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for the Degree of

Doctor of Philosophy

COARSE-GRAINED ROCKS OF

ROCKENSIDE ISLAND

CHRISTOPHER HARRIS

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Department of Geology and Mineralogy

and

The Queen's College, Oxford

Michaelmas 1982

FRONTISPIECE

Sister's Peak and Two Boats Village from Green Mountain



"What is man to rocks and mountains "

Jane Austen - Pride and Prejudice

[illegible] to those who have failed geology [illegible]

COARSE-GRAINED ROCKS OF ASCENSION ISLAND

by

CHRISTOPHER HARRIS

Department of Geology and Mineralogy

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ABSTRACT

The lavas and pyroclastics of Ascension Island contain a suite of coarse grained igneous blocks which range in composition from olivine-gabbro to peralkaline-granite paralleling, but extending beyond the compositional range of the volcanics. The lavas range from alkali-basalt through hawaiite, trachybasalt, trachyandesite and trachyte to comendite. True basalt is relatively rare and there is a scarcity of analyses with $57 < SiO_2 < 63$ wt %.

No high pressure mineral assemblages and hence no possible mantle fragments have been found. Petrographic and isotopic data suggest that a suite of gabbros from Dark Slope Crater crystallised from a magma derived from a MORB-like source. The remaining blocks and all the lavas evolved from magmas derived from a less depleted source.

The chemical variation seen in the lavas and blocks is best explained by crystal fractionation mechanisms in a relatively shallow magma chamber. The gabbroic blocks exhibit cumulus textures suggesting that they formed by accumulation of settling crystals. The intermediate to acid blocks compare much more closely in composition with the evolved lavas and are probably their slowly cooled equivalents. There is petrographic evidence that partial melting of intermediate coarse grained material gave rise to melts of granitic composition but these are not chemically equivalent to the acid lavas and blocks. A pegmatoid body crystallised in situ and closed system crystal fractionation alone resulted in a very similar sequence of mineral assemblages to the blocks and lavas and a peralkaline final liquid.

High $^{87}Sr/^{86}Sr$ ratios in the evolved lavas and blocks are attributable to contamination by a small quantity of highly radiogenic oceanic sediment.

Comparison with other oceanic volcanoes suggests that these differentiation processes are much less important in determining the evolutionary path of the magma than its apparent starting composition.

ABSTRACT

Ascension Island is the uppermost 850 m of a 3600 m single volcanic cone sited on magnetic anomaly 4, about 120 km west of the Median Valley of the Mid Atlantic Ridge and 50 km south of the Ascension Fracture Zone. About 57% of its surface is lava covered, the rest being a variety of pyroclastic and redistributed pyroclastic deposits.

The lavas display a trend to oversaturated peralkalinity ranging from basalt through hawaiite, trachybasalt, trachyandesite and trachyte to comendite (peralkaline rhyolite). Associated mainly with the pyroclastic deposits is a suite of coarse grained blocks ranging from dunite through gabbro, monzonite and syenite to peralkaline granite. The composition of these blocks, then, parallels the compositional range of the volcanic rocks.

Basalt-hawaiite lavas typically have non-glassy groundmasses with no preferred orientation of phenocrysts. These are olivine, pyroxene and plagioclase, the last normally being predominant. Trachybasalts show more textural evidence of flow and the trachyandesites display typically a trachytic groundmass and moderately well aligned phenocrysts, predominantly of plagioclase, though olivine and pyroxene also occur. The trachytes and comendites show trachytic texture and strongly aligned phenocrysts of anorthoclase to sanidine. Glass becomes more common in the groundmass as SiO_2 increases and a mainly glassy groundmass characterises the comendites. Obsidian is relatively common, associated with some of the acid flows or as loose blocks. These usually contain small microlites of K-feldspar. The proportion of mafic minerals to plagioclase in the phenocrysts of acid/intermediate lavas is much lower than that of the basic lavas. Plagioclase ranges from An_{83} Ab_{17} to Ab_{54} Or_{46} and there is no evidence of coprecipitation of plagioclase and K-feldspar; clinopyroxene from $Ca_{0.8}$ $Mg_{1.0}$ $Fe_{0.2}$ Si_2O_6 to $Ca_{0.8}$ $Fe_{1.2}$ Si_2O_6, there being very little sodium in the pyroxenes of the acid lavas. Olivine ranges from Fa_{13} to Fa_{100}. Minor minerals are quartz,

apatite, opaque oxides and sodic amphibole, which are all confined to the groundmass.

Coarse grained rocks are represented by cognate glomeroporphyritic clusters and true coarse grained blocks which may occur in lava or pyroclastics. The gabbroic blocks consist predominantly of olivine, plagioclase and clinopyroxene. Igneous lamination, alignment of grains and chemical variations which imply large scale layering typical of cumulates are seen in these blocks. One suite of gabbros has rare cumulus orthopyroxene, a mineral absent from the volcanics, and more commonly, exsolved orthopyroxene which suggests that it crystallised from a magma of tholeiitic affinity, a type not represented among the exposed lavas. Cumulus opaque oxides are found either in substantial proportions or not at all suggesting periodic precipitation of Fe-Ti oxides.

The intermediate blocks range from monzonite to quartz syenite and frequently show highly zoned feldspars with andesine cores and K-feldspar rims. As in the lavas there is no evidence of coprecipitation of plagioclase and K-feldspar. The ferromagnesian minerals are varied compared with those of the equivalent lavas, with amphibole and biotite replacing pyroxene (apparently subsolidus). There is no evidence suggesting amphibole was a cumulus phase. Apatite and zircon are ubiquitous in these blocks and they commonly contain a few percent of Fe-Ti oxides.

The quartz syenites grade into peralkaline granites though transitional assemblages are comparatively rare. The feldspar is perthitic in the granites and there may be up to 30% modal quartz, frequently occurring as granophyric intergrowths. The mafic minerals are arfvedsonitic amphibole and aegirine, which are intimately associated. Rarely ferrohedenbergite cores to the mafics may be seen in some blocks and fayalitic olivine may also occur. Other accessories are aenigmatite, zircon, eudialyte, dalyite and vlasovite. The last two are K and Na zirconium silicates respectively and reflect the strongly

peralkaline nature of these blocks.

The chemical variation exhibited by the lavas is that of a single chemical trend, showing considerable similarity to other oversaturated peralkaline volcanoes such as Aden and Bouvet. True basalt (SiO_2 < 51%) is rare and the most basic lavas are predominantly hawaiite. FeO^T, TiO_2, MgO, CaO and P_2O_5 decrease as SiO_2 increases, while K_2O and Na_2O increase. With SiO_2 < 65% the chemical composition of the blocks for a given SiO_2 content widely varies. This reflects the influence of processes of crystal accumulation on bulk chemistry. The acid blocks vary with SiO_2 in a very similar manner to the acid lavas which suggests they are simply slowly cooled equivalents. Rb, Zr, Nb and Y show positive correlations with SiO_2, Sr a negative correlation. Nb and Zr enrichment in the comendite relative to basalt suggest >86% fractionation.

Chemical and petrographic evidence strongly suggests that the evolution of the magmas was controlled by crystal fractionation. Comparison of block bulk chemistry and the trends shown by the lavas shows that the removal of selected block compositions may have controlled these trends. Tie lines between bulk block and residual liquid composition for a gabbroic block show similar trends to those of the lavas apart from FeO^T which is enriched in the residual liquid. This suggests that short term trends may have led to iron enrichment followed by periodic oxide fractionation to give overall iron depletion. Two element variation diagrams suggest olivine and plagioclase control in the basic lavas together with some oxide and apatite fractionation; and predominantly anorthoclase to sanidine control at the evolved end of the series. Least squares fractionation tests have, so far, been inconclusive mainly because the inclusion of an iron oxide phase in the 'mix' gives too many possibilities. Trace elements in the acid lavas and blocks become more incompatible as SiO_2 increases suggesting some form of complexing with F^- Cl^- etc., though the covariance of trace elements is good and regression lines

pass through the origin as would be expected if they were related by crystal fractionation.

A pegmatoid body occurring within hawaiite lavas in Cricket Valley crystallised *in situ*. It differs from the analysed lavas by having high (~13%) FeO, thus confirming the presence of more iron rich liquids. On slow cooling the crystals formed did not re-equilibrate with the supernatant magma and the resulting mineral assemblages are very similar to those seen in the blocks and lavas. The final liquid was oversaturated and peralkaline in character showing that such liquids can result from crystal fractionation alone. There is good evidence that Na is lost during the last stages of cooling.

Petrographic evidence for partial melting is seen in a suite of syenite blocks, the resulting liquid being quenched to a glass of granitic composition. However differences in K_2O/Na_2O and Zr content as compared with the values for granite blocks and comendite make this an unlikely origin for the acid liquids.

Sr and Pb isotopic analyses were performed on 13 samples. Pb results fall into two groups, the tholeiitic gabbros from Dark Slope Crater having MORB characteristics, and the lavas and other blocks having significantly more radiogenic Pb and presumably reflecting a different mantle source. Sr isotopes are uniformly unradiogenic (c. 0.7029) except in the evolved lavas and blocks where Sr concentrations are < 2 ppm and where $^{87}Sr/^{86}Sr$ ranges up to 0.7135. This is interpreted as being due to contamination by < 1% oceanic sediment, which is highly radiogenic around Ascension. The similarity between Sr ratios in the acid lavas and blocks is further evidence that they crystallised from the same liquids.

Chemical analyses of lavas were used to calculate their viscosities and densities. Density differences between lavas and phenocrysts suggest that settling of olivine, plagioclase and pyroxene could have occurred. The

viscosities of the basic lavas would allow settling (assuming they behaved as Newtonian fluids) but the acid lavas would have been too viscous unless significant quantities of F^-, Cl^- and H_2O were present.

Suitable assemblages for determining the temperature of mineral-mineral equilibria exist only in the blocks. The two pyroxene thermometer suggests the Dark Slope Crater blocks crystallised at 960-1050°C. Fe-Ti oxides in several gabbroic blocks from Dark Slope Crater, Middleton's and Lady Hill give calculated temperatures of 1000°C and low oxygen activities ($\ln aO_2 \sim -20$). These determinations are subject to large error due to high Al and Mg content. Plagioclase-liquid geothermometers applied to phenocryst-lava equilibria have not provided consistent temperatures. A model developed by Langmuir and Hanson has enabled crystallisation temperatures of the lavas to be predicted from their chemical analyses by considering major element distribution coefficients. For the Ascension lavas, this model predicts plagioclase would always have had a higher liquidus temperature than olivine (even in the most basic lavas). This is very unlikely since removal of compositions similar to those of the phenocrysts (and those calculated by the model itself) would result in a trend to lower SiO_2. The block assemblages suggest that olivine was the first phase to crystallise in the basic lavas. Experimental investigation is needed to resolve these problems.

REE contents of eight rocks show that the hawaiites have LREE enriched profiles approximately 100 x chondrite, so are likely to be far removed from the composition of the primary magma. The REE profiles for the eight rocks are consistent with crystal fractionation being the mechanism of evolution. There is a strong negative Eu anomaly in the salic blocks and lavas which is attributable to feldspar fractionation and a plagioclase rich cumulate from Dark Slope Crater shows a strong positive Eu anomaly which is to be expected.

Comparisons with other oceanic islands show that for a variety of different chemical trends differences in composition are already apparent in

the most basic members of the series. This suggests that low pressure fractionation does not control the composition of the final liquids even though it is the mechanism responsible for their evolution. It has been shown by previous authors that oversaturated peralkaline volcanics occur close to spreading centres and undersaturated volcanics some distance away. This must reflect source differences and/or differences in high pressure differentiation processes.

If the Dark Slope Crater gabbros crystallised from a MORB-like magma they are either fragments of ocean crust cumulates or they crystallised during an earlier, tholeiitic stage of the island's evolution. This latter origin requires that the island originated closer to the ridge and drifted away from it tapping a less depleted source region in the mantle. This would require a long lived mobile heat source capable of causing partial melting within the upper mantle. The former explanation simply requires a single melting event and while there is no indication why this should have occurred, this origin is more compatible with current volcanological and tectonic ideas.

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CHAPTER 1

INTRODUCTION

1.1 LOCATION

Ascension Island was discovered by the Portuguese explorer João da Nova on Ascension Day, 1501. The island is situated at latitude 7° 57' south longitude 14° 22' west. It is 92 km² in area and comprises the uppermost 850 m of a 3600 m single cone sited on magnetic anomaly 4, about 120 km west of the median valley of the Mid Atlantic Ridge and 50 km south of the Ascension Fracture Zone (Fig. 1.1). No explicit connection with either of these major structures has yet been found (van Andel and Heath, 1970; van Andel et al. 1972). Of the islands in the South Atlantic only Bouvetøya (latitude 54° 26' south, longitude 3° 24' east) is closer to the Mid Atlantic Ridge.

1.2 NON GEOLOGY

Ascension is a British possession and its 1980 population was approximately 1000 people. Employment is provided by the BBC whose Atlantic Relay Station is situated on the island, the Cable and Wireless Company and the US Airforce/NASA. Recently the island has been of great importance as a staging post in Britain's attempt to regain control of the Falkland Islands which lie some 4000 miles further south.

Normally Ascension receives only six scheduled flights per year from the UK and a similar number of visits by ship. The USAF, however, flies in supplies twice a week. Foreign Office permission is required for anybody intending to visit the island for periods longer than three days and in consequence it is difficult for anybody to visit the island unless they have a job, are visiting relatives or connected with research. There is no public transport once on the island, and no hotel or guest house.

High temperatures, low rainfall and persistent trade winds characterise the climate. This controls the vegetation which is desert-like at sea level

but above about 1500' contour, where the air is cooler and more humid, an almost tropical fauna exists. This is characteristic of the Green Mountain area.

The land fauna is almost entirely the result of introduction of species by man. These include wild donkeys and cats, rats and goats. The indigenous inhabitants are the land crabs and the birds. Turtles arrive in December/ January every year to mate and lay eggs.

1.3 HISTORY OF GEOLOGICAL RESEARCH

Ascension has attracted the attention of numerous geologists since before the visit of Charles Darwin in the 1830's (Darwin, 1844). Most prominent for general geology is the work of Daly (1925) in which descriptions of many of the volcanic forms and features may be found. Daly (1925) also considers some of the major petrographic and chemical features of the rocks. Renard (1889) also describes some of the petrographic features of the coarse-grained rocks which are the major topic of this thesis (see Section 1.6.1).

The rare minerals dalyite and vlasovite were identified in the ejected granite blocks, the former by van Tassel (1952), the latter by Cann (1967). van Andel and Heath (1970) and van Andel et al. (1972) have described the oceanography and tectonics of the sea floor around Ascension. Sr and Pb isotope data from a range of lavas are discussed by Gast et al. (1964) and these plus Nd by O'Nions and Pankhurst as part of a comparison of isotopic data from Atlantic islands (O'Nions and Pankhurst, 1974; O'Nions et al., 1978). Other accounts of the geology of Ascension Island are by Borley, in Sorenson (1974) and Roedder and Coombs (1967) who describe fluid inclusions in the granite blocks.

Ascension was first visited by geologists from Oxford in 1964 (Atkins, Baker, Bell and Smith) after which a brief account of the expedition was

published (Atkins et al., 1964). Later visits were made in 1965 (Bell and Smith) and 1979/80 (Atkins and Harris) to augment the collection of rocks made in 1964/5. Short publications of research based on these collections have been made but at time of writing, most of the work is unpublished.

The visit from December 1979 to January 1980 was made primarily to collect coarse grained blocks from existing and new localities. Unweathered samples of both coarse and fine grained rocks were collected for chemical and isotopic analysis. Other aspects of the field work included improvement of the existing geological map and an assessment of possible environments of deposition of xenolith bearing pyroclastic deposits (Chapter 2). Table 1.1 summarises the existing Ascension geological literature.

1.4 GENERAL GEOLOGY

1.4.1 Introduction

Ascension has the typical appearance of a large volcanic complex at a fairly advanced stage of evolution. Apart from the main eccentric cone of Green Mountain, it has at least 70 parasitic centres ranging up to 600 m in height. Before considering the nature, volume and distribution of the major rock types, it cannot be emphasised enough that Ascension Island is only the top 850 m of something like a 3600 m cone. This means that while the total volume of the cone is about 2350 km^3 the volume of the exposed part is only 26.32 km^3 (assuming that the pedestal is 50 km in diameter and 2000 km^2 in area and the profile is as drawn in Fig. 1.2).

There have been no eruptions observed in historic times but the extremely fresh nature of some of the flows suggests that they are comparatively recent (within the last 500 years?). In geological terms, then, the volcano is dormant rather than extinct.

The rocks investigated in this thesis therefore represent a very small percentage of the total volume of the volcano. It must also be recognised

that large volumes of material will have been explosively erupted and transported great distances (as fine grained ash, etc.) away from the cone.

Rock Types

Detailed classification of the various coarse and fine grained rocks will be given in the relevant chapters. An "in the field" guide to rock types is given in Table 1.2.

1.4.2 Lavas

About 57% of the exposed area of Ascension is covered by lava (Bell et al., 1972). The lavas form an assemblage of alkaline types ranging from basalt through hawaiite, trachybasalt, trachyandesite, trachyte to comendite (peralkaline rhyolites). This classification is based on chemical analyses, an explanation of which is given in Chapter 5. In the field the lavas were divisible into "basaltic" and "trachytic" types on the basis of their flow morphology and colour in hand specimen.

"Basaltic" lavas are black to grey and form extensive flows from central vents and cinder/scoria cones. The "trachytic" types form large domes which may or may not overflow to give extensive lava flows. Little Ascension (see map) is a good example and is comparable in size to the "basalt" flows. Minor occurrences of obsidian occur at the base of some of the trachytic bodies (e.g. Middleton's). Some typical lava types are shown in Plate 1.8.

1.4.3 Plutonic or Coarse Grained Blocks

A suite of coarse grained blocks is found in the lavas and pyroclastic rocks. This parallels and extends beyond the compositional range of the volcanics. These blocks are the principal subject of this thesis and are dealt with in detail in the succeeding chapters.

1.4.4 Intrusives

Because of the low erosion rates accompanying the dry climate, Ascension Island is not a deeply dissected volcano like Reunion, Madeira, St. Helena etc., and consequently there are very few dykes exposed and no other minor intrusives. The best example of a dyke is a basaltic intrusion south of Middleton's Ridge (see map). Others occur between Monkey Rock and Devil's Cauldron. These dykes resemble the lavas in grain size and texture and this is good evidence that they are feeders exposed very close to where they became lava flows.

1.4.5 Pyroclastics

The pyroclastic deposits have as yet received relatively little attention. They deserve detailed study on account of their large volume and extensive distribution but this is beyond the scope of this thesis. Those pyroclastics containing coarse grained blocks, however, are fully described in Chapter 2.

Much pyroclastic material is associated with small parasitic centres where scoria and cinders are interbedded with sheets of lava within the cones. These composite cones include Mountain Red Hill (see Plate 1.1) which is cut in half to reveal its internal structure in detail. It is a matter of some debate as to how much of the remaining pyroclastics have been deposited directly from sub aerial falls, or from reworking of such by wind, water and gravity. Deposits of ash and lapilli cover large areas of Green Mountain and its surroundings. These seem to have been deposited subaerially. Other deposits such as those found on Middleton's Ridge may be interpreted as ash etc., which has been deposited into standing bodies of water. Recent alluvial fan deposits associated with obvious stream beds are quite common, notably around Upper Valley Crater and Sandy Hill. These are relics of times when rainfall was much higher. The conglomerates found along the NASA road to Devil's Ashpit probably represent more "ancient" analogues of these

though some of the more widespread and poorly sorted are probably gravity rather than stream deposited.

A possible pyroclastic flow is exposed on the side of the Green Mountain road (G.R. 709204). This is shown in Plate 1.2 and may be seen to consist of obsidian plus welded pumice.

Other rocks of less importance are beach rock; a mixture of cemented shells and volcanic particles, and guano deposited by the large numbers of sea birds which was at one time worked as a source of phosphate.

1.4.6 Structural Features

A number of large scale structures which may have involved large scale movements were noted by Daly (1926). Cricket Valley (Plate 1.3) at the west of the island (G.R. 735215) is a possible explosion crater (Daly, 1926), though subsidence may have played a part in its origin (Atkins et al., 1964). The subsidence may have been related to the extension of one of the nearby trachyte bodies (e.g. Weather Post). Most of the faults on the island seem to be related to the emplacement of trachyte bodies. Small faults are found in the pumice deposits around Middleton's Ridge, the fault planes themselves stand out from the rest of the pumice, being better cemented, presumably by volatiles derived from the underlying trachyte. Many of the pyroclastic sequences are well bedded and laminated, with each bed maintaining a constant thickness and loading suggesting a lacustrine environment (Chapter 2). In the region around Spoon Crater (G.R. 695198) these beds show dips of 20-30° (Plate 1.4) which must therefore be post depositional. This uplift is again best related to trachyte emplacement.

1.4.7 History of Eruption

Both trachytic and basaltic lava (and pyroclastic material) have been extruded at various stages in the evolution of the volcano. Many centres (e.g. Devil's Riding School, Little White Hill, the South East Head fissure,

and Cross Hill) show both basic and intermediate/acid types and there is no justification for splitting up the evolution of the volcano into early trachytic and later basaltic phases and vice versa. Probably the most recent flows are those from Sisters Peak, East Crater and Gannet Hill.

1.5 TECTONIC SETTING

Ascension lies about 120 km west of the median valley of the Mid Atlantic Ridge, and some 50 km south of the Ascension Fracture Zone (Fig. 1.1) (van Andel et al., 1973) and now may be considered almost a mid plate volcano. This may not always have been the case and it may have formed on or very close to the ridge. Assuming present half spreading rates of about 2 cm yr^{-1} the maximum age is thus 6 Myr since the greatest distance it can have drifted is the 120 km from the ridge to its present position (Bell et al., 1972). The oldest dated rocks are 1.5 Myr (see Chapter 6).

1.6 DEFINITIONS

Previous accounts of the coarse grained rocks of Ascension refer to them as "xenoliths and projectiles of plutonic rock types ..." (Daly, 1925). "coarse grained ejected blocks" (Atkins et al., 1964) and "ejected blocks" (Fleet and Cann, 1967). Similar rocks from the Lesser Antilles and Azores are referred to as "plutonic blocks" by Arculus and Willis (1980) and Baker, M.J. (1970).

This thesis is concerned with all types of coarse grained material from grouped phenocrysts and xenocrysts to large blocks of cumulate gabbro. Terms like plutonic and xenolith are not used except where genetic connotations are needed. Not all coarse grained blocks are necessarily plutonic. For example, the pegmatoid in Cricket Valley can hardly be considered plutonic if , as evidence suggests, it crystallised at a depth of only 70-100 m (Chapter 4). Similarly, the majority of coarse grained blocks

occur in redistributed pyroclastics where they can hardly be described as xenoliths. Table 1.3 shows the classification scheme for coarse grained material. Xenoliths, blocks from pyroclastics etc., are grouped under the title coarse grained block, which is usually abbreviated to block.

1.7 AIMS AND SCOPE OF THIS THESIS

For the volcanologist, the geology of Ascension is both varied and fascinating and many important questions concerning the physical and chemical evolution of the volcano had been unanswered when this research was started.

In the previous sections dealing with the general geology of the island, it was stressed that only a small percentage of the total cone volume is exposed above sea level; that nearly half the island is covered by pyroclastics which are not amenable to chemical study; and that a lot of material erupted as pyroclastics would have been blown away from the island. Coarse grained blocks ejected from the volcano are for the most part well preserved and their constituent minerals may be easily analysed by microprobe methods. If it can be shown that the coarse grained rocks crystallised from the same magmas as the volcanic rocks, they will provide a valuable record of crystal fractionation and other possible differentiation processes. Volcanoes tend to be highly selective of the compositions they erupt, which means that a study of the lavas and their phenocrysts may not be comprehensive.

Accordingly, this thesis has two principal aims.

(i) To classify and fully describe all the coarse grained material collected.

(ii) To combine these data with chemical data from the lavas and identify the processes responsible for the range in chemical composition seen in the lavas.

Once this is achieved there are wider implications for two fields in particular:

(i) The position of Ascension within a plate tectonic framework and possible connections between its proximity to the Mid Atlantic Ridge and its petrochemistry.

(ii) As a source of data relevant to the possibility of mantle heterogeneity when compared with other oceanic islands.

The comparison between Ascension and other oceanic volcanoes forms the final part of this thesis.

CHAPTER 2

THE OCCURRENCE OF COARSE GRAINED BLOCKS

2.1 INTRODUCTION

Coarse grained blocks have been found in all the major rock formations and types of Ascension, but the most prolific sources are the various pyroclastic deposits. Map 1 gives the location, quantity and type of block for all the localities.

2.2 THE OCCURRENCE OF BLOCKS IN LAVA

There are two major localities where blocks may be found as xenoliths in lava (Porpoise Point (714267) and Crystal Bay (737189) to Pillar Bay (710178) flows) and several less important ones. Examples of blocks within acid to intermediate lavas are rare. This may be due to a combination of three factors:

(i) Acid/intermediate magmas crystallise as large domes which suggests that their rate of flow to the surface was slow. This diapir-like emplacement tended to push aside rather than incorporate the material through which it passed.

(ii) Chemical differences between lava and xenolith caused the latter to dissolve.

(iii) The source of the acid magmas lay above the level at which all or most of the coarse grained bodies occur.

(i) and (iii) seem the most plausible reasons for the paucity of blocks in acid lavas. It is shown in Chapter 5 that intermediate/acid blocks and lavas have the same composition and therefore would not be expected to react together.

2.2.1 East Crater (703258)

East Crater is a large basaltic scoria/lava cone in height above the surface 170 m. The southeast wall of the crater is breached by 300 m wide trachyandesite flow which turns rapidly through 270° to form the peninsula of Porpoise Point

(see maps) to the north east. The flow is rather complex near the cone itself, and blocks are found only near the edges of the flow (Fig. 2.1). The blocks themselves sometimes have a flat tablet form which is unique among Ascension Island blocks. Plate 1.5 shows a typical tablet from this locality. There is no microstructural control causing this cleavage so the fractures were probably caused by stress imposed on the original coarse grained body durings its breakup and transport to the surface. Similar fractures are described by Basu (1980) but in this case they are ascribed to stress induced by earthquakes in the upper mantle. This, of course, cannot be true for the Ascension example although volcanic earthquakes may have been the cause.

2.2.2 Crystal Bay-Pillar Bay Flows

Blocks of all types up to 10 cm diameter are found in hawaiite flows along the coast for about 4 km from Crystal Bay (747189) to Pillar Bay (710178). The temporal relationships of these flows are not clear due to later cone debris covering the flows in places along the coast, but it seems plausible that they are part of the same flow or series of flows from the same source. This source is impossible to identify due to later coverings of ash and cone debris inland (see maps).

2.3 IN SCORIA AND CINDER CONES

Numerous cones contain coarse grained blocks. The blocks themselves are invariably found to be gabbroic in composition.

2.3.1 Dark Slope Crater (673198)

This is the second largest source of blocks. They occur loose on the flanks of the cone, or enclosed within lava and scoria in the cone itself. The blocks range in size up to 70 cm in diameter and the largest of the Ascension blocks are found here. All are gabbroic and apparently represent

a cogenetic sequence from a single, mineralogically variable source.

2.3.2 Cross Hill (658233); Lady Hill (680219); Mountain Red Hill (705196); Wig Hill (763207)

These scoria cones have all yielded minor suites of gabbroic blocks, of similar appearance, but smaller size compared with those of Dark Slope Crater. Maximum size is only about 5 cm diameter. At both Cross Hill and Wig Hill only one specimen was found. In the collections at the Department of Earth Sciences at Cambridge, there is a gabbroic specimen from Coast Red Nipple but no specimens were found there during field work in 1979/80.

2.3.3 Green Mountain (720210); Bear's Back (715240)

Small (<4 cm) xenoliths are found in moderate quantities along Elliot's Path around Green Mountain. Very poor exposure (due to luxuriant vegetation) of this complex cone prevented a fuller investigation. Although not a cone the cinders around Bear's Back have yielded some small xenoliths. These are similar in nature to those found in the Green Mountain cinders and are presumably related.

