (Ritchie, 1968; Fitton & Gill, 1970).

Fitton & Gill (1970) expressed the view that considerable atmospheric oxidation of rock powders takes place during grinding due to the high local temperature, resulting in a low value for Fe0. They suggest that removal of the powder after 30 seconds grinding should show only slight oxidation and that the values can be used for most rocks.

Ritchie (1968) and Whipple *et al.*, (1984) have reported the effects of reduction on ferrous iron determinations. Whipple *et al.*, (1984) indicate that the use of tungsten carbide grinding equipment causes an increase in concentration of Fe0 due to the tungsten carbide acting as a powerful reducing agent. This is in contrast to the decrease due to atmospheric oxidation, proposed and demonstrated by Fitton & Gill (1970).

FIG. 30 EFFECTS ON THE Fe_2O_3 CONTENT OF CERTAIN IGNEOUS ROCKS DUE TO GRINDING OVER VARYING LENGTHS OF TIME



A test was carried out on three different rock samples from Arran, each powder in turn being ground in a tungsten carbide-barrelled Tema Mill for 30 seconds, followed by 3, 5, 8, 12, 15 and 20 minutes respectively (a small amount of powder being removed each time). Using the procedure of Wilson (1955), and the total iron oxide contents obtained by X.R.F., a series of plots of Fe_20_3 content of the rocks against time was drawn (Fig. 30). The diagram shows the increase in Fe_20_3 content with time, indicating much atmospheric oxidation of the samples occurs (in accordance with Fitton & Gill). The diagram also shows that for rocks of high Fe0 content the rate of oxidation to Fe_20_3 slows down with time, possibly caused by the increased involvement of tungsten carbide as a reducing agent due to the higher temperature.

The steeper slope associated with a shorter grinding time (tracing the curve back towards zero) would appear to prove that for powders of high Fe content, grinding for as little as 30 seconds produces a falsely high Fe_20_3 content due to immediate oxidation on commencement of grinding. Therefore even a very short mechanical grinding time does not give a true figure for Fe_20_3 content in Fe-rich rocks, although for Fe-poor rocks such as granites it appears to give a close approximation.

The conclusions of Fitton & Gill (1970), and Whipple *et al.*, (1984) for accurate determinations by hand grinding in an inert substance, such as acetone, would seem to be the only reliable method of analyzing for ferric/ferrous iron ratios for a wide range of rock compositions. For analysis of a great many samples, however, this is a time consuming process. For this reason all values for Fe have been expressed as Fe0 from X.R.F. analysis.

If the Fe_20_3 contents of the curves are traced back to zero grinding time, an approximate original Fe_20_3 composition can be obtained for the rocks analyzed. These approximations are seen to give Fe_20_3 /(Fe0 + Fe_20_3) ratios of 0.35 for the alkali gabbro (No. 47), 0.48 for the diorite (No. 21) and 0.51 for the granite (No. 20).

2:1.5 Normative calculations

Normative values have been calculated using the C.I.P.W. norm calculation computer program of N. Rock, run on a Harris Mainframe computer.

One problem in the calculation of the normative values is that ferric iron cannot be determined by X.R.F. analysis which displays total Fe as Fe0. The absence of Fe_20_3 creates difficulties particularly in the determination of the respective amounts of magnetite, hypersthene and olivine in the calculated normative mineralogy.

The suggested method of alleviating this problem in the program is the use of an $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ ratio of 0.15 for fresh rocks. However due to the altered nature of many of the rocks studied and the chemical variability of Fe^{3+} in igneous rocks (Le Maitre, 1976), this suggestion has not been followed here.

Instead, using the analyses reported by Le Maitre (1976) of the average ferric iron contents of numerous igneous rocks, a ratio of 0.33 has been adopted for the more basic rock types and a ratio of 0.50 for the acidic varieties (compare with approximate ratios obtained from Fig. 30 for similar rocks).

The boundary between these basic and acidic rocks is taken at a silica content of 60% for this purpose. These values are broadly in agreement with those calculated from mineral chemistry and modal mineralogy.

2:2 Trace element analysis

2:2.1 Sample preparation

For trace element analysis, the pressed powder pellet technique was used comprising 85% rock powder and 15% Bakelite resin R0214/1 as a binder.

This method produces a strong durable bricquette which will not disintegrate inside the spectrometer, also both surfaces of which are available for analysis.

The sample powder was dried at 110°C for one hour to remove any adsorbed $H_2\overset{+}{O}$. 8.5 gm. of powder was weighed out on to weighing paper. This was multiplied by 0.17647 to obtain the weight of Bakelite resin which was then added. These were thoroughly mixed in a plastic mixing bottle, each containing 6 glass balls, and were mixed for at least 30 minutes on a shaking table.

When homogenized, the powder was removed from the bottle, separated from the glass balls, and poured into a metal collar used to make the bricquette. This was then pressed with a perspex plunger to flatten the sample before being placed between the jaws of a hydraulic press. The sample was compressed at 20 tons pressure for 10 seconds, and was then removed from the collar and cured in an oven at 120°C overnight to harden the bricquette. This was then ready for use in the X.R.F.

2:2.2 Standards

The standards used for calibration of X.R.F. before analysis of the rock samples are listed below with their trace element concentrations. All the standards are used internationally.

Table 21: <u>XRF Standard Concentrations</u>

	Traces 1 PPM			
	Ba	U	Th	Pb
Pholgopite Mica Mg	4000			9
Biotite Mica Fe	145	60	150	13
Basalt BR	1050	3	12	8
Granite GA	850	4	17	30
Granite GH	22	18	90	45
Bauxite BX-N	34	8	55	135
Kyanite DT-N	130	2.3	13.5	28
Diorite DR-N	385	1.5	3	55
Feldspar FK-N	200	0.15	0.4	240
Granite GS-N	1400	8	44	53
Serpentine UB-N	30			18
Synth. Glass VS-N	1000			1000
Anorthosite AN-G	34			2
Basalt BE-N	1025	2.4	11	4
Granite MA-N	42	12	1	29
Andesite AGV-1	1220	1.89	6.5	36
Basalt BCR-1	678	1.72	6.04	13.6
Basalt BHV0-1	135	0.4	1.0	
Dunite DTS-1	2.35	0.0	0.01	12
Granite G2	1880	2.94	24.6	31
Peridotite PCC-1	1.2	0.0	0.01	11.5
Rhyolite RGM-1	800	5.8	15	21
Shale SCO-1	590	2.9	9.6	28
Syenite STMN-1	560	9.1	31	18
Diabase W2	174	0.5	2.4	
Basalt BIR-1	6			
Diabase DNC-1	118			
Mica Schist SDC-2	650	3.00	12	23
Gabbro MRG-1	50	0.3	1	10
Syenite SY-2	460	290	380	80
Dunite NIM-D	10		0.8	7

Table 21: XRF Standard Concentrations - contd:

	Traces 1 PPM			
	Ba	U	Th	Pb
Granite NIM-G	120	15	51	40
Lujavrite	450	14	66	43
Norite NIM-N	100	0.6	0.6	7
Pyroxenite NIM-P	46	0.4	1	6
Syenite NIM-S	2400	0.6	1	5
K Fspr. NBS-70a	180			
Na Fspr. NBS-99a	2300			
QMC Aplite I1	480			74
QMC Dolerite 13	690			10
QMC Pelite M2	1550			17
QMC Calc. Sil. M3	125			20

Table 22: XRF Standard Concentrations

Traces 2 PPM

	Rb	Sr	Y	Zr	Nb
Pholgopite Mica Mg	1300	25		20	120
Biotite Mica Fe	2200	5	25	800	270
Basalt BR	47	1320	30	250	100
Granite GA	175	310	21	150	10
Granite GH	390	10	70	150	85
Bauxite BX-N		112	118	520	
Kyanite DT-N				370	
Diorite DR-N	70	400	30	125	6
Feldspar FK-N	860	39	0.6	13	
Granite GS-N	185	570	19	235	23
Serpentine UB-N	6	10	11	8	
Synth. Glass VS-N	800	700		700	
Anorthosite AN-G	1	76	8	15	2
Basalt BE-N	47	1370	30	265	100
Granite MA-N	3600	84	1	27	173
Andesite AGV-1	67	660	21	225	15
Basalt BCR-1	47	330	39	191	14
Basalt BHV0-1	10	420	27	180	19
Dunite DTS-1	0.06	0.33	0.05	10	
Granite G2	170	478	11.4	300	13
Peridotite PCC-1	0.07	0.4		8	1
Rhyolite RGM-1	155	100	25	200	9.4
Shale SCO-1	115	170	24	135	10
Syenite STMN-1	120	700	46	1300	270
Diabase W2	21	192	23	100	6.8
Basalt BIR-1		107	16	18	2.3
Diabase DNC-1	4.7	144	18.5	39	3.2
Mica Schist SDC-2	120	180	42	300	18.5
Gabbro MRG-1	8	260	16	105	20
Syenite SY-2	220	275	130	280	23
Dunite NIM-D		3		20	

Table 22: XRF Standard Concentrations - contd:

Traces 2 PPM

	Rb	Sr	Y	Zr	Nb
Granite NIM-G	320	10	143	300	53
Lujavrite	190	4600	22	1.1%	960
Norite NIM-N	6	260	7	23	2
Pyroxenite NIM-P	5	32	5	30	
Syenite NIM-S	530	62	20	33	4
K Fspr. NBS-70a	550				
Na Fspr. NBS-99a					
QMC Aplite I1	130	170		60	
QMC Dolerite 13	42	260	50	190	
QMC Pelite M2	310	185	60	100	
QMC Calc. Sil. M3	25	500		290	

Table 23: XRF Standard Concentrations

	Traces 3 PPM		
	V	Cr	TiO_2 %
Pholgopite Mica Mg	0.5	100	1.63
Biotite Mica Fe	135	90	2.50
Basalt BR	235	380	2.60
Granite GA	38	12	0.38
Granite GH	5	6	0.08
Bauxite BX-N	310	300	2.37
Kyanite DT-N	160	240	1.40
Diorite DR-N	225	42	1.09
Feldspar FK-N	3	5	0.02
Granite GS-N	65	55	0.68
Serpentine UB-N	75	2300	0.11
Synth. Glass VS-N	600	700	1.08
Anorthosite AN-G	70	50	0.22
Basalt BE-N	235	360	2.61
Granite MA-N	4.6	3	0.01
Andesite AGV-1	123	12	1.06
Basalt BCR-1	404	16	2.22
Basalt BHV0-1	320	300	2.69
Dunite DTS-1	12	4000	0.00
Granite G2	36	9	0.492
Peridotite PCC-1	30	2730	0.014
Rhyolite RGM-1	14	4	0.27
Shale SCO-1	135	71	0.62
Syenite STMN-1		4	0.13
Diabase W2	259	92	1.062
Basalt BIR-1	312	373	0.96
Diabase DNC-1	148	270	0.484
Mica Schist SDC-2	105	66	1.0
Gabbro MRG-1	520	450	3.69
Syenite SY-2	52	12	0.14
Dunite NIM-D	40	2900	0.02

Table 23: XRF Standard Concentrations - contd:

Traces 3 PPM

	V	Cr	TiO_2%
Granite NIM-G	2	12	0.09
Lujavrite	81	10	0.48
Norite NIM-N	220	30	0.20
Pyroxenite NIM-P	230	2.4%	0.20
Syenite NIM-S	10	12	0.044
K Fspr. NBS-70a			0.01
Na Fspr. NBS-99a			0.007
QMC Aplite I1	7	7	0.05
QMC Dolerite 13	500	26	2.6
QMC Pelite M2	80	56	0.72
QMC Calc. Sil, M3	75	54	0.83

Table 24: XRF Standard Concentrations

	Traces 4 PPM		
	Zn	Cu	Ni
Pholgopite Mica Mg	290	4	110
Biotite Mica Fe	1300	4	35
Basalt BR	150	72	260
Granite GA	80	16	7
Granite GH	85	14	3
Bauxite BX-N	60	18	200
Kyanite DT-N	28	9	16
Diorite DR-N	145	50	16
Feldspar FK-N	10	2	3
Granite GS-N	48	20	34
Serpentine UB-N	92	28	2000
Synth. Glass VS-N	800	800	800
Anorthosite AN-G	20	19	35
Basalt BE-N	120	72	267
Granite MA-N	220	140	3
Andesite AGV-1	88	60	17
Basalt BCR-1	129	18	13
Basalt BHV0-1	105	140	120
Dunite DTS-1	48	7	2350
Granite G2	85	11	5
Peridotite PCC-1	42	10	2400
Rhyolite RGM-1	36	11	6
Shale SCO-1	105	28	30
Syenite STMN-1	240	4	3
Diabase W2	80	106	70
Basalt BIR-1	70	125	166
Diabase DNC-1	70	100	247
Mica Schist SDC-2	105	28	36
Gabbro MRG-1	190	135	195
Syenite SY-2	250	5	10
Dunite NIM-D	90	10	2050

Table 24: XRF Standard Concentrations - contd:

	Traces 4 PPM		
	Zn	Cu	Ni
Granite NIM-G	50	12	8
Lujavrite	400	13	11
Norite NIM-N	68	14	120
Pyroxenite NIM-P	100	18	560
Syenite NIM-S	10	19	7
K Fspr. NBS-70a			
Na Fspr. NBS-99a			
QMC Aplite I1	16	8	
QMC Dolerite 13	100	165	17
QMC Pelite M2	130	130	36
QMC Calc. Sil. M3	44	25	17

Table 25: XRF Standard Concentrations for La

Standard	La (PPM)	Standard	La (PPM)
Mica Mg	-	RGM-1	23
Mica Fe	190	SCO-1	29
BR	80	STM-1	150
GA	38	W 2	10.4
GH	25	BIR-1	0.63
BX-N	390	DNC-1	3.6
DT-N	-	SDC-2	42
DR-N	21	MRG-1	10
FK-N	1	SY-2	88
GS-N	75	NIM-D	0.2
UB-N	-	NIM-G	109
VS-N	-	MO,-L	250
AN-G	-	NIM-N	3
BE-N	82	NIM-P	2
MA-N	1	NIM-S	5
AGV-1	37	NBS-70A	-
BCR-1	25	NBS-99A	-
BHVO-1	17	QMC I 1	-
DTS-1	0.03	QMC I 3	-
G2	90	QMC M 2	-
PCC-1	0.09	QMC M 3	-

2:2.3 Analytical techniques

Trace elements were analyzed using a Philips PW1400 X-Ray Fluorescence Spectrometer. The analyses were obtained by averaging values over 3 - 4 runs.

Table 26: Operating conditions for trace element analysis

Element	Line	Collimator	Energy Window		kV	ma	Angle	Background	
			Upper	Lower					
V	KA	Fine	72	12	50	60	123.230	0.0	0.0
Cr	KA	Fine	62	12	50	55	107.125	1.64	1.64
Ni	KA	Fine	64	20	60	45	48.685	0.0	0.4
Cu	KA	Fine	64	22	60	45	45.090	0.5	0.5
Zn	KA	Fine	70	24	60	45	41.830	0.4	0.0
Rb	KA	Fine	84	24	70	40	37.990	0.4	0.4
Sr	KA	Fine	80	24	70	40	35.855	0.5	0.5
Y	KA	Fine	60	22	70	40	33.895	0.8	0.8
Zr	KA	Fine	80	22	70	40	32.100	0.4	0.4
Nb	KA	Fine	80	26	70	40	30.450	0.5	0.0
Ba	KA	Fine	72	28	70	40	15.540	0.0	0.18
Th	LA	Fine	66	22	70	40	27.470	0.52	0.3
La	LA	Fine	66	36	50	55	82.880	1.0	1.0
Pb	LB	Fine	64	20	70	40	28.325	0.3	0.3

Analytical errors for the trace elements have been determined by multiple runs of a number of samples and are tabulated below.

Table 27: Analytical errors for trace elements

Element:	V	Zn	Rb	Sr	Y	Zr	Cr
PPM	3.7	2.9	2.4	4.2	1.9	2.1	3.5

Element:	Nb	Ba	Th	La	Pb	Ni	Cu
PPM	0.5	6.4	1.3	1.7	1.6	5.3	2.8

The errors appear more significant than for the major elements when compared to their overall concentrations in the rocks. Error bars have been included on the relevant variation diagrams against silica. The whole rock analyses of the samples are displayed in Tables

Nominal detection limits for the trace elements using a Philips PW1400 XRF Spectrometer are given below with their upper limits of calibration.

Table 28: Detection and upper limits of standards for trace elements

Element	Detection limit (P.P.M)	Upper limit of standards (P.P.M.)
Ba	6	4000
Nb	2	960
Zr	2	11000
Y	2	143
Sr	2	4600
Rb	2	3600
Zn	1	1300
Cu	1	165 (800)
Ni	1	2400
V	1	520 (600)
Cr	3	4000 *
La	2	390
Pb	4	240 (1000)
Th	2	380

The values reported in brackets refer to the values of the synthetic glass standard VS-N.

* The highest value of a standard for Cr is 24,000 PPM in Pyroxenite NIM-D, but this standard was not used in the calibration.