2.4 IN PYROCLASTICS AND REDISTRIBUTED PYROCLASTICS

Pyroclastics provide the largest source of coarse grained blocks. A detailed general study of the pyroclastic rocks of Ascension Island is outside the scope of this work, but a fairly detailed study of those pyroclastics which contain blocks has been made. These block-bearing pyroclastics may be divided up into three main facies:

(i) NASA Road facies - found in the east of the Island.

(ii) The Middletons facies which occurs around Middleton's Ridge.

(iii) A series of "recent" alluvial fan deposits.

2.4.1 The NASA Road Facies

The NASA Road facies is the name proposed for the thin (1-5 m) but laterally extensive and predominantly rudaceous deposits which cover most of the southern and south eastern flanks of Green Mountain. Four localities of this facies have provided sources of blocks, namely the flanks of the west end of Cricket Valley, the Crystal Bay area, the road cuttings south of Mountain Red Hill and the road cuttings just west of Castle Hill (see Map 1 for detail). The road cuttings were made during construction of the NASA road built in 1965 and provide excellent sections through the sequence. At all these localities the suites of blocks are very similar, with a variety of intermediate and basic types.

Detailed sections of the NASA Road facies as seen above the west end of Cricket Valley and along the NASA road to Devil's Ashpit are shown in Figs. 2.2b and 2.3a. In all sections the common feature is the predominance of very coarse clasts and thin discontinuous horizons of laminated sands and muds. In all sections the majority of the coarse material is rather loosely consolidated and a red staining occurs throughout indicating a subaerial deposition.

The environment of deposition of this facies seems to be that of sporadic high energy followed by longer periods of quieter deposition resulting in the alternating rudaceous and fine laminated horizons. How much part volcanic processes played in the deposition of these deposits is not clear; it is possible that gravity and water (from rain) have been almost entirely responsible.

The south eastern ridge of Green Mountain provides a prolific source of coarse grained blocks and if the ridge is followed towards the summit of the peak, a transition is seen from loosely lying, thin deposits of the NASA Road facies into coarse grained block-bearing cinders, well bedded and well consolidated, dipping steeply down slope. This suggests that the

NASA Road facies has resulted from redeposition of the pyroclastics of the main peak into a scree/talus deposit.

2.4.2 Middleton's Ridge Facies

The Middleton's Ridge facies is used here to describe a thick sequence of white clays which contain discrete horizons of coarse grained blocks, unlike the NASA Road facies which contains blocks throughout. These sediments also differ from the NASA Road facies in being of a considerable (up to 50 m) thickness in places. Although the facies is confined mainly to areas on and adjacent to Middleton's Ridge, and at Palmer's, similar deposits have been recognised at Devil's Riding School (685204) in the valley south of Bear's Back and at the 5 mile post on the road up Green Mountain.

As can be seen from the logs (Figs. 2.3b and 2.4) this facies is characterised by the presence of a white to yellow clay which occurs both as matrix and as the main constituent of a bed. Very coarse grained units are much rarer than in the NASA facies and laminations are common throughout the sections. The clasts occurring in this facies at all localities are subangular to rounded and for these reasons the facies as a whole is interpreted as having been deposited (at least in part) in a lacustrine environment. Loading is seen in places (see plates and figures) and this is taken as further evidence that water saturated the deposit after deposition, although it does not necessarily mean that the deposit was subaqueous.

The coarser horizons must represent periods of high deposition as might be experienced during or immediately after an eruption. Most of the pumice and cinders occur in massive horizons with very little matrix. Presumably this was dumped by proximal eruptions. Thin bands of reworked pumice (as rounded pebbles) are seen in a number of places.

In summary then this widespread and rather complex facies seems to represent sporadic eruptions of pumice and cinders together with mass flows

of rubble and finer grained material into a sometimes lacustrine environment.

Middleton's Ridge (704210)

Here the thickest occurrence of the facies is found. The section (Fig. 2.4) is valid for a large area of the ridge although in some places there is a lower horizon of blocks present (this is not seen in Fig. 2.4 as the lower part is absent at the locality from which the section was taken).

In most places the section is very poorly exposed and detailed sedimentological study was not possible.

Where all three horizons of blocks are present the first is found to consist only of granites, and the upper two a mixture of syenite and gabbro, with no granite, showing that the eruptions introducing the blocks were either from different volcanic centres or were sampling different coarse grained bodies (or both).

Five Mile Post (708217)

Five Mile Post is most notable for being the source of the granite blocks in which the new mineral dalyite (van Tassel, 1952) and the rare mineral vlasovite (Fleet and Cann, 1967) were identified. These blocks are identical with the granites of the lowest block bearing horizons of Middleton's Ridge.

Very little of this exposure may be seen due to cactuses and other vegetation, so detailed study of the facies has not been made. The blocks are found at three locations up the road to Green Mountain above the 1500' contour. The facies is a loosely consolidated, extremely coarse conglomerate with rather rounded blocks of granite and volcanic fragments. Laminated sand and clay horizons are found sporadically distributed throughout the outcrop. Cinders and pumice occur unconformably on top of the block bearing facies.

The environment of deposition seems to be one involving high energy and the facies may represent a localised river deposit. The outcrop lacks the red staining seen in the NASA facies and has more affinities with the Middleton's facies, although no equivalent bed is found in the latter. It seems likely that this deposit was formed at the same time and from fairly similar constituents as the lower block horizon in the Middleton's facies; the differences probably reflect slightly different environments of deposition.

Devil's Riding School (684203)

This remarkable feature (Plate 1.3) consists of a series of concentric, saucer shaped rings of cinders and pumice making an approximately circular shape 1 km in diameter. The section shown in Fig. 2.2a compares well with parts of the Middleton's Ridge section (Fig. 2.4). The Riding School was almost certainly once a lake, the saucer shape of the sediments probably being due to subsidence of the lake floor, perhaps related to the extension of the Riding School trachyte flow. Coarse grained blocks of granite and syenite (1-5 cm diameter) are found in the basal breccia (Fig. 2.2a).

Upper Valley Crater Area (720232)

From the sections shown in Fig. 2.5a, b it may be seen that these deposits resemble those found on Middleton's Ridge. In one section a facies similar to that of Five Mile Post occurs. The overall shape of this bed and its contacts with the bed below suggest that it was a channel deposit (Fig. 2.5b). It is not laterally extensive but contains a number of basic and intermediate blocks.

2.4.3 Alluvial Fan Deposits

These sediments are among the most recent on the island and testify to periods when the rainfall must have been much higher than that experienced

during the 1979/80 visit. The type of block they contain must to a large extent reflect the type of block in the source material. The fan deposits in which blocks have been found consist of laterally extensive but thin units of boulders and smaller clasts, sand and clay. Blocks are comparatively rare. The fan between Mountain Red Hill and Spoon Crater (698200) has been the most prolific and ten blocks were collected. These are identical to the types found on Middleton's Ridge.

2.5 THE IN SITU OCCURRENCE OF COARSE GRAINED MATERIAL

Cricket Valley (737213) is a deep crater close to the NASA base at Devil's Ashpit (see Map II) at the eastern end of the island. Explanations of its origin include explosion crater (Daly, 1925) and cauldron subsidence, perhaps related to the extrusion of nearby Weather Post and White Hill trachyte domes (Atkins et al., 1964). Whatever the answer, the result is a 30-50 m deep section cut into the thick basalt sequence. A curious outcrop of a pegmatite-like body (i.e. pegmatoid) occurs at the west end of the valley at the base of a 50 m basalt cliff.

This outcrop of pegmatoid is a 3 m x 1.5 m irregular, but roughly ovoid mass. The rock consists of plagioclase, alkali feldspar, pyroxene and magnetite with accessory quartz, olivine and apatite. The texture is delicate throughout with apatite forming long slender needles and with numerous pore spaces between the grains. The texture is undisturbed at the boundary with the basalt and is unchilled at its margin. It is therefore suggested that this rock crystallised in situ. Since it is unchilled it cannot have been intrusive into cold basalt.

This rock is the only example on Ascension of a coarse grained body found in situ and therefore provides one of the few insights into possible mechanisms of formation of the coarse grained rocks. The pegmatoid, then, merits special consideration in the later chapters.

2.6 CONCLUSIONS

It has been stated that a wide variety of block types occur in many different rock types. It is possible that the distribution of these blocks may allow a reconstruction of the original coarse grained body to be made (assuming there is only one, albeit of complex shape in detail).

The reconstruction is possible, at least in principle, using those blocks whose eruptive centre is known. This includes those blocks found in the cones and most blocks which occur in lava. Most blocks in pyroclastics are not relatable to an eruptive centre (see Fig. 2.6).

Fig. 2.7 shows an idealised relationship between distribution of block type and coarse grained body morphology. If this simple model is applied to Ascension Island, the evidence such as it is would suggest a coarse grained body centred below the north eastern part of the island.

However, (a) the data on which this is based are imperfect, in particular the eruptive centres of the majority of the intermediate blocks and all of the acid blocks are unknown.

(b) the assumption that all blocks derive from a single body is without foundation.

(c) the occurrence of *in situ* coarse grained rock within the Cricket Valley basalt requires that alternative origins to simple accumulation of crystals in a single magma chamber be examined.

CHAPTER 3

PETROGRAPHY OF THE VOLCANIC ROCKS

3.1 INTRODUCTION

The published petrology on the lavas of Ascension is largely descriptive with very few analyses of individual phases. This chapter is not intended to give an exhaustive account of the lavas. Descriptions of representative lava types, in particular those rich in phenocrysts, are given. As stated in the introductory chapter, the study of the phenocrysts is considered complementary to that of the coarse grained blocks.

Because the pyroclastics are often fine grained, poorly consolidated and altered, they are difficult to study in thin section. This chapter concerns itself with the lavas rather than the volcanic rocks as a whole.

3.1.1 Previous Work on Lavas

Daly classified the lavas, on the basis of their petrography and selected chemical analyses, into basalts, trachytes, trachydolerite, trachyandesite and rhyolitic obsidian, and considered this the probable order of abundance (Daly, 1926, p.42). In this work the names basalt, hawaiite, trachybasalt, trachyandesite, trachyte and comendite are used. This classification is based on the alkalis vs. SiO_2 diagram (Fig. 5.24) and this basis for classification is discussed in Chapter 5. Relative volumes of the various lava types are particularly difficult to ascertain since the subsurface proportions of the various lava types and the pyroclastic material are not known. Relative volumes of lavas seem to be basalt/hawaiite > trachyte > trachybasalt > trachyandesite > comendite > obsidian. It must be emphasised that very few chemical analyses have been made on the pyroclastic rocks which cover almost half the island. It is possible that these would greatly affect the relative volumes of compositional types if they were included with the volcanics.

3.1.2 Variation in Groundmass

The mineralogy and texture of the groundmass provided a good indication

of the group to which a lava would be assigned on the basis of its chemical composition.

Basalt-hawaiite lavas typically have a non-glassy groundmass with no particular preferred orientation of phenocrysts or groundmass minerals. Plate 3.1 shows a typical basalt. With increasing SiO_2 wt% towards trachybasalt, more textural evidence of flow is seen in the groundmass. Trachybasalts commonly show felted textures. Trachyandesite shows typically trachytic groundmass (Plate 3.3) and moderately well aligned phenocrysts. The trachytes and comendites typically show trachytic texture and aligned phenocrysts. Glass is common in the groundmass of the more acid lavas, e.g. 17469 (White Hill) where SiO_2 = 70%. Glass is seen in the interstices between the groundmass K feldspar laths (Plate 3.2). The Little White Hill comendite (15146) (wt% SiO_2 = 72%) has a predominantly glassy groundmass (Plate 3.4), while the obsidians are nearly all glass. They invariably contain small acicular crystals of alkali feldspar which show flow alignment and the rock as a whole may show faint flow banding.

Some blocks of a rock type intermediate in grain size between the coarse grained blocks and the lavas were recovered from sediments in Cricket Valley. Plate 3.5 shows such a sample (NB. same magnification as previous plates) which is best described as a non-vesicular dolerite (optical measurements on the plagioclase suggest it is labradorite). It is possible that this block is from an intrusive body, of a type which is not exposed on Ascension Island due to low levels of erosion. It could perhaps be from the lower level of one of the dykes exposed on the island which at the surface are indistinguishable from the lavas of similar low position, presumably because they are feeders close to the surface.

Table 3.1 summarises the petrography of each lava type.

3.1.3 Phenocrysts

Phenocrysts may be thought of as single grain coarse-grained blocks

and form, in that sense, an integral part of this study. In general it is reasonable to assume that at least the outer rim of a phenocryst precipitated from the magma now quenched around it. Xenocrysts are accidentally incorporated from elsewhere and hence are likely to show evidence of disequilibrium which will take the form of irregularities in the grain shape.

Euhedral grains, then, suggest equilibrium with the surrounding magma and are thus likely to be phenocrysts. Irregular and/or embayed grains reflect disequilibrium (thermal and/or chemical) between themselves and the liquid, although this does not necessarily make them xenocrysts. Possible evolutionary paths for such grains are:

(I) Break up of coarse grained material into constituent crystals as a magma passes through it.

(II) Mixing of two different magma types giving two phenocryst assemblages. On homogenisation of the liquid the phenocrysts are likely to be in disequilibrium with it.

(III) Changes in pressure/temperature of the crystallising magma followed by the incomplete resorption of phenocrysts produced by this earlier crystallisation.

Types (I) and (II) may be considered as xenocrysts. It is, however, not often possible to determine which of these evolutionary paths (or combination) an irregularly shaped grain has followed.

In this thesis the term macrocryst will be used to describe a large crystal when no genetic connotation is intended. Examples of the use of grain morphology coupled with a detailed analytical approach to classify macrocrysts are given in Section 3.7.

3.1.4 Glomeroporphyritic Clusters

Many lavas from Ascension contain small glomeroporphyritic clusters each containing from 3 to about 30 grains and ranging in size up to about 2 cm. The mineralogy and number of grains per cluster for those in sectioned lavas are given in Fig. 3.2. As in the phenocrysts (Fig. 3.1) the main minerals are feldspar, clinopyroxene and olivine with feldspar dominant. It is noticeable that pyroxene is proportionally more abundant in the average cluster than it is in the average phenocryst assemblage which suggests that simple aggregation of settling phenocrysts does not, alone, account for the clusters observed.

The following possible mechanisms of formation are envisaged:

(i) simple aggregation of phenocrysts, possibly as a result of flow especially in the salic lavas.

(ii) nucleation of grains around some other large grain.

(iii) breakup of coarse grained material into small fragments by a magma passing through it.

(iv) breakup of cumulus material by eruption of its cognate magma.

The mineralogy and mode of formation of clusters are dealt with in detail in the next section where chemical data on clusters are presented.

3.1.5 Xenoliths of Volcanic Rock in Lava

These seem to be comparatively rare. One example is A63(1) in which two small (3 cm diameter) fragments of trachytic groundmass occur in a trachyandesite (Devil's Ink Stain). Minimal signs of reaction presumably indicate either similar chemical composition or a short time interval between engulfing of the xenolith and quenching of the liquid.

The real or apparent paucity of xenoliths of other volcanic rocks compared with the abundance of coarse-grained xenoliths is probably due to

(i) Lavas are likely to be in contact with volcanic wall rock only for

short periods, whereas coarse blocks are likely to remain in protracted contact with the lava either as refractory residues of partial melting and/or during other magma chamber processes (crystal settling, etc.).

(ii) Ease of digestion of volcanic rock relative to coarse grained rock due to finer grain size.

(iii) Difficulty in recognition of fine grained material as xenoliths within other lavas if both rock types have the same composition, e.g. basalt within basalt.

Mineralogy of Lavas

Phenocryst, xenocryst, clusters and some groundmass phases were analysed using the electron microprobe. The analytical procedure is outlined in Appendix A.3. All analyses presented in this chapter were made by the author during the course of this work. Tables 3.2 and 3.3 summarise the lava types analysed by microprobe.

3.2 FELDSPAR

Feldspar is the major phenocryst and groundmass phase in nearly all the Ascension Island lavas. Both plagioclase and alkali feldspar occur, and in the suite as a whole a remarkably wide range of feldspar compositions is found.

The feldspars are usually unaltered in appearance in both hand specimen and thin section, though some show evidence of reheating and/or chemical reaction with the melt.

3.2.1 Chemical Composition

Fig. 3.3 shows the range in composition of all analysed feldspar macrocrysts but not groundmass feldspars or feldspars from clusters. Unless otherwise stated the analyses are from the centre of each grain.

Analyses are scarce between Ab_{70} Or_{30} and Ab_{60} An_{40}. A few groundmass analyses are presented on Fig. 3.4. These proved difficult to obtain because they were often too small to contain the electron beam and the microprobe stage often proved difficult to reposition.

3.2.2 Intrasample Variation

Fig. 3.5 shows the intrasample variation of feldspar analyses. There are many lavas with compositions Ab_{70}-Or_{30} to Ab_{60} Or_{40} and from Ab_{60} An_{40} to Ab_{70} An_{30}. As stated previously analyses were made from the middle of each grain but since it is impossible to determine whether the middle of a grain is its core (i.e. the grain could be sectioned parallel and close to the rim), the compositional variation then is best considered as a combination of core compositions plus some zoning.

The variation within many samples is quite large though in others, especially at Ab_{65} Or_{35} it is very small, despite over 10 analyses being included within the ring on Fig. 3.5. Where 2 or 3 distinct macrocryst populations are present separate rings enclose them, e.g. H81L has feldspars of composition Ab_{70} An_{30} and Ab_{30} An_{70} with no intermediate compositions.

3.2.3 Zoning

Zoning of phenocrysts is rare in these lavas, given that many samples show a range of phenocryst compositions. About 1/3 of the crystals are optically zoned but microprobe analysis shows the chemical variation to be slight in most cases. Those samples whose feldspars show significant zoning are shown in Fig. 3.6. It can be seen that most zoning in plagioclase is normal zoning (i.e. towards more albitic compositions) indicating gradual cooling and precipitation of progressively more albitic compositions. Reverse zoning may be explained as:

(i) xenocrysts of more evolved compositions from coarse bodies acting as

sites for nucleation of feldspar of more basic affinities.

(ii) magma mixing where basic and more evolved magma mix. As a result of homogenisation of the liquid, any feldspar phenocrysts from the more evolved magma are likely to find themselves in a less evolved liquid probably at a higher temperature.

Feldspar in H6L is the only lava analysed so far to show reversed zoning.

3.2.4 Minor Elements in Feldspar

No analyses for Ba or Sr were made on these samples. Apart from these possibilities the only minor element in the feldspar of any abundance is Fe which may range up to about 0.5% (by weight).

3.2.5 Mineralogy vs. Rock Type

Table 3.1 shows the composition of feldspar phenocryst and groundmass expected in each major rock type. Those phenocrysts found in the basic and intermediate rocks range from An_{30} - An_{83}. These are euhedral to subhedral and range up to 0.5cm in length. The trachytes and more acid lavas have feldspar phenocrysts ranging from oligoclase to sanidine (Ab_{65} Or_{35}) in composition. These feldspars usually have rather rounded edges. Almost all the alkali feldspars are non perthitic, although possible albite exsolution may be seen in some phenocrysts of anorthoclase composition.

3.2.6 Feldspar-Liquid Relations

This is dealt with in detail in Chapter 5, but it is worth noting several points here.

(i) Only one feldspar type is in equilibrium within each lava, although initial compositions may be modified by zoning as the liquid composition changes. This is the behaviour ascribed by Carmichael et al. to "Acid liquids with one feldspar" (p.231). There is no evidence of simultaneous crystallisation of plagioclase and alkali feldspar.

(ii) The relative lack of zoning indicates that feldspars and liquid were well equilibrated. The lack of reversed zoning and mantling of one feldspar by another suggests that magma mixing was rare. Possible examples of mixing are discussed in section 3.6.1.

3.3 PYROXENE

All the pyroxenes in the Ascension lavas are Ca rich. No orthopyroxene, pigeonite or subcalcic augite has yet been identified. Coombs (pers. comm. to J.D. Bell) claims hypersthene to be present in the Cricket Valley basalt but this has not been confirmed from specimens in the Oxford collection (3 separate pieces analysed by microprobe). Fig. 3.1 shows that pyroxene is a slightly less abundant phenocryst phase than olivine and much less abundant than feldspar. Pyroxene is unaltered in nearly all samples and gives good totals and repeatable analyses using the microprobe. Reaction rims are present around pyroxene phenocrysts in the most acid lavas.

3.3.1 Chemical Composition

All the acceptable pyroxene analyses of macrocrysts have been plotted onto the pyroxene trapezium (Fig. 3.7) together with the trend for Skaergaard pyroxenes (from Deer et al., vol. 2A). It may be seen that the range for Ascension pyroxenes is extensive from magnesian augite to almost pure ferrohedenbergite, though the majority of analysed rocks contain the magnesian varieties. The Ascension pyroxenes show an almost horizontal variation with only a vague hint of the Skaergaard "kink" to subcalcic augite. In fact, some of the analyses may best be described as members of the diopside-hedenbergite series rather than augite. This flat range is normal for a suite of mildly alkaline lavas (e.g. Shiant, Gibb, 1973).

3.3.2 Intrasample Variation

As for the feldspars, analyses represented on Figs. 3.7 and 3.8 are

from the middle of each grain and the range is the variation among separate grains. Two features emerge from Fig. 3.8.

(i) The small variation in composition between pyroxenes in each sample, especially compared to that of the feldspar in the same blocks.

(ii) The large number of blocks whose pyroxene phenocryst analyses plot in the rectangle at the diopside end of the range. These are the lavas which have feldspar in the compositional range An_{40} - An_{70}.

3.3.3 Zoning

No compositional zoning was detected in any pyroxene with the microprobe although faint optical zoning may be seen in a few samples.

3.3.4 Minor Elements

The variation of molecular Al and Na in pyroxenes with Fe/(Fe+Mg) is shown in Fig. 3.9. It may be seen that Na increases slightly towards the Fe/(Fe+Mg) rich end and Al decreases sharply as the Fe/(Fe+Mg) increases from 0.1 to 0.5. There is very little acmite component in pyroxene phenocrysts of even the most evolved lavas, a fact which contrasts with the evolved blocks (q.v.). Carmichael (1962) considers this to be due to relatively low $P(O_2)$ in lavas. The sudden decrease in Al with Fe/(Fe+Mg) presumably reflects the evolving peralkalinity, i.e. Al decreasing relative to Na+K in the magma and hence being required for feldspar. The variation of molecular Al with Si is given in Fig. 3.10. The intermediate and basic rocks show varied amounts of Al substituting in tetrahedral (Si) sites whereas the pyroxenes of the acid lavas (those with high Fe/(Fe+Mg)) have little or no Al (see Chapter 4 for further discussion).

3.3.5 Variation in Texture with Chemistry and Rock Type

Most pyroxenes are fairly magnesian and colourless, but where molecular Fe exceeds molecular Mg they become green in colour; this deepens

as Fe/(Fe+Mg) increases. Those rocks with pyroxenes having molecular Fe > Mg are trachyandesites, trachytes and comendites although in many of the most evolved lavas, pyroxene is not a phenocryst phase.

3.4 OLIVINE

Olivine is found in the majority of basic lavas and in some of the more evolved types. In many the olivine shows a reaction rim of opaque oxides, but in only a few samples is the olivine completely iddingsitised. The fayalitic olivines in the evolved rocks always show fairly thick reaction rims, but in few cases is this considered to have influenced the core composition.

3.4.1 Chemical Composition

As with the pyroxene, there is a wide range in olivine composition. Fig. 3.11 shows the chemical composition of all analysed grains. Again these analyses are from the middle of the grains. Unlike the pyroxenes, a compositional gap is seen with no analyses between Fa_{45} and Fa_{58}. The only minor element in the olivine which is present in significant quantities (Ni was not determined) is manganese which increases from 0.2 to 3.5 wt% MnO as the Fe component increases. Mn^{2+} is able to substitute for Fe^{2+} in the M_2 site (Burns, 1970, p.63).

3.4.2 Intrasample Variation

Fig. 3.11 also show the intrasample variation of olivine analyses for these lavas. This is small for olivine throughout the compositional range.

3.4.3 Olivine Composition and Rock Type

The olivine "gap" as seen in Fig. 3.10 divides lavas of basalt-trachybasalt composition from those of trachyandesite-comendite. The majority of the basalt/hawaiites have olivine around Fa_{14-22}. Fa component in olivine correlates well with wt% SiO_2 (see Chapter 5).

3.5 OTHER PHASES

3.5.1 Iron-Titanium Oxides

Almost all the basic and intermediate lavas contain an opaque oxide phase in the groundmass and sometimes as phenocrysts. Unfortunately for geothermometry and barometry most lavas contain only one of the two common oxides (magnetite and ilmenite). The absence of oxides in the more evolved lavas is quite normal and is explained by Carmichael (1967) as being the result of elimination by the reactions ilmenite + acmite → aenigmatite + glass and magnetite + liquid → quartz + acmite (Carmichael et al., 1974, p.286). 15146 (SiO_2 = 70.61) is the only comendite analysed to contain an oxide phase. This is ilmenite, which is normal for these lava types (Carmichael et al., 1974). The majority of the evolved lavas, then, seem to lie in the "no oxide" field (Deer et al., 1977, fig. 282; Carmichael et al., 1974, fig. 5.40). This aspect of the lavas is further discussed in Chapter 7.

The basalts, hawaiites and trachybasalts commonly contain magnetite only. This is a common feature of alkali basalt suites explained by Carmichael et al. (1974) by the elimination of ilmenite in the reaction:

$$\underset{\text{(ilmenite)}}{2FeTiO_3} + \underset{\text{(anorthite)}}{2CaAl_2Si_2O_8} = \underset{\text{(Ti-cpx)}}{2CaTiAl_2O_6} + \underset{\text{(fayalite)}}{Fe_2SiO_4} + \underset{\text{(glass)}}{3SiO_2}$$

Low silica activity (as expected in an alkali basalt) will drive the reaction to the right, thus eliminating ilmenite.

Even when two coexisting magnetites and ilmenites occur, to apply the iron titanium oxide geothermometer/barometer of Buddington and Lindsley (1964) they must be coprecipitates. It is apparent in some lavas (Devil's Ink Stain especially) that one or both of the opaque oxides are xenocrysts. This invalidates any thermodynamic calculations. Two of the three lavas containing both oxides, also contain amphibole phenocrysts which are extremely rare in lavas but common constituents of some acid blocks.

Amphibole in these cases (see below) is considered to be the result of break-up of coarse material and it is possible that the opaque oxides found in the same lava are also xenocrystal material from these blocks which commonly contain both ilmenite and magnetite.

3.5.2 Amphibole

Rare amphibole macrocrysts in these lavas are probably xenocryst material resulting from break-up of coarse grained bodies. Numerous amphibole macrocrysts are found in a trachyandesite lava (A63(1)) but these show rounded edges, darker (reaction?) rims and in one case an amphibole is seen adhering to two feldspars. This is strongly suggestive of remnant coarse material. Compositionally the amphibole is similar to kaersutite having 4 wt% TiO_2 and being high in Mg, Al, Ca and Fe.

Amphibole is, nevertheless, commonly found in the ground mass of the acid lavas. Here very small grains occur in clusters (see Plate 3.11) showing very strong absorbtion and pleochroism from black to blue. These grains were too small for microprobe analysis (see Plate 3.11) but the colour suggests riebeckite or arfvedsonite.

3.5.3 Quartz

Quartz is confined to the most acid lavas, being found as rare small phenocrysts and more commonly as irregular patches in the ground mass (Plate 3.6). Because of the fine grained and often glassy nature of the ground mass in these lavas, it is not always possible to distinguish quartz as a crystalline phase even though the wt% SiO_2 is > 70.

3.5.4 Apatite

Apatite may be recognised as very fine needles in some of the P_2O_5-rich volcanic rocks, but it is not found in the trachyandesites-comendites.

3.5.4 Glass

Some basic/intermediate lavas contain glass:

(i) In the ground mass, occurring as dark isotropic material between the ground mass feldspars;

(ii) As inclusions in some of the phenocryst phases.

In both cases the glass patches have proved too small for analysis.

Glass is quite common in the trachytic and comenditic lavas. In the most evolved lavas, glass becomes the major ground mass constituent and in the obsidians, of course, it forms virtually the entire rock. Plate 3.2 shows a trachyte with small laths of sanidine, set in glass, forming the ground mass. Plate 3.4 shows the most evolved lava yet analysed (Little White Hill comendite) having flow banding and alignment of phenocrysts in a mainly glassy ground mass. Chemical analyses of some of these glasses were possible (particularly the obsidians) and these are dealt with in Chapter 5 along with the whole rock analyses.