2:3 Rare earth element analysis

Samples for rare earth element analysis were prepared in the method described for X-Ray Fluorescence analysis, but the powders were carefully weighed out at 0.5 gm. before being placed in special clean plastic containers for irradiation.

R.E.E. analyses for the Garabal Hill rocks were performed by Induced Neutron Activation Analysis (INAA) using facilities at the Imperial College Reactor Centre at Ascot.

The results obtained for the elements La, Ce and Yb were within 10% of the recommended values for the International Standard BCR-1. Lu was within 5% of the standard value and Nd, Sm and Eu were all within 15% of the recommended value.

Certain elements are impossible to analyze due to their short half lives, whilst others may be analyzed but with difficulty because of interferences by other elements.

Gd shows interference by Sm whereas Ho is complicated by the presence of any U (Henderson & Pankhurst, 1984). This is due to the interference by U fission products on the Ho line (e.g. 5 PPM of U gives an approximate increase of 0.5 PPM Ho - S. Parry, pers. comm.).

Sm values may also be rather unreliable if the rock specimens are ground using tungsten carbide equipment. This is due to interference of Sm by W (Henderson & Pankhurst, 1984: S. Parry, prs. comm.) although the interference is not a problem unless counting is done shortly after irradiation, the half life of W being less than that of Sm. As a consequence, whereas the other rare earth elements were analyzed over two counting runs, Sm was counted over one. The results obtained on the standard appear reasonable.

Analysis of the R.E.E.s was also attempted for the Bolton Hill rock suite, again by Neutron Activation Analysis using facilities at the Atomic Weapons Research Establishment Reactor at Aldermaston. However, R.E.E. values for these rocks were found to be very low, even for the light R.E.E.s. Concentration levels were either barely above or below the detection limits. These very low results are of little or no real use either in demonstrating a trend for hybridization or in suggesting the operation of other processes.

Table 29a: Arran Granitic & Intermediate Rocks

Sample No.	16	15	55	G	20	32	43
$Si0_2$	75.72	74.51	72.60	71.60	69.79	68.52	67.05
$Ti0_2$	0.24	0.34	0.43	0.49	0.67	0.73	0.82
Al_20_3	12.57	13.11	13.35	13.37	13.36	13.84	13.61
Fe0	2.73	2.92	3.97	3.78	5.77	5.55	6.13
Mn0	0.03	0.07	0.08	0.08	0.08	0.11	0.11
Mg0	0.18	0.38	0.48	0.67	0.71	1.53	1.61
Ca0	0.41	0.89	1.58	1.90	2.40	3.37	3.32
Na_20	3.61	3.82	4.36	4.32	4.06	3.58	3.69
K_20	4.40	4.44	3.57	3.82	3.43	3.05	2.84
P_20_5	0.04	0.06	0.10	0.10	0.18	0.16	0.18
Lol	1.10	0.88	0.98	0.70	0.70	0.58	1.00
Total:	101.04	101.44	101.55	100.83	101.24	101.32	100.37
Qz	36.54	32.51	29.26	27.31	27.33	26.21	25.91
Ab	30.52	32.10	36.63	36.44	34.09	30.01	31.32
Or	25.98	26.05	20.95	22.50	20.12	19.02	16.84
An	1.77	4.00	6.30	5.82	8.07	12.01	12.26
Di	0.00	0.00	0.72	2.51	2.23	2.97	2.61
Hy	1.38	1.84	2.24	1.48	2.87	3.83	4.43
Mt	1.97	2.10	2.72	2.72	4.17	3.96	4.40
Il	0.46	0.64	0.81	0.93	1.45	1.56	1.76
Ap	0.09	0.14	0.23	0.23	0.41	0.37	0.42
Cm	1.23	0.55	0.00	0.00	0.00	0.00	0.00

Sample No.	60	26	59	- 53	21	9X	29	22
$Si0_2$	66.55	62.60	62.32	60.97	60.15	57.71	57.67	53.90
$Ti0_2$	0.74	1.13	1.04	1.01	1.31	1.42	1.97	1.62
Al_20_3	14.37	14.22	14.29	14.25	14.32	14.59	14.98	13.88
Fe0	6.26	7.86	8.74	8.81	8.82	9.86	10.19	10.89
Mn0	0.13	0.14	0.17	0.16	0.16	0.21	0.20	0.18
Mg0	1.32	1.80	1.89	1.92	2.48	3.72	2.38	3.81
Ca0	3.52	3.94	4.86	4.89	5.44	5.90	6.04	6.88
Na_20	4.23	4.25	3.96	3.87	3.26	3.91	3.95	3.19
K_20	2.53	3.32	2.23	2.06	1.66	1.56	1.34	1.67
P_20_5	0.30	0.41	0.41	0.34	0.32	0.23	0.64	0.22
Lol	0.46	1.78	1.15	1.05	1.11	1.56	1.54	3.16
Total:	100.45	101.47	101.07	99.41	99.33	100.67	100.90	100.20
Qz	23.64	16.11	17.30	18.98	20.85	10.02	13.46	7.75
Ab	35.62	35.88	33.32	33.13	27.95	34.00	33.54	27.90
Or	14.88	19.58	13.10	12.32	9.94	9.24	7.95	11.42
An	12.73	10.48	15.12	15.64	20.94	17.82	19.29	18.68
Di	2.30	5.40	5.27	5.66	3.62	7.54	5.58	2.67
Hy	3.62	3.36	6.10	4.49	8.72	14.19	10.33	12.40
Mt	4.49	5.66	6.24	6.41	6.45	4.90	5.94	5.41
Il	1.97	2.52	2.53	2.52	2.72	2.71	3.76	3.19
Ap	0.69	0.95	0.94	0.80	0.75	0.53	1.49	0.53
Cm	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 29b: Arran - Intermediate Rocks

Sample No.:	10	43X	30	8
$Si0_2$	57.17	56.24	55.69	55.83
$Ti0_2$	1.42	1.29	0.86	1.62
Al_20_3	14.43	14.82	15.33	14.62
Fe0	10.12	10.20	8.29	11.35
Mn0	3.75	3.99	4.51	3.99
Mg0	6.23	7.35	6.90	5.28
Ca0	6.23	7.35	6.90	5.28
Na_20	3.58	3.72	3.16	3.63
K_20	2.30	1.67	1.55	2.17
P_20_5	0.23	0.18	0.11	0.26
Lol	1.10	1.82	2.47	1.00
Total:	100.80	101.73	99.04	99.83
Qz	3.88	6.75	9.91	7.83
Ab	30.33	31.48	27.63	30.99
Or	13.61	9.87	9.46	12.94
An	17.11	18.96	23.87	17.38
Di	9.48	13.65	8.89	6.14
Hy	12.30	11.44	14.09	15.40
Mt	5.00	5.90	4.13	5.54
Il	2.70	2.45	1.69	3.11
Ap	0.53	0.42	0.26	0.61

Table 29b. contd.: Arran - Intermediate Rocks

Sample No.:	13	17	12	56	11
$Si0_2$	55.83	55.41	54.92	54.92	54.60
$Ti0_2$	1.88	1.06	1.82	0.92	1.52
Al_20_3	13.59	13.64	13.39	15.02	14.26
Feo	12.17	10.17	11.10	9.53	12.24
Mno	0.18	0.17	0.17	0.16	0.22
Mg0	3.19	4.98	2.90	5.57	3.30
Ca0	6.33	8.02	6.29	8.20	6.72
Na_20	3.14	3.18	3.30	3.09	3.32
K_20	1.70	1.16	1.43	1.16	1.74
P_20_5	0.38	0.11	0.38	0.11	0.21
Lol	1.10	3.10	2.24	1.11	1.72
Total:	99.51	101.03	97.95	99.83	99.88
Qz	12.68	8.07	13.15	6.99	8.75
Ab	26.92	27.41	29.09	26.42	28.53
Or	10.18	6.98	8.80	6.93	10.44
An	18.24	19.91	18.26	23.98	19.20
Di	9.35	16.49	9.85	13.54	11.22
Hy	12.09	13.78	10.72	15.51	12.59
Mt	5.96	5.00	5.55	4.66	5.98
Il	3.62	2.05	3.61	1.77	2.94
Ap	0.89	0.26	0.92	0.26	0.49

Table 29c: Arran Gabbroic Rocks

Sample No.	49	39X	35	36	40X	41X	42
$Si0_2$	52.47	52.11	51.13	50.94	50.64	49.94	49.54
$Ti0_2$	1.25	1.28	1.81	1.01	1.33	1.34	0.81
Al_20_3	14.21	14.59	13.17	14.86	14.42	14.36	18.85
Fe0	10.28	12.23	15.58	10.53	12.60	12.81	8.52
Mn0	0.18	0.20	0.20	0.21	0.21	0.21	0.13
Mg0	5.11	6.12	5.35	6.65	6.35	6.42	6.10
Ca0	7.90	9.00	8.48	8.76	9.05	9.55	12.00
Na_20	2.88	2.99	2.77	2.78	3.09	2.81	2.72
K_20	1.24	0.89	0.73	0.28	1.11	0.91	0.58
P_20_5	0.19	0.13	0.16	0.09	0.13	0.13	0.07
Lol	2.79	1.04	1.54	1.60	2.02	2.20	1.34
Total:	98.52	100.61	100.92	97.76	100.95	100.70	100.67
Qz	6.96	1.24	3.88	5.10	0.53	0.93	0.00
Ab	25.39	25.41	23.50	24.41	26.34	24.07	23.11
Or	7.63	5.28	4.32	1.72	6.61	5.44	3.44
An	23.15	23.08	21.43	28.31	22.40	24.21	37.72
Di	13.58	17.34	16.52	13.31	18.21	18.79	17.71
Hy	15.15	18.92	18.92	18.66	16.84	17.05	10.60
Ol	0.00	0.00	0.00	0.00	0.00	0.00	1.51
Mt	5.16	5.93	7.56	5.23	6.17	6.25	4.14
Il	2.48	2.45	3.45	1.99	2.55	2.58	1.55
Ap	0.46	0.30	0.37	0.22	0.30	0.30	0.16

Sample No.	4	18	3	58	19	54	61	BC3
$Si0_2$	48.38	55.32	52.20	51.62	51.77	51.67	50.66.	50.63
$Ti0_2$	1.47	1.46	1.88	2.09	1.52	1.85	2.11.	1.95
Al_20_3	14.73	14.57	14.60	13.65	13.78	13.89	13.94	14.32
Fe0	13.94	10.84	13.86	14.86	12.79	14.10	15.44	14.61
Mn0	0.25	0.18	0.17	0.20	0.19	0.20	0.21	0.20
Mg0	7.06	4.677	4.00	4.46	5.25	4.73	4.88	5.10
Ca0	10.32	7.16	8.30	8.40	8.86	8.62	7.90	8.50
Na_20	2.47	3.33	3.29	3.04	3.08	3.20	2.95	2.90
K_20	0.27	1.55	1.10	1.03	0.84	1.05	1.21	1.18
P_20_5	0.14	0.17	0.21	0.25	0.22	0.22	0.17	0.16
Lol	1.30	1.15	0.90	1.21	1.55	1.30	1.24	1.10
Total:	100.46	100.53	100.53	100.83	99.87	100.86	100.76	100.82
Qz	1.21	7.68	5.20	4.62	4.75	1.95	2.39	2.01
Ab	21.14	28.27	27.85	25.73	26.42	27.11	25.00	24.56
Or	1.61	9.19	6.50	6.09	5.03	6.21	7.16	6.98
An	27.29	20.34	21.87	20.60	21.63	20.50	21.29	22.63
Di	19.53	11.80	15.18	16.38	17.92	17.52	14.17	15.53
Hy	19.34	14.24	12.60	14.83	14.50	15.83	18.06	17.05
Mt	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Il	6.71	5.25	6.70	7.15	6.16	6.80	7.47	7.01
Ap	2.83	2.79	3.58	3.98	2.93	3.52	4.02	3.71
Cm	0.33	0.39	0.49	0.58	0.52	0.51	0.39	0.37

Table 29d: Arran - Gabbroic Rocks

Sample No.:	BA1	51	38	14	37	BA2
$Si0_2$	54.11	53.65	53.62	53.40	52.91	52.89
$Ti0_2$	1.41	1.00	1.13	1.64	1.05	1.42
Al_20_3	15.45	15.79	15.18	14.63	15.32	14.65
Fe0	10.45	10.29	10.42	10.94	10.52	10.43
Mn0	0.20	0.18	0.18	0.19	0.20	0.19
Mg0	5.13	5.55	5.25	3.61	6.58	4.84
Ca0	8.23	9.17	8.36	7.04	8.88	7.78
Na_20	2.98	9.17	8.36	7.04	8.88	7.78
K_20	1.21	0.46	1.01	2.22	0.59	1.34
P_20_5	0.18	0.09	0.14	0.22	0.10	0.18
LoI	1.60	1.65	1.55	1.64	1.34	2.30
Total:	100.76	100.69	100.00	98.65	100.40	98.76.
Qz	7.16	7.95	5.70	7.32	3.63	8.69
Ab	25.36	23.88	26.91	26.94	24.62	23.37
Or	7.19	2.74	6.05	13.56	3.51	8.19
An	24.81	29.37	24.70	18.92	27.31	24.90
Di	12.48	13.14	13.58	13.25	13.49	11.46
Hy	14.76	15.83	15.39	10.85	20.06	14.92
Mt	5.08	4.93	5.11	5.46	5.10	5.20
Il	2.70	1.92	2.18	3.22	2.01	2.79
Ap	0.42	0.21	0.33	0.53	0.23	0.43

Table 29e: Arran - Alkali Gabbros

Sample No:	46	47	50
$Si0_2$	45.08	46.59	46.08
$Ti0_2$	1.82	2.09	2.38
Al_20_3	18.08	17.62	17.07
Fe0	10.89	11.96	13.11
Mn0	0.15	0.18	0.17
Mg0	4.36	4.73	4.24
Ca0	8.54	9.12	8.84
Na_20	3.86	3.95	3.64
K_20	0.62	0.71	1.58
P_20_5	0.21	0.28	0.32
LoI	3.80	1.58	1.55
Total:	97.50	98.84	99.00
Ab	29.11	27.75	22.54
Or	3.90	4.30	9.55
An	32.19	29.01	26.20
Ne	3.08	3.53	4.86
Di	9.56	12.91	13.85
Hy	5.18	4.97	4.84
Ol	7.11	6.74	6.32
Mt	5.63	6.00	6.41
Il	3.69	4.08	4.63
Ap	0.52	0.66	0.76

Table 30a: Bolton Hill Pegmatites & Granites

Sample No.	131P	166P	206P	205P	219P	218P	204P
$Si0_2$	91.21	80.31	76.30	79.60	77.39	76.44	68.90
$Ti0_2$	0.13	0.10	0.09	0.14	0.17	0.21	0.02
Al_20_3	3.47	10.96	14.33	11.36	12.08	12.58	17.06
Fe0	1.80	1.25	0.91	1.13	1.83	1.69	0.67
Mn0	0.11	0.02	0.03	0.03	0.11	0.04	0.03
Mg0	0.81	0.37	0.27	0.31	0.45	0.40	0.13
Ca0	1.76	1.80	0.68	0.95	1.12	1.50	1.00
Na_20	0.02	4.50	7.83	6.08	5.51	5.69	5.17
K_20	0.75	0.51	0.27	0.10	0.82	0.68	6.40
P_20_5	0.07	0.02	0.04	0.04	0.05	0.05	0.05
Lol	0.74	0.90	1.00	0.80	1.06	0.90	0.70
Total:	100.97	100.74	101.75	100.54	100.59	100.18	100.13
Qz	83.24	47.81	27.64	41.60	39.16	37.24	12.07
Ab	0.17	38.09	65.67	51.53	46.77	48.42	43.94
Or	4.42	3.01	1.58	0.59	4.86	4.04	37.99
An	7.15	8.23	3.09	3.44	5.25	6.85	4.50
Di	0.92	0.48	0.00	0.86	0.00	0.26	0.13
Hy	2.40	1.13	1.00	0.76	1.92	1.38	0.64
Mt	1.28	0.96	0.66	0.81	1.31	1.23	0.48
Il	0.25	0.19	0.17	0.27	0.32	0.40	0.04
Ap	0.16	0.05	0.09	0.09	0.12	0.12	0.12
Cm	0.00	0.00	0.03	0.00	0.22	0.00	0.00

Sample No.	165	200	130	138	162	121	191	217
$Si0_2$	82.91	81.76	72.15	79.90	78.70	77.69	77.66	69.84
$Ti0_2$	0.01	0.05	0.42	0.12	0.10	0.27	0.21	0.53
Al_20_3	11.37	10.77	13.67	11.83	12.50	11.45	12.90	14.03
Fe0	0.42	0.68	4.12	0.98	1.43	2.49	1.94	4.74
Mn0	0.01	0.01	0.11	0.05	0.04	0.07	0.06	0.07
Mg0	0.06	0.07	1.38	0.23	0.32	0.72	0.65	1.48
Ca0	0.79	1.81	2.65	0.43	1.23	1.48	1.68	2.91
Na_20	4.12	4.00	3.38	5.32	5.25	4.82	3.32	3.34
K_20	0.96	0.64	0.93	1.64	0.58	0.31	0.95	1.06
$P_2 0_5$	0.01	0.04	0.13	0.07	0.01	0.04	0.04	0.13
Lol	0.70	0.22	1.30	0.80	1.10	1.20	0.80	1.30
Total:	101.36	100.05	100.24	101.37	101.26	100.54	100.21	99.43
Qz	53.07	52.03	41.46	41.24	42.60	44.32	50.43	38.32
Ab	34.59	33.83	28.85	44.70	44.29	40.99	28.22	28.73
Or	5.63	3.78	5.54	9.62	3.42	1.84	5.64	6.37
An	3.82	8.67	12.41	1.66	6.02	7.12	8.11	13.81
Di	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hy	0.36	0.65	4.96	0.92	1.34	2.65	2.29	5.33
Mt	0.30	0.48	3.01	0.72	1.05	1.83	1.40	3.50
Il	0.02	0.10	0.81	0.23	0.19	0.52	0.40	1.02
Ap	0.02	0.09	0.30	0.16	0.02	0.09	0.09	0.31
Cm	2.13	0.33	2.63	0.69	1.03	0.60	3.48	2.46

TABLE 30b

BOLTON HILL GRANITES

SAMPLE NO.	139	163	6	161	103	222	228a	228b	224a	224b	5	201	156	110
SiO_2	77.03	76.58	76.13	75.31	75.42	75.98	77.35	77.51	77.40	77.61	73.66	69.84	71.57	70.26
TiO_2	0.05	0.12	0.05	0.15	0.14	0.11	0.13	0.13	0.07	0.08	0.23	0.47	0.37	0.41
Al_2O_3	14.13	13.32	13.57	13.20	12.52	11.43	12.37	12.40	12.05	12.40	13.52	13.49	14.01	14.13
FeO	0.34	1.78	1.44	1.81	1.53	1.12	1.44	1.43	0.78	0.92	2.01	4.62	3.71	4.41
MnO	0.00	0.05	0.05	0.05	0.03	0.10	0.12	0.11	0.11	0.11	0.08	0.11	0.09	0.14
MgO	0.14	0.49	0.55	0.67	0.34	0.24	0.26	0.27	0.14	0.15	1.20	1.48	1.33	1.27
CaO	0.36	1.10	2.02	2.75	1.86	0.88	1.25	1.13	1.06	0.61	1.61	3.60	2.51	3.35
Na_2O	7.85	5.16	5.46	4.69	5.18	4.86	5.36	5.09	5.18	4.78	5.51	4.69	4.55	3.03
K_2O	0.52	1.00	0.62	0.72	1.03	1.91	1.21	1.18	2.70	3.27	1.50	0.28	0.99	0.39
P_2O_5	0.05	0.04	0.06	0.04	0.05	0.05	0.06	0.06	0.05	0.05	0.14	0.14	0.12	0.12
LOI	0.60	1.00	1.00	0.96	1.30	1.66	1.60	1.62	1.06	1.05	1.38	1.22	1.20	2.26
TOTAL	101.07	100.64	100.95	100.35	99.40	98.34	101.15	100.93	101.60	100.03	101.04	99.94	100.45	99.77
Qz	29.00	39.63	36.81	38.61	37.73	39.19	38.55	40.76	34.91	35.68	31.04	32.20	33.80	42.83
Ab	66.02	43.75	46.11	39.87	44.62	42.48	45.49	43.31	43.98	40.40	46.38	40.10	39.16	26.23
Or	3.05	5.92	3.66	4.27	6.20	11.66	7.17	7.01	16.01	19.30	8.90	1.67	5.87	2.36
An	1.45	5.21	9.61	12.93	8.04	3.88	5.83	5.24	1.69	2.70	7.17	15.12	11.65	16.20
Di	0.00	0.00	0.00	0.43	0.87	0.25	0.00	0.00	2.81	0.00	0.00	1.69	0.00	0.00
Hy	0.45	1.96	1.88	2.10	0.98	1.59	1.34	1.34	0.11	0.91	3.96	4.55	4.64	6.99
Mt	0.24	1.29	1.05	1.35	1.13	0.84	1.05	1.05	0.19	0.66	1.37	3.39	2.70	3.27
Il	0.09	0.23	0.28	0.29	0.27	0.22	0.25	0.25	0.13	0.15	0.42	0.90	0.71	0.80
Ap	0.12	0.09	0.14	0.09	0.12	0.12	0.14	0.14	0.12	0.12	0.30	0.33	0.30	0.28
Cm	0.13	1.86	0.40	0.00	0.00	0.00	0.13	0.85	0.00	0.02	0.40	0.00	1.15	3.00

TABLE 30c

BOLTON HILL INTERMEDIATE ROCKS

SAMPLE NO.	107	216	116	117	157	128	4	209	126	202	3	210	2	108	220	221
SiO_2	69.08	68.63	68.15	66.75	66.24	64.53	63.60	61.95	61.66	62.18	58.76	57.86	54.99	55.41	54.25	71.93
TiO_2	0.52	0.67	0.67	0.67	0.63	0.90	0.87	0.98	1.04	0.43	0.86	0.47	0.55	1.08	0.77	0.20
Al_2O_3	14.10	13.94	14.31	14.37	13.85	15.26	14.71	15.59	15.68	13.80	16.13	15.84	15.72	16.07	15.00	13.69
FeO	5.19	4.67	5.44	5.50	6.68	7.41	6.67	7.67	8.06	6.03	9.18	7.22	9.01	9.60	10.13	3.30
MnO	0.11	0.11	0.09	0.10	0.13	0.18	0.15	0.18	0.18	0.13	0.22	0.13	0.19	0.18	0.21	0.09
MgO	1.39	1.34	1.40	1.57	2.05	2.10	1.98	2.04	2.11	3.82	2.68	4.91	5.80	4.32	6.03	0.90
CaO	3.99	5.12	4.34	4.01	4.03	4.66	4.85	4.55	5.32	6.38	5.91	6.72	6.37	6.52	6.96	2.14
Na_2O	3.27	3.02	2.99	3.07	2.93	3.27	4.35	3.48	3.17	4.55	3.32	3.24	4.11	3.80	3.35	5.74
K_2O	0.70	0.69	0.91	0.82	0.93	1.14	0.57	1.26	0.93	0.43	0.98	1.26	0.77	0.68	0.93	1.08
P_2O_5	0.11	0.15	0.17	0.18	0.14	0.24	0.24	0.26	0.29	0.18	0.22	0.08	0.13	0.24	0.11	0.05
LOI	1.97	2.50	1.40	1.80	1.80	1.22	2.25	1.25	1.24	2.09	1.10	2.30	2.20	2.25	2.30	2.23
TOTAL	100.43	100.84	99.87	98.84	99.41	99.91	100.24	100.81	100.98	101.02	100.36	100.03	99.84	100.15	99.84	101.35
Qz	37.08	36.43	36.32	35.71	34.33	27.94	23.93	24.44	24.52	11.76	17.00	12.26	4.41	6.65	6.42	29.47
Ab	27.98	25.92	25.63	26.70	25.33	27.67	37.48	29.97	27.17	39.25	28.51	28.05	35.52	33.02	28.98	49.14
Or	4.18	4.14	5.45	4.98	5.61	6.74	3.43	7.58	5.57	2.59	5.88	7.62	4.65	4.02	5.62	6.46
An	19.29	22.80	20.68	19.24	19.49	21.56	19.26	21.25	24.81	16.31	26.65	25.58	22.69	24.34	23.70	7.90
Di	0.00	1.66	0.00	0.00	0.00	0.00	3.08	0.00	0.00	12.71	1.39	5.33	7.19	13.58	8.96	0.00
Hy	5.35	3.92	5.25	5.88	7.62	7.64	4.60	7.69	8.10	5.82	13.83	16.43	19.68	11.35	19.60	3.81
Mt	3.84	3.44	3.99	4.09	4.93	5.37	4.93	5.67	5.80	4.47	4.49	3.57	4.44	4.45	4.91	2.40
Il	1.00	1.29	1.29	1.31	1.22	1.71	1.68	1.90	2.00	0.83	1.66	0.91	1.07	2.02	1.50	0.38
Ap	0.26	0.35	0.40	0.43	0.33	0.56	0.57	0.61	0.68	0.19	0.52	0.19	0.31	0.53	0.26	0.12
Cm	0.97	0.00	0.95	1.63	1.07	0.76	0.00	0.88	0.50	0.00	0.00	0.00	0.00	0.00	0.00	0.23

TABLE 30d

BOLTON HILL PALE DIORITES

SAMPLE NO.	211	212	134a	190	xxx	140	145	146	154	133	129	132	101	100	136
SiO_2	56.45	55.12	53.87	54.34	53.26	53.37	53.11	53.13	51.69	51.37	51.04	50.85	50.85	50.88	50.55
TiO_2	0.44	0.47	0.44	0.43	0.46	0.48	0.53	0.56	0.69	0.54	0.60	0.47	0.52	0.56	0.47
Al_2O_3	14.77	14.82	15.68	18.43	17.75	15.58	16.42	15.34	15.77	16.86	15.39	16.63	16.52	16.63	14.89
FeO	7.50	8.34	7.44	7.53	7.77	8.35	9.32	9.38	10.10	9.46	9.91	8.61	9.39	10.41	9.10
MnO	0.17	0.18	0.19	0.15	0.14	0.16	0.18	0.19	0.24	0.22	0.21	0.21	0.21	0.23	0.17
MgO	6.03	6.48	7.78	4.79	5.22	6.88	6.02	7.26	7.00	6.81	7.71	7.59	7.70	7.19	9.77
CaO	7.25	7.23	7.95	8.90	8.99	8.33	8.39	8.85	8.26	8.88	9.51	9.86	9.30	7.65	9.64
Na_2O	5.24	5.25	3.72	2.51	4.75	4.59	2.35	1.88	3.22	1.80	1.53	2.18	2.24	2.90	1.61
K_2O	0.62	0.56	1.15	1.02	1.29	0.62	1.31	1.09	1.05	1.55	1.31	1.12	1.35	0.85	1.58
P_2O_5	0.09	0.11	0.10	0.02	0.04	0.11	0.09	0.05	0.08	0.08	0.10	0.08	0.09	0.08	0.06
LOI	1.52	2.51	1.75	2.00	2.00	2.00	2.10	2.20	2.30	1.85	2.40	1.78	2.09	1.98	2.30
TOTAL	100.08	101.07	100.07	100.12	101.67	100.47	99.82	99.93	100.40	99.42	99.71	99.38	100.26	99.35	100.14
Qz	1.84	2.04	1.80	9.73	0.00	0.00	6.61	7.87	2.47	7.04	5.21	4.25	2.30	2.58	1.11
Ab	45.05	45.16	31.94	21.59	34.80	39.34	20.29	16.23	28.43	15.57	13.27	18.85	19.26	25.13	13.89
Or	3.72	3.36	6.89	6.13	7.63	3.71	7.90	6.57	6.32	9.36	7.93	6.76	8.10	5.14	9.52
An	15.23	15.51	23.06	36.66	23.37	20.38	31.05	30.86	25.75	34.13	32.07	33.03	31.55	30.61	29.33
Ne	0.00	0.00	0.00	0.00	2.94	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Di	15.30	14.50	13.22	6.68	17.28	16.96	8.92	11.15	11.80	8.51	12.78	13.40	12.04	6.35	15.43
Hy	14.07	14.10	18.29	12.40	6.13	10.04	19.33	21.44	18.69	21.77	22.38	20.44	20.87	23.71	26.48
Ol	0.00	0.00	0.00	0.00	3.07	3.63	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mt	3.68	4.09	3.65	5.34	3.75	4.08	4.61	4.63	4.96	4.69	4.92	4.25	4.61	5.15	3.35
Il	0.85	0.91	0.85	0.83	0.88	0.92	1.03	1.09	1.32	1.05	1.17	0.91	1.00	1.09	0.91
Ap	0·21	0·26	0·23	0·05	0·09	0·26	0·21	0·12	0·21	0·19	0·24	0·19	0·21	0·19	0·14

TABLE 30e

BOLTON HILL PALE DIORITES

SAMPLE NO.	223	134b	193	xx	102	213	135	142	192
SiO_2	50.34	49.88	49.75	49.39	49.43	49.19	49.06	48.60	47.94
TiO_2	0.72	0.60	0.56	0.64	0.54	0.55	0.65	0.75	0.62
Al_2O_3	15.66	14.95	16.63	12.73	17.27	16.17	14.73	16.22	16.62
FeO	10.41	10.59	9.81	9.17	9.54	9.64	12.00	10.89	10.57
MnO	0.23	0.24	0.20	0.20	0.22	0.21	0.23	0.20	0.22
MgO	7.34	8.70	7.38	9.23	7.25	6.99	8.39	8.12	8.03
CaO	10.02	10.12	9.17	10.04	10.20	10.25	10.46	10.76	10.96
Na_2O	1.65	2.04	3.21	1.92	1.65	3.16	1.96	2.41	1.93
K_2O	1.21	0.68	0.99	0.76	1.38	0.70	0.47	0.86	0.86
P_2O_5	0.12	0.08	0.06	0.38	0.09	0.09	0.02	0.10	0.10
LOI	1.72	2.13	2.60	2.70	1.77	2.15	2.40	2.40	2.20
TOTAL	99.42	100.01	100.36	97.16	99.34	99.10	100.37	101.31	100.05
Qz	3.95	2.60	0.00	2.57	23.6	0.00	0.70	0.00	0.00
Ab	14.26	17.58	27.79	17.15	14.27	27.50	16.87	20.56	16.64
Or	7.30	4.09	5.99	4.74	8.33	4.25	2.83	5.12	5.18
An	32.30	30.22	28.74	25.54	36.47	28.71	30.57	31.19	34.48
Ne									
Di	14.51	16.67	13.02	20.08	12.00	18.87	18.16	18.00	16.31
Hy	20.81	22.20	11.56	23.49	20.52	8.02	20.87	11.03	16.98
Ol	0.00	0.00	6.75	0.00	0.00	6.55	0.00	7.19	3.36
Mt	5.15	5.23	4.87	4.47	4.72	4.76	3.65	5.20	5.22
Il	1.40	1.16	1.09	1.29	1.05	1.08	1.26	1.44	1.20
Ap	0·28	0·19	0·14	0·93	0·21	0·21	0·05	0·23	0·24

TABLE 30f

BOLTON HILL DARK DIORITES

SAMPLE NO.	X	214	106	229	118	119	215	105	124	104	115	122	114X	108X	226	112
SiO_2	50.97	49.62	46.10	49.60	49.34	48.52	48.77	48.06	47.78	46.32	46.58	44.92	45.78	44.90	47.12	46.65
TiO_2	1.36	0.85	1.21	0.89	1.37	1.37	1.35	1.13	1.40	1.18	0.88	1.47	0.91	1.21	0.72	0.75
Al_2O_3	15.60	16.17	16.03	15.24	17.22	16.80	15.68	15.47	15.90	15.96	16.15	15.87	16.40	17.18	17.40	16.49
FeO	13.98	11.44	12.66	11.54	13.17	13.46	14.65	11.84	15.00	12.70	13.74	16.87	14.20	12.67	11.83	13.26
MnO	0.25	0.25	0.29	0.29	0.30	0.25	0.26	0.23	0.29	0.27	0.27	0.28	0.27	0.25	0.23	0.27
MgO	4.54	5.88	8.04	7.23	4.50	4.50	5.14	7.63	5.48	8.25	6.24	5.83	6.61	6.76	7.06	7.29
CaO	8.31	7.65	10.66	8.62	7.95	7.87	5.97	9.29	7.30	9.63	10.00	9.53	10.01	8.78	9.29	9.52
Na_2O	2.92	3.91	1.46	2.73	2.13	3.50	4.08	2.28	3.65	1.54	2.11	1.92	1.86	2.94	2.41	2.36
K_2O	0.70	1.08	1.29	0.97	1.28	0.87	0.95	1.34	0.69	1.62	1.02	1.08	1.20	0.27	0.74	0.97
P_2O_5	0.17	0.10	0.19	0.14	0.16	0.24	0.21	0.18	0.19	0.16	0.13	0.18	0.12	0.18	0.09	0.11
LOI	2.30	2.60	2.56	2.37	2.53	2.60	2.40	2.12	2.57	2.60	2.55	1.99	2.56	2.52	2.06	2.56
TOTAL	101.10	99.55	100.50	99.62	99.95	99.98	99.46	99.57	100.25	100.23	99.67	99.94	99.92	97.66	99.49	100.23
Qz	5.11	0.00	0.00	2.85	5.33	0.00	0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ab	24.92	34.02	12.58	23.68	18.44	30.31	35.44	19.73	31.50	13.31	18.32	16.52	16.11	25.47	20.98	20.38
Or	4.17	6.56	7.70	5.88	7.74	5.26	5.76	8.10	4.16	9.78	6.18	6.49	7.26	1.63	4.50	5.85
An	27.67	24.08	34.06	27.17	34.46	28.25	22.28	28.70	25.50	32.57	32.45	32.07	33.67	33.72	35.51	32.22
Di	10.77	11.84	15.25	12.96	4.04	8.49	5.64	14.18	8.53	12.46	14.65	12.44	13.57	8.01	9.31	12.62
Hy	15.49	6.17	14.92	19.62	20.38	14.32	15.80	16.19	9.62	15.06	13.69	11.41	11.17	16.06	16.25	9.28
Ol	0.00	9.69	6.42	0.00	0.00	3.43	0.00	4.59	10.07	7.82	5.81	9.46	9.09	6.01	5.86	11.36
Mt	6.80	5.69	6.23	5.72	6.51	6.66	10.67	5.85	7.40	6.27	6.83	8.30	7.03	6.26	5.90	6.54
Il	2.61	1.66	2.34	1.74	2.67	2.67	2.64	2.20	2.72	2.29	1.72	2.84	1.77	2.36	1.41	1.46
Ap	0.40	0.24	0.45	0.33	0.38	0.57	0.50	0.43	0.45	0.38	0.31	0.42	0.28	0.43	0.21	0.26