3.6 MINERALOGY OF PHENOCRYST POPULATIONS AND GLOMEROPORPHYRITIC CLUSTERS

3.6.1 Phenocryst Populations

As stated in the Introduction to this Chapter, the distinction between phenocrysts and xenocrysts is difficult to make and often based on assumptions. Hence the term macrocryst was introduced for use in describing large crystals (which may be either phenocrysts or xenocrysts) for which no genetic connotation is implied.

In sample H39L there is unequivocal evidence that the large feldspar macrocrysts which make up 10-20% of the rock (by volume) are xenocrysts. Plate 3.8 shows an anorthoclase macrocryst and the margin of a coarse grained block contained within the lava. Texturally the phenocryst margins are identical to those of the block and Fig. 3.12 shows the feldspar xenocrysts

and feldspars from the block (C_3) to have identical chemical composition.

Visual confirmation of the fragment breaking off the block is not needed to classify these macrocrysts as xenocrysts, since their chemical composition is incompatible with that of the ground mass (Fig. 3.12). This example is discussed in detail in Section 4.14 (partial melting) and by Harris and Bell (1982).

Reversed zoning has already been noted in specimen H6L (Section 3.2.3) and this is similar to a case described by Cox et al. (1970) from Little Aden, where plagioclase phenocrysts have cores of An_{50} and rims of An_{80}. In Lava H6L it is impossible to say whether the reversed zoned feldspars have resulted from the break-up of a more evolved coarse grained body, or from the passage of a basic magma through a more evolved phenocryst-bearing magma (i.e. magma mixing).

A63L, a trachyandesite from the Devil's Ink Stain (South East Head) provides the most varied collection of macrocrysts. These are:

euhedral: plagioclase (An_{40}), olivine, clinopyroxene

embayed: plagioclase (An_{60} cone 40 mm) olivine, clinopyroxene

The ground mass feldspar ranges from plagioclase An_{40} to possible KFsp (??) and other groundmass minerals are ilmenite, magnetite, amphibole; macrocrysts also occur plus a xenolith of trachyte.

The problem here is that the euhedral and embayed macrocrysts are of approximately the same chemical composition. Plagioclase macrocrysts which are embayed, nevertheless retain a euhedral outline.

Plate 3.8 shows such a grain together with a euhedral plagioclase. Plate 3.3 shows an embayed and a euhedral olivine macrocryst also in close vicinity

The type of embayment shown in the feldspar which pervades the whole grain is most likely to be due to preferential melting along cleavage planes (Cox et al., 1979). It seems, then, that a rise in temperature

without a great change in bulk chemical composition affected these grains. As the magma then cooled, new euhedral feldspar crystallised together with some nucleation of feldspar along the edges of the existing partially melted grains. Heating of the magma in this way may be the result of a sudden influx of more basic (i.e. hotter) magma into an already occupied chamber. The density contrast would help to prevent mixing, hence A63L composition remained the same.

3.6.2 Mineralogy of Glomeroporphyritic Clusters

In the introduction four main modes of origin of clusters were proposed:

(i) Simple aggregation of phenocrysts into clusters perhaps as a response to flow. A possible example of this type is shown in Plate 3.9 and chemically in Fig. 3.13. Although these two specimens bear different numbers, they are in fact from the same flow (Little Ascension). No embayed crystals are found and the analyses of minerals in the clusters and the phenocrysts are very similar.

(ii) Nucleation of grains around pre-existing grains seems to be very rare in these lavas and is confined to small opaque grains which are sometimes found nucleating around olivine and pyroxene grains. Nothing involving plagioclase as described by Betton (Betton, D.Phil. thesis 1978, plates 3.9 and 3.10) has been found in the Ascension Island lavas.

(iii) Break-up of coarse material to give small xenoliths. Lava H39L, described in the previous section, has xenocrysts derived from fragmented blocks and if a number of these grains still adhered, they would be assigned to this group. Very few clusters of this type are found in this lava which must reflect the efficiency of separation of the grains (see Section 4.14).

Another example of this type is in A63(1) from Devil's Ink Stain trachyandesite flow, where feldspars and an amphibole fragment are found

adhering. Amphibole is a common constituent in the intermediate coarse grained blocks but occurs only in a handful of lavas where it is rounded in shape and rimmed by opaques. This is good evidence that these clusters are fragmented blocks and the separate amphiboles are xenocrysts. Other examples of this type of cluster are found in the lava from the Dark Slope Crater composite cone, which contains small angular fragments of material identical to some of the coarse grained blocks.

(iv) A possible example of the break-up of cumulus material by its cognate magma is illustrated in Plate 3.10 where a small cluster of cumulus plagioclase and intercumulus pyroxene (showing classic ophitic texture) is seen. The cluster is not embayed and its constituent minerals have chemical compositions indistinguishable from those of the surrounding phenocrysts. The shapes of the plagioclase both in the cluster and as phenocrysts are remarkably similar. This evidence suggests that the cluster formed as a part of a coarse grained body which was later disrupted by the same magma giving entrained fragments of cumulus material.

Many of the clusters are not easy to interpret and cannot be ascribed to one particular mode of formation. H39L (Fig. 3.12) contains small clusters (C_1 and C_2) which resemble type (i) in texture yet are more evolved than the phenocrysts and do not appear to be fragments of the associated blocks. Lava 15006 (Cocoanut Bay) contains a variety of clusters (Fig. 3.14). C_1, C_2 and C_3 could be type (iii) or (iv) and C_4 could be type (i), (iii) or (iv) using chemical composition as a guide.

For the majority of glomeroporphyritic clusters, chemical and textural relationships with the enclosing lava do not provide sufficient information to elucidate their origins.

3.7 SUMMARY

(i) The lavas range from basalt to comendite and relative abundances, at

the surface, are basalt/hawaiite > trachyte > trachybasalt > trachyandesite > comendite > obsidian.

(ii) Feldspar is the major phenocryst phase but olivine and clinopyroxene are also present as phenocrysts in most rocks.

(iii) Orthopyroxene has not been observed in the lavas. This is typical of mildly alkaline suites (Coombs, 1963).

(iv) Pyroxene, feldspar and olivine exhibit a wide range of chemical composition with, in the case of feldspar and pyroxene, a paucity of analyses in mid range and in olivine a gap in compositions. Intrasample variation is high in feldspar and low in pyroxene and olivine.

(v) It seems that in no magma coprecipitated alkali feldspar and plagioclase.

(vi) Some lavas exhibit a highly varied assemblage of macrocrysts (phenocrysts + xenocrysts) which are difficult to interpret.

(vii) Xenocrysts may be characterised by irregularity and embayment but chemical incompatibility (e.g. K feldspar in basalt) is required to distinguish between xenocrysts and resorbed phenocrysts. In some cases special circumstances may indicate macrocrysts to be xenocrysts (e.g. observing grains in the process of being detached from blocks).

(viii) Many lavas contain glomeroporphyritic clusters which may have had a variety of origins. Fragments of blocks cannot positively be recognised unless they show chemical incompatibility with their host lava.

CHAPTER 4

MINERALOGY AND PETROGRAPHY OF THE BLOCKS

4.1 INTRODUCTION

In this chapter, the blocks are grouped according to the geographically isolated suites in which they were found, but in some cases seemingly identical suites are described together. As far as possible the basic blocks are described before the acid blocks.

Nomenclature is kept as simple as possible. These blocks are best described as gabbros, monzonites, syenites or granites depending on their feldspar composition.

The first part of this chapter (from Section 4.2. to 4.10) deals with each suite and the second part (4.11 onwards) deals with aspects such as partial melting, residual liquid composition, evidence for immisicibility, which are common to a number of these suites.

4.2 DARK SLOPE CRATER GABBROIC BLOCKS

This suite is gabbroic in the sense that the plagioclases are calcic ($> An_{50}$). They consist of three major minerals: plagioclase, pyroxene and olivine. The modal proportions for a randomly selected collection of blocks are shown in Fig. 4.1. Accessory minerals are orthopyroxene, chrome-spinel, Fe-Ti oxides and apatite. Iron oxides may reach rock forming (> 10 modal %) proportions in two blocks (DSA3, HDSA5, and DS24). Alteration is variable and this usually affects olivine which shows a range of textural and chemical responses. Table 4.1 lists the mineralogy of the 20 blocks analysed by the electron microprobe. These were selected to enable as wide a textural and mineralogical range as possible to be investigated.

MINERALOGY

4.2.1 Plagioclase

This ranges from An_{96} - An_{48}, there being no alkali feldspar. Fig. 4.2

shows the range of analyses and the intrasample variation. The majority of these blocks have feldspars with compositions between An_{92} and An_{78}. Six blocks show feldspar with An between 48 and 69. There seems to be a compositional gap between An_{70} and An_{78}.

The plagioclases are unzoned both optically and chemically and the intrasample variation is quite small (usually < 10% An) in all except two blocks. These two contain isolated patches of intercumulus plagioclase and the variation is possibly due to slight differences in composition between isolated liquid pockets as crystallisation approached 100%.

4.2.2 Pyroxene

Orthopyroxene has been observed as a primary phase only in two blocks (15227(4) - Plate 4.3 and 15227(13)) but is relatively common as a reaction product where olivine and plagioclase are in contact. Clinopyroxene is also a product of this reaction (Plate 4.1) which is discussed in Section 4.2.3. In specimen 15227(4) the orthopyroxenes are intercumulus phases, but these are distinct from the reaction type and are not associated with olivine. Analyses of orthopyroxene are plotted on Fig. 4.3.

Clinopyroxene which is absent from only one block (17317N), shows a limited range in chemical composition. All are highly magnesian (Fig. 4.3) and as with the feldspars, two compositionally distinct groups appear to be present. Fig. 4.4 shows the intrasample variation and a striking feature is that there is little variation in Fe/(Fe + Mg) but often a significant variation in Ca/(Fe + Mg). This may be due to two reasons:

(i) The electron beam lay across opx/cpx boundaries; this may be the case for those rocks containing both pyroxenes but blocks with no opx show this variation.

(ii) The range may be due to fine scale exsolution of opx from cpx. This is rarely seen optically but it is significant that in those rocks in which it is seen, the variation in Ca/(Mg + Fe) is largest.

Fig. 4.5 is a portion of the pyroxene quadrilateral with analyses from 15227(4) and 15227(13) which show a large variation in Ca content. 15227(4) contains both orthopyroxene and clinopyroxene which both show fine scale exsolution lamellae. The range in chemistry seen on Fig. 4.5 is presumably the result of a series of analyses where the electron beam contained a varying proportion of the lamellae. Specimen 15227(13) contains both cumulus orthopyroxene (Plate 4.3) and orthopyroxene formed by reaction between olivine and plagioclase. The pyroxenes in this block appear to show a very wide range of compositions, some even plotting in the field of metastable sub-calcic augites. It is thought however that these are "spurious" analyses of areas straddling ortho/clinopyroxene boundaries.

Exsolution in augites is especially common in basic plutonic rocks of tholeiitic affinities (Deer et al., 1977, p.342) and the unmixing of Ca-poor pyroxene from the augites of these blocks suggests that they crystallised from a liquid of tholeiitic affinities. Exsolution is not seen in the clino-pyroxenes of blocks from any other locality and is not found in clinopyroxene phenocrysts in the lavas.

4.2.3 Olivine

Fig. 4.6 shows the range in olivine composition (Fa_3 to Fa_{29}) and the intrasample variation. Some specimens have a wide range in olivine composition (15227(5), 15227(13) and DS56) relative to the other blocks, which vary less than 10%. Most analyses lie between Fa_{10} and Fa_{20}.

Further investigation of blocks showing a large range in olivine composition suggests that chemical change in the olivine has occurred, probably the result of secondary reheating when the blocks were engulfed by magma. In 15227(5) and 15227(13) the olivines have an opaque phase occurring along an unusually well defined cleavage (Plate 4.2). Two sections of 15227(13) were made, one from very close to the block/lava contact (and

parallel to it), and the second from the interior of the block.

The olivines from the interior do not show opaque veins (as in Plate 4.1) but those from the margin show a well developed network of opaques throughout the whole grain. There are three distinct compositional groups (Fig. 4.5):

(i) Normal olivines with no opaque veins - group A.

(ii) The olivine from between the opaque veins - group B.

(iii) The opaque blebs - group C.

Similar networks of opaques in olivine have been produced by experimental alteration (Haggerty and Baker, 1967). Their Figs. 11, 18 and 19 greatly resemble Plate 4.2. They were produced by oxidising olivine at 950°C for 72 hours. The absence of the texture inside the Dark Slope blocks may be due to thermal insulation of the interior.

Many of the olivines altered in this fashion also possess large rims of orthopyroxene. This is evidence that the orthopyroxene forms from oxidation reactions rather than crystal liquid reactions. Breakdown of olivine to give orthopyroxene is well documented (e.g. Muir et al., 1957).

$$\underbrace{3Fe_2SiO_4 + 3Mg_2SiO_4}_{\text{components of olivine}} + O_2 \rightarrow \underbrace{2Fe_3O_4}_{\text{mgt}} + \underbrace{6MgSiO_3}_{\text{opx}}$$

In the Haggerty and Baker (1967) example, the opaque blebs within the olivine are iron oxide rather than a fayalitic olivine and it may be that in this example the fayalitic blebs are a mixture of the Fe_3O_4 produced by the reaction plus the original olivine. The reaction above requires equal amounts of Fa and Fo and the highly forsteritic olivine between the blebs may be the additional Fo left as this reaction proceeded.

4.2.4 Opaque Minerals

Chrome Spinel

This is found ubiquitously in the olivine rich blocks (Plate 4.4). Chemically the chrome spinels are very similar.

Fe-Ti Oxides

About half the Dark Slope blocks contain Fe-Ti oxides (Table 4.1). These minerals may be used as a guide to temperature of crystallisation and oxygen activity so their study merits special consideration despite low modal abundances (See Chapter 7). Table 4.2 summarises the occurrence of Fe-Ti oxides in all blocks in which they are found.

The presence of exsolution limits the value of these minerals as geothermometers. This is seen in DS24 where lamellae of exsolved ilmenite occur in magnetite. Such grains are confined to the edges of the block and are presumably related to reheating and oxidation by the engulfing magma (cf. olivine section). Oxidation of magnetite is discussed by Haggerty (1976) who considers the reaction

$$\underset{\text{(ulvospinel)}}{6Fe_2TiO_4} + O_2 = \underset{\text{(Mgt)}}{2Fe_3O_4} + \underset{\text{(Ilmenite)}}{6FeTiO_3}$$

to be responsible for the exsolution. Chemical compositions and inferred equilibrium T and aO_2 are given in Chapter 7.

4.2.5 Texture of Dark Slope Blocks

It is important to consider the textures of these blocks in conjunction with their mineralogy. This suite is the largest and the blocks have suffered much less alteration than most.

Grain Size

Maximum grain size is about 8 cm diameter. Fig: 4.7 (a) and (b) shows

histograms of maximum grain size and average grain size in each block vs. frequency. Fig. 4.7(c) is maximum grain size - average grain size, which is a crude measure of equigranularity,vs. frequency. None of the three main minerals consistently forms the largest grains in a block, and for most blocks the largest grains are not just one mineral. This suggests that in general mechanical sorting is responsible for the grain size differences rather than chemical factors which could have influenced mineral growth rates.

Grain Shape and Rock Fabric

These blocks show classic cumulus textures as in examples described by Wager et al. (1960). Fig. 4.8 is taken from their work and their scheme of nomenclature is used here. However in using these names, genetic connotations are not intended. Thus if a block is described as having cumulate texture, it refers only to the shape and relative orientation of its minerals and does not necessarily imply that the block formed by crystal settling (see McBirney and Noyes, 1979 and Irvine, 1982 for discussion).

Orthocumulates

None of these blocks may be classified as an orthocumulate. The block most like the orthocumulates of Wager et al., is 15227(4), see Fig. 4.8, where in places cumulus plagioclase occurs with intercumulus clino and orthopyroxene. Elsewhere in the block the textures are more like the plagioclase-pyroxene adcumulates described below.

Adcumulates

Because of the almost complete absence of intercumulus minerals and evidence of intercumulus liquid, these blocks are best described as adcumulates. Zoning is absent, thus there is no way of distinguishing cumulus material from later adcumulus growth.

The following classification is convenient:

(i) Olivine adcumulates (dunites)

(ii) Plagioclase adcumulates

(iii) Plagioclase + olivine adcumulates

(iv) Plagioclase + pyroxene adcumulates

(v) Plagioclase + pyroxene + olivine adcumulates

(vi) Opaque adcumulates

Olivine Adcumulates

These may be >99% olivine, but most contain a few percent of intercumulus plagioclase and pyroxenes. Cr-spinel is a ubiquitous accessory mineral. It is considered to have crystallised early as it is found in small rounded grains, often included in much larger olivines. The average grain size of this group is quite coarse, in the region of 3-4 mm diameter. Smaller grains of olivine are rounded and presumably have experienced less adcumulus growth than the larger, sometimes irregular and interlocking grains. Plate 4.4 shows an example.

Plagioclase Adcumulates

As with olivine, blocks consisting of pure plagioclase are found (see Plate 4.5). These are, in general, fine grained (average grain size 1.5 mm) and tend to be equigranular. Very small amounts of intercumulus olivine, pyroxene opaques (ilmenite and magnetite) may occur (< 1% in many cases). With increasing olivine they grade into plagioclase-olivine adcumulates. In some of these blocks narrow bands of fine grained pyroxene are found (see later

Plagioclase + Olivine Adcumulates

These are similar to the plagioclase adcumulates except that significant (10-15%) olivine is found as irregular, but not entirely intercumulus grains (Plate 4.1). No zoning is seen either in olivine or plagioclase but it seems

that the olivine is part cumulus and part adcumulus. Clino and orthopyroxene rim the olivine in some cases and are explained as being the result of oxidation of the olivine. In some grains, though, this may be a reaction with the last liquid portion.

Optical zoning is seen in some plagioclases though these show negligible differences in chemical composition. This zoning is in any case irregular and patchy and does not suggest the presence of cumulus cores surrounded by adcumulus rims.

Plagioclase-Clinopyroxene Adcumulates

In general there is strong preferred orientation of both plagioclase and pyroxene. In all cases there is little evidence for adcumulus growth and the grains (especially pyroxene) show elongate rectangular grain shapes. There seems to be no intercumulus material which either suggests that cumulus minerals were packed solid (very unlikely) or that crystal growth in situ has given these well defined and regular grain shapes.

In 17317Y, clinopyroxene shows a linear orientation. Plates 4.6 and 4.7 are sliced respectively parallel and perpendicular to the orientation. Note the lack of intercumulus material and the interlocking grain boundaries indicative of some adcumulus growth

Orthopyroxene is found in 15227(4) which is best classified in this group and this occurs with a poikilitic relationship with the plagioclase. This orthopyroxene provides evidence for a coexisting liquid of tholeiitic character.

Opaque Oxide Adcumulates

Three blocks (HDSA(5), DS24 and DSA3) contain appreciable (> 10%) amounts of Fe-Ti oxide. In the other (200+) blocks examined, none have > 1% opaques

(not including oxidation products of olivine etc.) and many have none at all. The absence of opaques is considered typical of adcumulates (Wager et al., 1960). Orthocumulates usually contain 1-10% oxide minerals crystallised from the trapped residual liquid (Fig. 4.8).

HDSA(5) contains about 60-70% magnetite and ilmenite plus plagioclase, clinopyroxene and some iddingsitised olivine. DS24 contains about 30% ilmenite/magnetite with plagioclase and clinopyroxene (no olivine) and DSA3 contains about 10% ilmenite/magnetite with plagioclase, clinopyroxene and a small amount of iddingsitised olivine. These rocks show particularly interesting textures.

DSA3 is otherwise a fairly typical plagioclase-pyroxene adcumulate with typically adcumulate grain boundaries. The opaques though show an irregular and rounded grain shape and often lie along other grain boundaries, and in a significant number of cases they project into pyroxene. There is no sign of reaction between pyroxene and opaque and no zoning is seen in the pyroxene. This rock is unique in that it is the only Dark Slope gabbro to contain quenched residual liquid, which resembles the basalt lavas in texture and to some extent has reacted with the surrounding crystals. The petrogenetic significance of residual liquid (= mesostasis) is discussed in Section 5.6.6.

DS24 exhibits similar textural relations between pyroxene and oxides and HDSA5 contains rounded pyroxene grains which are completely or partially surrounded by oxides. In these cases adjacent pieces of pyroxene often show optical continuity.

Associated with the oxides in all the blocks is apatite, a mineral not found in any other Dark Slope block. Apatite/oxide rich rocks have been described by Philpotts (1967) who ascribes their origin to liquid immisicibility between P-Fe rich and silicate rich liquids (see Section 4.15).

Layering and Other Planar Structures

Uneven distribution of minerals throughout a block is relatively common.

Layering, however, is much rarer, being recorded in only three blocks (DSA5, DS23, DS36). This is surprising since the majority of blocks show very distinct preferred orientation. Figs. 4.9-10 are sketches of the layering seen in two of these blocks (DS23 and DS36) showing the grain size and modal proportions in each layer. A large number of phases have been analysed in all three blocks and in no case has the variation in composition of minerals between layer exceeded the intra-layer variation, which is in any case very small. This layering, then, seems to be due to sedimentary processes rather than chemical or pressure/temperature changes.

The only other type of layered structure seen in the Dark Slope Crater blocks are bands of clinopyroxene which occur in some of the plagioclase adcumulates. These bands are 1-2 grains in thickness (1/4 mm) and have no specific orientation and criss-crossing bands are seen in HDSC(2) (Plates 4.8 and 4.9). Where the bands occur, the adjacent feldspar shows zones of anomalous birefringence (Plate 4.10). On analysis these are found to be significantly richer in Ab component compared with parts of the same grain away from the pyroxene band, and with the other feldspars in the block. Two possible modes of origin are:

(i) The bands represent crystallisation of trapped liquid which have crystallised at lower temperatures giving pyroxene and a more sodic plagioclase.

(ii) The bands were cracks along which magma from above (more evolved) passed giving pyroxene and the sodic plagioclase.

The veinlike nature of the bands and the fact that they occur as flat planes suggests (i) is very unlikely. The plagioclase seems to have reacted with the magma to give a more sodic composition hence this seems similar to examples of infiltration metasomatism described by Irvine (1980).

Summary of Textural Evidence

(i) Grain size varies, but most specimens are approximately equigranular.

(2) There is very little intercumulus material, hence these blocks may be considered as adcumulates. Only one block shows any evidence of quenched residual liquid. This suggests that the suite must have been almost completely solid at the time of eruption.

(3) No chemical zoning is seen in any mineral (apart from the special case, HDSC(2)), so adcumulus growth must have been isochemical. The crystallisation of the intrusion must therefore have been slow.

(4) Oxide rich blocks are very rare and these show unusual textures which may be related to immiscibility.

(5) Although layering in individual blocks is rare, large modal differences between blocks of the suite imply large scale layering of the present body.

(6) Planar bands of pyroxene are found which suggest that residual fluids travelled along fractures in already solid cumulus material. Infiltration metasomatism of the feldspar seems to have occurred.

4.2.6 The Nature of the Coarse-Grained Body

On the assumption that the blocks are all derived from a single plutonic mass (there being no evidence to the contrary), an attempt may be made to reconstruct the parent body by analogy with well documented intrusions such as the Skaergaard and Bushveld bodies. Sympathetic changes in composition of olivine, pyroxene and plagioclase (Fig. 4.11) suggest crystallisation from an evolving, fractionating magma intruded as a single pulse (cf. Skaergaard) rather than as successive pulses (e.g. Rhum).

Fig. 4.13 represents an attempt to place the blocks in a relative stratigraphic order on the basis of the cumulus phases they contain and the composition of these phases. (It should be noted that there is no scale on the vertical axis on Fig. 4.13 and it cannot be assumed to be linear).

Variation in Modal Proportions

This is seen to vary considerably with relative height in the proposed

intrusion (Fig. 4.13), but certain features may be noted.

(i) The earliest cumulates are olivine rich (dunites).

(ii) Plagioclase enters as a cumulus phase before clinopyroxene.

(iii) The most evolved blocks are plagioclase rich.

The down temperature sequence of liquidus phases olivine, olivine + plagioclase, olivine + plagioclase + clinopyroxene is similar to the experimentally determined "melting relations" of Bender et al.(1978) for tholeiitic basalt at low pressure (Fig. 4.12).

Liquid Composition

With no intercumulus material, it is impossible to determine the composition of liquids in equilibrium with a particular cumulus assemblage. In addition, the initial liquid composition is not known unlike Skaergaard where it can be estimated with reference to the composition of its fine grained marginal facies.

Further consideration of the nature of the parent liquid is given in Chapter 6, but several points may be stated here.

(i) There are tholeiitic affinities in this liquid not seen in the lavas.

(ii) Assuming that the volume of a particular block type in the original intrusion is proportional to the volume of blocks collected, then the rapid change in mineral composition ar the top of Fig. 4.13 suggests that the liquid composition changed rapidly at the later stages of crystallisation. This would be consistent with a high proportion of the original liquid having been crystallised at this stage.

(iii) If the blocks are a random sample of the intrusion, a sudden crystallisation of iron oxides is suggested. This could be due to super-saturation of Fe or the crossing of the immiscibility field by the liquid (Roedder, 1978, Philpotts, 1967). Relatively late appearance of iron oxides (see Fig. 4.13) can be ascribed to a highly reduced parental magma (cf. Skaergaard).

(iv) Appearance of opx would be consistent with a sudden decrease in Fe oxide content of the liquid (Deer et al., Vol.2A, p.338).

4.3 MIDDLETON'S RIDGE GABBROS

Three main block suites are found at this locality:

(i) Gabbros

(ii) Monzonites - syenites - quartz syenites

(iii) Granites

The latter two groups are closely related and are almost certainly part of the same body. These are described in Section 4.10. The gabbros are all very similar and consist of plagioclase, clinopyroxene, olivine and Fe-Ti oxides. The ubiquitous accessory oxides and the presence of quenched residual liquid make these gabbros distinct from those of Dark Slope Crater. Fig. 4.14 shows the modal proportions of the three major phases and an indication of the volume percentage of mesostasis.

Mineralogy

4.3.1 Plagioclase

This ranges from An_{81} to An_{60} (Fig. 4.15) and the intrasample variation is small (3-10 An %). There is no alkali feldspar in these blocks, but most plagioclases contain 0.1-0.2 wt % K_2O. Some show a slight amount of optical zoning but this is within the analytical error of the probe.

4.3.2 Pyroxene

Clinopyroxene only is present and this has a very small compositional range (Figs. 4.16 and 4.17). Pyroxenes in these blocks do not exhibit the apparent large range in Ca/(Fe + Mg) relative to Fe/(Fe + Mg) seen in some of the Dark Slope blocks, hence no fine scale exsolution is suggested.

Fig. 4.18a shows the variation of molecular Al and Ti with Si. The

good inverse correlation indicates that both Al and Ti substitute for Si in tetrahedral sites. This suggests low pressure crystallisation (Le Bas, 1962). Kushiro (1960) describes the variation of Al and Ti with Si for a variety of volcanic suites and the Middleton's gabbro distribution of Fig. 4.18a lie in Kushiro's alkali basalt (i.e. no normative Qz or Ne) suite. Undersaturated volcanic suites may contain pyroxenes with considerable Al and Ti substitution (for Si) which results from low Si concentration relative to tholeiites (Deer et al., 1977; Le Bas, 1960).

Fig. 4.18b shows the variation of Na with Mg/(Mg + Fe). As the pyroxene becomes more iron-rich, the Na content increases, presumably with falling temperature. Pyroxenes from a single sample show a wide range in Al and Ti content. In H7(1), slight optical zoning can be correlated with Al and Ti enriched rims.

These pyroxenes contain inclusions of residual liquid (Plate 4.11) and of iron sulphide, which may be due to sulphide/silicate immiscibility (Section 4.15.2).

4.3.3 Olivine

As in the pyroxenes, the Fe/Mg ratio in olivine shows little variation (Fig. 4.17b). Except for 15226(11) compositions lie between Fa_{23} and Fa_{28}. 15226(11) has a wider range of compositions which may be related to oxidation, suggested by opaque patches in the olivines. Oxidation of Dark Slope olivines is described in Section 4.2.4 but the network patterns in those examples are not seen here.