TABLE 31a

GARABAL HILL - GRANITIC & ACID HYBRID ROCKS

SAMPLE NO.	1a	2	123	102	29	106	11	104	15	26	10	27	17	137	136	3
SiO_2	65.53	61.67	61.18	60.70	59.54	59.07	58.44	58.32	57.50	57.37	57.32	57.24	57.27	57.22	57.12	63.36
TiO_2	0.55	0.64	0.69	0.85	0.75	0.89	0.87	0.90	0.87	1.03	0.85	0.85	0.95	0.97	0.97	0.67
Al_2O_3	15.22	16.32	17.22	16.57	18.40	17.48	13.05	17.89	18.01	17.47	17.73	15.89	17.90	17.26	17.74	16.64
FeO	3.93	5.02	5.36	5.85	5.86	6.05	7.80	6.33	6.58	6.79	6.23	7.42	6.78	6.85	6.82	4.31
MnO	0.07	0.10	0.09	0.08	0.11	0.09	0.18	0.08	0.08	0.11	0.11	0.14	0.10	0.11	0.10	0.07
MgO	2.40	3.22	2.87	2.84	3.26	2.95	6.94	3.15	3.98	3.32	4.04	5.51	3.60	3.87	3.60	3.06
CaO	3.02	4.41	4.50	3.79	5.27	4.32	6.38	4.87	6.07	4.53	6.11	5.42	5.13	5.20	5.19	3.78
Na_2O	3.85	3.72	4.27	3.95	3.74	4.17	2.82	4.37	4.13	4.29	4.63	3.36	4.11	3.92	4.06	4.16
K_2O	3.68	2.75	3.12	3.58	1.99	3.44	1.97	3.25	1.73	3.30	0.96	2.82	2.91	2.94	2.93	2.94
P_2O_5	0.16	0.18	0.21	0.32	0.24	0.31	0.21	0.33	0.33	0.45	0.28	0.27	0.28	0.38	0.30	0.20
LOI	1.30	1.40	1.30	1.20	1.20	1.70	1.70	1.40	1.50	1.50	1.60	1.40	1.40	1.30	1.30	1.20
TOTAL	99.71	99.52	100.81	99.73	100.36	100.47	100.36	100.69	100.78	100.16	99.86	100.32	100.43	100.02	100.13	100.39
Qz	19.56	15.89	9.87	10.90	12.88	7.19	11.37	5.03	7.32	4.54	7.34	6.63	4.95	10.36	5.07	15.63
Ab	33.04	32.02	36.23	33.85	31.85	35.65	24.13	37.16	35.12	36.71	39.78	28.67	35.04	34.31	34.68	35.42
Or	22.06	16.53	18.49	21.42	11.83	20.54	11.77	19.30	10.27	19.72	5.76	16.80	17.32	17.97	17.48	17.48
An	13.61	20.09	18.70	16.93	24.73	19.05	17.35	19.74	25.66	18.92	25.19	20.15	22.01	12.52	21.78	17.56
Di	0.44	0.80	1.91	0.00	0.00	0.46	10.79	1.14	2.00	0.69	3.07	3.43	1.48	0.00	1.85	0.00
Hy	6.86	9.05	10.33	11.52	12.68	11.65	18.48	12.03	13.93	13.02	13.46	18.29	13.97	15.23	13.19	8.87
Mt	2.88	3.70	2.59	2.85	2.86	2.95	3.80	3.05	3.20	3.30	3.06	3.70	3.29	3.41	3.33	3.12
Il	1.06	1.24	1.32	1.64	1.44	1.71	1.67	1.72	1.66	1.98	1.64	1.63	1.82	1.91	1.86	1.28
Ap	0.38	0.42	0.49	0.75	0.56	0.73	0.49	0.77	0.77	1.05	0.66	0.63	0.65	0.91	0.70	0.47
Cm				0·09	1·11									3·32		0·24

Table 31b: Garabal Hill - Hybrids

Sample No.:	18	138	135	16	23	116	21
$Si0_2$	56.84	56.39	55.93	54.95	54.90	53.98	53.77
$Ti0_2$	0.97	0.99	0.93	9.84	0.89	1.01	1.18
Al_20_3	17.40	17.56	17.93	16.27	15.95	18.49	12.49
Fe0	6.79	7.09	7.18	7.73	7.26	7.37	12.26
Mn0	0.1	0.10	0.11	0.13	0.12	0.09	0.19
Mg0	3.98	4.10	3.85	6.89	6.69	4.62	6.43
Ca0	5.06	5.71	5.94	6.61	4.96	7.25	8.71
Na_20	4.14	3.93	4.28	3.70	4.45	4.17	2.46
K_20	2.73	2.59	2.41	1.63	2.51	1.73	1.35
P_20_5	0.36	0.39	0.33	0.19	0.23	0.25	0.18
LoI	1.60	1.40	1.30	1.60	1.90	1.40	1.50
Total:	99.88	100.25	100.19	100.54	99.86	99.86	100.52
Qz	4.90	4.87	2.95	2.53	0.00	1.60	8.62
Ab	35.56	33.45	36.53	31.56	38.35	35.75	18.45
Or	16.38	15.45	14.37	9.71	15.11	10.36	8.05
An	21.19	22.88	22.84	23.20	16.47	27.03	20.63
Di	0.74	2.59	3.90	7.01	5.74	6.36	18.61
Hy	15.05	14.31	13.29	20.10	17.81	12.94	16.91
Ol	0.00	0.00	0.00	0.00	0.66	0.00	0.00
Mt	3.39	3.46	3.50	3.77	3.58	3.36	6.04
Il	1.87	1.90	1.78	1.61	1.69	11.95	2.27
Ap	0.85	0.91	0.77	0.44	0.54	0.59	0.37

TABLE 31c GARABAL - HILL DIORITES

SAMPLE NO.	115	105	86	85	77	82	121	80	22	101
SiO_2	53.07	52.72	51.78	51.89	51.17	50.91	48.09	49.87	51.88	51.79
TiO_2	1.06	1.03	0.97	0.99	1.03	0.92	1.34	0.86	1.06	1.13
Al_2O_3	18.99	17.42	19.54	18.84	17.82	16.92	15.00	15.89	18.87	14.09
FeO	6.84	8.18	8.37	7.84	9.13	10.87	10.49	10.29	7.01	8.30
MnO	0.09	0.13	0.14	0.14	0.16	0.17	0.18	0.16	0.10	0.14
MgO	4.55	6.59	5.20	5.05	6.62	7.19	9.58	7.70	4.92	8.43
CaO	7.10	7.07	8.04	7.18	8.51	9.04	8.11	9.98	6.76	9.00
Na_2O	4.14	3.68	4.04	4.14	3.46	2.88	2.78	2.54	2.84	2.84
K_2O	2.05	1.98	1.34	1.39	1.53	1.40	1.07	0.48	1.36	2.19
P_2O_5	0.29	0.27	0.38	0.36	0.33	0.-5	0.43	0.26	0.37	0.24
LOI	1.90	1.40	1.20	2.30	1.80	1.60	2.00	1.40	3.00	2.90
TOTAL	100.19	100.47	100.00	99.12	100.56	100.95	99.07	99.73	98.17	98.05
QZ	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ab	36.50	31.35	32.26	34.17	28.04	22.22	24.16	24.37	45.91	26.21
Or	12.30	11.78	4.83	4.87	5.06	4.13	6.49	2.88	8.43	10.25
An	27.13	22.63	34.58	32.68	31.88	29.45	26.02	29.64	25.54	27.58
Di	5.49	8.86	2.61	1.31	7.02	12.47	10.10	15.43	4.17	11.44
Hy	5.94	9.35	18.48	22.42	8.93	21.17	10.71	15.26	7.10	10.13
Ol	8.16	11.38	2.94	0.00	4.43	5.52	16.22	7.59	3.36	5.22
Mt	1.68	1.99	2.04	1.95	2.23	2.64	2.61	2.53	3.01	4.08
Il	2.05	1.97	1.86	1.94	1.98	1.76	2.62	1.66	2.11	2.18
Ap	0.68	0.63	0.89	0.86	0.77	0.12	1.02	0.61	0L90	0.56

TABLE 31d GARABAL HILL - GABBROS

SAMPLE NO.	10X	5	83	129	108	6	119	12	113	114	87	9	28	79
SiO_2	50.92	50.81	50.74	49.94	49.38	49.05	48.73	48.77	48.47	48.38	47.90	48.02	49.89	51.37
TiO_2	0.92	2.24	0.62	0.50	0.81	1.73	1.13	0.57	0.82	0.93	1.14	0.91	0.86	1.09
Al_2O_3	12.79	13.41	10.29	14.83	13.76	15.66	14.49	16.04	14.27	12.54	14.84	16.16	11.40	18.46
FeO	10.38	13.32	13.26	9.41	9.90	10.85	10.13	9.09	9.68	10.95	10.26	11.29	11.01	9.18
MnO	0.20	0.19	0.21	0.17	0.17	0.18	0.18	0.15	0.16	0.19	0.16	0.17	0.21	0.14
MgO	10.98	6.42	14.73	10.88	10.38	8.83	10.04	10.84	11.72	12.04	11.01	9.50	12.12	5.84
CaO	8.05	9.21	7.94	10.19	9.67	9.46	8.94	10.00	9.59	10.19	8.85	9.47	8.91	6.25
Na_2O	1.82	1.91	1.51	1.59	1.89	2.35	2.02	1.69	1.23	1.38	1.47	1.68	1.80	1.33
K_2O	1.56	1.66	0.29	0.83	1.60	0.36	1.37	1.34	0.95	0.98	1.96	0.85	1.16	1.47
P_2O_5	0.05	0.23	0.21	0.03	0.13	0.16	0.22	0.06	0.03	0.19	0.13	0.19	0.22	0.36
LOI	2.20	0.90	0.60	1.90	2.00	1.30	1.80	1.80	2.30	2.20	2.00	1.30	2.10	2.20
TOTAL	99.87	100.30	100.40	100.27	99.79	99.93	100.05	100.35	99.22	98.97	99.72	99.54	99.68	97.72
Qz	1.38	5.13	1.54	2.10	0.00	0.87	0.00	0.00	2.00	0.00	0.00	0.00	0.00	0.00
Ab	15.72	16.21	12.76	13.61	16.32	20.04	17.52	14.47	10.71	11.58	12.69	14.43	15.56	11.49
Or	9.41	9.60	1.71	4.96	9.65	2.14	8.30	8.01	5.78	5.88	11.82	5.10	7.00	11.89
An	22.62	23.34	20.44	31.28	24.88	31.40	27.13	32.65	31.53	35.53	28.72	34.59	20.06	30.26
Di	14.44	17.33	14.20	14.91	18.83	10.48	13.68	13.87	13.90	19.81	12.32	9.65	19.14	11.69
Hy	29.38	17.08	41.24	27.01	19.12	25.30	22.53	18.61	29.55	24.76	19.12	27.78	24.62	26.66
Ol	0.00	0.00	0.00	0.00	4.39	0.00	3.05	6.66	0.00	4.57	7.72	0.67	8.67	2.95
Mt	5.10	6.46	6.42	4.60	4.89	5.31	5.01	4.46	4.82	5.35	5.06	5.54	2.72	4.05
Il	1.79	4.27	1.18	0.96	1.57	3.32	2.20	1.10	1.60	1.79	2.21	1.76	1.67	2.12
Ap	0.12	0.53	0.49	0.52	0.31	1.07	0.52	0.14	0.07	0.45	0.31	0.45	0.52	0.85

TABLE 31e

GARABAL HILL - HORNBLENDE GABBROS

SAMPLE NO.	109	24	14	13	122	128	8	107	118	117	120	139	84	1
SiO_2	50.52	50.47	49.68	49.52	48.92	48.75	48.33	48.29	48.03	47.57	46.86	49.87	50.14	47.00
TiO_2	0.51	1.16	1.09	0.92	1.13	1.63	1.41	1.23	1.69	1.70	1.55	1.71	0.58	1.06
Al_2O_3	13.64	15.20	13.35	15.66	14.50	13.47	14.29	15.21	15.32	14.97	15.65	15.64	12.88	14.26
FeO	10.36	9,30	10.58	8.88	9.71	10.56	11.00	9.29	11.51	11.50	11.74	8.76	10.53	9.81
MnO	0.20	0.16	0.18	0.15	0.16	0.15	0.16	0.15	0.19	0.17	0.17	0.14	0.19	0.17
MgO	11.14	8.98	10.99	10.21	9.68	10.56	10.48	10.54	9.46	10.15	9.94	8.82	12.00	11.78
CaO	7.73	9.36	9.41	9.44	8.89	8.41	11.15	10.33	9.74	10.41	9.83	8.47	8.78	10.00
Na_2O	1.89	2.79	1.98	2.10	2.12	2.00	1.79	1.80	2.02	2.03	1.71	2.80	1.90	1.53
K_2O	1.53	0.88	1.04	1.26	1.54	1.70	0.46	1.16	1.92	1.86	1.90	1.40	1.92	1.44
P_2O_5	0.25	0.17	0.25	0.08	0.23	0.09	0.12	0.06	0.39	0.33	0.041	0.38	0.11	0.09
LOI	2.00	2.00	1.70	1.80	2.20	2.30	1.80	1.90	1.70	0.50	1.70	1.80	1.40	2.70
TOTAL	99.77	100.47	100.25	100.02	99.08	99.62	100.99	99.96	101.97	101.19	101.46	99.79	100.43	99.87
Qz	0.49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ab	15.49	23.91	16.95	18.04	18.46	17.34	15.22	15.49	13.34	17.23	12.44	24.91	12.83	13.92
Or	6.97	5.27	6.22	7.56	9.37	10.29	2.73	6.97	9.41	8.28	11.43	8.42	12.23	8.89
An	30.55	26.73	24.79	30.08	26.29	23.35	29.79	30.55	28.21	30.21	29.63	26.48	22.46	26.02
Di	17.10	15.56	16.85	13.69	14.24	15.21	20.31	17.10	11.87	15.79	11.01	11.13	14.75	14.22
Hy	32.21	20.51	26.21	20.79	21.07	20.55	20.26	17.43	26.15	18.45	22.51	19.73	31.56	25.39
Ol	0.00	0.81	1.09	3.48	2.94	4.60	2.22	5.52	0.14	5.37	4.32	1.55	0.02	4.60
Mt	5.11	4.54	5.18	4.35	4.83	5.23	5.37	4.57	5.63	5.58	5.74	4.33	5.20	4.73
Il	2.38	2.23	2.10	1.78	2.21	3.18	2.70	2.38	3.24	3.24	2.98	3.31	1.13	2.00
Ap	0.14	0.40	0.59	0.19	0.55	0.21	0.28	0.14	0.91	0.77	0.96	0.90	0.26	0.20

Table 31f: Garabal Hill - Hornblendites

Sample No.:	103	132	125	126
$Si0_2$	48.30	45.48	45.24	45.19
$Ti0_2$	1.73	1.40	2.07	1.69
Al_20_3	14.36	5.96	15.28	13.58
Fe0	11.03	18.66	11.12	11.16
Mn0	0.15	0.28	0.14	0.17
Mg0	9.43	16.56	11.48	12.59
Ca0	8.92	9.32	10.26	10.11
Na_20	2.53	0.50	1.19	1.41
K_20	1.49	0.19	1.62	1.39
P_20_5	0.33	0.10	0.05	0.04
LoI	2.00	2.10	2.40	2.50
Total:	100.27	100.55	99.86	99.83
Ab	21.72	4.28	10.30	12.22
Or	8.93	1.14	9.85	8.41
An	23.81	13.63	29.51	27.30
Ne	0.00	0.00	0.00	0.00
Di	15.37	26.46	17.95	19.21
Hy	11.61	31.82	9.46	5.94
Ol	9.00	10.60	13.24	17.86
Mt	5.41	9.15	5.50	5.53
Il	3.34	2.69	4.03	3.29
Ap	0.78	0.23	0.12	0.09

Sample No.:	7	127	110	124	111
$Si0_2$	44.83	43.81	43.61	42.55	42.06
$Ti0_2$	1.78	2.75	2.34	2.37	2.59
Al_20_3	14.13	11.22	8.92	9.77	9.62
FeO	11.84	13.25	14.19	14.27	14.91
MnO	0.14	0.16	0.18	0.18	0.18
MgO	11.53	13.75	14.72	14.97	14.94
CaO	10.87	11.04	11.45	12.31	12.41
Na_20	1.47	1.48	1.15	0.99	0.95
K_20	1.05	0.69	0.35	0.55	0.53
P_20_5	0.06	0.05	0.05	0.03	0.04
LoI	1.90	2.40	2.80	2.50	2.50
Total:	99.60	100.60	99.76	100.49	100.73
Ab	12.64	10.44	10.00	3.58	2.33
Or	6.33	4.14	2.13	3.30	3.18
An	29.48	22.29	18.67	20.96	20.74
Ne	0.03	1.23	0.00	2.68	3.16
Di	20.37	26.60	31.82	33.08	33.52
Hy	5.93	4.75	6.54	4.49	4.79
Ol	16.60	18.59	19.07	20.21	20.34
Mt	5.82	6.50	7.06	7.02	7.27
Il	3.45	5.31	4.57	4.58	5.00
Ap	0.14	0.12	0.12	0.07	0.09

Table 31g: Garabal Hill - Pyroxenites (81, 78) and Peridotites (133, 112)

Sample No.	81	78	133	112
$Si0_2$	50.93	49.88	43.74	42.55
$Ti0_2$	0.64	0.86	0.52	1.12
Al_20_3	4.21	3.43	3.80	2.33
$Fe0$	13.40	15.59	13.09	18.40
$Mn0$	0.26	0.27	0.21	0.26
$Mg0$	16.17	17.45	23.90	22.83
$Ca0$	13.63	11.88	10.30	11.25
Na_20	0.35	0.29	0.07	0.00
K_20	0.11	0.14	0.10	0.03
P_20_5	0.13	0.09	0.07	0.02
LoI	0.40	0.30	3.10	0.90
Total:	100.23	100.18	98.90	99.69
Qz	2.35	1.71	0.00	0.00
Ab	2.96	2.45	0.62	0.00
Or	0.65	0.83	0.61	0.18
An	9.59	7.63	10.16	6.33
Di	46.15	40.96	34.04	40.21
Hy	30.31	37.17	17.97	6.82
Ol	0.00	0.00	29.04	34.79
Mt	6.48	7.51	6.57	9.99
Il	1.22	1.63	1.03	2.15
Ap	0.30	0.21	0.17	0.05

Table 32a: Arran - Granitic Rocks

Sample No.	16	15	55	G	20	32	43
Rb	129.0	140.6	110.2	124.6	79.2	80.6	78.3
Ba	1106.1	1092.2	1142.3	905.2	1036.3	907.6	944.4
Sr	80.2	123.1	146.2	141.5	225.1	197.0	220.4
Y	61.1	48.2	57.2	63.3	50.1	46.2	45.6
Nb	22.7	20.1	18.9	20.7	16.3	17.0	16.6
Zr	346.1	330.1	337.7	317.6	277.2	290.2	280.7
Th	22.1	24.0	15.1	20.7	10.7	12.1	18.7
Pb	10.8	14.2	20.1	15.2	10.2	15.8	16.3
V	7.2	22.4	13.1	38.3	27.7	68.0	88.9
La	61.0	47.5	36.2	45.1	50.2	31.0	44.6
Zn	53.1	69.6	79.2	60.3	39.1	57.0	63.0
Cr	6.4	6.2	0.4	5.4	2.6	18.7	33.5
Ni	4.3	4.2	5.3	11.2	4.6	13.8	9.9
Cu	2.2	5.5	16.1	8.3	24.2	26.7	37.7

Sample No.	60	26	59	53	21	9X	29	
Rb	52.0	87.1	56.0	56.3	32.6	46.3	34.7	62.0
Ba	861.1	820.2	590.3	686.3	658.0	534.8	621.0	516.2
Sr	238.2	243.2	262.7	254.3	287.1	255.0	366.1	284.1
Y	46.0	50.0	50.0	52.0	41.8	49.0	55.2	36.1
Nb	15.0	17.2	16.0	13.4	13.7	14.1	20.7	12.7
Zr	305.0	256.7	216.6	216.0	211.2	182.0	210.2	153.0
Th	13.1	10.6	10.1	11.3	7.5	12.0	7.5	10.0
Pb	14.1	8.0	15.7	14.0	16.2	12.3	11.0	11.0
V	82.0	100.1	111.7	110.8	150.1	263.8	108.4	291.3
La	30.3	25.4	30.4	30.8	20.4	34.0	37.4	20.1
Zn	66.0	78.5	94.9	89.1	72.2	90.3	104.2	334.1
Cr	12.8	27.7	22.2	0.0	43.8	24.4	1.6	25.9
Ni	17.5	27.7	22.2	13.0	28.7	45.6	6.2	24.6
Cu	10.0	16.0	22.7	26.2	35.1	30.7	18.8	56.1

Table 32b: Arran - Intermediate Rocks

Sample No.	10	43X	30	8	13	17	12	56	11
Rb	76.8	58.6	33.0	69.3	48.0	34.0	39.6	39.3	47.3
Ba	574.8	599.9	553.0	726.5	528.5	363.1	593.0	430.2	549.5
Sr	265.6	242.1	263.5	342.2	296.5	193.3	326.2	213.3	307.2
Y	44.0	45.3	33.0	42.3	46.5	41.1	46.1	38.1	41.6
Nb	15.2	11.7	9.0	12.1	10.0	9.0	14.3	10.0	12.2
Zr	166.0	173.6	123.5	173.0	172.0	146.2	142.5	155.5	131.0
Th	11.7	5.8	10.0	9.7	7.0	6.0	6.2	5.2	10.4
Pb	8.3	14.2	10.3	10.0	1.08	8.2	12.1	9.2	6.1
V	255.1	234.6	252.5	289.3	229.5	246.1	215.3	183.8	276.0
La	27.0	25.5	22.0	28.3	21.2	19.3	24.4	11.0	23.4
Zn	76.2	85.5	71.6	87.0	85.3	90.4	101.1	82.7	116.6
Cr	36.6	29.8	57.4	28.2	29.4	53.1	10.4	65.2	15.3
Ni	26.4	29.8	57.4	28.2	29.4	53.1	10.4	65.2	15.3
Cu	33.0	119.3	57.2	48.6	22.1	66.2	46.2	96.7	36.2

Table 32c: Arran - Gabbroic Rocks

Sample No.	49	39X	35	36	40X	41X	42
Rb	19.9	31.7	22.7	8.8	44.3	33.7	25.2
Ba	383.7	316.2	297.4	165.1	402.2	336.0	193.7
Sr	272.2	193.3	276.2	173.3	193.7	190.7	262.2
Y	36.6	42.3	32.4	38.7	41.9	41.2	21.7
Nb	12.7	7.0	7.2	6.2	8.9	9.3	4.2
Zr	150.7	125.5	86.2	110.1	119.7	116.3	54.3
Th	12.5	3.7	4.0	3.1	5.3	6.0	4.7
Pb	10.5	20.1	13.2	7.2	14.0	12.4	6.6
V	257.5	300.8	468.6	220.1	309.8	321.8	189.2
La	16.1	14.3	12.0	6.2	14.0	10.5	5.1
Zn	80.3	119.2	85.1	92.7	135.2	132.0	55.0
Cr	71.9	74.9	25.4	24.9	85.3	71.5	59.6
Ni	55.7	65.5	35.2	73.2	73.2	73.6	73.3
Cu	71.6	119.8	126.2	86.1	122.9	188.2	53.7

Sample No.	4	18	3	58	19	54	61	BC3
Rb	9.0	44.1	29.4	30.3	22.2	28.1	38.8	39.1
Ba	134.1	489.5	461.2	434.4	355.1	380.2	434.6	388.0
Sr	198.9	291.1	336.0	272.2	256.1	273.3	267.7	277.1
Y	36.2	39.6	32.7	39.1	37.9	35.2	39.5	36.4
Nb	5.2	13.3	10.6	9.2	9.0	6.2	15.1	9.2
Zr	95.5	104.0	148.1	137.7	122.6	125.5	135.5	103.0
Th	6.3	9.2	4.0	3.9	4.2	2.0	4.8	7.4
Pb	7.2	14.8	7.0	7.7	9.2	8.7	11.2	14.9
V	329.2	282.9	424.4	397.5	293.5	386.2	612.9	514.1
La	3.3	24.1	14.9	11.9	12.0	12.0	15.8	17.8
Zn	101.7	94.0	81.1	96.6	94.3	99.1	104.4	100.1
Cr	70.3	57.9	2.4	0.0	16.0	0.2	0.0	37.8
Ni	70.4	40.2	12.7	25.0	33.6	33.2	67.3	66.6
Cu	125.3	75.9	45.1	73.7	89.1	84.4	105.5	80.3

Table 32d: Arran - Gabbroic Rocks

Sample No:	BA1	51	38	14	37	BA2
Rb	33.3	13.0	30.2	74.2	17.2	34.0
Ba	415.1	301.8	403.3	707.3	232.2	433.5
Sr	296.7	314.4	311.3	293.0	224.6	281.5
Y	33.3	28.7	31.6	40.1	37.7	36.5
Nb	10.7	7.2	6.6	12.1	5.6	10.5
Zr	133.3	112.7	105.5	153.0	112.7	36.5
Th	4.7	3.0	5.3	9.6	4.3	5.5
Pb	11.6	6.5	9.3	11.2	9.9	9.5
V	265.7	253.8	208.7	309.1	232.2	292.5
La	20.6	13.0	14.3	29.7	9.1	19.0
Zn	89.6	76.6	73.5	93.8	102.2	89.8
Cr	52.5	7§.6	46.3	24.0	30.6	54.7
Ni	42.3	45.0	42.6	23.2	93.2	52.2
Cu	61.8	64.6	60.2	33.7	33.6	61.9

Table 32e: Arran - Alkali Gabbros

Sample No.	46	47	50
Rb	20.0	25.7	57.7
Ba	355.0	358.1	164.0
Sr	397.5	532.6	508.2
Y	26.5	34.7	32.2
Nb	4.5	7.2	6.1
Zr	129.4	170.1	193.6
Th	0.0	0.0	0.0
Pb	13.3	6.2	17.0
V	231.1	233.4	255.6
La	8.0	6.1	4.1
Zn	82.8	68.0	77.7
Cr	76.1	69.4	45.1
Ni	36.9	35.6	43.7
Cu	72.2	98.7	118.2

TABLE 33a

BOLTON HILL - PEGMATITES & GRANITES

SAMPLE NO.	131	166	206	205	219	218	204	165	200	130	138	162	121	191	219
Rb	14.7	27.9	5.3	1.5	14.7	16.7	80.3	14.0	16.3	1.0	3.5	5.7	8.0	14.8	24.3
Ba	57.0	86.5	44.4	48.7	141.3	155.5	466.7	55.1	143.7	68.3	184.5	100.5	64.1	95.5	141.5
Sr	43.0	50.9	44.3	26.5	58.0	53.3	50.3	114.8	120.0	38.5	42.5	91.5	87.8	182.2	189.0
Y	7.5	17.9	16.3	12.0	8.5	167.	9.0	8.9	8.7	11.0	7.3	10.8	12.5	4.9	12.5
Nb	4.3	6.8	12.5	10.7	4.6	6.3	6.7	3.3	5.0	5.7	2.7	5.0	3.5	2.3	7.5
Zr	15.0	105.1	43.1	25.3	151.4	121.5	26.0	179.5	194.3	19.0	95.3	145.5	189.3	95.7	23.5
Th	1.0	4.5	10.3	6.7	11.3	13.7	5.0	5.6	3.0	4.5	2.5	3.3	3.0	4.5	4.3
Pb	2.1	4.9	8.8	9.5	4.7	2.7	22.7	3.5	3.5	5.9	2.9	4.7	4.5	2.5	2.7
V	84.3	10.7	11.3	11.2	21.8	22.0	8.5	3.5	8.8	7.1	5.5	18.0	20.9	28.3	66.5
La	10.8	20.7	18.5	11.0	28.5	33.1	14.0	13.3	12.6	14.1	10.7	19.3	10.7	10.4	14.1
Zn	15.3	32.7	17.0	21.0	24.0	24.5	16.1	19.5	11.0	11.3	16.5	25.5	24.7	42.5	54.5
Sc *											1.3				
Cr	7.1	8.3	8.9	4.9	20.2	11.1	19.9	0.3	3.0	12.0	10.1	2.8	13.2	14.8	14.8
Ni	3.7	30.3	63.0	3.1	5.3	9.7	2.2	99.0	3.5	2.0	70.4	107.5	88.2	74.5	5.8
Cu	1.3	0.8	3.4	8.0	2.0	4.9	7.7	3.8	2.5	5.2	2.2	1.0	23.0	1.7	5.7

* ANALYSIS PERFORMED BY NEUTRON ACTIVATION ANALYSIS

TABLE 33b

BOLTON HILL GRANITES

SAMPLE NO.	139	163	6	161	103	222	228a	228b	224a	224b	5	221	156	110	201
Rb	10.8	24.8	8.8	11.8	16.5	44.7	31.8	35.9	37.3	47.0	9.3	30.0	17.0	7.4	6.9
Ba	34.9	106.1	100.7	160.7	121.0	282.7	253.3	254.9	354.5	430.3	67.0	239.3	169.5	72.0	36.1
Sr	112.5	86.7	150.3	87.5	183.7	29.0	37.0	38.8	31.5	34.3	91.1	59.7	154.0	226.0	81.0
Y	6.3	8.0	9.0	5.8	7.7	26.7	24.7	23.2	24.7	25.5	9.5	10.7	6.7	7.5	11.3
Nb	2.7	3.0	2.9	3.8	4.3	11.1	10.7	11.0	11.0	12.3	4.7	5.1	2.9	5.1	6.5
Zr	132.9	90.1	144.3	87.5	1117.5	85.2	94.7	98.3	79.3	82.0	193.7	108.1	97.1	94.5	134.3
Th	2.7	2.5	4.1	2.1	3.0	13.0	11.5	11.3	12.1	12.3	2.1	4.5	4.3	1.7	3.0
Pb	2.7	5.5	4.1	4.4	3.9	8.1	6.7	6.2	13.1	13.0	1.1	4.3	5.9	4.5	4.3
V	16.7	44.1	36.3	36.3	56.9	10.8	12.8	11.3	10.2	9.3	32.5	50.0	64.8	84.8	96.7
La	13.7	13.7	11.5	10.8	11.3	28.7	30.0	27.0	27.3	25.3	10.6	18.5	12.4	10.4	9.5
Zn	24.0	31.0	24.5	35.3	45.0	24.0	15.7	17.0	15.5	15.0	21.3	46.0	36.5	50.0	44.5
Sc *	0.3	1.6			3						9		3.6	6.6	
Cr	2.3	14.7	18.0	10.1	13.5	0.2	5.6	6.1	31.0	19.1	24.7	39.8	22.9	7.8	32.1
Ni	76.3	55.8	59.6	37.8	3.3	3.4	1.4	33.8	5.1	58.8	4.3	27.2	37.7	3.1	31.5
Cu	5.8	0.7	2.0	2.6	10.2	0.0	3.2	0.0	0.0	0.0	2.3	1.2	2.2	16.3	10.0

* PERFORMED BY NEUTRON ACTIVATION ANALYSIS

TABLE 33c BOLTON HILL - INTERMEDIATE ROCKS

SAMPLE NO.	107	216	116	117	157	128	4	209	126	202	3	210	2	108	220
Rb	13.9	20.9	16.3	15.0	17.5	22.1	15.1	28.3	19.0	12.1	18.6	33.7	14.8	15.3	29.7
Ba	111.0	126.0	158.2	153.5	104.0	140.9	122.2	176.7	165.5	78.3	185.6	199.0	106.5	89.0	21.30
Sr	232.7	200.7	250.2	244.3	166.0	236.5	150.0	218.0	246.6	193.3	193.3	180.8	162.1	197.1	170.7
Y	11.8	21.3	14.7	16.1	12.3	15.5	12.5	24.3	22.5	15.3	16.0	22.7	19.3	15.4	18.5
Nb	4.0	7.5	8.3	8.0	5.6	8.5	8.3	6.5	10.5	5.0	6.0	6.5	5.9	5.5	6.1
Zr	180.0	263.0	263.8	223.5	117.3	153.9	160.3	32.7	243.7	98.6	77.3	32.7	33.1	147.4	117.2
Th	0.9	1.9	1.0	2.7	2.3	3.3	4.2	0.3	3.0	3.5	3.7	0.5	3.7	2.0	1.3
Pb	3.2	4.8	4.5	4.5	3.6	4.8	5.2	7.0	3.2	5.3	3.7	6.8	2.3	2.5	5.0
V	110.6	90.2	64.2	68.2	126.8	109.4	313.3	235.5	101.1	188.4	210.3	235.5	313.3	278.2	348.5
La	8.9	12.0	12.1	12.2	11.7	10.8	10.3	11.0	12.1	9.5	10.4	12.0	8.2	7.9	6.0
Zn	39.0	47.7	61.5	60.5	67.5	68.5	63.5	86.3	87.0	48.0	96.0	67.7	77.8	68.3	83.8
Sc *			14	14		26	16		29		21		33	27	
Cr	7.7	12.6	14.0	18.9	30.6	28.3	30.0	20.1	10.1	83.7	46.7	101.6	24.4	20.4	46.2
Ni	45.7	37.7	2.5	3.0	28.4	22.9	19.6	31.4	3.8	29.2	31.4	25.5	15.5	38.5	19.0
Cu	9.1	3.3	7.8	8.0	21.4	14.8	10.1	12.3	19.3	46.2	35.5	44.4	101.9	79.3	68.6