4.3.4 Opaque Oxides

Six of the sectioned rocks contain Fe-Ti oxides, and sulphide inclusions have been found in the pyroxenes of H7(5). Of the analysed rocks, two contain only magnetite (the same composition) and one (H7(5)) both ilmenite and magnetite. H7(5) contains about 10 modal % opaques. Most of this is

magnetite but rounded inclusions of ilmenite are seen in some magnetite grains under reflected light. The two oxides appear therefore to be comagmatic and the rock is potentially useful for temperature and aO_2 determination (see Section 7.5.3).

4.3.5 Minor Phases

Apatite, zircon, sphene are not found in these blocks.

4.3.6 Textures

These gabbros show a wide range of textures and exhibit several features not seen in the Dark Slope Crater gabbro suite. They are most notable for the presence of up to 15% quenched residual liquid.

Grain Size

As in the Dark Slope Crater suite, grain size is variable, although for these blocks it is difficult to quantify owing to the poikilitic nature of the pyroxene in most blocks. Two blocks have significantly finer grained plagioclase (average 1.5 mm diameter) while the remainder have plagioclase between 2.5 and 5 mm. Olivine is, in general, small and rather rounded (0.5 - 1.5 mm).

Grain Shape

Plagioclase occurs as euhedral laths which may have slightly rounded edges in some sections. Many are in completely crystallised enclosing euhedral glass patches. This aspect is dealt with in Section 4.3.7. Olivine is always found as subhedral rounded grains but in one specimen it shows intercumulus characteristics. Pyroxene invariably occurs as large poikilitic patches up to 1-2 cm diameter enclosing plagioclase and olivine. In some blocks euhedral (presumably cumulus) pyroxene is seen but this is associated with the poikilitic variety (see Plate 4.12). The opaque minerals, where

present, show similar poikilitic texture to the pyroxene, but on a much smaller scale. Large irregular opaques are seen in H7(5).

Rock Fabric

Three textural types may be recognised:

(i) Plagioclase ± olivine orthocumulates

(ii) Plagioclase ± olivine mesocumulates

(iii) Plagioclase hetradcumulates

Examples between the three types are common but ideally the orthocumulates contain euhedral olivine and plagioclase with subordinate interstitial pyroxene and opaques (Plate 4.13). The mesocumulates contain both subhedral (cumulus?) pyroxene with some poikilitic pyroxene and these may grade into the hetradcumulates where plagioclase is surrounded by an equal modal proportion of pyroxene (Plate 4.14).

Layering and other large scale textural features are absent from these blocks. Some preferred orientation of feldspars in the orthocumulates is seen, although this is much less pronounced than in the Dark Slope Crater blocks. Sometimes minerals are preferentially clustered in different parts of a slide (usually olivine or pyroxene) but the small size of each block (usually <10 cm diameter) and paucity of blocks relative to the Dark Slope Crater suite precludes a more detailed textural study.

4.3.7 Nature of the Quenched Residual Liquid

Quenched residual liquid is represented by a largely glassy mesostasis and evidence of this is seen in all Middleton's gabbros, even hetradcumulate blocks such as 15226(18) (Plate 4.14), which contains thin films along some of its grain boundaries. The amount of mesostasis may range up to 14% by volume (Fig. 4.14). Similar material in coarse grained blocks from St. Vincent has been termed interstitial scoria (Lewis, 1964; Arculus and Willis, 1980).

The reasons why this material is considered to be quenched residual

liquid are:

(i) The minerals bounding the mesostasis are sharply euhedral and show no signs of melting (see Section 4.14).

(ii) The chemistry and mineralogy rule out any possibility of this being a secondary (e.g. zeolitic) material (see below).

Texture and Mineralogy

The mesostasis consists of small quench crystals of plagioclase (some swallow tailed - see Plate 4.15) and rods of opaque mineral which form a criss-crossed network set in glass (Plates 4.15 and 4.16). Often the mesostasis is too fine grained to distinguish individual minerals, in which case it appears opaque. The composition of the minerals is not accurately known as they are too fine grained to contain the probe beam, and in most cases the mesostasis is destroyed during polishing of the section. Low overall Ti content in the opaque patches suggest that the opaque mineral is magnetite rather than ilmenite.

Small patches of mesostasis may be found within the individual grains. In plagioclase these take the form of elongate patches parallel to the grain edges and with "negative" crystal shape (Plate 4.12). This must be due to incomplete recrystallisation of the plagioclase, rather than partial resorption which manifests itself as rounded melt patches (Plate 3.7). Pyroxene and olivine contain subspherical patches of mesostasis in some blocks (15243D, H7(5) etc.) which have the same character as the intergranular mesostasis (see Plate 4.11). See Chapter 5, Section 6 for details of chemical composition of residual liquid.

4.3.8 Nature of the Original Intrusion

This is difficult to ascertain but, given the similarity in composition and texture of these blocks, it seems likely they came from the same place within an original coarse grained body. Some further tentative

speculations are as follows:

(i) The analysed blocks containing magnetite are also those whose mafic and femic minerals are most enriched in Fe and Na respectively. This suggests the fractionation of an initially reduced parental magma.

(ii) The predominance of ortho- and mesocumulates implies a more rapid deposition rate (with consequent trapping of residual liquids) than has been inferred for the Dark Slope Crater intrusion.

(iii) The intrusion was disrupted before crystallisation was complete, hence the occurrence of quenched residual liquid in many cases.

(iv) The blocks with the most mesostasis have the least evolved olivine, pyroxene and plagioclase (H28(1), H28(3), H7(1) and H99(1)). This may be due to progressively slower crystallisation as the intrusion cooled.

Unlike the Dark Slope Crater blocks, these are amenable to direct measurement of evolved liquid composition, although the inhomogeneous nature of the glass and quench crystals makes this very inaccurate. However, a block similar to these Middleton's gabbros from Green Mountain contains residual liquid quenched to glass (Section 4.9) without abundant quench crystals. Further discussion of fractionation trends is deferred to Chapter 5, Section 5.6.

4.4 BLOCKS FROM OTHER CONES

Seventeen blocks were collected from Mountain Red Hill, seventeen from Lady Hill and one from Cross Hill (for details see Chapter 2). These blocks are similar in size, mostly 3-5 cm in diameter. They are often altered and rather friable.

Mineralogy

Three blocks from Mountain Red Hill and one from Lady Hill were investigated by microprobe.

4.4.1 Plagioclase

Fig. 4.19 shows that the feldspar is all plagioclase (An_{46-72}). Normal zoning is seen optically in plagioclase of all the blocks and this accounts for the range in compositions in Fig. 4.19.

4.4.2 Pyroxene

Both clino- and orthopyroxene are found in these blocks (e.g. H83(14) and H83(10)). All the clinopyroxene analyses are remarkably similar (Fig. 4.20) but the orthopyroxenes of H83(14) and H83(10) are rather different in Fe/(Fe + Mg). It is possible that the orthopyroxenes are reaction products of olivine (see Dark Slope olivine section, 4.2.3)

Fig. 4.21 shows the variation of molecular Ti and Al with molecular Si. Orthopyroxene shows no variation for either but in the clinopyroxenes there is a wide range of amounts of Al and Ti substitution for Si. This variation is found in analyses from the same block. Although all these analyses came from the middle of a grain, a thin section is two dimensional and the middle is not necessarily the core. These variations may reflect zoning even though this was not detected optically. The paucity of Al in the orthopyroxene is consistent with an igneous origin (Deer et al., 1977).

4.4.3 Olivine

In contrast to the pyroxene, olivine exhibits a wide range in chemical composition (see Fig. 4.20) especially in block H83(14) where olivine analyses range from Fa_{16-45}. The pyroxene analyses require an equilibrium olivine composition of c. Fa_{35} and the wide variations on either side of this value may be the result of secondary oxidation (cf. Section 4.2.4), although alteration textures (reaction rims around olivine, pyroxene etc.) mask textural evidence that could substantiate this point.

4.4.4 Opaque Minerals

It is very difficult to distinguish primary opaque oxides from altered olivine and pyroxene. The Mountain Red Hill blocks contain opaque minerals as small rounded blebs; interstitially between plagioclase and often as inclusions within olivine and pyroxene. All these blocks are magnetite bearing. H95(7) (Lady Hill) is much richer in opaques (about 15 modal % magnetite + ilmenite) which seem to be primary.

4.4.5 Optical Mineralogy of the Cross Hill Block

This is similar in texture and mineralogy to those from Lady Hill and Mountain Red Hill. The assemblage is olivine, clinopyroxene and plagioclase (An_{55} by the Michel-Levy method). Opaque minerals are absent.

4.4.6 Accessory Minerals

Apatite is found in H83(10) where it has a yellow stain, possibly due to alteration. No other minerals such as zircon, sphene have yet been identified and quartz, not surprisingly given the plagioclase composition, is absent.

4.4.7 Textures

The blocks are plagioclase orthocumulates. Table 4.3 gives mineral assemblages for all the blocks examinedin thin section with notes on their textures. Plagioclase occurs as orientated laths (e.g. H83(10)) and the pyroxene is usually poikilitic. Olivine grain shapes are obscured by alteration rims, and alteration may be obscuring the presence of mesostasis. Grain size is fairly constant (between 1 and 2 mm).

The blocks are unusual as some show evidence of partial melting. The feldspars show sieved edges (Section 4.14) but the glass is to a large extent hidden by alteration products and has itself, perhaps, been altered. These blocks are among the most basic to show evidence of partial melting.

4.5 CRYSTAL BAY - PILLAR BAY - COCOANUT BAY

Hawaiite lava outcrops along the south west of the island from Pillar Bay to Crystal Bay (see map) interrupted only by the trachyte of Cocoanut Bay and the cinder cone of Coast Red Nipple. Given the lack of exposure of the flows inland, it is impossible to determine whether or not these lavas are part of the same flow. Petrographically and chemically they are similar.

The blocks collected exhibit a remarkable range in mineralogy and texture and while they are not obviously part of a single suite (cf. those of Dark Slope Crater), they are here treated as one. They are, unfortunately, uniformly small (max. 10 cm diameter).

Mineralogy

Six blocks, representative of the major types were selected for probe analysis with due consideration for size and lack of alteration.

4.5.1 Feldspar

A wide range of feldspar compositions occurs, from An_{78} to An_{37} and from $Ab_{78}\ Or_{22}$ to $Ab_{58}\ Or_{42}$. This is primarily due to normal zoning in the feldspars of H49(2) and the inclusion of analyses from the mesostasis of H49(1) (see Fig. 4.22 and 4.23). Two blocks (H49(16) and H71(1)), which contain modal quartz, contain only K-feldspar. A gap in the compositions occupied only by a relatively large mesostasis feldspar of anorthoclase composition would presumably be closed if more mesostasis feldspars were analysed. H49L is a lava specimen which contains a small inclusion of cumulate gabbro.. It has been discussed in Chapter 3 as a glomeroporphyritic cluster, but it shows great textural similarity with the more basic blocks from this suite. A range in compositions is seen in the cores of alkali feldspars in H49(16) and H71(1). This may be due to variable amounts of

albite exsolved from the hypersolvus feldspars. Perthites and their significance are discussed in Section 4.10.

4.5.2 Pyroxene

All the blocks contain clinopyroxene, and two contain orthopyroxene. As in the Dark Slope blocks, orthopyroxene may have two possible origins:

(i) Primary crystallisation from the magma.

(ii) A reaction product from olivine oxidation.

In both cases the blocks have suffered considerable reheating, which manifests itself as partial melting textures, hence the second explanation is feasible. However in both blocks, the orthopyroxene grains are discrete and in H71(1) exhibit fine exsolution lamellae, presumably of clinopyroxene. Exsolution is not seen in the orthopyroxenes around olivine in the Dark Slope blocks which suggests that in H71(1), at least, the orthopyroxene may be primary.

The variation in chemical composition of the clinopyroxenes is given in Fig. 4.24, and the intrasample variation in Fig. 4.25. In all but H49(16) this is small. In the two quartz modal blocks, clinopyroxenes have a greenish tint but this is not due to high sodium content ($Na_2O < 0.5$ wt %).

Fig. 4.26 is molecular Al and Ti vs. Si. Orthopyroxenes show little substitution of Al and Ti but the clinopyroxenes Al and Ti may substitute for 0.25 molecules of Si (out of two). The basic blocks contain substantial Al in tetrahedral sites but as the clinopyroxene becomes more iron rich (in the two quartz bearing blocks) Al is not present in any quantity. This must be due to the onset of peralkalinity in the acid magmas (i.e. excess molecular Na and K over Al).

4.5.3 Olivine

Only two blocks contain olivine (H49L and H71(1)) and in these it is rare. Fig. 4.27 shows the range in composition of the olivine. Although in

all cases surrounded by a reaction rim, the olivine is fresh in the cores.

4.5.4 Minor Minerals

Quartz occurs as small rounded to interstitial grains in H71(1) and H49(2). Magnetite is found in three blocks but ilmenite appears to be absent. Apatite is found in H49(2), where it occurs as large, apparently cumulus crystals (Plate 4.18). Apatite fractionation is discussed in Chapters 5 and 8. This is the finest example of cumulus apatite in all examined blocks. Minerals associated with alteration are biotite and amphibole, which replace pyroxene in H64(6) and H49(2). In the latter block, the biotite shows the effects of partial melting, so at least some of the alteration must have taken place before transport to the surface.

4.5.5 Textures

The blocks may be divided into two groups:

(i) Plagioclase orthocumulates

(ii) K-feldspar adcumulates.

Other features of interest include evidence of melting (in H71(1), H49(2) and H49(16)); mesostasis (in H49(1) and H64(6)) which is some sort of agglomerate.

Plagioclase Orthocumulates

Euhedral laths of plagioclase are surrounded by intercumulus pyroxene though not to the same extent as the heteradcumulate 15226(18) (Plate 4.14). The plagioclase may exhibit oscillatory zoning (e.g. H49(1)) but very little difference in composition is seen between rim and core. Oscillatory zoning has recently been interpreted in terms of interface kinetics (Allegre *et al.*, 1981). Other intercumulus minerals include magnetite (in H49(1)), apatite (ditto) and olivine. Mesostasis is seen in H49(1), where it is identical to the enclosing lava (texturally and mineralogically) which suggest that the block is cognate. This permits the deduction of a fractionation trend (see

Section 5.6).

K-Feldspar Adcumulates

Irregular grain contacts between the feldspars characterise this group (Plate 4.19). This is considered to have resulted from adcumulus growth of new material onto existing grains to give feldspars with an essential lath shape, but highly irregular boundaries. Accessory phases such as quartz, pyroxene, and zircon lie in interstices between the grains. Exsolution of albite is present in small quantities in some grains.

Other Textural Features

H47(1) contains small subrounded, rather perthitic K-feldspar with partially sieved edges. Between the grains is a matrix of K-feldspar and rather altered mafics. It is suggested that this fine grained material represents mesostasis (with some reaction with the cumulus crystals subsequent on cooling). In other cases of partial melting described, the contacts between two different minerals are the places where most melt is produced rather than contacts between two grains of the same mineral (i.e. simple binary eutectic has a lower melting point than the pure end members). This example has not behaved like this (see Plate 4.29). The K-feldspar in the mesostasis is non-perthitic which suggests it may be subsolvus. Some plagioclase should therefore be present but this slide has not been probed.

Complete crystallisation of H47(1) before quenching would presumably have produced a block like H71(1), the addition of K-feldspar to the cumulus grains resulting in irregular boundaries. H64 is a block of diameter 20 cm and is an agglomeration of a variety of rock types. H64(6) is a plagioclase orthocumulate block and other fragments of H64 are K-feldspar adcumulates like H71(1). Amphibole and biotite replace much of the pyroxene and a fine grained volcanic matrix is present. The block is probably part of a vent agglomerate.

Partial melting is seen in H71(1), H49(16) and H49(2). These examples are similar to those described from East Crater, in Section 4.14. H49(16) is notable for the dark colour of its glass.

Evidence of strain is seen in one pure feldspar block (H67(1) - Plate 4.21). The feldspar shows well developed, but irregular kink bands. Perhaps this was caused by strain imposed during eruption.

4.6 EAST CRATER

A suite of syenite and monzonite blocks collected from East Crater exhibits superb textural evidence of partial melting. This is fully described in Section 4.14 with details of mineralogy and textures of the blocks themselves.

4.7 NASA ROAD FACIES BLOCKS

Blocks of all types (gabbro-granite) were collected from the red rubble which is found around the SW flanks of Green Mountain (see Chapter 2). This suite is variable, but in many cases the blocks are rather altered, making them friable and rather difficult to study in thin section.

4.7.1 Feldspar

Four blocks were analysed by microprobe (Fig. 4.28). H61(2) and H60(4) contain plagioclase. A certain amount of zoning is seen in thin section and probe analysis shows this to be normal zoning. In H13(1) and 17428(9) a considerable range in analyses was obtained (Fig. 4.29). Plagioclase (An_{30} - An_{40}) forms the cores of the feldspar and the rims range up to Ab_{64} Or_{36} (in H13(1)) and Ab_{48} Or_{52} (17428(9)). This range is in part due to exsolution which is present in the K-feldspar as fine lamellae.

4.7.2 Pyroxene

Ortho- and clinopyroxene have been analysed in three out of the four blocks. Fig. 4.30 gives their chemical compositions and Fig. 4.31 the intra-sample variation. In all three cases, the orthopyroxene consists of small grains associated with olivine and hence is considered to be a reaction product as in some of the Dark Slope blocks. This argument is supported by the wide range of compositions of the orthopyroxene from 17428(9). Clinopyroxene has a much more limited compositional range.

4.7.3 Olivine

None of the blocks prepared for probe analysis were found to contain olivine but it is found in some of the thin sections. Plate 4.26 shows an altered olivine grain in a gabbro (H57(16)). Common reaction products are biotite and amphibole (see Section 4.7.5).

4.7.4 Other Minerals

Quartz is found only in the Five Mile Post type granite block found incorporated in the NASA facies in Cricket Valley (for description see Section 4.10). H60(4) contains an intergrowth of magnetite and ilmenite and pyroxene, though the two opaques could not be distinguished under reflected light. They are presumably coexisting primary phases since magnetite oxidised to ilmenite is slightly pink in reflected light. Amphibole and biotite are common as alteration products of clinopyroxene and olivine, and apatite is found in H61(2) and H42(2).

4.7.5 Textures

It is convenient to divide the blocks into four groups:

(i) Granites - indistinguishable from Five Mile Post granites.

(ii) K-feldspar adcumulates.

(iii) Amphibole-biotite gabbros (altered).

(iv) Olivine-pyroxene gabbros.

Group (i) are identical to some of the granites collected from Five Mile Post and Middleton's Ridge (q.v.). These have probably been reworked from other pyroclastic deposits. Group (ii) are identical to the K-feldspar adcumulates of Crystal Bay in texture, though they show a much greater range in zoning of feldspar (Plate 4.19) and may be slightly less evolved varieties. Groups (iii) and (iv) are probably intergradational, the only distinguishing feature being alteration. They are plagioclase (+ olivine, where present) orthocumulates and are extremely similar to the blocks found in the south coast lavas. It may be that these rocks are from the same source. Plate 4.26 shows an altered olivine-pyroxene gabbro (H57(16)) from Cricket Valley (NASA facies sediments) where the reaction pyroxene + opaque ($+H_2O$) biotite is well illustrated. Usually biotite is found as a reaction product of opaques and amphibole which presumably indicate slightly different fluid composition and/or conditions during alteration than Plate 4.26.

4.8 UPPER VALLEY CRATER BLOCKS

These blocks are extremely similar to the gabbroic blocks of the NASA facies, but are less abundant, smaller in size and generally more altered. Two blocks (A22(4) and H35(4)) were analysed by microprobe.

4.8.1 Mineralogy

Plagioclase

Fig. 4.32 shows the range in composition of the plagioclase (An_{48} - An_{82}). Normal zoning is seen with A22(4) having the more calcic cores.

Pyroxene

Fig. 4.33 shows pyroxene compositions. H35(4) contains only

clinopyroxene but both ortho and clinopyroxene occur in A22(4). The orthopyroxene in A22(4) is rare and again seems due to olivine alteration.

Olivine

Both blocks contain olivine, which although it has oxide rims, is quite fresh in the cores. Compositions are similar, Fa_{36} to Fa_{45} (Fig. 4.34).

4.8.2 Textures

These blocks are plagioclase-orthocumulates, with additional cumulus olivine ± opaques. Where the pyroxene is altered, the amphibole is in structural continuity and takes the original intercumulus shape of the pyroxene (Plate 4.25). In places amphibole has completely replaced the pyroxene (A22(1)) and retains the poikilitic texture. In these blocks amphibole appears to be crystallising at a very late stage in the cooling history of the block and may be subsolidus. On the evidence of the specimens available this suite probably came from the same body as the NASA and South Coast lava gabbros.

4.9 GREEN MOUNTAIN

Although fifteen blocks were collected from this locality, only six are sufficiently unaltered and coherent to enable them to be studied in thin section and by microprobe. Table 4.4 summarises the petrography of these blocks.

4.9.1 Mineralogy

Only two blocks were analysed; 15254-1 and 15243-(B) (both gabbros). Figs. 4.35-4.37 give the pyroxene, feldspar and olivine compositions of these blocks. 15243(B) shows slight optical zoning of pyroxene and plagioclase but this is chemically insignificant. 15254-1 has plagioclase with cores of An_{49} and rims An_{30} which makes it somewhat transitional between gabbro and

monzonite.

4.9.2 Texture

15243(B) is texturally and chemically identical to the Middleton's gabbros and is therefore considered as part of the Middleton's gabbro suite. It does however have one important difference, namely, the mesostasis, which is in places glassy and in large enough patches to make probe analysis feasible. Thus the composition of coexisting cumulus phases and liquid is known which has important implications for fractionation trends (Section 5.6). Plate 4.22 shows this glassy mesostasis.

Block 15368a is interesting because it shows partial melting textures (Plates 4.2.3 and 4.2.4). These are comparable to examples described in Section 4.14. This block is among the most basic blocks to exhibit melting textures. Blocks 15243(A), 15243(D) and H42(1) are similar to the altered gabbro/monzonite types already described from the South Coast lavas, NASA Facies and Upper Valley Crater deposits.

4.10 ACID BLOCKS

The major suite of acid blocks is found on Middleton's Ridge and its surrounds (e.g. Five Mile Post, Palmers, Devil's Riding School). They range from mafic (quartz-bearing) monzonites, to peralkaline granites and may be divided into three groups:

(i) Mafic monzonites

(ii) Quartz syenites

(iii) Granites and granophyres.

Mineralogy

4.10.1 Feldspar

Plagioclase occurs in the monzonites but the only plagioclase in Groups

(ii) and (iii) is exsolved albite in the perthitic K-feldspar. Fig. 4.38 is a plot of the analysed feldspars from all the acid blocks. Fig. 4.39 shows the intrasample variation. It may be seen that some feldspars are $An_{\sim 50}$ but these are from the cores of grains, the rims being albite/oligoclase. Similar zoning is found in the quartz syenites (15226(1) and (2)) which have cores of An_{30} and rims of K-feldspar (Or_{35}). Some feldspar from 15226(1) lying very close to pure albite in composition, and thus off the main trend, have exsolved from the K-feldspar. The Five Mile Post feldspars have no Ca and range in composition from pure albite to Or_{82}, the range being entirely due to exsolution of albite from original sanidine. Intermediate compositions result when the electron beam overlaps different exsolution patches. The unexsolved feldspars which occur in some Five Mile Post blocks are Or_{33} Ab_{66}. No primary oligoclase or albite is found in the granites and nearly all blocks show perthitic K-feldspar. The feldspars obviously crystallised well above the solvus (Roedder and Coombs, 1967) and the granites are 'hypersolvus' in the sense of Tuttle and Bowen (1958).

4.10.2 Pyroxene

The one analysed monzonite (15226(17)) contains a quite magnesian augite (Fig. 4.40). The quartz syenites (15226(1) and 15226(4)) contain subcalcic augite (Fig. 4.40). This composition is very rare for Ascension blocks (or lavas) and it may be that a reaction occurred reducing the pyroxene Ca component as amphibole formed (these pyroxenes are rimmed by amphibole - Plate 4.27). The pyroxenes of the granites are not representable on the Wo, En, Fs triangle since they contain Na, and little or no Ca. Fig. 4.4 shows the analyses plotted on Ac-En-Fs triangle. No analyses have been found between En_{55} Fs_{45} and Ac_{80} Fs_{20} except in block H15231H which is a rare non-perthitic granite with calcic pyroxene rimmed by aegirine/augite (as in Plate 4.40 of 15231A). Analyses from these zoned pyroxenes come some way

towards filling the gap in these analyses.

Aegirine-augite (Ac_{80}-Fs_{20}) is a common constituent of the Five Mile Post granites along with arfvedsonitic amphibole and some aenigmatite. These pyroxenes contain virtually no Al or Mg and can be presented by the chemical formula (Na, Ca) (Fe^{3+}, Fe^{2+}) [Si_2O_6]. For charge balance molec. Fe^{3+} = Na - (Al - (Al^{VI} + 2Ti)) (Neuman, 1976). Fig. 4.43 is molec. Na vs. Ca and a very good straight line correlation is seen. Where Ca is some distance below the line, as in some analyses, the molecular Ti is correspondingly high.

The Ti content of aegirines is usually small (Deer et al., 1977) but in aegirine-augites up to 2.5 wt % TiO_2 is not uncommon. In some Ascension "aegirines" TiO_2 is > 5 wt % (e.g. K17318) (see Table 4.6). This aegirine also contains 1.00 wt % ZrO_2 and the addition of these elements is presumably indicative of late stage crystallisation. Zoning is common in the aegirines of these granites, particularly with regard to the Zr and Ti content which increase towards the rim, Ca decreasing.

The high Ti content of an aegirine may be regarded as solid solution between Na Fe^{3+} Si_2O_6 (acmite) and $Na(Mg, Fe)_{0.5}$ $Ti_{0.5}$ Si_2O_6 (neptunite) (Deer et al., 1977). In these analyses Ti vs. Fe molecular shows a good inverse correlation (Fig. 4.44) suggesting this is the case. Ti and Si show very little correlation indicating that Ti does not substitute into four fold sites. The analysis from K17318 with 5.87 wt % TiO_2 thus contains about 35 wt % of the neptunite molecule (Table 4.6) (see also Ferguson, 1977).

4.10.3 Aenigmatite

Aenigmatite is found in numerous granite blocks, though it is not as common in the collection as Roedder and Coombs (1967) suggest (see Table 4.7). The three analyses show a remarkable similarity (from different blocks). They differ from the ideal formula given by Deer et al. (1977), Na_2 Fe_5^{2+} TiO_2 [Si_6O_{18}] by containing 0.32 formula amounts of Mn substituting for Fe^{2+}. Aenigmatite is closely associated with aegirine and in one block, H30(3),

aegirine seems to replace it (Plate 4.28). This reaction may be used with the generally antipathetic relationship between aenigmatite and Fe-Ti oxides (Nicholls and Carmichael, 1969) to place these granites in temp-aO_2 space (Section 7.5.5). The reaction eliminating Fe-Ti oxides may account for their almost complete absence in these granites.

4.10.4 Amphibole

Amphibole is present in blocks of all three groups as:

(i) Reaction rims around pyroxene

(ii) Complete replacement of pyroxene

(iii) 'Primary'(?) magmatic phase

This aspect is dealt with in the textures section (4.10.7).

The amphibole varies in composition from edenite (in the monzonites and syenites) to arfvedsonite in the granites. Chemical variation is best represented on the Na + K, Mg, Fe^{2+} triangle of Fig. 4.41. A more continuous range in chemistry is seen than that of the pyroxenes. Amphibole compositions are less 'useful' than pyroxene compositions for making petrogenetic deductions and their study has to some extent been neglected. They exhibit similar $Fe^{2+}/(Fe^{2+} + Mg^{2+})$ to the coexisting pyroxenes (Fig. 4.42) but contain additional Na and K. In all cases, if Fe was completely trivalent, the totals would not be increased to 100% hence H_2O is likely to be present (probably 1-3% by weight).

4.10.5 Biotite

Biotite, as distinct from phlogopite has total Fe/Mg > 2:1. In these rocks it occurs associated with amphibole in the monzonites and syenites but is only found in one granite block (of the non-perthitic type) (Plate 4.39). Perhaps this is because the granites do not contain Fe-Ti oxides. Remarks made about amphibole chemistry also apply here. Deer et al. (1962) suggest

that colour is a good guide to the amount of Fe^{3+} relative to Fe^{2+} in the mineral. In these blocks, the biotite is usually brown and since TiO_2 is moderate (<4% by weight), Fe^{3+} must be low-moderate as high Fe^{3+} would result in a green colour. Total Fe/(Mg + Fe) ratios are higher than those of the pyroxene and amphibole they are replacing, which suggests iron oxides have been involved. Even with all Fe calculated as Fe_2O_3 totals are in the range 95-98 wt %. H_2O contents seem therefore to be in the range 3-7 wt % which suggests that biotite only formed where H_2O was abundant.

Olivine

Olivine is found in several syenites and granites though in only one block (H30(3)) was it analysed. This was almost pure fayalite (only 0.28 wt % Mg) though 5.38 wt % MnO_2 was present. While fayalite is not unstable in silica rich melts, the grains are invariably surrounded by pyroxene and amphibole and seem to be one of the earliest phases to have crystallised.

Quartz

This is chemically uninteresting but texturally varied; details follow in Section 4.10.7.

4.10.6 Accessory Minerals

Apatite

This is present in the monzonites in some quantity (Plate 4.29) as small acicular crystals often included by the other minerals, but is completely absent in the syenites and granites. This must be because P_2O_5 has already been removed from the magma by apatite fractionation before crystallisation of syenite and granite (see Chapter 5).

Opaque Minerals

Small grains of opaque oxide are found in the monzonites and syenites,

but not in the granites which seem to be in the 'no oxide' field of Nicholls and Carmichael (1969) - see Section 7.5.5.

Zirconium Silicates

Zircon is found in almost all blocks of these three groups together with the rare mineral eudialyte and still rarer vlasovite (Na_2 Zr Si_4O_{11}) and dalyite (K_2 Zr Si_6O_{15}). These minerals are discussed in Section 4.12.

Textures

Modal proportions of quartz, feldspar and mafics of these blocks are given in Fig. 4.45.

4.10.7 Monzonites

Only three blocks of this type have been found (Table 4.5) at Middleton's/Five Mile Post but they show textural and chemical similarity to some of the intermediate blocks already discussed.

Plagioclase laths form the cores of the feldspars and overgrowths of oligoclase-albite surround this to give an interlocking feldspar texture similar to that of H71(1) and H13(1) (NASA facies, Plate 4.19). Mafic minerals lie along the feldspar grain boundaries and the opaque oxides lie at grain interstices. Small needles of apatite occur throughout the blocks both as inclusions in the feldspar and clustered with the mafics (Plate 4.29). Apatite is rare as inclusions in the cores of the plagioclase though not in the rims. Amphibole is the predominant mafic mineral but in places it retains a core of calcic pyroxene. Biotite is less abundant than amphibole and seems in places to be replacing it (Plate 4.30) and where opaques and amphibole are in contact a reaction may be seen;

	+Na + K (in fluids)		+K, +Fe + Ti	
Cpx	→	amphibole	→	biotite
(Fe-augite)		+ Ca		

These reactions seem to be subsolidus as, to a large extent, structural continuity is seen from pyroxene to amphibole to biotite and reactions may be seen such as in Plate 4.29 which obviously occurred *in situ*. Quartz is present in small quantities as small irregular grains. No granophyric texture is seen.

4.10.8 Quartz-Syenites

Although there is a great deal of textural and mineralogical variation in these syenites, they do not seem to overlap with the granite group. Fig. 4.45 shows the modal proportions to be different from the granites and monzonites in that they are almost pure feldspar (K-feldspar). The absence of aegirine (except as rare rims to augite) and aenigmatite and the zirconium silicate, dalyite and vlasovite is a significant chemical difference.

The feldspars show interesting textures. In most blocks a clear euhedral core is surrounded by an inclusion filled rim (Plate 4.31) with higher Or content (see Fig. 4.40 - rock 15226(4)). Perthitic texture is seen in several blocks and is of the rod type (Deer *et al.*, 1966). Replacement patches of clear and inclusion free albite in K-feldspar are much rarer.

The mafics vary greatly in form and habit. Olivine is seen mantled by amphibole, biotite and opaques in two blocks. Augite and ferroaugite may be found in cores surrounded by biotite and amphibole, or as discrete grains which exhibit typical interstitial texture. These are rather altered and in 15226(5) and (7) are rimmed by green ferrohedenbergite or aegirine-augite (no analysis) - see Plate 4.32. Amphibole occurs as discrete grains in many blocks, presumably where complete replacement of pyroxene occurred. Biotite is found either as discrete grains, or as a replacement of amphibole, where it may be seen enclosing and rimmed by opaque minerals (Plate 4.33). Perhaps this is a response to reheating caused by the disruption and transportation

to the surface of the original body. A possible reaction is:

$K_2(Mg\ Fe^{2+},\ Fe^{3+}\ Ti)_6\ [Si_6\ Al_2\ O_{20}]O_2$ (biotite)

↓

Fe-Ti oxide (magnetite, since in these biotites Fe >> Ti)

\+

K-feldspar + olivine + 'liquid'

Small low birefringent patches are associated with the opaques within the biotite and may be K-feldspar; and small grains of a high birefringence mineral (olivine?) are found associated with the opaque rims. Le Maitre (1974) describes similar melted biotites. Opaque minerals are much less abundant than in the monzonites. Large masses of opaque mineral occur in the cores of a few amphiboles (no analyses) and may be iddingsitised olivine.

Granophyric veins, found in several specimens of this group, are considered to be liquids (?eutectic) which have penetrated the solid mass after a small amount of fracturing had taken place. The syenite must have been almost completely solid since in places these veins cross large feldspar grains which have broken in half (Plate 4.34). The veins range up to about 2 mm in thickness and consist almost entirely of fine grained perthite, quartz and granophyric intergrowths of the two, especially at the edges of the veins. The granophyric nature suggests affinities with the granites (q.v.) and it is possible that the syenites are in fact the less evolved lower levels of the same coarse-grained body as the granite blocks.

4.10.9 Granites

Granite blocks are found at Five Mile Post, Middleton's, Devil's Riding School, Palmers and in the NASA facies. The Devil's Riding School types are different from the rest which all belong to the Five Mile Post type.

Five Mile Post Type

These have been previously described by van Tassel (1952), Cann (1967),

and Roedder and Coombs (1967). The last named classify the granites into three groups:

(i) Perthitic aegirine - arfvedsonite granites ± dalyite

(ii) Sanidine-aegirine-arfvedsonite granites with largely unexsolved alkali feldspar

(iii) Sanidine-oligoclase granites

This classification is not considered useful for the blocks collected in 1979/80. These 70+ blocks are probably more representative of the suite than the smaller number of blocks studied by Roedder and Coombs (1967). Non-perthitic blocks are rare and no oligoclase (or albite) bearing (other than exsolved) granites were collected in 1979/80. The feldspar is invariably perthitic and the exsolution type varies from rods to complete exsolution of albite in large patches (Plates 4.35 and 4.36). In some blocks completely recrystallised feldspar may be seen to lie in thin films along grain boundaries. This feldspar is almost pure Or (Fig. 4.39). The thermodynamic significance of unmixing of feldspars is considered by Roedder and Coombs (1967).

The feldspar grains are varied in shape from perfectly euhedral to almost completely anhedral but the other minerals (aegirine, arfvedsonite and aenigmatite) invariably show euhedral grain shapes. The granites contain many miarolitic cavities into which these minerals project and here the feldspar shows perfect crystal faces. The amphibole and pyroxene are often difficult to distinguish when no cleavage is seen. Aegirine is usually greener and less pleochroic than the black/brown to dark green arfvedsonite. In some blocks aegirine seems to be replacing arfvedsonite (Plate 4.37) and in other cases the reverse seems to be true (Plate 4.38). The reaction involved is probably

$$10\ Na\ Fe^{3+}\ Si_2O_6 + 2\ H_2O \rightleftharpoons 2\ Na_3\ Fe^{2+}_4\ Fe^{3+}\ Si_8O_{22}\ (OH)_2 + 2(Na_2\ 0.2\ SiO_2) + 2\ O_2$$

Conditions which would cause the reaction to proceed to the left might be high $Na_2O.SiO_2$ activity, to be expected in a peralkaline liquid. This is further discussed in Section 7.5.5.

Rarer textural and mineralogical types include the non-perthitic granites (e.g. 15231A) which contain a less sodic amphibole and aegirine (Plate 4.40) around relict calcic pyroxene and a unique block (15231D) which is the only biotite bearing 'granite'. The mafics show reactions from the core to the rim (Plate 4.39) as seen in the syenites (i.e. augite/ferroaugite → amphibole → biotite). This block has unexsolved K-feldspar (see Fig. 4.39).

The Devil's Riding School granites have a similar mineralogy to the Five Mile Post blocks. They do not contain aegirine, dalyite or vlasovite but the feldspar is similar in composition to the unexsolved feldspar of 15231A, and the amphibole is very similar in chemistry (see Fig. 4.42). Texturally these types are rather different. The Devil's Riding School granites have much smaller grain size and although both types have granophyric texture it is finer and more abundant in the Riding School granites and the rock has an almost porphyritic appearance (Plate 4.41). This seems to indicate that these granites are faster cooled equivalents of the Five Mile Post ones. Fast cooling would enhance the likelihood of granophyric texture forming and would account for the general lack of perthitic texture compared to Five Mile Post types.

4.10.10 Minor Localities

There are several places where only one block was found. These are tabulated in Table 4.8 along with the petrography of each block.

4.10.11 Vesicular Feldspar Blocks

In the alluvial fan deposits around Lower Valley Crater, blocks were found which are similar in appearance in hand specimen to the East Crater syenites, being feldspathic with a small modal % of dark minerals. On

closer study the feldspars were found to be highly vesicular, giving the blocks an extremely low density, and to show evidence of partial melting. All attempts to section these blocks failed due to their extreme friability.

Blocks collected in the Azores in 1980 have very similar textures being fresh, and in places showing evidence of plastic deformation. In thin section the feldspar is glassy in places where it has melted. An attempt to produce melting in East Crater blocks experimentally failed to reproduce textures described in Section 4.14 but produced very similar textures to those described above.

Small samples of H34(1), a comparatively unmelted East Crater syenite, were placed in a Pt. crucible and heated in air to 1100, 1200 and 1300°C for approximately ½ hour. At 1200°C, little melting had taken place but at 1300°C (above the melting point of anorthoclase) the feldspar melted and on quenching in air the melted feldspar was partly glassy and highly vesicular and small patches of dark glass had been produced where cpx-feldspar contacts had behaved as binary mixtures. This evidence suggests that the blocks were suddenly heated (presumably by engulfing in a basic magma) to temperatures just above the melting point of anorthoclase for a short period, then suddenly quenched. This is in contrast to the melted East Crater blocks described in Section 4 which must have been heated to temperatures below the pure anorthoclase melting point, but above the anorthoclase-quartz, anorthoclase-pyroxene mixture 'eutectic' melting points.

4.11 MINERALOGY OF THE CRICKET VALLEY PEGMATOID

Cricket Valley is a 100 m deep depression close to the NASA station at Devil's Ashpit at the east end of the island. Daly (1925) considered it to be an explosion crater whereas Atkins et al. (1964) suggested cauldron subsidence related to the extrusion of the nearby Weather Post and White Hill trachyte domes as its origin. Whatever the mechanism responsible one result is a

30-50 m deep section cut in the thick basalt sequence (see Chapter 2 for details).

Exposed in the basalt wall at the west end of the valley is a pegmatoid body roughly ovoid in shape, about 3 m x 1 m in dimension and with its long axis horizontal. This pegmatoid has a well defined if irregular outline and in places lava is enveloped by it.

Two features indicate that the pegmatoid is not a large xenolith. First, there is no sign of the partial melting that would be expected in a block of this composition caught up in a basalt magma (Harris and Bell, 1982); secondly, the pegmatoid shows no cataclastic or other disruption effect and, indeed, preserves very delicate crystalline textures at its contact with the enclosing basalt. The pegmatoid has no chilled margin and so could not have intruded cold, solid basalt, although it could have been emplaced into warm semi-solid basalt.

4.11.1 Other Examples of Pegmatoid Bodies

Pegmatoids described in the literature include those in the Picture Gorge basalt, Oregon (Lindsley et al., 1971) and the Makaopuhi prehistoric lava lake, Hawaii (Evans and Moore, 1968; Moore and Evans, 1967). Although the mineralogy of these bodies is similar to that of the Ascension example there are several important differences. The pegmatoids in most of these examples are lens-shaped, with matching walls and an en echelon distribution. The explanation offered for this configuration is that residual liquid from the semi-crystallised lava filled in cracks which were torn open in the host basalt while it was still plastic (i.e. semi-molten). A single amoeboid pegmatoid from the Picture Gorge basalt is interpreted as having formed before the enclosing host rock has achieved a rigid framework (i.e. earlier than the others) yet was coherent enough to permit segregation of interstitial liquid into an irregular body with sharp boundaries. Least squares fractionation

tests on the en echelon pegmatoids of Picture Gorge suggested that they formed when the basalt was 50-75% crystallised. (No calculation was made for the amoeboid example). Similar calculations for the Ascension pegmatoid (using the programme written by Wright and Doherty, 1970) suggest that the pegmatoid composition would be reached after only 30-40% crystallisation. It seems unlikely that this amount of solidification would give the basalt sufficient tensile strength to provide a framework into which residual liquid may flow.

4.11.2 Petrography

Different sections of the Ascension pegmatoid show some variation in texture and mineralogy but unless stated otherwise, features described below are common to all parts. Table 4.9 gives modal proportions of the four pieces of pegmatoid analysed by microprobe.

The rock has a framework of relatively large, euhedral laths of feldspar, pyroxene and opaque minerals with the interstices occupied by later formed minerals or left as spaces, presumably once filled by fluid. The feldspars exhibit strong normal zoning though many possess cores which are comparatively unzoned. The pyroxenes form the largest crystals (up to 5 mm long) and are unzoned except for their rims which exhibit marginally higher birefringence. Most pyroxene grains are surrounded by a thin rim of opaque minerals (Plate 4.42). Large skeletal crystals of opaque mineral occur throughout but are particularly concentrated in specimen H59B (Plate 4.42) taken from the rim of the pegmatoid. These three minerals, together with long needles (up to 5 mm) of apatite (Plate 4.42) and rare olivine (Plate 4.43) make up this early formed framework.

The crystals occupying the interstices in the framework consist of:

(i) Euhedral, but in places completely crystallised K-feldspar. These are not resorbed since the glassy patches present show negative crystal shapes (Plates 4.44 and 4.45).

(ii) An intergrowth of augite and zoned feldspar formed around some of the initially crystallised pyroxene (Plate 4.47).

(iii) A fibrous intergrowth interstitial between the feldspar laths of (i), shown by microprobe analysis to be K-feldspar and silica (structural state unknown) (Plate 4.43).

(iv) Green rims of aegirine-augite round some pyroxenes (Plate 4.46). This feature is confined to a few areas only of some thin sections studied and is not found in H59B, taken from the margin of the pegmatoid.

(v) Some of the interstitial cavities are filled with crypto-crystalline quartz (verified by XRD) (Plate 4.44). Cristobalite is reported to line some vugs in tholeiites of the Alae lava lake (Peck et al., 1966) and is attributed to deposition by pneumatolytic fluids at c. 800°C, the silica having been extracted from the surrounding rocks or magmas. In the Ascension example it is difficult to imagine the leaching of SiO_2 from surrounding material by deuteric fluids since there is no evidence of alteration. It seems more likely that an SiO_2 rich vapour was the final product of differentiation.

4.11.3 Order of Crystallisation

From the textural evidence this may be summarised as follows. Plagioclase, apatite, pyroxene, opaques and some olivine crystallised initially. Then augite and feldspar crystallised as an intergrowth followed by incompletely crystallised K-feldspar, possibly during a period of more rapid cooling. The last stages of crystallisation produced small euhedral laths of K-feldspar and some small grains of augite (Plates 4.44 and 4.45), then a fine grained intergrowth of "quartz" and K-feldspar (Plate 4.43). Crypto-crystalline quartz occurs in vugs in the rock and it is possible that this crystallised from a residual SiO_2 rich vapour. Lindsley et al. (1971) ascribe the presence of aegirine to crystallisation from the vapour state and it is possible that the aegirine-augite veins in this example have a similar paragenesis. The fact that these features are confined to some portions of

the pegmatoid indicates localisation of the vapours responsible.

4.11.4 Mineralogy

(i) Feldspar

Fig. 4.46 shows the extreme variation in composition of analysed feldspars from four different slices of the pegmatoid. H59B is from the edge of the body and is partly coarse, partly fine-grained. This variation is evidence of the extreme differentiation in liquid composition which has taken place. Analyses plotted are from single points of zoned crystals. The density of analyses is not directly proportional to the volume of feldspar of a given composition but gives a reasonable indication of this. Analyses of K-feldspar and late stage crystals received a disproportionately high number of analyses.

In Fig. 4.46 the compositions of pegmatoid feldspars are divided into zones A-C. The compositions marked P are analyses of phenocrysts from the host basalt. One analysis is significantly more calcic than the rest (An_{52}). This is from the margin of the body (H59B) and may be a basalt phenocryst accidentally incorporated into the pegmatoid. The total range of feldspar compositions is from $Or_2\ Ab_{56}\ An_{42}$ to $Or_{53}\ Ab_{46}\ An_1$.

The analyses in Group A are from the large framework feldspars. The most calcic end of the composition range in the group are analyses of cores and the most sodic from the rims. There are many analyses plotting at the most calcic and indicative of initial feldspar precipitation throughout the pegmatoid at the same temperature. The analyses from group B are from the clinopyroxene-feldspar intergrowths and may be classed as anorthoclase in composition. The further away from the pyroxene core a point is, the more potassic the analysis. Group C analyses are from the small euhedral, and sometimes incompletely crystallised feldspars which are sometimes found projecting into the cavities. These feldspars are zoned, with progressively

more Or component towards the rims (e.g. Plate 4.45). It is worth noting that these feldspars do not lie close to the feldspar minima for any realistic pH_2O (i.e. Ab_{60} Or_{40}). This is discussed in the section on changes in liquid composition. Analyses of feldspar from the K-feldspar/silica intergrowth were contaminated by the silica but relative amounts of Na_2O and K_2O suggest they are more potassic than group C feldspars.

No perthitic textures are found in any of these alkali feldspars, a feature ubiquitous in alkali feldspars of the coarse grained acid blocks, but absent in sanidine phenocrysts in the lavas. pH_2O of the crystallising pegmatoid is not likely to have been significantly higher than the pressure of the overburden, i.e. about 15 bars (50 m basalt of density 2.65 gcm^{-3}) and possibly significantly less. This means that the solvus temperature would be well below that of the solidus and the absence of unmixing in these alkali feldspars must be due to the rapid rate of cooling relative to that of acid blocks.

A compositional gap is seen at around the potassic part of group B and the sodic part of group C. This may be due to a change in cooling rate or possibly analysis bias. There is no evidence for the resorbtion of the missing feldspar compositions. Representative analyses are given in Table 4.10.

(ii) Pyroxene

In contrast to the feldspars, the pyroxenes show a relatively restricted range of compositions even though pyroxene was precipitating simultaneously with feldspar throughout the latter's wide range of compositions. All the pyroxene analysed is calcic, and pigeonite or orthopyroxene have not been detected. Representative analyses are given in Table 4.11.

Analyses from the core portions (about 95%) of the large pyroxenes lie in the area A in Fig. 4.47. The range in compositions does not seem to be

due to fine scale exsolution, but to some extent is due to slight inhomogeneities between each analysed piece, e.g. analyses from H59(1) are more calcic than those of 17428B. The narrow, higher birefringent rims lie in group B (Fig. 4.47) and have significantly higher Fe/(Fe + Mg) as do the analyses from the feldspar/pyroxene intergrowth surrounding these pyroxenes. The small augite crystals associated with the euhedral K-feldspar (Plate 4.42) belong to group C. These are the most iron rich pyroxenes so the trend of pyroxene compositions is to a relatively small amount of iron enrichment.

There is little variation in the Al and Ti content of these pyroxenes, both remaining less than 0.08 molcules per formula unit (6 oxygens).

The pyroxene in one sample of pegmatoid (17428B) displays green rims of aegirine-augite. Representative analyses are given in Table 4.12 (recalculated so that molecular $Fe^{3+} = Na^{+}$, i.e. charge balance maintained). Plotted onto an Ac-En-Fs triangle (Fig. 4.48) the analyses show an unusual trend from core to rim, given the oversaturated nature of the liquid. A typical undersaturated augite-aegirine and a typical oversaturated augite-ferroaugite-aegirine trend are shown together with that of the Picture Gorge pegmatoid pyroxenes. These Ascension pegmatoid pyroxenes compare closely with the undersaturated trend because of the absence of significant iron enrichment.

That the analyses in Table 4.12 show high totals where significant amounts of Fe total are recalculated as Fe^{3+} to preserve ideal charge balance. This suggests that the substitution varies somewhat from the ideal Na Fe^{3+} Ca (Mg, Fe^{2+}).

(iii) Olivine

Only one grain of olivine was found in the four sections of pegmatoid analysed, though it is present in other thin sections. The olivine analysed is represented on Fig. 4.47 (Fo 28-32) and shown in Plate 4.43. It is

surrounded by a reaction rim of opaque minerals and on textural grounds must be regarded as an early formed mineral.

(iv) Fe-Ti Oxides

Large (up to 4 mm) skeletal grains of Ti-magnetite occur in the pegmatoid. Texturally these are very similar to those of the Picture Gorge pegmatoid (compare Plate 4.42 with Plate 4A of Lindsley et al.). Only one type of oxide is found and this is a titaniferous magnetite containing exsolved lamellae of ilmenite along {111} planes. These are presumably the results of oxidation of an initially homogeneous magnetite-ulvospinel solid solution. As Fe^{2+} is oxidised to Fe^{3+} the remaining Ti must exsolve as ilmenite (Haggerty, in Rumble, 1976). Probe analyses across exsolution lamellae give compositions on a tie line between ilmenite and Usp_{28} M_{72}. The most Ti rich analysis is 92% ilmenite. This range in compositions is caused by the inability of the ilmenite lamellae to contain the electron beam, the 92% ilmenite analysis occurring at mid traverse when the maximum area of lamelli is contained by the beam.

The absence of two primary coexisting Fe-Ti oxides and/or phases such as aemigmatite precludes the assessment of oxygen activity and temperature. $Magnetite_{ss}$ is particularly susceptible to oxidation especially when a vapour is present, for which there is abundant evidence in this rock and this degree of oxidation is easily obtainable without affecting the ferromagnesian minerals (see Lindsley et al., 1971 for an explanation). A discussion of changes in the liquid composition with crystallisation is given in Chapter 5, Section 5.7.

4.11.5 Possible Mode of Formation of the Ascension Pegmatoid

The pegmatoid and its host lava have identical Sr and Pb isotopic composition (Harris et al., in press). Enrichment of SiO_2, alkalis and P_2O_5

and depletion of MgO in the Cricket Valley pegmatoid relative to its host lava are consistent with its having crystallised from a more evolved liquid than the hawaiite (H81L). Two possible hypotheses for the origin of the pegmatoid are advanced here:

(i) The basalt and pegmatoid were once two separate magmas, the latter being the more differentiated. The basalt magma then erupted through the pegmatoid magma. Differences in viscosity and density calculated for all possible temperatures, using the model of Bottinga and Weill, 1970, 1972, prevented mixing and the higher density of the more evolved iron rich pegmatoid meant that only a small amount was carried to the surface (Fig. 4.49). Once at the surface the pegmatoid fraction remained liquid as the basalt was quenched then crystallised slowly with the thick hawaiite flow providing effective insulation.

(ii) The basalt and pegmatoid separated as immiscible liquids from an originally homogeneous magma. The pegmatoid is richer in FeO^T and P_2O_5 (see Chapter 5) than the lava and these elements are known to be concentrated into the mafic conjugate immiscible liquid (Roedder, 1978; Phillpotts, 1979). However no evidence of immiscibility on a thin section scale (as described by Phillpotts (1978), De (1974) etc.) has been recognised in either the pegmatoid or the enclosing lava, hence this remains an unsubstantiated hypothesis.

Whatever its origin the pegmatoid presents a record of crystallisation of a relatively slowly cooled magma and provides an important link between the lavas of Ascension and the coarse grained blocks whose parent bodies are not exposed. The pegmatoid as described is a unique outcrop, but others may be present within the relatively undissected volcano.

4.12 ZIRCONIUM SILICATES

In addition to zircon, three other zirconium silicates have been identified in the granites. Dalyite was described by van Tassel (1952) (the

first occurrence); vlasovite by Fleet and Cann (1967) (the second occurrence); and eudialyte by Harris et al. (in press). Table 4.13 summarises the occurrence of analysed vlasovite, zircon, dalyite and eudialyte.

4.12.1 Dalyite

Dalyite (K_2 Zr Si_6O_{15}) occurs as interstitial anhedral grains between mafics, quartz or feldspar. It is usually unaltered and displays no cleavage or twinning. This is contrary to the information given by van Tassell (1952). Plate 4.5 shows a typical dalyite grain. Dalyite shows no apparent reaction with any other mineral in the blocks and is not seen as a reaction rim around zircon.

4.12.2 Vlasovite

Although vlasovite (Na_2 Zr Si_4O_{11}) is more common and more easily recognisable than dalyite, it was first described in these blocks by Fleet and Cann (1967) some fifteen years after dalyite. In thin section, it may be interstitial between grains, as in dalyite, or it may be subhedral (Plate 4.48). It invariably shows one good cleavage in thin section. In some blocks it is seen as a reaction rim around zircon (Plates 4.49-4.51).

Dalyite is very similar to vlasovite, especially when the latter shows no cleavage, and also to quartz, especially in thicker than normal sections. Numerous single crystal X-ray diffraction photographs were taken of both minerals. Tables 4.14 and 4.15 show calculated d spacings which agree extremely well with those from Tikhonenkova and Kazakova (1961), Fleet and Cann (1967) and van Tassel (1952).

4.12.3 Petrogenesis

The occurrence of these minerals is no doubt due to the strongly peralkaline nature of these rocks. An excess of alkalis over alumina is characteristic of these blocks and this excess is accounted for to some extent by the sodic pyroxenes and amphiboles. It is possible that some excess

alkalis and silica could have combined with Zr in the last liquid fractions to crystallise as zirconium silicates.

It must be emphasised that in no block do dalyite and vlasovite occur together even though more than 70 thin sections of different blocks have been studied. This is especially remarkable as the granites are otherwise identical (both petrographically and chemically; see Chapter 5) though dalyite granites have a slight tendency to contain more miarolitic cavities. Zircon may be present in both types of granite and may be surrounded by vlasovite in vlasovite granites.

Any hypothesis accounting for the occurrence of these two minerals must explain why they do not occur together, but at present this is not possible. There are few published data on the system Na_2O-ZrO_2-SiO_2 and none at all on K_2O-ZrO_2-SiO_2. Michel-Levy synthesised vlasovite from Na, ZrO_2 and SiO_2 and Ahmed and Mackenzie (1978) synthesised vlasovite during experimental studies of eudialyte (see Chapter 7).

A possible explanation for the occurrence of dalyite is that at the late stages of crystallisation both Na and K were present with Zr and silica, but that the Na was lost due to volatilisation leaving K, Si and Zr to form dalyite. A possible origin of vlasovite is that it formed from sodium disilicate liberated when aegirine altered to form arfvedsonite (for which there is reasonable petrographic evidence) in the reaction

$$\underset{\text{(Aegirine)}}{10Na\ Fe^{3+}\ Si_2O_6} + 2H_2O \rightleftharpoons \underset{\text{(arfvedsonite)}}{2Na_3\ Fe_4^{2+}\ Fe^{3+}\ Si_8O_{22}\ (OH)_2} + 2(Na_2O.2SiO_2) + 2O_2$$

The sodium disilicate could have reacted with zircon to give vlasovite or with Zr left in the last liquids.

This does not explain why the minerals do not occur together. A detailed study of fluid inclusions, and some experimental work on the K_2O-ZrO_2-SiO_2 system is needed to resolve these problems.

4.12.4 Eudialyte

This is found in only three granite blocks (H30(1), H17318, 17318P) from Five Mile Post, and only in H30(1) does it occur in reasonable amounts (0.1-0.25 modal %). All the chemical data for the Ascension eudialyte is from this rock.