* PERFORMED BY NEUTRON ACTIVATION ANALYSIS

Table 33d : Bolton Hill - Pale Diorites

Sample No.	211	212	134a	190	XXX	140	145
Rb	12.2	11.5	21.7	16.3	18.3	6.3	33.7
Ba	85.3	67.3	205.7	178.7	211.3	86.3	226.0
Sr	186.7	67.4	160.8	195.5	186.4	112.5	153.7
Y	14.3	26.3	15.6	15.8	16.2	15.0	153.7
Nb	5.5	5.0	6.0	3.5	4.1	3.0	4.3
Zr	29.5	33.3	32.0	66.3	18.2	42.9	67.5
Th	1.0	2.9	3.7	3.5	2.4	3.9	2.5
Pb	2.2	4.4	1.1	1.8	3.1	4.8	5.0
V	215.5	298.7	185.5	294.3	295.0	267.7	313.8
La	11.0	10.5	8.1	7.6	7.9	8.2	8.3
Zn	57.5	70.5	52.0	64.5	55.3	63.5	80.3
Sc *	-	-	-	-	-	-	34
Cr	146.5	77.3	122.0	127.9	99.7	131.6	110.1
Ni	29.9	34.5	43.0	21.4	24.3	42.3	23.6
Cu	57.0	62.5	55.9	87.3	86.7	74.5	22.6

* Performed by Neutron Activation Analysis

Table 33d contd: Bolton Hill - Pale Diorites

Sample No.	146	154	133	129	132	101	100	136
Rb	20.7	19.5	30.5	29.0	28.5	28.2	20.1	26.5
Ba	154.5	159.2	186.4	254.1	206.5	200.7	109.1	134.5
Sr	128.7	144.5	146.3	135.0	156.9	135.7	159.2	113.3
Y	17.5	19.5	16.0	15.3	17.3	15.2	16.7	14.0
Nb	4.0	3.3	5.0	4.0	4.6	4.9	5.1	3.3
Zr	56.3	41.0	30.5	32.3	41.9	30.0	34.0	35.5
Th	3.9	4.6	2.3	3.0	3.0	2.1	4.4	4.5
Pb	4.4	4.9	2.0	4.0	3.7	3.6	4.2	3.9
V	305.1	370.6	287.5	328.3	291.3	284.4	284.4	362.3
La	7.7	9.7	6.1	4.5	6.6	6.0	5.3	6.6
Zn	74.3	89.0	66.3	76.3	60.3	66.3	72.0	64.3
Sc *	-	41	-	-	-	-	36	-
Cr	116.0	130.3	42.8	176.8	74.2	107.0	48.1	119.8
Ni	33.7	28.7	28.5	31.9	25.9	31.0	21.3	65.5
Cu	65.0	59.1	83.7	73.8	131.3	55.2	91.9	92.7

* Performed by Neutron Activation Analysis

TABLE 33F

BOLTON HILL - PEGMATITES & GRANITES

SAMPLE NO.	X	214	106	229	118	119	215	105	124	104	115	122	114x	108x	226	112
Rb	9.9	31.0	24.8	24.2	24.5	17.7	16.5	21.0	15.0	21.0	19.5	22.1	21.5	8.0	19.0	19.9
Ba	133.0	226.3	157.3	154.3	143.0	103.8	196.2	130.2	143.1	186.3	136.4	144.6	163.7	152.3	149.3	89.1
Sr	206.2	164.3	185.8	192.0	234.5	205.0	161.5	176.2	191.9	185.5	172.5	190.7	192.4	147.5	168.3	144.1
Y	46.3	35.0	16.1	34.3	32.5	35.1	46.5	17.3	41.0	17.5	25.5	29.3	25.7	19.0	16.5	19.1
Nb	8.5	8.8	4.9	9.5	9.0	8.3	10.5	6.0	9.0	4.2	5.5	7.4	6.1	6.3	4.7	7.0
Zr	85.0	47.3	27.2	65.5	128.3	45.0	48.4	34.4	53.2	33.7	32.2	64.6	40.2	32.4	29.7	34.4
Th	4.0	3.5	4.8	4.3	2.8	1.1	4.4	0.8	2.0	0.8	3.5	0.4	1.5	1.3	2.7	3.0
Pb	4.7	5.0	0.0	7.0	2.1	2.2	5.3	2.0	3.9	4.2	3.0	3.5	1.2	2.4	1.5	3.0
V	392.3	383.5	430.9	414.7	310.7	363.0	431.2	396.3	512.2	404.5	442.0	640.6	441.9	418.5	414.5	384.7
La	8.7	13.0	3.3	12.0	7.1	8.3	11.5	3.1	6.7	4.3	7.7	5.4	4.2	3.9	3.5	7.8
Zn	128.5	109.0	89.0	114.0	116.5	119.7	136.5	84.0	137.5	88.0	100.0	123.5	101.8	95.5	89.0	95.0
Sc *									55				55	50		53
Cr	32.2	26.9	148.3	24.2	6.0	0.2	34.6	154.3	1.1	90.6	19.3	0.9	20.0	121.2	39.2	0.3
Ni	13.3	19.5	31.3	7.5	15.6	2.7	34.9	30.0	9.8	47.7	6.0	11.0	9.3	39.4	26.5	9.6
Cu	35.0	31.5	93.9	35.3	32.3	30.7	64.9	75.7	35.0	101.3	45.3	50.1	46.4	81.3	49.0	73.4

* PERFORMED BY NEUTRON ACTIVATION ANALYSIS

TABLE 34a

GARABAL HILL - GRANITIC & ACID HYBRIDS

SAMPLE NO.	1a	2	123	102	29	106	11	104	15	26	10	27	17	137	136	3
Rb	73.5	62.3	89.9	113.5	60.5	99.0	51.2	102.1	66.3	111.1	28.3	91.3	74.8	103.2	73.0	71.6
Ba	425.0	495.7	587.7	697.3	480.0	655.5	520.3	680.1	433.0	656.3	453.2	647.5	450.5	646.3	572.8	416.6
Sr	580.6	541.1	496.6	487.7	640.0	588.7	467.0	557.7	679.0	515.0	746.2	515.0	566.3	528.1	565.9	707.5
Y	14.7	18.0	20.3	26.7	21.0	16.5	33.0	23.3	20.9	23.3	21.3	23.3	24.6	23.0	23.0	14.6
Nb	13.9	10.2	10.4	18.6	11.7	4.6	15.1	15.3	10.1	21.2	10.0	13.0	13.3	16.1	13.6	10.2
Zr	157.3	157.3	163.3	243.5	202.3	55.3	165.5	236.7	160.6	167.3	210.1	182.2	165.6	227.9	166.8	180.5
Th *				20.2				11.7						14.3	9.1	
V	40.1	72.0	75.5	124.4	131.1	141.4	187.4	156.6	160.0	158.8	133.1	180.0	152.2	185.0	166.6	31.5
La	29.5	23.5	23.3	47.4	23.3	31.5	22.6	40.2	26.0	40.9	22.7	28.0	28.5	42.8	30.9	20.1
Ce *				86.9				75.4						79.1	66.1	
Nd *				41.8				33.4						38.3	34.7	
Sm *				7.22				6.69						6.67	6.15	
Eu *				1.40				1.43						1.54	1.49	
Yb *				2.58				2.17						2.27	2.19	
Lu *				0.29				0.24						0.28	0.24	
U *				4.8				4.1						4.6	3.0	
Zn	59.0	61.3	66.3	68.0	78.5	72.0	90.3	74.5	54.0	79.3	55.5	93.3	80.3	78.5	76.7	62.7
Cr	56.3	58.0	59.2	74.7	61.0	168.5	70.3	66.9	70.6	177.1	280.1	229.0	185.5	84.4	49.0	55.7
Ni	64.0	56.5	42.0	44.7	66.0	59.5	116.5	51.4	54.5	49.0	58.3	87.3	52.4	70.1	50.0	58.4
Cu	7.0	18.5	41.7	71.3	7.0	80.039.5		37.6	42.7	135.0	55.7	29.5	13.5	200.5	12.8	4.5

* PERFORMED BY NEUTRON ACTIVATION ANALYSIS

Table 34b: Garabal Hill - Hybrids

Sample No.	18	138	135	16	23	116	21
Rb	92.3	80.1	61.3	42.2	76.0	60.3	47.3
Ba	629.9	606.6	399.8	308.2	446.0	307.1	251.1
Sr	509.5	550.4	554.4	529.2	385.3	854.6	675.6
Y	24.7	25.2	21.5	20.0	20.2	20.4	40.3
Nb	18.1	14.7	10.6	7.1	10.3	9.0	13.9
Zr	270.2	183.1	137.2	93.4	157.3	121.8	83.5
Th *	-	-	5.7	3.2	-	2.7	6.4
V	176.5	177.5	201.2	198.3	162.2	195.9	306.4
La	32.0	31.3	30.1	29.9	22.3	22.5	19.2
Cr *	-	-	57.5	42.1	-	48.2	41.6
Nd *	-	-	31.0	22.1	-	23.0	28.1
Sm *	-	-	5.71	4.24	-	6.65	6.95
Eu *	-	-	1.4	1.42	-	1.63	1.35
Yb *	-	-	1.86	1.84	-	1.88	1.15
Lu *	-	-	0.23	0.23	-	0.23	0.52
U *	-	-	2.1	1.2	-	1.4	2.6
Zn	79.3	79.6	80.6	80.6	76.4	58.5	98.6
Cr	131.2	220.5	55.8	284.2	186.0	112.7	88.2
Ni	57.3	53.6	47.3	141.3	143.6	61.1	82.5
Cu	36.5	107.3	196.7	248.5	39.6	61.3	239.7

* Performed by Neutron Activation Analysis

TABLE 34c

GARABAL HILL - DIORITES

SAMPLE NO.	115	105	86	85	77	82	121	80	22	101
Rb	56.3	41.4	43.8	47.9	56.0	52.2	58.0	31.0	55.1	50.8
Ba	318.1	200.1	211.7	220.1	228.3	253.6	245.5	186.3	133.6	238.0
Sr	919.4	888.4	904.4	927.5	880.4	787.7	613.4	753.7	580.7	488.7
Y	22.3	20.4	13.3	14.5	17.2	16.3	22.5	21.3	23.0	22.0
Nb	10.6	8.7	4.0	4.4	3.0	3.8	5.5	1.1	4.3	9.8
Zr	101.7	147.3	36.6	36.6	40.5	50.7	45.2	41.5	118.2	139.0
Th *		0.9	0.7		0.6	0.5				0.4
V	290.1	286.8	222.2	304.0	247.7	343.8	340.9	322.0	309.3	257.0
La	21.5	22.7	17.4	16.9	16.1	8.7	13.0	10.5	17.5	19.9
Ce *		45.6	32.5		32.8	18.9				41.5
Nd *		24.2	22.5		20.7	12.3				24.2
Sm *		5.30	3.50		4.39	3.39				4.28
Eu *		1.45	1.77		1.69	1.11				1.44
Yb *		1.83	0.85		1.28	1.42				2.18
Lu *		0.24	0.11		0.17	0.22				0.23
U *		0.5	0.1		TRACE	0.1				0.2
Zn	56.7	80.3	89.3	81.0	85.5	102.7	94.7	95.7	62.0	72.3
Cr	306.6	392.4	107.2	327.7	148.4	219.5	286.4	550.3	441.6	469.5
Ni	54.6	163.7	58.7	67.3	89.7	107.6	144.5	109.6	44.5	171.5
Cu	51.0	100.5	36.0	35.5	109.3	285.3	24.6	283.7	245.5	55.0

* PERFORMED BY NEUTRON ACTIVATION ANALYSIS

TABLE 34d

GARABAL HILL - GABBROS

SAMPLE NO.	10X	5	83	129	108	6	119	12	113	114	87	9	28	79
Rb	48.6	51.8	2.0	28.2	54.4	19.6	49.2	44.2	28.7	34.0	26.0	24.0	29.0	35.2
Ba	198.5	304.4	10.5	170.4	210.5	99.6	240.0	216.3	158.8	180.2	110.3	191.1	160.4	134.3
Sr	491.3	456.5	436.0	648.9	536.2	567.0	556.7	624.4	508.8	457.3	661.2	619.3	293.0	683.6
Y	18.8	30.5	18.0	15.1	20.9	21.4	20.3	17.2	15.2	25.6	19.4	17.2	22.2	14.7
Nb	5.5	4.6	2.8	3.2	6.0	7.0	4.1	3.8	4.0	5.0	3.8	4.1	7.6	4.7
Zr	55.7	61.3	37.5	51.0	62.2	33.66	46.2	50.7	45.3	56.3	51.7	42.4	98.5	43.0
Th *		1.1	0.5							0.4				
V	309.0	411.1	376.7	298.2	303.9	330.0	323.3	282.4	283.9	336.6	329.7	348.9	356.1	249.9
La	9.0	16.9	10.4	7.3	7.2	11.0	6.7	7.5	5.0	10.6	8.0	8.7	11.1	15.5
Ce *		38.2	22.7							22.8				
Nd *		22.4	13.4							15.6				
Sm *		6.44	3.93							5.65				
Eu *		2.10	1.03							1.45				
Yb *		2.62	1.64							2.20				
Lu *		0.35	0.25							0.30				
U *		0.4	TRACE							TRACE				
Zn	88.5	98.3	127.0	83.1	79.7	94.0	76.0	72.3	84.0	89.6	69.7	95.2	112.0	87.5
Cr	333.2	184.5	986.6	274.0	388.8	223.3	400.2	501.1	374.9	678.9	510.1	497.7	576.5	470.5
Ni	137.5	90.7	316.4	126.3	176.0	99.3	148.6	175.5	173.5	175.0	131.5	118.3	199.9	71.7
Cu	38.5	182.7	52.0	20.0	501.5	111.5	63.5	73.5	37.3	191.7	84.3	57.4	11.5	181.5

* PERFORMED BY NEUTRON ACTIVATION ANALYSIS

TABLE 34e GARABAL HILL - HORNBLENDE GABBROS

SAMPLE NO.	109	24	14	13	122	128	8	107	118	117	120	139	84	1
Rb	43.5	40.2	55.5	51.5	49.2	52.0	58.0	30.0	42.0	78.3	62.8	46.6	32.3	53.0
Ba	179.1	182.4	184.6	192.3	222.3	243.3	249.4	174.4	193.9	284.2	262.3	200.5	115.2	260.3
Sr	522.6	550.1	536.5	616.5	563.0	468.1	518.3	588.7	585.5	496.0	562.3	608.7	538.9	560.1
Y	16.7	24.3	20.0	14.9	22.0	30.2	25.6	16.5	21.1	30.7	23.4	23.1	15.5	20.2
Nb	5.3	7.0	4.5	5.5	3.3	8.7	6.1	4.6	6.0	8.6	6.5	12.2	4.5	4.2
Zr	60.0	72.5	56.7	512.1	44.0	87.3	70.9	55.3	47.7	53.6	47.0	89.0	45.3	47.3
Th *			4.4				0.4		0.5					
V	324.4	296.6	335.5	266.5	280.0	319.9	333.6	269.4	366.8	379.5	360.7	279.7	322.5	315.1
La	11.0	10.2	20.4	9.0	8.0	12.1	9.5	8.5	11.7	12.2	11.5	16.8	10.5	5.4
Ce *			28.7				26.4		24.5					
Nd *			16.5				17.2		24.5					
Sm *			5.43				5.55		4.33					
Eu *			1.41				1.43		1.26					
Yb *			1.91				2.07		1.66					
Lu *			0.32				0.28		0.23					
U *			1.51				0.2		0.1					
Zn	99.7	80.7	92.0	71.0	72.3	78.5	86.5	71.3	95.7	92.3	94.5	74.7	88.3	77.0
Cr	477.4	436.6	418.9	462.2	427.0	304.3	361.7	498.8	402.5	355.5	383.9	440.0	456.9	497.1
Ni	140.5	102.3	142.7	142.0	144.3	138.3	132.7	159.3	105.5	117.3	124.3	140.3	226.7	187.3
Cu	31.0	145.5	98.4	106.5	24.0	10.0	52.7	160.7	148.0	139.5	29.5	41.0	28.5	27.0