This block is dalyite-bearing and indistinguishable in mineralogy and texture from other members of its group and its whole rock chemistry and modal proportions are shown in Table 4.17. A light brown to colourless, low birefringence mineral infrequently occurs between quartz, mafic and perthite grains. Plate 4.51 shows a typical grain in rock H30(1) also in contact with dalyite with which there is no apparent reaction. It must be noted that only small amounts of the eudialyte are available and therefore a complete X-ray and chemical investigation has not been possible. The data presented below confirm this mineral as eudialyte.

Optical Properties of Eudialyte

The mineral studied has moderate relief and is irregularly fractured, but no cleavage is visible in the section available (see Plate 4.52). It is optically biaxial with $2v_\gamma \sim 70°$ and shows very weak pleochroism with β slightly brownish and α colourless. Birefringence is low and often slightly anomalous in patches. Zoning is also visible but restricted to small areas.

X-ray Study

The eudialyte was identified by X-ray diffraction experiments using a 114.6 mm diameter Gandolfi camera. A powder-type diffraction pattern was obtained from a single crystal measuring 0.03 mm across using Ni-filtered $Cu_K\alpha$ radiation and was indexed with the aid of the Powder Diffraction File (card nos. 8-355 and 25:814). The cell dimensions, based on hexagonal indexing, were calculated by least squares from the twenty-eight lines shown

in Table 4.18. Comparison of these results with the powder diffraction data obtained by Edgar and Blackburn (1972) for eudialyte from the Kipawa Lake area, Canada is also shown in Table 4.18. The eudialyte from rock H30(1) has a slightly larger unit cell than the Kipawa Lake sample which can probably be attributed to the higher Y + REE content of the Ascension Island eudialyte (see Table 4.19).

Analyses of eudialyte in H30(1) are given in Table 4.19. Table 4.21 shows the structural formula of one analysis assuming the formula $Na_4(Ca, Fe^{2+}, REE, Y)_2\ Zr\ Si_6O_{17}\ (OH\ Cl)_2$ proposed by Gossner (1930) and Hey (1962). This is compared with the eudialyte from Kipawa Lake, Canada (Edgar and Blackburn, 1972). The Ascension example fits the formula well although as with the Kipawa Lake eudialyte, Si is rather high. It is possible that some of the REE substitute for Zr as well as (Ca, Fe) since in the analyses with highest REE, Zr is always rather low. The determination of Fe^{3+}, OH, Cl and F has not been possible. It is probable that only a small amount of the total Fe is Fe^{3+} since (Zr, Al, Ti) is only 0.04 formula units deficient.

This eudialyte is remarkable for the presence of 10-12% REE and Y. The rare earth content of this and other minor phases such as apatite and zircon is to be the subject of a later section.

Details of the analytical procedure is given in the appendix. The analysis of Eu has proved impossible because of its low abundance and the severity of interferences on both $EuL\alpha_1$, from $PrL\alpha_2$ and $SmL\beta_2$ (Exley, 1981). However the probe detection limit is below the level of the Sm-Gd join. Since there is no observable $EuL\alpha$ peak, there must be an Eu anomaly. Fig. 4.50 shows the position of the Eu detection limit (Chondrite-normalised).

4.12.5 Petrogenesis

Eudialyte is most commonly found in pegmatite and syenitic peralkaline rocks of both over and undersaturated types. Ascension Island granites are rather peralkaline (with a small amount of normative sodium

metasilicate) and very oversaturated (see analysis of H30(1), and modal proportions Table 4.17). It is obvious on textural grounds (Plate 4.52) that eudialyte formed at a very late stage in the rock's crystallisation history. It is possible that the mineral formed from hydrothermal fluids after the rock had solidified but the lack of alteration in the rock as a whole seems to preclude this. It is also possible that the eudialyte formed as an alteration of dalyite but in Plate 4.52, eudialyte occurs adjacent to dalyite with no evidence of reaction.

The high rare earth content of this eudialyte seems, therefore, to be due to its late-stage crystallisation from the residual magmatic fluid. The chondrite-normalised REE patterns for the core, the rim and a point midway between are shown in Fig. 4.50. Y is plotted in place of Ho on ionic radius considerations, as recommended by Eby (1975). The Ascension eudialyte is seen to be very slightly LREE enriched (Ce_N/Y_N 1.86 - 2.49 and Ce_N/Yb_N 3.5 - 4.2). This can be contrasted with Exley's data on rare earth-enriched sphenes and allanites from the Skye epigranites, also considered to be the late crystallisation products of residual magmatic fluids. The two Skye examples illustrated show highly fractionated REE patterns (Ce_N/Y_N = 40 - 100).

Zoning is seen in the Ascension eudialyte in thin section and has been investigated for any difference in REE content between rims and cores of grains. The cores of analysed grains are found to be slightly more REE enriched (this is also seen in grains not represented by analyses in this paper). There seems to be no noticeable change in fractionation of the REE pattern from rim to core, the three REE patterns in Fig. 4.50 remaining approximately parallel.

Fig. 4.51 shows the chondrite-normalised REE pattern for H30(1) whole rock. A strong negative Eu anomaly is present which suggests that the suspicion of an Eu anomaly in the eudialyte is justified. This type of anomaly is strongly suggestive of feldspar fractionation at some time during

the earlier history of this magma. It can also be seen that the whole rock REE profile is rather different in shape from the profile exhibited by the eudialyte contained within it, showing a much stronger enrichment of light REE. This type of relationship is seen in a number of peralkaline rocks where eudialyte, despite being the major REE bearing mineral, has a heavy REE enriched pattern, and the whole rock a light REE enriched pattern (Fryer and Edgar, 1977).

Fryer and Edgar (1977) suggest that this late stage enrichment of heavy REE does not occur because of the preferential concentration of these elements by the eudialyte but is due to complexing involving Na and F in late stage magma and postmagmatic fluids. Complexes involving heavy REE are more stable than those with light REE and the liquids left at the last stages will hence be enriched in heavy REE. Consequently the last mineral to crystallise, which in the case of H30(1) is eudialyte, will be much richer in heavy REE than the whole rock.

Late stage sphenes and allanites from the Skye granites do not show any heavy REE enrichment (Fig. 4.50) and consequent indication of REE complexing. It is presumably the extreme peralkaline nature of the Ascension granites which makes the REE behaviour in late stage fluids so different from that of the Skye granites. H30(1) has the highest $^{87}Sr/^{86}Sr$ ratio of the two granites and one comendite analysed (Chapter 6). It may not be a coincidence that it is also eudialyte bearing. In order to explain the high Sr ratios, contamination by small quantities of oceanic sediment was postulated. This would have resulted in Ca (from $CaCO_3$) being introduced into the magma which is very low in CaO. This favours the formation of eudialyte rather than vlasovite (Michel-Levy, 1962) in experimental systems and may be the reason why eudialyte is present in this granite.

4.13 PARTIAL MELTING

Textural evidence of partial melting is seen in a variety of block types from a number of localities. This section will concentrate on the syenite blocks of East Crater.

4.13.1 Textural Evidence of Partial Melting

A brief description has been given by Cox et al. (1979). Somewhat similar are the partially melted granite blocks from Mt. Elephant, Australia, described by Le Maitre (1974). Textural evidence of reheating and melting of the Ascension syenite lies in the cracking, clouding and sieve-textured edges of the feldspar and especially in the occurrence of glass. Pyroxene too is replaced patchily by glass and an opaque phase. The glass in these blocks varies in colour, being usually light brown to colourless, but darker brown when adjacent to pyroxene and opaque minerals (see Plate 4.53).

The preservation of glass means that the liquid was rapidly quenched and this presumably occurred when the lava containing the block was exposed to air on eruption. Glass alone is not considered to be a priori evidence of partial melting since it is also found in a suite of gabbro cumulate blocks where it is considered to be quenched intercumulus liquid. In these blocks euhedral plagioclase and clinopyroxene crystals project into the glass which contains quench crystals of feldspar and opaque mineral and shows no reaction against the enclosing grains.

Partially melted blocks have been recovered from a number of localities (e.g. Green Mountain, Mountain Red Hill - see previous sections). In most cases the blocks are small and altered, thus petrographic study is difficult. The melted blocks are usually small in number so comparisons are difficult to make. However the syenite blocks of East Crater flow (plus three monzonite gabbros) are numerous (~40 specimens) relatively large (up to 25 cm diameter) and reasonably fresh, enabling a detailed study of glass chemistry to be made with statistical accuracy. This section is therefore mainly concerned with

the partial melting features of blocks from East Crater.

Table 4.21 gives the SiO_2 composition of the glass, petrography. location of all partially melted blocks.

4.13.2 The Syenite Blocks

Microprobe analyses of major phases and modal proportions and whole rock analyses of East Crater blocks are given in Tables 4.22 and 4.23 and Fig. 4.52. Plates 4.53-4.58 are photomicrographs of typical specimens.

The mineralogy of the syenites is fairly uniform (Fig. 4.52). All comprise predominantly anorthoclase feldspar, together with augite, opaque mineral, possible orthoclase, and rare olivine, apatite and zircon. In altered blocks biotite and/or amphibole rim or replace the augite. This latter alteration occurred before the partial melting since the biotite and amphibole, where present, are affected by reheating in a similar manner to the pyroxenes.

In hand specimen many of the blocks are rather friable although some which have suffered considerable melting are compact. There is negligible variation in the texture of all blocks from this locality and it is therefore assumed that they once formed part of the same coarse grained body.

4.13.3 The Enclosing Lava

Two chemical analyses of different specimens of the lava from different parts of the flow are shown in Table 4.23 and representative analyses of all the phases in the lava are shown in Fig. 4.53. Also shown are the analyses of feldspars from a small block contained in the lava and analyses from a glomeroporphyritic cluster.

In hand specimen the lava is seen to contain up to 25-30% feldspar phenocrysts. In thin section these are found to have rounded and sieved edges identical to those of the feldspars adjacent to the partially melted patches in the coarse grained blocks and must therefore be considered to be xenocrysts from them. They are, moreover, indistinguishable in chemistry from feldspars

in the blocks (see Figs. 4.52 and 4.53) and it seems they have resulted either from complete disintegration of coarse grained solid material consequent on partial melting into individual grains, or from disruption of a magma containing these xenocrysts as phenocrysts by a further pulse of magma resulting in mixing and transportation to the surface before complete resorption of the feldspars. Two generations of olivine are also seen: as euhedral phenocrysts, and as iron oxide-rimmed euhedral grains often found in glomeroporphyritic clusters. These varieties are chemically distinct (see Fig. 4.53).

A simple mixing diagram (Fig. 4.54) suggests that the two lava analyses H39L and H31L differ in chemistry only because of differing xenocryst percentages. Removal of 20% xenocrysts of composition A from H31L would produce a lava with chemistry identical to H39L. This model is in good agreement with observed features since H31L contains about 25% feldspar xenocrysts, H39L about 5-10% feldspar xenocrysts, and the feldspar composition A is close to the average xenocryst analyses of H39L (Fig. 4.53).

4.13.4 Nature of the Glass and Associated Phases in the Syenites

Approximately thirty syenite blocks have been recovered from East Crater flow and investigated. Chemical analyses of the glass and all its associated phases (both pre- and post-partial melting) have been made from nine blocks (including two blocks which show no glass, although evidence of reheating is present).

In all these blocks the effects of melting are greatest between two grains of different minerals. Very little if any glass is found between two grains of the same mineral. In simple terms this may be considered an effect of the mutual lowering of melting point. Although melting along quartz-pyroxene or pyroxene-biotite contacts in principle should occur, its products cannot in practice be adequately distinguished since they are always affected

by those of melting along the much more abundant, adjacent quartz-feldspar or pyroxene-feldspar contacts. The partial melts, then, may be considered to form between feldspar and each of the accessory phases as two-phase and more rarely as multiphase systems.

Glass is most abundant along quartz-feldspar contacts in blocks where quartz is present (see Plate 4.55). In rocks with high degrees of melting, e.g. H33(4) no quartz is found, possibly because it has all melted. Feldspar-pyroxene contacts show a wide range of melting behaviour. In some cases pyroxene of normal appearance is surrounded by a brown to colourless glass. In other cases it is replaced patchily or completely by opaque minerals and glass. Although the glass varies considerably in colour in these cases there is very little chemical variation between the colourless and the brown types other than an extra 2-5% FeO in the latter. The glass may change colour within an individual melt patch, becoming lighter in tint away from the pyroxene. It seems, therefore, that inhomogeneity may exist in melts even on this small scale. Opaque minerals are mainly associated with the pyroxene but where opaque grains are in contact with feldspar alone, very little glass is found, although what little does occur tends to be dark brown in colour.

Feldspar-biotite boundaries are considerably less affected by melting than pyroxene-feldspar and quartz-feldspar boundaries in the same block. Biotite is found in some East Crater blocks as an alteration product of pyroxene and where pyroxene and biotite occur together there is more glass around the pyroxene than the biotite. In some blocks the biotite shows blackened edges and in a few cases is partially replaced by glass and opaques. Le Maitre (1974) suggested that the glass in the Mt. Elephant granites formed because the biotite dissociated releasing water, which allowed a limited amount of partial melting between quartz and feldspar. In the Ascension example where biotite occurs in the same partially melted area as quartz and feldspar, there is no more melting than in the same block where there is no

biotite present.

The two minor phases zircon and apatite show very little tendency to melt even in the blocks with relatively high degrees of partial melting. Plate 4.54 shows euhedral zircon in a partially melted area.

A feature of partial melting common to many blocks is the occurrence of quench crystals of varying mineralogy and development. Euhedral alkali-feldspar crystals have nucleated for the most part along the edge of the ancestral feldspars but in some cases radiate from a point, forming spherical masses (Plates 4.56 and 4.57). Much smaller acicular pyroxene and possibly opaque oxide quench crystals are seen both singly and as spheroids with radiating structure. Quench crystals are considerably less well developed in quartz-feldspar melts than in pyroxene-feldspar melts of the same block. This may be a function of the higher viscosity of the more acid liquid with a low bridging ion/network-forming ion ratio and lower content of network modifiers. Again, it might be that the pyroxene-feldspar liquid is likely to have been at a temperature closer to that of its solidus and thus retained substrate features favouring rapid heterogeneous nucleation.

A closer investigation into the opaque minerals present showed that there were two main types, magnetite and an iron silicate (see Table 4.24). Magnetite occurs mainly as primary grains associated with the pyroxene, often as small inclusions and perhaps also as quench crystals associated with the partial melt. The origin of the iron silicate is less easy to explain. The larger grains are sometimes found to have fayalitic olivine in the cores and must therefore be an alteration of the olivine. Chemical analyses of this opaque silicate (Table 4.24) are similar to those of greenalite (Deer et al., 1962, p.168) apart from higher Mn and Mg. The low totals of the East Crater opaque silicates are consistent with the material having about 8% H_2O (assuming most of the Fe to be divalent). Small grains of chemically identical (see Table 4.24) material are found adjacent to, and sometimes within, the partially melted pyroxenes. Three possible modes of formation are suggested:

(i) All of the opaque silicate formed by the alteration of fayalitic olivine. The great similarity of all the analyses in Table 4.24 supports this argument. In a number of cases, however, the opaque silicate is intimately associated with pyroxene and magnetite and these would have to be fragmented altered olivine which has become mixed into the melted pyroxene or altered olivine inclusions within the pyroxene.

(ii) The opaque silicate associated with the pyroxene could result from alteration of the pyroxene or magnetite which is often seen as inclusions within the pyroxene. This mode of origin seems extremely unlikely given the similarity in chemical composition of all the opaque silicate glasses in Table 4.24.

(iii) The opaque silicate is in fact an iron rich silicate glass and represents a conjugate mafic liquid to the acid glass caused by immiscibility on melting and formation of liquid. The low totals shown by the opaque silicate could in part be caused by Fe being present as Fe^{3+} (as one might expect in a glass of this kind). If all this is true then the totals would be much closer to 100%. Examples of experimental and observed conjugate liquids are described by Roedder (1979) and Philpotts (1979).

This third hypothesis must be considered unlikely for the following reasons;

(i) Even assuming all the Fe to be Fe^{3+} the totals are still slightly low, suggesting some H_2O to be present. The acid glass is apparently dry hence any coexisting mafic glass should also be dry as one would expect a hydrated basic liquid to lose water more rapidly than a conjugate acid liquid.

(ii) The opaque silicates show rather irregular shapes which are unlike those in any previously described conjugate acid/basic pair (Philpotts, 1979) and the large size (≅ 0.1 mm) is much larger than any previously described example (< 10μ, Philpotts, 1979).

4.13.5 The Variation in Chemistry of the Glass

The partial melting features seen in these blocks are best explained as resulting from breakup of a single solid coarse grained body by explosive eruptions and subsequent immersion of its fragments in a more basic magma. After a relatively short period of time, perhaps as short as hours, the xenolith-bearing magma was extruded. During this time temperatures were above the melting point of the quartz-feldspar, pyroxene-feldspar and biotite-feldspar 'mixtures' and partial melting occurred. Decompression is unlikely to have played a significant part in the melting since all blocks show features of a low pressure assemblage.

It seems reasonable, then, to assume that the melts in these blocks all formed at the same conditions of pressure and temperature. In the case of pressure this is likely to have been close to 1kb since the liquids contained a vapour phase whose exsolution is indicated by vesicles in the glass (see Plates 4.55 and 4.58) (Robertson and Wyllie, 1971; Le Maitre, 1974). The variation in chemistry of the glasses is therefore likely to be due to:

(i) The length of time during which the material was heated, assuming the same P and T (i.e. the degree of partial melting).

(ii) The mineralogy of the blocks (i.e. modal percentage).

(iii) The chemistry of these minerals.

(iv) Possible contamination by the surrounding magma.

Fig. 4.52 snows the compositions of the feldspar and pyroxene in the blocks and these may be compared with the chemistry of the glass in each block (Table 4.25). Those blocks with the most evolved pyroxene and feldspar show the most acid glass composition. Those blocks with low degrees of partial melting (see Table 4.22) show a high variation in glass composition between pyroxene-feldspar contacts and quartz-feldspar contacts. Different melt patches with the same mineralogy show good agreement in glass chemistry. Block H33(4) shows the highest degree of melting and a very consistent glass

chemistry. This block has no modal quartz possibly because any original quartz was removed during the 28% partial melting suffered by this rock. Because of the greater ease of diffusion and mixing in a relatively highly melted block differences in chemistry between melts formed from quartz and feldspar and pyroxene and feldspar would disappear. In some of the blocks with higher degrees of partial melting it might be thought possible that contamination of the partially melted areas by the enclosing lava may have occurred. There is, however, no evidence for this at the edges of the blocks and there is nothing anomalous about the chemistry of the glass in block H33(4) showing 28% melting compared with those blocks showing only 3% melting (see Table 4.22).

Previous accounts of partial melting (such as Maaløe and Printzlau, 1979) devote considerable attention to melt geometry. In the Ascension blocks the distribution of the melt fraction depends on the distribution of pyroxene and quartz and the shape to a large extent reflects the outline of the original pyroxene or quartz grains (see Plates 4.53-4.58).

4.13.6 Petrological Implications

The volume of partial melt formed in the Ascension syenite blocks is in most cases small and direct evidence that these semi-discrete patches were able to coalesce to form a mobile mass (= a magma) and hence produce rocks is lacking (although what this should be is by no means clear). Ascension Island has a fairly large volume of quite acid (>65% SiO_2) volcanic rocks and a suite of true granite blocks and it may be that partial melting of intermediate coarse grained material has played a role in producing these evolved magmas.

We have seen that liquids with a silica content of 70-75% may have been produced by 5-30% melting. A simple explanation of this is that the small amount of quartz in the rocks is able to contribute more melt than the other phases thus enriching the liquid in SiO_2. Comparing the analyses of the

granite blocks and the most acid volcanics (Table 4.23) with the glass analyses of similar Wt% SiO_2 (i.e. between 70 and 77) the only elements which are significantly different are Ca, Na and K. The small amount of CaO in the glasses (0.5 - 1 Wt%) must be due to the contribution of clinopyroxene to the melt. Total alkalis in the glass are slightly less than that of the granite block and comendite but perhaps of more significance is the difference in K_2O/Na_2O (Wt%) ratio.

Fig. 4.55 shows the variation of K_2O/Na_2O with Wt% SiO_2 for Ascension glasses and volcanic rocks. The more basic glasses are from naturally melted blocks from other localities on Ascension which show a more varied bulk chemical composition and mineralogy than that of the East Crater syenites. The difference in the two curves in Fig. 4.55 implies that Na is lost relative to K during the formation and possibly after solidification of the glass. Bailey and Macdonald (1970) consider that peralkaline glasses as obsidian are unlikely to have lost glass after solidification.

Fig. 4.52 shows that in H33(4) and 17360(1) the idiomorphic quench crystals of alkali feldspar have a much higher Or content than the original feldspar of the block. This could only be the case if a significant increase in K_2O/Na_2O had occurred before quenching. Significant amounts of Na must have been lost during the production of the melt.

For the acid glasses from East Crater to be representative of a magma parental to the rocks of granite composition it would be necessary for their K_2O/Na_2O ratios to be changed, possibly by some form of selective enrichment of Na via volatiles. This high K_2O/Na_2O ratio is also seen in granitic glass from Mt. Elephant, Australia, (Le Maitre, 1974) where K_2O = 7% and Na_2O = 4%. This is an important difference between observed granite liquids formed by partial melting and granites which may have formed by partial melting.

Trace element data for these glasses have so far proved difficult to obtain due to the small size of the samples and so differences between partial

melt and granite (observed) trace element chemistry cannot yet be discussed. However, it may be noted that the Zr content of the blocks is likely to be almost entirely contained in zircons. Zircon is an extremely refractory phase and retains its euhedral shape in otherwise melted patches (Plate 4.54). Thus any melt produced from 20-30% melting (i.e. granitic) is likely to be significantly poorer in Zr than the parent material. The Ascension granites, however, have Zr contents more than three times higher than those of the East Crater syenites. This evidence strongly suggests that the Ascension granites have not formed from wholly liquid fractions produced by partial melting of the syenite blocks as described. It might be thought that a partial melt containing a disproportionate quantity of relict zircons could have separated to form the granites but the petrographic features of the zircons in the granites do not give evidence of this.

4.14 THE ROLE OF IMMISCIBILITY IN ASCENSION MAGMAS

There are now several accepted examples of liquid immiscibility in igneous rocks. The earliest recognised examples occur in rocks of unusual composition, e.g. nephelinites and apatite and magnetite rich rocks (Philpotts, 1963). More recently evidence has accumulated which suggests immiscibility may be a common feature in magmas of more 'normal' composition such as tholeiites (De, 1970; Philpotts, 1979) including the Skaergaard intrusion (McBirney, 1978). Several features of the Ascension blocks suggest that immiscibility occurred in Ascension magmas.

4.14.1 Fluid Inclusions

Roedder and Coombs (1967) described fluid inclusions from a small number of granite blocks from Five Mile Post. Apparently primary inclusions of (i) silicate liquid (quenched to a glass) and (ii) halite crystals in solution + gas bubble occur. The random distribution of these types throughout

the rocks implies immiscibility of the original silicate liquid and saline fluid. This is not, though, evidence for silicate liquid immiscibility.

4.14.2 Sulphide-Silicate Immisicibility

Block H7(5) from Middleton's Ridge is the most opaque-rich gabbro from this locality (≈ 10% modal magnetite + ilmenite). Small opaque inclusions are found in the pyroxene and olivine. These proved, on analysis, to be pyrrhotite (Fe_{1-x} S). In this example iron is slightly less than one per formula unit. Sulphides have not been identified in any other block.

Immiscibility of sulphides and silicate-oxide systems is well documented in basic intrusions (Wager and Brown, 1969). The liquids separate when sulphur is about 0.025 - 0.1 wt%. The sulphide becomes concentrated in the residual liquid as fractionation proceeds. Eventually the two liquid field is reached and droplets of sulphide separate. In this case they must have been caught up in the accumulating and growing crystals.

4.14.3 Apatite-Opaque Rich Blocks

In nearly all blocks which contain opaque minerals, apatite is present in small but significant amounts (∿ 3 modal percent in the pegmatoid). In the only three Dark Slope Crater blocks to contain significant modal oxides, apatite is also present (DS24, HDSA5 and DSA3). Apatite is not found in any other Dark Slope block.

Philpotts (1967) describes some almost pure apatite-oxide rocks associated with anorthosites (at Nelson, Virginia (USA) and Lake St. John, Quebec). He concluded that the apatite/magnetite rocks crystallised from a liquid which had become immiscible with the main anorthositic liquid. This idea led Philpotts to investigate the magnetite-apatite 'diorite' system. Large 2 or 3 liquid fields were found (Fig. 4.56). A 30-40% apatite + magnetite component is needed before the two liquid field is reached. As described in the Dark Slope Crater section (4.2.6), the textures of these opaque minerals are

somewhat unusual rounded opaque masses surrounding plagioclase and pyroxene and in some places pyroxene blebs are completely surrounded by opaques, maintaining optical continuity between separate pieces.

In the previous section on Dark Slope gabbros it was proposed that the iron oxide rich blocks are part of a thin opaque rich horizon formed when the magma suddenly became saturated with FeO and P_2O_5 causing sudden precipitation. The textures exhibited, though, are not like the cumulus opaques in say the Bushveld (Wager and Brown, 1960) or any other gabbro intrusion. It is possible that the oxide-rich blocks result from liquid immiscibility. The magma may have fractionated into the two liquid field causing an iron oxide/apatite rich liquid to separate. This being denser would have sunk onto the accumulating crystals on the floor of the intrusion (if this is indeed where they accumulate). This hypothesis is at least able to explain the unusual textures shown by the opaques.

This explanation is, perhaps, unlikely, but in view of the recent revival of silicate liquid immiscibility, deserves some consideration.

4.14.4 The Pegmatoid

The above hypothesis could equally well be applied to the pegmatoid. The amount of apatite and magnetite it contains is not sufficient to place it in the two liquid field, however. Field evidence strongly suggests that it crystallised in situ and was once a liquid within a liquid. This does not imply immiscibility occurred since there is no evidence that one liquid split into two immiscible fractions. This is further discussed in Section 4.11.5.

4.15 COMPARISONS BETWEEN THE BLOCKS AND THE PHENOCRYSTS IN LAVAS

4.15.1 Modal Proportions

In basic blocks, the modal proportion of mafics to plagioclase is much

higher on average than in the phenocryst assemblages containing grains of the same composition. This is presumably because olivine and pyroxene settle much faster in magmas than plagioclase (see Chapter 7). The comparison between granite blocks and the acid lavas is less meaningful because the blocks contain sodic pyroxene and amphibole rather than ferrohedenbergite and olivine. The proportion of mafics in the blocks is significantly higher than in the phenocrysts of the acid lavas.

4.15.2 Mineralogy

The following differences are interesting:

(i) Some blocks from Dark Slope Crater have both ortho and clinopyroxene and many clinopyroxenes show exsolution of calcium poor pyroxene. This is the only suite of blocks to show this and no pyroxene phenocrysts exhibit exsolution. It seems that these blocks crystallised from a magma with tholeiitic affinites. Isotopic data suggests that these blocks originate from a different mantle source (see Chapter 6).

(ii) The pyroxene phenocrysts range from magnesian augite to ferrohedenbergite with almost no magnesium and very little sodium. The acid blocks do not contain ferrohedenbergite, having both aegirine and amphibole instead. Amphibole is however found in the groundmass of some acid lavas (see Chapter 7).

(iii) The granite blocks contain sodium and potassium zirconium silicates. This reflects their peralkalinity and possibly results from reaction of sodium/potassium silicate with Zr in the last stages of crystallisation. These zirconium silicates are not found in the acid volcanics. The excess sodium and potassium(?) silicate is presumably in the glassy groundmass.

(iv) The acid blocks contain perthite, the sanidine phenocrysts in the acid lavas show no exsolution. This is most likely a reflection of the faster cooling of the lavas.

(v) Opaque oxide phenocrysts are not common in the lavas but the blocks

contain both magnetite and ilmenite, and are hence evidence that these phases were involved in crystal fractionation.

(vi) Figs. 4.57 and 4.58 show tie lines for coexisting pyroxene-olivine and plagioclase-olivine in blocks and lava. Olivine composition is comparatively insensitive to bulk composition changes other than MgO/FeO (Roedder and Emslie, 1971) so differences in plagioclase compositions for the same olivine composition in blocks or phenocrysts imply differences in crystallisation conditions. In the case of zoned plagioclases the core compositions were plotted. There are no significant differences beween either sets of tie lines which give any indication of differing crystallisation conditions either between block suites, or between blocks and phenocryst assemblages.

CHAPTER 5

BULK CHEMICAL VARIATION IN BLOCKS AND LAVAS

5.1 INTRODUCTION

Sixty one lavas and 28 blocks have been analysed (see Table 5.1). The 15 analyses from Daly's (1925) account have been ignored in this chapter because of uncertainty in method.

The localities were resampled (and later analysed) in the course of the Oxford expeditions in 1964 and 1965. Many of the analyses of lavas in this thesis were taken from unpublished data by Bell et al. (1965-70). Additional samples of lava were analysed during the course of this work as were nearly all the block analyses. The analysis of blocks is hindered by the oxidised nature and small size of many of the samples.

The trace elements Y, Rb, Nb, Zr, Sr (plus in very few cases) Ta, Hf, Th, Sc, Co + REE were made on selected samples. Details of analytical procedure may be found in the appendices. Analyses of lavas and blocks with procedure and analyst are given in Table 5.1.

5.1.1 Fe Oxidation State

Early analyses have separate determination of FeO and Fe_2O_3 (by wet chemical methods) but later analyses (this work) have only total iron determined. Since the Fe_2O_3 content of a lava (or block) is likely to reflect aO_2 conditions during cooling rather than at the time of crystallisation, iron is represented as total iron FeO^T. This is especially important for use in the calculation of norms since Fe_2O_3 is allocated to magnetite rather than silicates (olivine and pyroxene). So high Fe_2O_3 results in higher normative silica.

5.1.2 Index of Differentiation

There are numerous choices of index of differentiation such as Differentiation Index (D.I.) (Thornton and Tuttle, 1952) and Solidification Index (S.I.) (Kuno, 1970). In a study on volcanics from Aden, Hill (1974) considers that SiO_2 is the best choice of index. D.I. and S.I. run into

difficulties at the most evolved end of the series since they are based on normative Q, Or, Ab and do not take normative ns into account. The Ascension volcanics are remarkably similar to those of Aden and in this thesis the variation diagrams use SiO_2 as a measure of differentiation, since in the Ascension lavas wt% SiO_2 shows a wide range (from 47.16 to 74.00) and as in the Aden lavas, the salic rocks do not have quartz phenocrysts. MgO is a useful index for the more basic rocks but becomes meaningless for the more evolved rocks (SiO_2 > 62) since they contain no significant MgO.

5.2 MAJOR ELEMENT VARIATION IN LAVAS

Figs. 5.1 - 5.9 show the variation of wt% TiO_2, Al_2O_3, FeO^T, MgO, CaO, Na_2O, K_2O, P_2O_5 and $Na_2O + K_2O$ vs. SiO_2. Of these TiO_2, CaO, MgO, FeO^T and the alkalis show a good correlation with SiO_2. Al_2O_3 and P_2O_5 much less so. TiO_2, FeO, MgO, CaO show -ve correlation, K_2O and for the most part Na_2O show +ve correlation.

CaO and MgO show the most straightforward pattern, a continuous decrease with increasing SiO_2 until each become zero (at SiO_2 = 65 and 62 respectively). FeO^T and TiO_2 also show continuous decrease as SiO_2 increases but in both cases the distribution shows an inflection. TiO_2 becomes suddenly less steep at SiO_2 = 60 (Fig. 5.1) and FeO^T at SiO_2 = 65, although this is less pronounced (Fig. 5.3).

K_2O shows a continuous increase as SiO_2 increases but Na_2O, while it parallels K_2O for the basic and intermediate lavas, shows an inverse correlation with SiO_2 > 65. This may in part be due to a 'constant sum effect' (Chayes, 1964). Al_2O_3 has a very diffuse pattern for SiO_2 < 60 but above this value there is good -ve correlation (Fig. 5.2) with SiO_2. P_2O_5 is more diffuse, but the overall pattern is one of negative correlation with SiO_2 (Fig. 5.8).

Total alkalis vs. SiO_2 is of particular importance as a guide to

classification. Fig. 5.9 shows $Na_2O + K_2O$ vs. SiO_2 and the nomenclature from Chapter 3 superimposed upon it. As may be seen on Fig. 5.9, there is a "Daly gap" with analyses scarce between trachybasalt and trachyte. The series as a whole is 'transitional' in that it lies between the tholeiite field and the field of more undersaturated alkaline series such as Tristan da Cunha (etc.). One analysis plots in the tholeiite field. This rock is a pyroclastic notable for its very low Na_2O content. This may be due to analytical error or loss of Na due to volatilisation which might be more likely in a pyroclastic than a lava. Either way the lava is not a representative of a tholeiitic suite.

CaO and FeO^T may be plotted against MgO and Figs. 5.10 and 5.11 show that a good positive correlation is seen for CaO but FeO^T shows slight negative correlation for the highest MgO contents. This is an indication that some iron enrichment occurred on differentiation of the most basic end members of the suite. The lavas with high MgO and lower FeO^T are not noticeably olivine phyric so this iron depletion in high Mg rocks is not due to their being high in olivine to the exclusion of iron in the groundmass.

5.3 MINOR ELEMENTS vs. SiO_2

Included here are Nb, Zn, Y, Sr, Rb (see Table 5.1) analysed by XRF (see Appendix) and Th, Ta, Hf, Co, Sc analysed in four lavas by INAA. The second group will not be considered in detail as only four lavas were analysed.

Nb, Zn, Y, Rb, Th, Ta, Hf show strong positive correlation with SiO_2 (Figs. 5.12 - 5.18) showing them to be incompatible, i.e. strongly partitioned into the melt as crystallisation proceeds. Sr shows negative correlation with some degree of point scattering (Fig. 5.19), Sc shows good negative correlation and Co no particular pattern (the latter two with only four data points).

5.4 OTHER PLOTS

5.4.1 A.F.M.

The lavas are plotted onto an A.F.M. triangle in Fig. 5.20. This shows the lack of iron enrichment and the dichotomy between the basic-intermediate and acid lavas.

5.4.2 Norms

Ne normative lavas are rare in comparison with Hy and Hy-Qz normative lavas. The non Qz-normative analyses are plotted onto a Ne-Di-Fo-Hy double triangle in Fig. 5.21. The analyses straddle the Di-Fo join with approximately equal numbers of Ne and Hy normative analyses, though the amount of Ne is small in Ne normative lavas.

As stated in Section 5.1.1, there is some confusion as to the amount of FeO/Fe_2O_3 in the magmas susceptible to oxidation as they cooled so are not likely to give a true value for magmatic Fe_2O_3. Coombs (1963) considered that 1.5 wt% Fe_2O_3 was an acceptable quantity in the basic magmas. This low value is confirmed by the low aO_2 values calculated for a sample of Middleton's gabbro which presumably crystallised from such a magma (see Section 5.6). Experimental work by Cooper and Bailey (1974) suggested that peralkaline and obsidians had very low Fe_2O_3/FeO. For these reasons, the norms have been calculated assuming all iron to be divalent. The norms will become less Ne normative/more silica normative if more Fe total is put into the norm calculations as Fe_2O_3. Fig. 5.21 again demonstrates the transitional nature of the series.

Those lavas with <10% normative An may be plotted on to the Qz-Ab-Or normative triangle (Fig. 5.22) with the Qz-feldspar cotectic of Bowen and Tuttle and are seen to approach the cotectic at the most salic end of the series. This line of evidence forms part of the case for an origin via crystal fractionation presented in Section 5.8.

5.4.3 Peralkalinity

Peralkaline rocks are those with molecular $Na_2O + K_2O > Al_2O_3$ (Bailey and Schairer, 1966). Fig. 5.23 shows the lavas plotted on a portion of the molecular SiO_2, Al_2O_3, ($Na_2O + K_2O$) triangle where an easy division into peralkaline and aluminous rhyolites and trachytes may be made (only the evolved $SiO_2 > 57$ wt% lavas are plotted, since basic lavas contain many constituents not representable on this figure). It may be seen that only a minority of lavas are peralkaline and these are the more salic ones. The Qz-Ab cotectic is marked and it may be seen that the most evolved lavas approach it (as in Fig. 5.22).

5.5 BLOCKS

5.5.1 Major Elements (Fig. 5.24)

Where the lava variation diagrams for the most part show good correlation (Fig. 5.2), similar plots for the blocks are much more diffuse. This is particularly so of the SiO_2 poor end of the series where variation of the proportions of cumulate minerals gives considerable variation in chemical composition between blocks which must be closely related. Positive correlation with SiO_2 is shown by Na_2O, K_2O and negative correlation by CaO, FeO^T, MgO. P_2O_5 and MnO_2 show no real correlation.

The variation shown by the alkalis is broadly similar to that shown by the lavas. Na_2O rises to a peak value at SiO_2 = 62-65 then falls off presumably due to the combined effects of increase in alkali feldspar content over anorthoclase and the constant sum effect. K_2O continues to rise for increasing SiO_2. . $Na_2O + K_2O$ vs. SiO_2 is a good illustration of the constant sum effect at high SiO_2 values.

FeO^T, MgO and TiO_2 show similar variation with SiO_2. At low SiO_2 they have varied values and show no correlation, but at $SiO_2 > 50$-55 the values become constant (for MgO this is zero wt%). Again this distribution is

controlled by the presence and quantities of the cumulus phases in the blocks. Some blocks contain magnetite in large quantities while others have very little. Consequently for a given SiO_2 value a wide range of TiO_2 and FeO^T values may occur. Similarly gabbros with high olivine content and high plagioclase content may be closely related (as in Dark Slope Crater xenoliths) but can have completely different MgO values for the same SiO_2 content.

CaO and Al_2O_3 both show reasonable negative correlation with SiO_2. This is no doubt related to the change in composition of feldspars with crystallisation. CaO reaches zero at SiO_2 = 70 but Al_2O_3 continues to drop and like the lavas shows good correlation with SiO_2 at high SiO_2 values.

P_2O_5 shows a very similar distribution to that of the lavas. P_2O_5 content in blocks depends almost entirely on whether they contain apatite. In blocks of $SiO_2 > 65$, P_2O_5 is effectively zero.

5.5.2 Minor Elements vs. SiO_2 (Fig. 5.25)

Of these, Nb, Zr, Y and Rb show quite good positive correlation with SiO_2. These elements are considered strongly incompatible and their partition into the melt relative to crystals is shown by strongly fractionated patterns. Nb and Zr show the best correlation with SiO_2, both with a rather "hyperbolic" shape. Y shows a less good correlation as does Rb.

Sr exhibits negative correlation but the correlation is only moderate. At $SiO_2 > 67$, Sr is zero.

Only four blocks were analysed for Th, Ta, Hf, Sc and Co. Th, Ta and Hf show strongly fractionated incompatible patterns (i.e. positive correlation with SiO_2). Co and Sc, negative but scattered correlation with SiO_2.

5.5.3 Other Plots

Blocks are plotted onto the normative Qz-Ab-Or system in Fig. 5.22 and show very similar distribution to lavas, except that the most salic blocks are much closer to (and in some cases sit on?) the ternary minimum. The

plot is only valid for rocks with <10% normative An hence any block in this plot is fairly salic. Since the chemical variation for salic lavas and blocks is very similar, it is scarcely surprising that blocks and lava show similar distribution in Fig. 5.22. Other diagrams such as AFM and Ne-Ol-Di-Hy are much less useful for basic to intermediate blocks than lavas as they tend to accentuate differences in composition caused by variation in cumulus minerals.

Both granites and comendites (lavas) contain normative sodium metasilicate (ns). The granites contain vlasovite which was considered in Chapter 5 to be the result of combination of Zrcomplexed in the residual liquid and the sodium silicate in the melt. Table 5.2 gives the CIPW norms for the acid lavas and blocks. The lavas contain a higher % ns which may be because more sodium is lost by volatilisation in the slower cooling granites. The granites contain higher (in general) wt% SiO_2 (Table 5.1).

5.6 INTERCUMULUS LIQUID

As described in Chapter 4, several blocks contain intercumulus liquid. In only one block (15243(B), a gabbro), was analysis possible. In this block, the mesostasis occurs as intergranular material quenched to a glass in several places (Plate 4.22), and also in the form of glass inclusions within pyroxene and olivine grains. Glass inclusions also occur in plagioclase but these were invariably destroyed on polishing.

Analyses of the mesostasis are presented in Table 5.23. It may be seen that analyses of intergranular glass have $K_2O > Na_2O$ while those from the glass inclusions have $K_2O < Na_2O$. Two possible explanations may be put forward.

(i) Crystallisation of residual liquid onto the edges of the grains and the appearance of quench crystals may mean that the present glass composition where $K_2O > Na_2O$ is in part due to non-equilibrium crystallisation onto

pre-existing material (especially sodic feldspar).

(ii) Na_2O was lost relative to K_2O before the liquid was quenched to a glass (or possibly after it was solid). There is good evidence in the partially melted blocks that the liquid produced lost Na while molten (see also Harris and Bell, 1982).

(ii) seems most likely so the analyses of blebs within pyroxene are probably most reliable since loss of Na would have been more difficult from these melt patches than from the intergranular liquid. These glass blebs contain quench crystals of opaque minerals so only those blebs with little or none were analysed.

Differences in wt% CaO, MgO and SiO_2 between olivine and pyroxene enclosed blebs were found so disequilibrium addition onto the host minerals seems to have had some effect on the glass composition.

5.6.1 Glass Chemistry

Fig. 5.26 shows glass-whole rock tie lines [glass compositions are given in Table 5.3]. The whole rock value used is not that of 15243B or 15368D but H99(2), the only Middleton's gabbro analysed (the largest and least altered). Since all the blocks have similar mineral compositionsand modal proportions (it was shown in 4.9 that 15243B belongs to the Middleton's gabbro group) except for the opaque rich block H7(1), this is considered legitimate.

Also shown in Fig. 5.26 are approximate major element trends with SiO_2 as x axis (i.e. measure of differentiation). Several features are worth comment:

(i) Al_2O_3, CaO, MgO and K_2O liquid-block tie lines parallel the distribution of the volcanic analyses.

(ii) Na_2O is less parallel to the volcanic analysis distribution, perhaps due to loss of Na_2O before quenching.

(iii) FeO^T and TiO_2 show positive correlation with SiO_2 whereas the volcanic

analyses have a distribution which has negative correlation with SiO_2.

5.6.2 Discussion

The quenched glass in these blocks is assumed to have been in equilibrium with the cumulus crystals on quenching, hence tie lines between block and glass composition must approximate to the trend of differentiation shown by this particular magma. If this is so then it is necessary to explain why iron and titanium enrichment is seen in this example and not in the volcanic suite as a whole.

A possible explanation is that the block selected for whole rock analysis, while being representative of the vast majority of Middleton's gabbros, contains little or no Fe-Ti oxides. One block (H7(1)) contains substantial (15-20%) Fe-Ti oxides (Section 4.3) and presumably others not represented by the collection could contain much more (cf. Dark Slope Crater). Thus it seems that Fe-Ti oxides are only cumulus phases when FeO^T is sufficiently concentrated and the short term trend is therefore to iron enrichment (shown by the block-glass tie line) while in the long term it is to iron depletion via periodic fractional crystallisation of oxides. Because Fe-Ti oxides are so much denser than the melt (see Chapter 7) they sink rapidly, hence they may be expected to form narrow layers in the cumulate pile though with substantial proportions of oxide.

5.6.3 Amount of Fractionation

This example gives us a chance to determine the amount of fractionation required to produce a given change in liquid composition. If the bulk composition of H99(2) is taken as a starting point for liquid composition and the average volume of mesostasis is 10% then 90% fractionation has been required to give the liquid composition preserved as mesostasis. Application of the lever rule gives a figure of 96% fractionation before SiO_2 reaches 70%.

5.7 CRYSTALLISATION OF THE PEGMATOID AND ITS BULK CHEMISTRY

5.7.1 Chemical Composition

Two different pieces of pegmatoid and one sample of host lava have been analysed. These analyses are presented in Table 5.4 [H59(1) and (2)]. In Section 4.11 it was compared with examples of pegmatoids from Hawaii and Picture Gorge (Canada) and in the latter case the suggestion was that residual liquid flowed into cracks in the semi-plastic cooling basalt when it was 50-75% solid (from least squares fractionation tests).

As stated in Section 4.11, calculations using the mixer programme of Wright and Doherty (1970) were made (Table 5.5). It can be seen that only about 30% removal of suitable crystals from H81L is needed to produce a liquid with the bulk composition of H59. It seems unlikely that this amount of solidification would give the basalt sufficient tensile strength to allow tension gashes to form into which residual liquid may have flowed. Two other important points concerning the chemical composition of the pegmatoid may be made.

(i) Inhomogeneity. It was shown in Fig. 4.47 that analyses of feldspar and pyroxene from H59B (the rim) are less evolved than those from the other samples of pegmatoid analysed. Presumably this is due to crystallisation proceeding inwards from the edge of the pegmatoid. Thus the small differences in composition between H59(1) and H59(2) are easily explicable in terms of slight variance in distance from the edge of the body. Aegirine-augite and silica in vugs are confined to certain parts of the body and this is likely to be the cause of some inhomogeneity.

(ii) The iron and titanium contents (12.64 FeO^T and 3.20 TiO_2 - see Table 5.1) are higher than for any analysed lava (max. 10.66 wt% FeO^T) hence the liquid from which the pegmatoid crystallised was an unusual composition. High Fe-Ti oxide (modal %) composition is a feature of a small number of

gabbroic cumulates and in some cases this may reach 70% (Chapter 4, Dark Slope Crater). It has been demonstrated earlier in this chapter that there is no iron enrichment in the volcanic suite yet where quenched intercumulus material has been analysed, the bulk rock-residual glass tie lines do show iron enrichment. This was interpreted in Section 5.6.3 as iron oxides being a periodic liquidus phase so that FeO is continually being enriched until iron oxides precipitate and the cycle perhaps begins again, the overall trend being of iron depletion as SiO_2 increases. For the pegmatoid to have 12.64 wt% FeO^T it must have been captured by the enclosing basalt at some stage when iron oxides were close to becoming liquidus phases (i.e. fairly concentrated). The subsequent rise in temperature resulting from heating from surrounding basalt magma would have prevented it from crystallising before reaching its present position.

5.7.2 Change in Liquid Chemistry

That the mineralogies exhibited by the pegmatoid at successive stages of its cooling match assemblages found in the lava and blocks indicates a similar mechanism of petrogenesis, namely crystal fractionation and a common liquid line of descent. From the change in feldspar composition the change in liquid chemistry may be schematically represented on the Qz-Or-Ab-An tetrahedron (Fig. 5.27) after Carmichael et al. (1969). The K feldspar-"quartz" intergrowth must result from crystallisation at the isobaric minimum (point H). It is difficult to explain how the feldspars of the pegmatoid become progressively more Or rich until they lie well to the Or side of the Ab-Or cotectic (Fig. 5.27, point C). However a possible explanation is that the liquid began to lose alkalis, particularly Na, as it became highly evolved, and possibly peralkaline (i.e. molecular $Na_2O + K_2O > Al_2O_3$). With continued loss of Na, a feldspar which would otherwise have crystallised at the same composition (at the eutectic, Fig. 5.27, point F) will, in fact, become more

K rich. Harris and Bell (1982) have shown that Ascension peralkaline glasses formed by partial melting lost considerable amounts of Na relative to K in the molten state. This feature of the feldspars combined with the occurrence of aegirine-augite rims round the pyroxene, indicates that the last pegmatoid liquids were oversaturated and peralkaline in character. Since it seems reasonable to assume that nothing was added to the pegmatoid as it crystallised (except perhaps H_2O) the rock presents strong evidence that peralkalinity may result from crystal fractionation. This example also indicates that in the final stages of crystallisation the liquid is modified by loss of Na which presumably occurs only when molecular alkalis exceed molecular aluminium.

In recent years some doubts have been expressed concerning the importance of crystal settling in magmas which inadvertently give the impression that crystal fractionation may not occur. It is interesting to note that in the Ascension pegmatoid crystal-liquid equilibria (i.e. crystal fractionation) controlled the chemical evolution of the liquid without settling of the crystals. Thus for this example, at least, crystal settling and crystal fractionation are not synonymous.

5.8 CRYSTAL FRACTIONATION MODELS

Differentiation is synonymous with fractionation and crystal fractionation is one such differentiation process (others being immiscibility, volatile transfer, etc.). The operation of crystal fractionation during the evolution of this suite is implied by the large and varied suite of cumulate blocks. There are two ways of assessing its nature and importance; (i) non rigorous and graphical comparison of block and lava composition; (ii) mixing calculations using various computer programmes.

5.8.1 Comparison of Block and Lava Chemistry

Fig. 5.24 shows major elements vs. SiO_2 for all analysed blocks. Superimposed on these are the same variation diagrams for the lava analyses. It may be seen that in most cases the block compositions parallel that of the lavas closely with the basic block analyses providing extensions to the basic end of the lava series. It is this type of pattern that would be expected if the basic blocks are cumulates formed during the evolution of the volcanic series. The exceptions to this are FeO^T and TiO_2. This may be due to Fe-Ti oxides sinking very rapidly which would concentrate them, in layers, or only being periodic liquidus phases as suggested in Sections 5.6.3 and 7.7. These plots then are very good evidence that the volcanic series is related by crystal fractionation.

Fig. 5.24 also shows that the compositions of the volcanics and blocks are very similar at the acid end of the series. This is perhaps an indication that the granites are slowly cooled equivalents of the acid lavas rather than an accumulation of crystals settled out from the magmas producing acid lavas.

Fig. 5.25 shows the trace elements Nb, Zr, Y, Sr, Rb, Th, Ta and Hf vs. SiO_2 for some blocks with the patterns from the limited number of lavas analysed superimposed. This lack of data on the lavas limits the use of this approach, but in general trace element patterns for blocks and lavas are the same. Zr, Y, Rb show good agreement while Nb is similar but rather more hyperbolic in the block pattern. Sr is rather higher in blocks than lavas of the same SiO_2 content. Since Sr is partitioned into crystallising plagioclase this is an indication that the blocks contain cumulus plagioclase.

5.8.2 Inspection of Variation Diagrams

Simple inspection of the wt% oxide vs. wt% SiO_2 plots (Figs. 5.1-5.11) allow constraints to be placed on crystal fractionation. This may be summarised as follows:

(i) At the SiO_2 poor end of the series FeO^T shows a decrease with SiO_2 which is greater than can be controlled by olivine fractionation (Fig. 5.3). This implies fractionation of an iron oxide phase. As SiO_2 increases the FeO content in olivine increases so it would be more feasible for olivine fractionation to control the decrease in total iron.

(ii) TiO_2 is also seen to decrease with SiO_2. This cannot be explained by fractionation of a Ti bearing phase like clinopyroxene as these have been shown in Chapters 4 and 5 to contain < 5 wt% Ti. This also suggests loss of a Ti rich phase such as ilmenite ($TiO_2 \sim 40.00\%$) or magnetite (TiO_2 15%).

(iii) Al_2O_3 gives a good inverse correlation with SiO_2 where $SiO_2 > 60$. Fig. 5.2 shows the locus for feldspar compositions and it can be seen that the depletion of Al_2O_3 in the acid lavas may be explicable by feldspar fractionation.

(iv) CaO vs. SiO_2 (Fig. 5.5) suggests plagioclase and/or clinopyroxene fractionation.

(v) P_2O_5 decreases to almost nothing in the acid lavas. If P_2O_5 is almost all contained in apatite then apatite fractionation must have occurred. The very scattered P_2O_5 content of the basic end of the series does not enable the SiO_2 content at which apatite fractionation began to be determined. It seems likely that large ranges in P_2O_5 contents in the basic lavas may be a reflection of the presence/absence of cumulus apatite. The maximum P_2O_5 content is almost 2 wt% (17364), which seems well above that of apatite saturation (Watson, 1978).

(vi) FeO^T decreases more sharply than MgO except for SiO_2 < 52%. This must have been achieved by removal of FeO^T via iron (titanium) oxides.

The trace element silica variation diagrams also give information about fractionation. Sr shows negative correlation with SiO_2 suggesting feldspar fractionation and the continued increase of Zr suggests that zircon was not a fractionating phase. Indeed the trace elments Nb, Zr and Y show a slightly

upward curve at SiO_2 > 65 wt%. This may be explained by complexing of these elements with F^-, Cl^- etc. (see Chapter 4.12 and 8.2 for further discussion) which makes them even more incompatible.

Bailey and McDonald (1975) have plotted various incompatible trace element compositions from trachytic to comenditic obsidians (from Kenya) against each other. They argue that while the plots are linear and show good correlation, most fail to pass through the origin and hence are not likely to be relatable by crystal fractionation. Similar plots for Ascension volcanics (Figs. 5.28, 5.29) show less good correlation (probably influenced by phenocryst abundances - especially Rb, a problem not encountered by Bailey and McDonald as they only analysed obsidians) but the lines of best fit pass much closer to the origin in every case (especially Nb vs. Zr, Nb vs. Y, Nb vs. Rb and Zr vs. Rb which are very close to the origin). Hence in the case of the Ascension lavas, fractional crystallisation is a much more plausible differentiation mechanism.

5.8.3 Amount of Fractionation

For a closed system undergoing continuous crystal fractionation, the Rayleigh Law gives

$$\log \frac{C_L}{C_o} = (K_D - 1) \log F \qquad (1)$$

[where C_o = initial concentration of an element in a magma

C_L = the final concentration

K_D = relevant distribution coefficient of element between crystals and melt

F = amount of fractionation]

The amount of fractionation required to go from composition A - B may be calculated. This is not possible for the whole of the suite since the K_D for a given element will change considerably as the cumulus phases change. The amount of fractionation may be calculated in small steps with little

change in fractionate but addition of these amounts of fractionation to determine the total will result in a large compound error.

Using the range of concentration of a typical incompatible element such as Nb, the minimum amount of fractionation to produce the comendites (A35) from the basalts (H81L) by crystal fractionation may be deduced.

Assuming K_D for Nb between magma and fractionate to be zero, the amount of fractionation required is calculated from equation (1) as 86% - similarly 85% for Zr. K_D must be greater than zero over some stages of the magma evolution, particularly when zircon is a cumulus phase. Hence the real value of F must be greater than 86%.

5.8.4 Numerical Fractionation Tests

The least squares programme of Wright and Doherty (1970) was used to determine the feasibility of the lavas being related by crystal fractionation. These tests are limited in many cases because the composition of the settling crystals is not likely to have remained constant over large changes in SiO_2 content.

For the basic to intermediate end of the series, these tests have not been especially successful because of

(i) uncertainty of compositions of the fractionating phases (especially feldspar), and

(ii) There are probably five major phases involved (olivine, clinopyroxene, plagioclase, magnetite and ilmenite) and the programme gets confused because of this.

Tables 5.6 (i & ii) give the results of these tests for the transition 15209 (basalt) to H48L (hawaiite) and from H48L to A63L (trachyandesite). The feldspar problem was minimised by using a composition of An_{70} for the 15209 → H48L mix and An_{60} for H48L → A63L. Reasonable agreement is seen between the observed and calculated analyses. Plagioclase is the most important fractionating phase and significant amounts of oxides would seem

to be involved. For the basalt to hawaiite olivine is much more important than pyroxene but in the hawaiite to trachyandesite the reverse is so. This is to some extent in agreement with the type of crystallisation sequence envisaged for the Middleton's gabbro blocks.

In Chapter 3 it has been shown that in the more acid lavas ($SiO_2 > 65$) the phenocrysts are much less varied and this makes the application of the computer test for fractionation much easier. Results of these tests are given in Table 5.6 (iii-vi). Na_2O is sometimes rather high in the computed extracts. This may be due to the loss of Na_2O as volatiles associated with the peralkalinity of the lavas. Apart from sodium, it is possible to produce reasonable agreement between computed and observed "extracts" by removal of sensible quantities of phenocrysts (with compositions taken from real analyses) from a starting composition. It must be stressed that this is not proof that crystal fractionation is the controlling mechanism behind a particular change in composition, only that it is a possible mechanism.

5.9 CONCLUSIONS

1) Most elements show a good correlation with SiO_2 content of the lavas. Similar variation diagrams for blocks are less well correlated. This is because their bulk composition is controlled by processes of crystal cumulation in addition to being dependent on the chemistry of the parent magma.