* PERFORMED BY NEUTRON ACTIVATION ANALYSIS

TABLE 34f GARABAL HILL - HORNBLENDITES

SAMPLE NO.	103	132	125	126	7	127	110	124	111
Rb	52.0	4.0	55.5	54.0	32.2	10.6	4.2	10.0	13.4
Ba	321.3	104.4	249.1	245.2	195.0	49.3	14.0	51.2	33.0
Sr	522.2	162.6	422.3	379.1	480.3	303.3	190.5	171.4	212.3
Y	32.6	30.4	35.4	30.7	31.2	37.8	36.2	34.7	40.8
Nb	12.2	3.9	10.6	8.5	7.8	11.3	9.3	8.9	11.0
Zr	100.4	58.2	81.6	94.6	56.0	77.4	62.2	67.3	68.4
Th *					0.4				
V	334.0	636.4	372.7	384.4	356.5	327.7	455.5	465.2	481.9
La	18.2	1.1	10.6	7.7	5.8	6.7	3.0	5.0	0.6
Ce *					22.2				
Nd *					18.4				
Sm *					5.81				
Eu *					1.69				
Yb *					2.34				
Lu *					0.32				
U *					TRACE				
Zn	91.5	163.5	75.3	79.0	78.0	85.7	89.7	92.5	94.0
Cr	488.2	429.1	506.0	490.9	434.0	511.2	535.2	406.8	432.3
Ni	132.0	267.5	158.3	148.5	154.5	192.7	195.0	200.5	191.3
Cu	37.0	315.3	8.0	53.7	819.6	14.3	41.5	24.0	209.4

* PERFORMED BY NEUTRON ACTIVATION ANALYSIS

Table 34g: Garabal Hill - Pyroxenites (81, 78) & Peroditites (133, 112)

Sample No.	81	78	133	112
Rb	0.0	0.0	0.6	0.0
Ba	1.8	0.9	8.4	0.0
Sr	132.0	79.6	90.3	27.7
Y	42.2	34.5	21.1	22.2
Nb	2.5	5.0	2.7	1.8
Zr	55.3	50.8	34.7	40.1
V	420.4	531.1	427.0	646.6
La	7.3	3.8	4.1	1.2
Zn	181.3	149.5	99.3	120.5
Cr	545.3	470.0	727.7	783.2
Ni	229.5	281.5	639.6	341.7
Cu	65.0	137.5	264.3	19.7

Table 35a: <u>Arran Mixing Calculations (Granite amd Medium Gabbro)</u>

	Average	Average	9			20			32		
%	Granite	Gabbro	Actual	Estimated	Residuals	Actual	Estimated	Residuals	Actual	Estimated	Residuals
SiO_2	75.11	51.31	71.60	71.52	0.08	69.79	69.83	-0.04	68.52	68.54	-0.02
Al_2O_3	12.84	14.65	13.37	13.11	0.26	13.36	13.24	0.12	13.84	13.39	0.45
TiO_2	0.29	1.20	0.49	0.43	0.06	0.77	0.49	0.28	0.83	0.54	0.29
FeO	2.83	11.74	3.78	4.18	-0.40	5.77	4.81	0.96	5.55	5.29	0.26
MgO	0.28	6.42	0.67	1.21	-0.54	0.71	1.64	-0.93	1.53	1.97	-0.44
MnO	0.05	0.20	0.08	0.07	0.01	0.08	0.07	0.01	0.11	0.09	0.02
CaO	0.65	9.05	1.90	1.92	-0.02	2.40	2.51	-0.11	3.37	2.97	0.40
Na_2O	3.72	2.91	4.32	3.60	0.72	4.06	3.54	0.52	3.58	3.50	0.08
K_2O	4.42	0.76	3.82	3.87	-0.05	3.43	3.61	-0.18	3.25	3.41	-0.16
			Sums of squares of residuals 1.04			Sums of squares of residuals 2.19			Sums of squares of residuals 0.73		
			Granite 84.9%			Granite 77.8%			Granite 72.4%		
			Gabbro 15.1%			Gabbro 22.2%			Gabbro 27.6%		

TABLE 35b

ARRAN MIXING CALCULATIONS (GRANITE & MEDIUM GABBRO)

	SAMPLE NO. 43			21			9x			10		
%	ACTUAL	ESTIMATED	RESIDUALS	ACTUAL	ESTIMATED	RESIDUALS	ACTUAL	ESTIMATED	RESIDUALS	ACTUAL	ESTIMATED	RESIDUALS
SiO_2	67.05	66.93	0.12	60.15	60.18	-0.03	57.71	57.76	-0.05	57.17	57.10	0.07
Al_2O_3	13.61	13.45	0.16	14.52	13.97	0.55	14.49	14.16	0.33	14.63	14.20	0.43
TiO_2	0.92	0.60	0.32	1.41	0.86	0.55	1.42	0.96	0.46	1.42	0.98	0.44
FeO	6.13	5.85	0.28	8.82	8.42	0.40	9.86	9.34	0.52	10.12	9.56	0.56
MgO	1.61	2.36	-0.75	2.98	4.13	-1.15	3.92	4.77	-0.85	4.05	4.92	-0.87
MnO	0.11	0.10	0.01	0.16	0.14	0.02	0.2	0.16	0.05	0.17	0.16	0.01
CaO	3.32	3.50	-0.18	5.44	5.92	-0.48	5.90	6.79	-0.89	6.23	6.99	-0.76
Na_2O	3.69	3.45	0.24	3.26	3.21	0.05	3.91	3.13	0.78	3.58	3.11	0.47
K_2O	2.84	3.18	-0.34	1.66	2.13	-0.47	1.56	1.74	-0.18	2.30	1.66	0.64
		Sums of squares of residuals 0.97			Sums of squares of residuals 2.53			Sums of squares of residuals 2.71			Sums of squares of residuals 2.65	
		Granite 66.0% Gabbro 34.0%			Granite 37.3% Gabbro 62.7%			Granite 26.8% Gabbro 73.2%			Granite 24.6% Gabbro 75.4%	

Table 35 c: Arran Mixing Calculations (Granite and Medium Gabbro)

%	Sample No. 43X			22			38		
	Actual	Estimated	Residuals	Actual	Estimated	Residuals	Actual	Estimated	Residuals
SiO_2	56.24	56.21	0.03	53.90	53.80	0.10	53.62	53.59	0.03
Al_2O_3	14.87	14.28	0.59	13.88	14.45	-0.57	15.18	14.47	0.71
TiO_2	1.29	1.01	0.28	1.62	1.10	0.52	1.13	1.11	0.02
FeO	10.20	9.90	0.30	10.89	10.78	0.11	10.42	10.88	0.54
MgO	4.19	5.16	-0.97	4.01	5.01	-1.00	5.25	5.83	-0.58
MnO	0.20	0.17	0.03	0.18	0.18	0.00	0.18	0.19	-0.01
CaO	7.35	7.32	0.03	6.88	7.14	-0.26	8.36	8.24	0.12
Na_2O	3.72	3.08	0.64	3.19	3.00	0.19	3.14	2.99	0.15
K_2O	1.67	1.51	0.16	1.67	1.16	0.51	1.01	1.11	-0.10
	Sums of squares of residuals			Sums of squares of residuals			Sums of squares of residuals		
	1.89			1.97			1.08		
	Granite 20.6%			Granite 10.7%			Granite 9.6%		
	Gabbro 79.4%			Gabbro 89.3%			Gabbro 90.4%		

Table 35 d: Arran Mixing Calculations (Granite and Coarse Gabbro)

Sample No.	G	20	32	43	21	9X	10	43X	22	38	
SiO_2	0.01	-0.11	0.12	0.04	-0.07	0.11	0.03	0.02	0.12	0.09	
Al_2O_3	-0.33	-0.23	0.64	0.33	0.86	0.69	0.80	0.99	-0.12	1.17	
TiO_2	0.04	-0.12	0.10	0.09	0.12	-0.04	-0.07	0.27	-0.09	-0.60	
FeO	0.75	-0.42	-0.40	-0.54	-0.09	-1.21	-1.23	-1.60	-1.99	-2.59	
MgO	0.30	0.60	-0.02	-0.17	-0.18	0.29	0.00	0.26	-0.36	0.83	
MnO	-0.01	-0.01	0.02	0.01	0.02	0.05	0.01	0.04	0.00	0.01	Residuals
CaO	-0.13	0.00	0.55	0.01	-0.12	-0.47	-0.53	0.48	0.74	0.65	
Na_2O	-0.69	-0.48	0.03	0.18	-0.06	0.65	0.33	0.50	0.03	-0.01	
K_2O	0.09	0.24	-0.24	-0.43	-0.64	-0.39	0.43	-0.07	0.26	-0.36	
Sums of Squares of residuals	1.24	0.89	0.94	0.68	2.44	2.70	2.73	4.20	4.72	9.68	

Table 35 e: <u>Arran Mixing Calculations (Granite and Alkali Gabbro)</u>

Sample No	G	20	32	43	21	9X	10	43X	22	38	
SiO_2	-0.13	0.00	-0.06	0.12	-0.05	0.11	0.02	0.03	0.04	0.14	
Al_2O_3	-0.04	-0.34	-0.06	-0.54	-0.75	-.1.18	-1.12	-1.04	-2.41	-1.16	
TiO_2	-0.02	0.15	0.14	0.13	0.19	0.05	0.02	-0.17	0.01	-0.49	
FeO	-0.15	1.27	0.68	0.78	1.30	1.58	1.67	1.45	1.40	0.84	
MgO	-0.11	-0.33	0.54	0.19	0.57	1.16	1.22	1.22	0.71	1.90	Residuals
MnO	0.22	0.01	0.03	0.03	0.05	0.09	0.05	0.07	0.04	0.04	
CaO	0.27	0.26	0.90	0.42	0.60	0.38	0.57	1.42	0.28	1.68	
Na_2O	0.59	0.32	-0.16	-0.06	-0.51	0.13	-0.20	0.06	-0.60	-0.65	
K_2O	-0.19	-0.36	-0.40	-0.63	-0.99	-0.81	-0.01	-0.52	-0.24	-0.87	
Sums of squares of residuals	0.49	2.16	1.81	1.53	3.46	6.08	5.90	6.99	8.77	9.91	

Table 36a: **Bolton Hill Mixing Calculations (Granite and Dark Diorite)**

%	Average Granite	Average Dark Diorite	156 Actual	156 Estimated	156 Residuals	110 Actual	110 Estimated	110 Residuals	107 Actual	107 Estimated	107 Residuals
SiO_2	76.89	47.79	71.54	0.04	70.26	70.26	0.00	69.08	68.95	0.13	
Al_2O_3	12 88	16.17	14.01	13.49	0.52	14.13	13.63	0.50	14.10	13.76	0.34
TiO_2	0.13	1.31	0.37	0.35	0.02	0.41	0.40	0.01	0.52	0.45	0.07
FeO	1.45	13.70	3.71	3.70	0.01	4.41	4.26	0.15	5.19	4.73	0.46
MgO	0.52	6.07	1.33	1.54	-0.21	1.27	1.79	-0.52	1.39	2.01	-0.62
MnO	0.52	0.26	0.09	0.09	0.00	0.19	0.10	0.09	0.11	0.11	0.00
CaO	1.50	8.53	2.51	2.79	-0.28	3.35	3.11	0.24	3.99	3.38	0.61
K_2O	0.94	1.01	0.94	0.95	-0.01	0.39	0.96	-0.57	0.70	0.96	-0.26
			Sums of squares of residuals 0.39			Sums of squares of residuals 0.92			Sums of squares of residuals 1.15		
			Granite 81.6% Diorite 18.4%			Granite 77.1% Diorite 22.9%			Granite 73% Diorite 27%		

Table 36b: **Bolton Hill Mixing Calculations (Granite & Dark Diorite)**

	116			117			157			128		
%	Actual	Estimated	Residuals	Actual	Estimated	Residuals	Actual	Estimated	Residuals	Actual	Estimated	Residuals
SiO_2	68.15	68.25	-0.10	66.75	66.68	0.07	66.24	66.16	0.08	64.53	64.55	-0.02
Al_2O_3	14.31	13.87	0.44	14.37	14.03	0.34	13.85	14.09	-0.24	14.26	-0.02	
TiO_2	0.67	0.49	0.18	0.67	0.54	0.13	0.63	0.56	0.07	0.90	0.63	0.27
FeO	5.44	5.14	0.30	5.50	5.74	-0.24	6.68	5.95	0.73	7.41	6.67	0.74
MgO	1.40	2.19	-0.79	1.57	2.46	-0.89	2.05	2.56	-0.51	2.10	2.88	-0.78
MnO	0.14	0.11	0.03	0.15	0.12	0.03	0.18	0.13	0.05	0.23	0.17	0.06
CaO	4.34	3.62	0.72	4.01	3.96	0.05	4.03	4.08	-0.05	4.66	4.49	0.17
K_2O	0.91	0.96	-0.05	0.82	0.98	-0.14	0.93	0.96	-0.03	1.14	0.97	0.17
	Sums of squares of residuals			Sums of squares of residuals			Sums of squares of residuals			Sums of squares of residuals		
	1.46			0.99			0.85			1.28		
	Granite 69.9%			Granite 65.2%			Granite 63.3%			Granite 57.4%		
	Diorite 30.1%			Diorite 34.8%			Diorite 36.7%			Diorite 42.6%		

Table 36c: **Bolton Hill Mixing Calculations (Granite & Dark Diorite)**

	4			209			126			3		
	Actual	Estimated	Residuals	Actual	Estimated	Residuals	Actual	Estimated	Residuals	Actual	Estimated	Residuals
SiO_2	63.60	63.72	-0.12	61.95	62.04	-0.09	61.66	61.57	0.09	58.76	58.73	0.03
Al_2O_3	14.71	14.39	0.32	15.59	14.57	1.02	15.68	14.61	1.07	16.13	14.94	1.19
TiO_2	0.87	0.67	0.20	0.98	0.74	0.24	1.04	0.75	0.29	0.86	0.87	-0.01
FeO	6.67	7.09	-0.42	7.67	7.76	-0.09	8.06	7.88	0.18	9.18	9.11	0.07
MgO	1.98	3.08	-1.10	3.60	3.38	0.22	3.49	3.43	0.06	3.68	3.99	-0.31
MnO	0.20	0.15	0.05	0.23	0.16	0.07	0.23	0.16	0.07	0.22	0.16	0.06
CaO	4.85	4.73	0.12	4.55	5.12	-0.57	5.32	5.19	0.13	5.91	5.89	0.02
K_2O	0.57	0.97	-0.40	1.26	0.98	0.28	0.93	0.98	-0.05	0.98	0.98	0.00
	Sums of squares of residuals			Sums of squares of residuals			Sums of squares of residuals			Sums of squares of residuals		
	1.69			1.55			1.28			1.51		
	Granite 54.0%			Granite 48.5%			Granite 47.3%			Granite 37.6%		
	Diorite 46.0%			Diorite 51.5%			Diorite 52.7%			Diorite 62.4%		

Table 36d: Bolton Hill Mixing Calculations (Granite & Dark Diorite)

	108			220		
	Actual	Estimated	Residual	Actual	Estimated	Residual
$Si0_2$	55.41	55.30	0.11	54.25	54.24	0.01
Al_20_3	16.07	15.31	0.76	15.00	15.44	-0.44
$Ti0_2$	1.08	1.00	0.08	10.13	10.98	-0.85
Fe0	9.60	10.49	-0.89	10.13	10.98	-0.85
Mg0	4.32	4.62	-0.30	5.83	4.84	0.99
Mn0	0.18	0.22	-0.04	0.21	0.21	0.00
Ca0	6.52	6.69	-0.17	6.96	9.97	-0.01
K_20	0.68	0.99	-0.31	0.93	0.99	-0.06
	Sums of squares of residuals 1.50			Sums of squares of residuals 1.97		
	Granite 26.3% Diorite 73.7%			Granite 22.2% Diorite 77.8%		

Table 36e:

Bolton Hill Mixing Calculations (Granite & Pale Diorite)

%	Average Granite	Average Pale Diorite	5			221			202		
			Actual	Estimated	Residuals	Actual	Estimated	Residuals	Actual	Estimated	Residuals
SiO_2	76.89	47.94	73.66	73.66	0.04	71.93	71.99	-0.06	62.18	62.27	-0.09
Al_2O_3	12.88	16.62	13.52	13.30	0.22	13.69	13.53	0.16	14.80	14.79	0.01
TiO_2	0.13	0.62	0.23	0.19	0.04	0.20	0.22	-0.02	0.43	0.38	0.05
FeO	1.45	10.57	2.01	2.48	-047	3.30	3.05	0.25	6.03	6.10	-0.07
MgO	0.52	8.03	1.20	1.37	-0.17	0.90	1.40	-0.50	3.82	4.35	-0.53
MnO	0.05	0.22	0.13	0.07	0.06	0.14	0.08	0.06	0.18	0.14	0.04
CaO	1.50	10.40	1.61	2.51	-0.90	2.14	3.05	-0.91	6.38	6.04	0.34
K_2O	0.94	1.08	1.50	0.96	0.54	1.08	0.96	0.12	0.43	1.01	0.58
			Sums of squares of residuals 1.40			Sums of squares of residuals 1.18			Sums of squares of residuals 0.74		
			Granite 88.7% Diorite 11.3%			Granite 82.7% Diorite 17.3%			Granite 49.0% Diorite 51.9%		

Table 36f: **Bolton Hill Mixing Calculations (Granite & Pale Diorite)**

	210			211			212			140		
	Actual	Estimated	Residuals	Actual	Estimated	Residuals	Actual	Estimated	Residuals	Actual	Estimated	Residuals
SiO_2	57.86	57.74	0.12	56.45	56.42	0.03	55.12	55.19	-0.07	53.37	53.48	-0.11
Al_2O_3	15.84	15.34	0.50	14.77	15.52	-0.75	14.82	15.69	-0.87	15.58	15.92	-0.34
TiO_2	0.47	0.45	0.02	0.44	0.48	-0.04	0.47	0.50	-0.03	0.48	0.53	-0.05
FeO	7.22	7.45	-0.23	7.50	7.89	-0.39	8.34	8.32	0.02	8.35	8.87	-0.52
MgO	4.91	5.46	-0.55	6.03	5.83	0.20	6.48	6.18	0.30	6.88	6.63	0.25
MnO	0.17	0.16	0.01	0.20	0.17	0.03	0.23	0.05	0.16	0.19	-0.03	
CaO	6.72	7.36	-0.64	7.25	7.79	-0.54	7.23	8.20	-0.97	8.33	8.74	-0.41
K_2O	1.26	1.03	0.23	0.62	1.04	-0.42	0.56	1.05	-0.49	0.62	1.05	-0.43
	Sums of squares of residuals			Sums of squares of residuals			Sums of squares of residuals			Sums of squares of residuals		
	1.07			1.23			1.84			0.80		
	Granite 34.2%			Granite 29.3%			Granite 24.7%			Granite 18.7%		
	Diorite 65.8%			Diorite 70.7%			Diorite 75.3%			Diorite 81.3%		

Table 36g:

Bolton Hill Mixing Calculations (Granite & Pale Diorite)

	145			154			138			132		
	Actual	Estimated	Residuals	Actual	Estimated	Residuals	Actual	Estimated	Residuals	Actual	Estimated	Residuals
SiO_2	53.11	53.01	0.10	51.69	51.57	0.12	51.37	51.41	-0.05	50.85	50.78	0.07
Al_2O_3	16.42	15.95	0.47	15.77	16.15	-0.38	16.86	16.18	0.68	16.63	16.25	0.38
TiO_2	0.53	0.53	0.00	0.69	0.62	0.07	0.54	0.56	-0.02	0.47	0.57	-0.10
FeO	9.32	8.95	0.37	10.01	9.41	0.69	9.46	9.49	-0.03	8.61	9.68	10.07
MgO	6.02	6.69	-0.67	7.00	7.08	-0.08	6.81	7.14	-0.33	7.59	7.29	0.30
MnO	0.18	0.19	-0.01	0.24	0.20	0.04	0.22	0.20	0.02	0.21	0.20	0.01
CaO	8.39	8.81	-0.42	8.26	9.27	-1.01	8.88	9.34	-0.46	9.86	9.53	0.33
K_2O	1.31	1.06	0.25	1.05	1.06	-0.01	1.55	1.07	0.48	1.12	1.08	0.04
	Sums of squares of residuals			Sums of squares of residuals			Sums of squares of residuals			Sums of squares of residuals		
	1.04			1.64			1.01			1.50		
	Granite 17.8%			Granite 12.8%			Granite 11.9%			Granite 9.8%		
	Diorite 82.2%			Diorite 87.2%			Diorite 89.1%			Diorite 91.2%		

Table 36 h: Bolton Hill Mixing Calculations (Granite and Pale Diorite

	193			102		
	Actual	Estimated	Residual	Actual	Estimated	Residuals
$Si0_2$	49.75	49.61	0.14	49.43	49.47	-0.04
$Ti0_2$	16.63	16.39	0.24	17.27	16.42	0.85
Ti0	0.56	0.59	-0.03	0.54	0.59	-0.05
Fe0	9.81	10.00	-0.19	9.54	10.08	-0.54
Mg0	7.38	7.56	-0.18	7.25	7.63	-0.38
Mn0	0.20	0.21	-0.01	0.22	0.20	0.02
Ca0	9.17	9.85	-0.68	10.20	9.93	0.27
K_20	0.99	1.07	-0.08	1.38	1.07	0.31

193	102
Sums of squares of of residuals 0.63	Sums of squares of of residuals 1.24
Granite 6.2%	Granite 5.3%
Diorite 93.8%	Diorite 94.7%

Table 37a:

Garabal Hill Mixing Calculations (Granodiorite & Diorite)

	Average Granodiorite	Average "Diorite"	104			27			137		
%			Actual	Estimated	Residuals	Actual	Estimated	Residuals	Actual	Estimated	Residuals
SiO_2	61.18	51.04	58.32	58.29	0.03	57.24	57.22	0.02	57.22	57.21	0.01
Al_2O_3	17.22	16.65	17.49	17.06	0.43	16.09	17.00	-0.91	17.26	17.00	0.26
TiO_2	0.69	1.01	0.90	0.78	0.12	0.85	0.81	0.04	0.97	0.81	0.16
FeO	5.36	9.22	6.33	6.42	-0.09	7.42	6.83	0.59	6.85	6.85	0.00
MgO	2.87	7.40	3.15	4.12	-0.97	5.31	4.60	0.71	3.87	4.61	-0.74
MnO	0.09	0.15	0.08	0.11	-0.03	0.14	0.11	0.03	0.11	0.11	0.00
CaO	4.50	8.22	4.87	5.52	-0.65	5.42	5.92	-0.50	5.20	5.93	-0.73
Na_2O	4.27	3.32	4.37	4.01	0.36	3.36	3.91	-0.55	3.92	3.90	0.02
K_2O	3.12	0.93	3.25	2.52	0.73	2.82	2.28	0.54	2.94	2.28	0.64
			Sums of squares of residuals			Sums of squares of residuals			Sums of squares of residuals		
			1.88			2.52			1.58		
			Grandiorite 72.4%			Granodiorite 61.7%			Grandiorite 61.6%		
			Diorite 27.6%			Diorite 38.3%			Diorite 38.4%		

Table 37b: **Garabal Hill Mixing Calculations (Granodiorite & Diorite)**

	136			18			138			135		
%	Actual	Estimated	Residuals	Actual	Estimated	Residuals	Actual	Estimated	Residuals	Actual	Estimated	Residuals
SiO_2	57.12	57.05	0.07	56.84	56.89	-0.05	56.39	56.29	0.10	55.93	55.82	0.11
$Al2_03$	17.54	17.00	0.54	17.30	16.98	0.32	17.56	16.95	0.61	17.53	16.93	0.60
TiO_2	0.79	0.82	0.05	0.97	0.82	0.15	0.99	0.84	0.15	0.93	0.85	0.08
FeO	6.82	6.88	-0.06	6.79	6.99	-0.20	7.09	7.16	-0.07	7.18	7.34	-0.16
MgO	3.80	4.65	-0.85	3.98	4.78	-0.80	4.10	4.98	-0.88	4.25	5.19	-0.94
MnO	0.10	0.11	-0.01	0.11	0.12	-0.01	0.10	0.12	-0.02	0.11	0.12	-0.01
CaO	5.19	5.97	-0.78	5.06	6.07	-1.01	5.71	6.23	-0.52	5.94	6.41	-0.47
Na_2O	4.06	3.90	0.16	4.14	3.87	0.27	3.93	3.83	0.10	4.28	3.78	0.50
K_2O	2.93	2.26	0.67	2.73	2.20	0.53	2.59	2.10	0.49	2.41	2.00	0.41
	Sums of squares of residuals			Sums of squares of residuals			Sums of squares of residuals			Sums of squares of residuals		
	2.12	2.18	1.71	2.46								
	Granodiorite 60.5%			Granodiorite 57.8%			Granodiorite 53.2%			Granodiorite 48.7%		
	Diorite 39.5%			Diorite 42.2%			Diorite 46.8%			Diorite 51.3%		

Table 37c: Garabal Hill Mixing Calculations (Granodiorite & Diorite)

	16			116			105		
%	Actual	Estimated	Residuals	Actual	Estimated	Residuals	Actual	Estimated	Residuals
SiO_2	54.95	54.90	0.05	53.98	53.94	0.04	52.72	52.59	0.13
Al_2O_3	16.27	16.87	-0.60	17.59	16.82	0.77	16.42	16.75	-0.33
TiO_2	0.84	0.88	-0.04	1.01	0.92	0.09	1.03	0.96	0.07
FeO	7.73	7.71	0.02	7.37	8.08	-0.71	8.18	8.56	-0.04
MgO	6.89	5.65	-0.73	5.02	6.06	-1.04	7.59	6.63	-0.04
MnO	0.13	0.13	0.00	0.09	0.13	-0.04	0.13	0.14	-0.01
CaO	6.61	6.76	-0.15	7.25	7.12	0.13	7.07	7.59	-0.52
Na_2O	3.70	3.69	0.01	4.17	3.60	0.57	3.68	3.48	0.20
K_2O	1.63	1.79	-0.16	1.73	1.58	0.15	1.98	1.30	0.68
	Sums of squares of residuals			Sums of squares of residuals			Sums of squares of residuals		
	2.02			2.54			1.60		
	Granodiorite 39.4%			Granodiorite 29.4%			Granodiorite 17.2%		
	Diorite 60.6.			Diorite 70.6%			Diorite 82.8%		

Table 37d: Garabal Hill Mixing Calcualtions (Granodiorite & Gabbro)

	104	27	137	136	18	138	135	16	116	105	
SiO_2	0.12	0.00	0.11	-0.07	0.03	-0.07	0.11	0.08	0.13	0.10	
Al_2O_3	0.95	-0.29	0.97	-0.72	1.11	1.48	1.55	0.53	2.07	1.20	
TiO_2	0.10	0.01	0.13	0.13	0.12	0.12	0.05	-0.08	0.05	0.03	
FeO	-0.24	0.40	-0.18	-0.25	-0.40	-0.29	-0.39	-0.26	-1.01	-0.73	
MgO	-1.32	-0.03	-1.47	-1.62	-1.61	-1.78	-1.91	0.11	-2.35	-0.57	Residuals
MnO	-0.03	0.02	0.01	-0.02	0.01	0.02	-0.01	0.00	-0.05	-0.02	
CaO	-0.78	-0.66	-0.89	-0.95	-1.19	-0.72	-0.67	-0.40	0.14	-0.82	
Na_2O	0.67	-0.13	0.43	0.59	0.73	0.61	1.04	0.66	1.32	1.08	
K_2O	0.61	0.36	0.48	0.49	0.34	0.27	0.16	-0.45	-0.19	0.27	
Sums of squares of residuals	4.14	0.83	4.36	5.83	6.06	6.42	7.76	1.17	12.63	4.15	

APPENDIX 3 - FLUID GEOCHEMISTRY

3:1 Preparation of samples - the crush-leach method.

Sample preparation was carried out using the crush-leach method of Shepherd *et al.*, (1985).

Samples were ground for 3 minutes each (to maximise the usefulness of the data) using a tungsten carbide-barrelled Tema mill, this also being to ensure breakage of all inclusions (dominantly being in quartz).

2 gm. samples of powder were then washed with 20 cm^3 of distilled water before being centrifuged to remove suspended solids. This produced liquids containing the soluble contents of the fluid inclusions ready for analysis.

Solutions were analyzed for the cations Na, K, Ca, Mg and Fe by conventional Atomic Absorption Spectro-photometry (Beckman model 24), the contents being analyzed by reference to the absorbance of known Standards.

The solutions were analyzed colourimetrically for the anions Cl^- and F^- as proposed by Shepherd et al., (1985). (The methods of determination of Cl^- and F^- are shown in Appendix 3:2).

3:1.1 Drawbacks of the crush-leach method.

Analyses of fluid inclusions carried out using this procedure are merely semi-quantitative, only referring to the concentration of the elements in the volume of leachate not to their concentration in the fluid inclusions (as the volume of the fluid inclusions is unknown). Therefore the analyses have little meaning as values but are useful for comparing as ratios.

Other major problems may arise if the host mineral of the fluid inclusions is itself soluble in water, then the leachate will also include elements present in the host, although this would not appear to be of great concern in this study where the rocks are composed of insoluble silicates. Shepherd *et al.*, (1985) have also indicated that only the inclusion-bearing minerals should be ground (after previously being separated) to obtain accurate analyses, although the rocks analyzed here are not of a coarse enough grainsize to permit separation of individual crystals, consequently the whole-rocks have been used. This may result in the adsorption and retention of interfering ions on mineral surfaces reducing accuracy of analyses. However, any additions to the results due to this effect are believed to be small.

3:2 Anion analysis by colourimetric methods

3:2.1 Colourimetric determination of fluoride

Zirconyl ions form both monomolecular and bimolecular coloured complexes with Erichrome Cyanine R in hydrochloric acid solution. When a limited quantity of fluoride is present in the reacting mixture, Zirconyl ions react preferentially with it forming a complex of the composition $ZrOF_2$. This reaction withdraws Zirconyl from the coloured compled resulting in the reduction in total colour of the Zirconyl Erichrome Complex colour system.

Special solutions:

Reagent A:	1.80 g, Erichrome Cyanine R dissolved in distilled water and diluted to 1 litre.
Reagent B:	0.265 g. Zirconyl chloride Octa-hydrate dissolved in 50 cm^3 distilled water. 700 cm^3 of concentrated hydrochloric acid was added and made up to 1 litre with distilled water.
Reference Solution:	To 10 cm^3 of Reagent A, added 100 cm^3 distilled water and 7 cm concentrated hydrochloric acid made to 10 cm^3 with distilled water.
Fluoride Standard:	0.221 g NaF ("Analar") dissolved in 1 litre of distilled water (1 cm^3 = 100 PPM). Subsequent working Standards prepared by diluting from this stock.

Method: 20.0 cm^3 aliquot of Sample diluted to 50.0 cm^3 with distilled water. 5.0 cm of Reagent A is added followed by 5.0 cm^3 of Reagent B and mixed well.

Spectrophotometer was adjusted to 0 absorbance with Reference Solution at 527 nM.

Standards were selected in the range of 0.0 - 10.0 PPM fluoride.

The concentration is obtained by plotting absorbance versus concentration F^-.

Samples were analyzed using a Beckman model 24 Spectrophotometer.

3:2.2 Colourimetric determination of chloride

For trace amounts of chloride ion, a determination is carried out using a Mercury (II) thiocyanate - which depends on the displacement of thiocyanate ions by chloride. This is done in the presence of iron (III) ions, and a highly coloured iron (III) thiocyanate complex is formed. The intensity of colour is proportional to the original chloride ion concentration.

$$2Cl^- + Hg(SCN)_2 + 2Fe^{3+} = HgCl_2 + 2[Fe(SCN)]^{2+}$$

(range 0.5 - 100 micrograms chloride ion/cm^3)

Method: 20 cm^3 aliquot of the chloride solution was put in a 25 cm^3 flask. 2.0 cm^3 of 0.25 M ammonium iron (III) sulphate ($Fe(NH_4)(S0_4)_2$ 12 H_20) in 9 M nitric acid was added, followed by 2.0 cm^3 of a saturated solution of mercury (II) thiocyanate in ethanol.

After 10 minutes the absorbance of the sample solution was measured and also the blank, in 5 cm^3 cells in a Spectrophotometer, at 460 nM against water in a reference cell.

The amount of Cl ions in the sample corresponds to the difference between the two absorbances and is obtained from the calibration curves.

The calibration curve is from a standard NaCl solution with 10 micrograms Cl^- per cm^3. This covers the range of 0 - 50 micrograms as above with absorbance being plotted versus micrograms of Cl^-.

Samples were analyzed using a Beckman model 24 Spectrophotometer.

Table 38: Fluid Inclusion Analyses

	Arran Suite				Bolton Hill					Garabal Hill			
Sample No.	20 (Granite)	43X (Xenolithic Diorite)	BA2.1.1/1 (Diorite)	36 (Gabbro)	BH 228 (Granite)	BH 103 (Granite)	BH 128 (Tenacite)	BH 2 (Quartz Diorite)	BH 124 (Diorite)	GH 102 (Grano-diorite)	GH 23 (Quartz diorite)	GH 77 (Diorite)	GH 108 (Gabbro)
PMM													
Na (± 1.0)	32.0	37.0	9.0	5.0	52.0	38.0	29.0	53.0	38.0	24.0	28.0	22.0	16.0
K (± 0.4)	19.2	15.8	2.9	2.5	15.9	19.1	17.0	14.6	11.9	15.4	15.9	7.8	6.0
Ca (± 0.4)	0.3	0.2	1.3	7.0	1.7	0.2	6.0	14.2	6.4	1.2	0.8	2.8	5.5
Fe (± 0.1)	8.1	14.0	4.5	0.8	0.9	2.1	0.5	0.0	0.7	3.5	1.8	0.1	0.0
Mg (± 0.2)	0.7	1.0	1.3	1.5	0.3	1.0	1.3	4.4	2.2	0.8	0.6	1.4	4.1
Cl (± 0.5)	52.4	46.0	4.2	4.0	27.6	66.0	42.6	61.6	28.4	28.4	36.2	19.8	21.2
F (± 0.1)	4.6	0.4	0.2	0.2	0.5	0.4	0.4	0.6	0.5	1.4	1.0	0.2	1.3