2) Studies on intercumulus liquid chemistry suggests that the depletion of iron and titanium in the lavas as SiO_2 increases is due to periodic crystallisation of Fe-Ti oxides. The Cricket Valley pegmatoid and this intercumulus liquid give evidence for more Fe rich magmas than the exposed lavas.

3) The volcanic rocks trend towards oversaturated peralkalinity though only the most evolved rocks are themselves peralkaline. The crystallisation in

situ of a pegmatoid demonstrates that oversaturated peralkaline liquids may be produced from liquids of intermediate composition without addition of alkalis from outside the system. Na seems to be lost though once peralkalinity is achieved.

4) Visual comparison of block and lava compositions, major and trace element data and least squares fractionation tests do not give any indication that the fractional crystallisation is not the mechanism by which the volcanic series has evolved.

5) Fractionation tests for the evolved lavas indicate that feldspar fractionation was the dominant control. The type of feldspar fractionating changes from andesine to anorthoclase to sanidine as the magmas become more evolved. Some fractionation of pyroxene and olivine (+ loss of volatiles) may also be involved.

6) The behaviour of Nb, Zr and Y suggests complexing in the SiO_2 rich (and peralkaline) lavas. This is good evidence for relatively high F and Cl contents in these magmas.

7) The basic blocks have a much more varied chemistry than the basic lavas. This is a reflection of their origin by crystal accumulation. The granite blocks have a very similar chemistry to the acid lavas showing them to be the slowly cooled equivalents of the same liquids.

CHAPTER 6

K-Ar AGES OF LAVAS AND Pb AND Sr ISOTOPE CONSTRAINTS ON THE GENESIS OF THE ASCENSION VOLCANICS AND ASSOCIATED BLOCKS

6.1 INTRODUCTION

The K-Ar dates are from unpublished data of F.B. Atkins, P.E. Baker, J.D. Bell and D.G.W. Smith. In the present study 13 samples (both lava and blocks) were selected for Sr and Pb analysis. These samples exhibited a wide range of chemical and petrographic features (Table 6.2). Details of analytical techniques are given in Section A.3 of the Appendix.

6.2 PREVIOUS WORK

Gast et al. (1968) presented precise data on Pb and Sr for five lavas. Their principal findings were (i) homogeneous but, for an oceanic volcano, unusually high Pb^{208}/Pb^{204} (39.0 - 39.5) and Pb^{206}/Pb^{204} (19.4 - 19.7) with more normal Pb^{207}/Pb^{204} (15.6 - 15.7) and (ii) high Sr^{87}/Sr^{86} (up to 0.7073) in some of the more evolved rocks (trachytes). They attributed the strontium isotope features to source differences and rejected contamination by seawater or pelagic sediments as a likely cause of the high Sr^{87}/Sr^{86}. Later research (Sun, 1980) confirmed the Pb results of Gast et al. (1968) but O'Nions and Pankhurst (1974) failed to find significant variation in Sr^{87}/Sr^{86} in the basic and intermediate rocks.

6.3 PETROGRAPHY OF SAMPLES ANALYSED FOR Pb AND Sr

Table 6.1 summarises chemical and petrological details of these rocks. For more detail on the blocks in general see Chapter 4. Of particular interest is the nature of basic cumulate blocks DS4 and DS44 and the differences between them and the other analysed specimens. DS4 and DS44 belong to a substantial suite of gabbroic blocks collected from the walls and on the flanks of Dark Slope Crater, a mixed basaltic lava and scoria cone in the south west of the island (see Chapter 4). Features such as the presence of orthopyroxene both as an intercumulus phase and as exsolution lamellae in

augites indicate that these blocks crystallised from a tholeiitic magma. In contrast the rest of the blocks and the exposed volcanics have the petrography and chemistry of members of a mildly alkaline suite.

6.4 RESULTS

Whole-rock K-Ar ages (Table 6.2) determined by Dr. N.H. Gale and J. Symonds at Oxford and Professor J. Dymond at Oregon State University range up to 1.5 ± 0.2 Myr. Using these data and known spreading rates, Bell et al. (1972) suggested that if Ascension had originated on the Mid-Atlantic Ridge, its age was ~7 Myr. This is consistent with the siting of Ascension Island on magnetic anomaly 4 (van Andel and Heath, 1970).

Table 6.3 summarises the Sr results. It can be seen that Sr^{87}/Sr^{86} ratios are homogeneous for most of the rocks (≅0.7029) but for those with high SiO_2 (which also have high Rb and low Sr) the ratio is much higher (up to 0.71352 ± 7). Figs. 6.1 and 6.2 are plots of Sr^{87}/Sr^{86} vs. SiO_2 and Sr respectively. A sudden rise to high ratios is seen in both curves at SiO_2 > 70 wt% and Sr < 15 ppm. These results confirm and significantly extend the range of isotopic compositions reported by Gast et al. (1968).

Table 6.4 reports the Pb isotopic compositions of samples of lavas and blocks. Figs. 6.3 and 6.4 show plots of Pb^{207}/Pb^{204} and Pb^{208}/Pb^{204} vs. Pb^{206}/Pb^{204} respectively. The majority of points cluster together with the data of Gast et al. (1968) and the repeated analyses of these rocks by Sun (1980). However, two samples lie well away from the rest on both plots (Figs. 6.3 and 6.4). These are the gabbroic cumulate blocks DS4 and DS44 from Dark Slope Crater which exhibit tholeiitic affinities. Also plotted on Figs. 6.3 and 6.4 is the position of the M.O.R.B. field of Cohen et al. (1980). DS4 and DS44 are seen to have considerable affinities with M.O.R.B. at least as regards Pb data.

6.5 DISCUSSION

Fig. 6.5 is a plot of Sr^{87}/Sr^{86} vs. Pb^{206}/Pb^{207}. This affirms the M.O.R.B. character of the Pb and Sr isotopic composition of DS4 and DS44, and also shows the agreement between data for the rest of the rocks and those previously published.

There are two obvious hypotheses for the origin of the Dark Slope Crater gabbroic cumulates which satisfy both isotopic and petrological data.
(i) They are fragments of ocean crust cumulates which would, of course, have M.O.R.B. characteristics. (ii) They crystallised from a M.O.R.B.-like magma at an early stage in the island's evolution. At this time the island was much closer to the Mid Atlantic Ridge and the source region in the mantle produced depleted partial melts (i.e. having tholeiitic rather than alkaline character, low Sr^{87}/Sr^{86} and less radiogenic Pb). Migration of the island away from the ridge transferred it to a position for which the underlying mantle was less depleted and magmas from this led to the formation of an alkaline suite with more radiogenic Sr and Pb. If this is so, samples dredged from the base of the Ascension pedestal might include older lavas of tholeiitic character.

The specimens with high Sr^{87}/Sr^{86} are blocks and lavas with SiO_2 > 70 wt% which, because of the highly fractionated nature of the silicic magma, contain very low amounts of Sr. This is what would be expected if contamination by a material with high Sr^{87}/Sr^{86} ratio had occurred. The lavas of Kerguelen in the Indian Ocean also have relatively high Sr^{87}/Sr^{86} ratios (Fig. 6.5) but since these do not vary with Sr concentration they are more easily explicable in terms of variability in source regions (Vidal and Dosso, 1978).

Most acceptable models for magma chamber evolution show the evolved salic magma concentrating at the roof of the magma chamber. Hence they are much more susceptible to contamination from fragments of roof sinking into it than is the less evolved magma occurring at lower levels.

6.6 POSTULATED CONTAMINANTS

(i) Relict Continental Crust

This material would be 100+ myr in age. It was suggested by Daly (1925) and Honnorez (1971) that the granite blocks are fragments of ancient continental crust left behind after the opening of the South Atlantic. The petrological similarity between granite blocks and the comendite lavas together with the similarity in Pb^{206}/Pb^{204}, Pb^{207}/Pb^{204} and Pb^{208}/Pb^{204} over the whole suite of analysed rocks (with the exception of the Dark Slope Gabbros) suggest otherwise. The possibility that continental crust with high Sr^{87}/Sr^{86} ratio could have been assimilated to produce the trend shown seems remote given the need for the contaminant to have a very similar Pb composition to the Ascension magmas.

(ii) Seawater

The Sr in seawater has a Sr^{87}/Sr^{86} ratio of 0.709 which could not alone account for the Sr^{87}/Sr^{86} ratio of 0.71352 ± 7 found in sample H30(1).

(iii) Oceanic Sediments

Oceanic sediments in the region of Ascension contain very high concentrations of Sr. The nearest locality sampled by Turekian (1964) is at 01°S, 12°W and contains 1470 ppm Sr. Dasch (1969) reports that the Sr^{87}/Sr^{86} ratio of oceanic sediment near Ascension is 0.7213.

Clear field evidence of caldera collapse, littoral volcanism and explosive eruptions exists on Ascension Island (see Chapter 2), hence the physical conditions favourable for a magma to mix with oceanic sediment did exist. A small amount only of pelagic sediment of the composition stated above need be introduced into the silicic magma in the roof zone of the magma chamber to modify significantly the Sr^{87}/Sr^{86} ratio. The amount of contaminant needed is difficult to quantify since the concentration of Sr in

the acid magma would decrease after homogenisation if fractionation of feldspar subsequently occurred, since Sr is more strongly partitioned into feldspar than magma of this composition. Some idea of the amount of contamination is desirable, however, for determining its effect on the Pb isotopic composition. Calculation of this requires a knowledge of the initial Sr and Pb concentrations of the original granite magma. If it is assumed that no Sr is lost subsequent to homogenisation then the value obtained for the amount of contaminant is the minimum necessary to give the observed Sr^{87}/Sr^{86} ratio. It is also necessary to assume complete assimilation of the contaminant and thus complete homogenisation of the Sr^{87}/Sr^{86} ratio.

Using the contamination equations of Moorbath et al. (1981) and the previously stated values of Sr and Sr^{87}/Sr^{86} for pelagics, it emerges that the amount of contaminant needed to change the Sr^{87}/Sr^{86} ratio from an assumed original value of 0.703 to its value in H30(1) 0.71352 ± 7 is 0.08%. Assuming the mean Pb isotope ratios for oceanic sediment of Stacey and Kramers (1975) (Pb^{206}/Pb^{204} = 18.81) and a plausible Pb concentration of 100 ppm, the Pb^{206}/Pb^{204} ratio in the granite magma before 0.2% contamination would have been 19.531. This also assumes that no Pb is lost from the magma after assimilation and homogenisation of Pb.

This value of Pb^{206}/Pb^{204} is 0.016 greater than the observed value of 19.515, and hence insignificant compared with the range (0.332) in the alkaline suite. Even if the degree of Sr fractionated after contamination required the amount of contaminant to be an order of magnitude greater, no significant effect on the Pb isotopic composition would be observed. Another consequence of feldspar fractionation is that magmas may acquire higher Sr^{87}/Sr^{86} ratios from feldspars which settle into them and need not come into contact with the original contaminant themselves.

H30(1) has the highest Sr^{87}/Sr^{86} ratio so is presumably the rock which has suffered the larges amount of contamination. This blocks is distinguished

from the other granite (H30(2)) with lower Sr^{87}/Sr^{86} by the occurrence in it of 0.5 modal % eudialyte (found in only three granites so far). Eudialyte is an unusual mineral to find in oversaturated peralkaline plutonic rocks. The Ascension granites usually contain dalyite or vlasovite, both late stage zirconium silicates. Experimental study of vlasovite (Michel-Levy, 1962) indicates that the addition of $CaCO_3$ to the system favours the crystallisation of eudialyte relative to vlasovite. The possibility then arises that the eudialyte in H30(1) is an indication of the addition of $CaCO_3$-rich pelagic sediment.

A hydrothermal system charged with sea water and convecting within the volcanic structure might also affect the transfer of Sr from pelagic sediments into the silicic magma. A large flux would be necessary, given the low solubility of Sr in sea water. Oxygen isotope and other data necessary to test this hypothesis are not yet available.

Baker and McReath (1972) did not consider contamination and postulated that partial melting of early formed acid differentiates could account for the high Sr^{87}/Sr^{86} ratios in the evolved rocks. A mica phase rich in K (and hence Rb) could have accumulated sufficient ^{87}Sr in about 10 /lyr (Baker and McReath, 1972). This time is presumably calculated using the maximum Sr^{87}/Sr^{86} value for the evolved rocks of Gast et al. For the Sr^{87}/Sr^{86} value of H30(1) (0.7135) much longer would be needed. This is not reconcilable with Ascension's position on the flank of the Mid Atlantic Ridge and the calculated age of the island, based on spreading rates, of Bell et al. (1972). Baker and McReath themselves admit that such a two stage model does not explain the other chemical features of Ascension and it was concluded in Section 4.14 and by Harris and Bell (1982) that the granites were unlikely to have been formed by partial melting of intermediate coarse grained material on trace element grounds.

6.7 CONCLUSIONS

It would appear that this work offers no support for the contention that the Ascension granite blocks are fragments of old continental material (Daly, 1975; Honnorez, 1971). A suite of gabbroic blocks seem either to be fragments of oceanic crust, or slowly cooled equivalents of early tholeiitic M.O.R.B.-like magmas. Contamination of the evolved magmas by material with high Sr^{87}/Sr^{86} ratios is required to explain the Sr isotope data. The most likely candidate is oceanic sediment, though the additional effects of sea water contamination must not be ruled out. The isotopic data are consistent with the evolved blocks (granites) and lavas (comendites) sharing the same liquid line of descent.

Chapter 6 - Addendum

Contamination by Radiogenic Strontium from Oceanic Sediment?

In Chapter 6 high $^{87}Sr/^{86}Sr$ ratios in some salic blocks and lavas were attributed to the incorporation [by the evolving magma] of oceanic sediment, containing highly radiogenic Sr. Because these rocks are very young (no rocks from Ascension have been dated by K-Ar at >1.5 ± 0.2 Ma) it was assumed that the initial $^{87}Sr/^{86}Sr$ ratios were equal to those observed. It has since been pointed out (B.R. Doe, M.F. Thirlwall: pers. comm.) that in rocks such as these, with high Rb/Sr ratios, an age correction may be significant even for an age less than 1.5 Ma.

The age correction is approximated by $(^{87}Rb/^{86}Sr) .\lambda t$, directly proportional to Rb/Sr ratio and age. The accurate determination of the Sr content of these samples is therefore particularly important as it is in the region of 2 ppm so that a small error in Sr will result in a much larger inaccuracy in Rb/Sr. (Rb concentrations are of the order of 100 ppm).

The four rocks with high $^{87}Sr/^{86}Sr$ (originally analysed by the much less accurate X.R.F. method) have now been re-analysed for Rb and Sr by mass spectrometric isotope dilution employing a mixed spike. The results are given in Table 6.3a together with the calculated age corrections and the corrected $^{87}Sr/^{86}Sr$ ratios assuming an age of 1.5 Ma for all samples.

Table 6.3a shows that it is probable that contamination affected H30(1), H30(2) and possibly 15255. The only other possibility is that these samples are older than the others.

Table 6.3b gives the calculated age of the samples assuming that no incorporation of radiogenic Sr occurred and an initial ratio of 0.7029, which is the mean initial value of $^{87}Sr/^{86}Sr$ in those rocks with small Rb/Sr and hence a minimal age correction.

Discussion

It may be seen from Table 6.3b that the two granite blocks, H30(1) and H30(2), would require ages of 4.5 Ma and 3.5 Ma respectively to give the observed $^{87}Sr/^{86}Sr$ ratios from initial $^{87}Sr/^{86}Sr$ ratios as low as 0.7029. Three possible explanations are:

(i) These rocks crystallized during earlier stages of the island's evolution and were incorporated in material erupted more recently of which representative samples range in age up to 1.5 ± 0.2 Ma [1]. No K-Ar age determinations have been made on the blocks themselves.

(ii) Contamination by sea water now seems much more likely. The affected rocks contain 2-3 ppm Sr and ocean water 7.5 ppm Sr, thus sea water is enriched in Sr relative to the rocks in question. H30(2) is within the sea water range of $^{87}Sr/^{86}Sr$ (= 0.709) and an age of 2 Ma for H30(1) would bring it, too, within the sea water range.

(iii) The rocks are of similar age to the volcanic suite, their high $^{87}Sr/^{86}Sr$ ratios being due to contamination by radiogenic Sr from oceanic sediments as originally suggested. It is also possible that circulating sea water itself transferred Sr from oceanic sediment into the magma giving increased $^{87}Sr/^{86}Sr$ ratios due to both sea water and oceanic sediment.

The great similarity in major and minor element chemistry between the salic lavas (comendites) and blocks (peralkaline granites) strongly suggests that the granites are the slowly cooled equivalents of the comendites. It seems unlikely, therefore, that the granite blocks crystallized some 3 Ma before eruption of the equivalent lavas. The difference in apparent age between H30(1) and H30(2) which on the basis of petrography, obviously once belonged to the same coarse-grained body, is much more easily explained in terms of varying amounts of contamination by radiogenic Sr.

Ascension Island is situated some 120 km west of the median trough of the Mid-Atlantic Ridge and straddles magnetic anomaly 4 (van Andel et al, 1973) indicating a maximum age for the island of 7 Ma. The granite blocks have petrographic features such as miarolitic cavities which suggest a high level of emplacement (i.e. within the oceanic lithosphere). Magma must have been tapped from its mantle source, emplaced within the oceanic lithosphere and allowed to differentiate strongly over 4.5 Ma ago to account for the apparent age of H30(1). Rejection of the contamination hypothesis would require Ascension to have been in existence longer than the dating of samples suggests is the case and at present there seems to be no evidence to indicate this is so.

CHAPTER 7

PHYSICAL PROPERTIES OF THE ASCENSION MAGMAS

7.1 INTRODUCTION

It has been postulated in Chapter 5 that the chemical variation shown by the lavas is a result of crystal fractionation. This chapter considers the constraints imposed on this mechanism by the physical properties of the magmas themselves. These include density, viscosity, temperature and oxygen activity (≡ fugacity) and they may be deduced from chemical analyses of lavas and analyses of the phenocryst and block assemblages.

7.2 DENSITY

The density of a silicate liquid may be calculated from its chemical analysis using the model of Bottinga and Weill (1970). This method converts the analysis into partial molar volumes and uses experimentally determined coefficients of expansion to calculate the density of the silicate liquid at given temperatures above the liquidus. In practice the variation with temperature is small. The densities of selected lavas were computed using a program written by Dr. D.G. Fraser based on Bottinga and Weill's model. Table 7.1 gives the results for a variety of lavas at 1250°C (i.e. well above the liquidus). The range is from 2.76 gcm^{-3} (basalt) to 2.33 gcm^{-3} (comendite).

Densities of possible phenocrysts show a considerable variation with SiO_2 content of the magma. Olivine and clinopyroxene precipitated by a magma increase in density as the magma becomes more salic since the ratio of Fe/Mg in the mineral increases. Feldspar, on the other hand, decreases in density as Na/Ca increases (labradorite to albite) then increases as K/Na increases from albite through anorthoclase to sanidine. Fig. 7.1 is based on fig. 1 of McBirney and Noyes (1979) and shows the variation of density with SiO_2 content of the magma for possible phenocrysts. Densities of minerals were calculated from fig. 1 of McBirney and Noyes (1979) and the composition of each precipitating mineral was taken to be that of the rims of its phenocrysts

(in practice zoning is negligible for olivine and pyroxene). Also plotted on Fig. 7.1 are the densities of magmas from Table 7.1.

7.2.1 Implication of Density for Crystal Settling

It is easily seen from Fig. 7.1 that the density contrast between magnetite, olivine, pyroxene and magma of appropriate composition is significant, the minerals all having the higher density. This is not the case for feldspar. In the SiO_2 poor magmas the density of plagioclase is similar to that of the magma, thus settling of plagioclase would not be as efficient as that of pyroxene, olivine or magnetite and in those magmas with the lowest wt% SiO_2 plagioclase flotation must have been a possibility.

Whether or not a crystal sinks in a magma is dependent not only on the crystal being denser but also on the viscosity of the melt, its structural type and the size of the crystal. These factors are discussed in the next section. The density of the Skaergaard liquid increased as it evolved (McBirney and Noyes, 1979) due to increasing iron. Iron continually decreases with increasing SiO_2 in the Ascension lavas which is an important factor in their decrease in density with SiO_2. If significant iron enrichment had occurred, the settling of feldspar would have been much less feasible.

There is good evidence (Chapters 4 and 5) that there has been significant iron enrichment in some liquids whose 'preservation' must be regarded as fortuitous. Densities calculated from the analysis of the residual liquid from 15243D (a gabbroic block - see Chapter 5.6) and the Cricket Valley pegmatoid are plotted on Fig. 7.1 and it can be seen that they closely approach that of feldspar. Changing iron content in the basic liquids may have exerted an important control over the modal mineralogies of the gabbroic blocks. High Fe content would cause much greater differences in settling velocities of feldspar and the ferromagnesian minerals which could lead to olivine rich and feldspar rich layers when the crystals eventially settled.

7.3 VISCOSITY

Using the model of Shaw (1972), Arrhenius plots of ln η vs. $10^4/T$ were obtained for selected lavas (Fig. 7.2). Assuming approximate liquidus temperatures for the various magmas, the relationship between wt% SiO_2 and viscosity may be determined. Temperatures are assumed to lie on the line indicated on Fig. 7.2. Table 7.2b gives viscosities for the six lavas and it can be seen that the acid magmas are approximately six orders of magnitude more viscous than the most basic, though these figures were made assuming the melt was free of H_2O,Cl,Fetc., which, if they were present, would have an important influence on viscosity (see below).

7.3.1 Constraints on Crystal Settling Due to Viscosity

For a given particle size, and using the density contrast between crystal and magma of Fig. 7.1 , the initial settling velocity of a crystal may be calculated using Stokes' equation:

$$V = \frac{2r^2 g(\rho_1 - \rho_2)}{9\eta}$$

where V = the velocity of a sphere of radius r and density ρ_1 in a liquid of density ρ_2 and viscosity η. This velocity would not be expected to remain constant due to the effect of later addition to the crystal, but it gives a good indication of the likelihood of a particular mineral being removed by settling.

Table 7.2a gives calculated initial settling velocities for 1 cm diameter spherical phenocrysts of olivine, pyroxene and feldspar in the six magmas from Fig. 7.2. It may be seen that lavas H5L and A63L crystals would settle relatively fast (>100 m per year). However, in A29L, Ob4, Ob3 and A35 settling does not appear to proceed very rapidly. Feldspar, postulated as the major fractionating phase in the salic magmas (see Chapter 5) is not likely to settle in those magmas with $SiO_2 > 65$.

7.3.2 Possible Role of H_2O and Volatiles in Crystal Settling

Silicate melts probably contain linked chains of Si and O, each Si linked to the next by an oxygen molecule (bridging oxygen) (see Wood and Fraser, 1976 for a review). H_2O dissolved in a magma as OH^- together with Cl^-, F^- etc. react with the oxo-bridges causing depolymerisation of the Si-O chains thus reducing the viscosity of the liquid. Because H_2O, F^- and Cl^- have relatively low molecular/atomic weights, addition of only a small weight percent will greatly affect the slope of the Ahrennius plots of Fig. 7.2.

As an example, the comendite + 5% H_2O (A35) would have a very similar viscosity to the basalt (H5L) - see Table 7.2b. The presence of Cl^- and F^- would presumably have a similar effect (not included in Bottinga and Weill's model). 5% H_2O is quite water rich and Bailey and Cooper (1978) concluded from experimental work that peralkaline acid lavas were erupted H_2O free and never contained any H_2O. Certainly the microprobe analyses of the obsidians Ob1-5 support this, having close to 100% totals. There is no data on F^-. If the Ascension magmas evolved in a closed system, this seems to suggest that the basic magmas were also water free.

7.4 OTHER OBJECTIONS TO CRYSTAL SETTLING ON PHYSICAL GROUNDS

When the crater of Kilauea Iki was filled to a depth of 100 m in 1959 the basalt contained phenocrysts of olivine that were 2-3 mm in length. When recently drilled the olivine crystals were found to have settled very little and far less than that predicted by Stokes' Law. Lava flows and sills in which settling has been demonstrated indicate that olivine may sink in a hot agitated liquid but not in one that is static and has begun to nucleate other phases (McBirney and Noyes, 1979). Certainly the evolving Ascension magmas would be expected to be hotter than the Kilauea Iki lava lake.

McBirney and Noyes (1979) reassessed the crystallisation history of the Skaergaard intrusion and concluded that the crystallising magma did not behave as a Newtonian fluid, hence Stokes' Law did not apply. Their evidence concerned the density relations of the minerals and the evolving liquid. Plagioclase was always less dense than the liquid, the ferromagnesian minerals denser, yet plagioclase was abundant in the lower zones of the layered series and ferromagnesian minerals are important constituents of the rocks formed under the roof. McBirney and Noyes (1979) explained this paradox by postulating that the majority of the intrusion crystallised in situ and the non-Newtonian properties of the liquid prevented plagioclase floating and ferromagnesians from sinking.

There is no way, at present, that it can be assessed whether the Ascension magmas were either Newtonian or non-Newtonian but the possibilities should at least be considered.

As shown in Section 4 and 5, the pegmatoid from Cricket Valley crystallised in situ and the residual liquid still managed to evolve from hawaiite to peralkaline acid composition by crystal fractionation without settling. It should be remembered therefore that crystal fractionation and crystal settling are not always synonymous.

7.5 TEMPERATURES AND OXYGEN ACTIVITY FROM MINERAL-MINERAL EQUILIBRIA

7.5.1 Clinopyroxene-Orthopyroxene Geothermometer

Numerous attempts (e.g. Wood and Banno, 1974; Wells, 1977) have been made to calibrate the temperature dependence of the reaction

$$\underset{\text{(Opx)}}{Mg_2Si_2O_6} \rightleftarrows \underset{\text{(Cpx)}}{Mg_2Si_2O_6}$$

between coexisting ortho and clinopyroxene. The most recent and perhaps the

most widely accepted is that of Wells (1977) who from experimental data derived the following empirical relationship for temperature and pyroxene composition:

$$T = \frac{7341}{3.355 + 2.44\, X_{Fe}^{Opx} - \ln K} \qquad (1)$$

where $K = \dfrac{a_{Mg_2\,Si_2O_6}^{Cpx}}{a_{Mg_2\,Si_2O_6}^{Opx}}$ and $a_{Mg_2\,Si_2O_6}^{Cpx/Opx} = X_{Mg}^{M_2} \cdot X_{Mg}^{M_2} \cdot \gamma_{Mg_2\,Si_2O_6}$

Local charge balance is assumed in that tetrahedral Al is completely coupled to octahedral Al. It is assumed that Mg^{2+}, Fe^{2+}, Mn^{2+}, Na^{+} and Ca^{2+} occupy M_2 sites and Mg^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+}, Ti^{4+} and Cr^{3+} occupy M_1 sites.

$$\therefore \quad X_{Mg_2\,Si_2O_6}^{M_2} = \left(\frac{Mg^{2+}}{Ca^{2+} + Mg^{2+} + Fe^{2+} + Mn^{2+} + Na^{+}}\right) M_2$$

$$\text{and} \quad X_{Mg_2\,Si_2O_6}^{M_1} = \left(\frac{Mg^{2+}}{Mg^{2+} + Fe^{2+} + Fe^{3+} + Al^{3+} + Ti^{4+} + Cr^{3+}}\right) M_1$$

It is also assumed that Mg^{2+} and Fe^{2+} mix randomly between sites. The pyroxenes were recalculated using a program written by D.G. Fraser and adapted to run on a Commodore PET by S. Beswetherick. The program assigns cations to M_1 and M_2 sites using the method of Wood and Banno (1973) and from this calculates activities which are substituted into the equation of Wells (1977) (equation (1)). Results are given in Table 7.3.

7.5.2 Discussion of Results

Davies and Boyd (1966) showed that the opx-cpx thermometer was almost completely pressure insensitive and the data of Wells (1977) show that for Al_2O_3 content in cpx up to 12 wt%, K is not related to the amount of Al_2O_3.

This thermometer, in spite of its apparent reliability and wealth of supporting data is not especially useful for the Ascension rocks, because only some blocks and no lavas contain the necessary pyroxenes. It is also apparent from Chapter 4 that although quite a large number of blocks contain two pyroxenes, the orthopyroxene from many has formed by reaction with olivine and hence is not likely to have formed in equilibrium with the clinopyroxene in the block. Even in the two genuine cases of two coexisting and apparently comagmatic pyroxenes, fine scale exsolution is found and this results in considerable variation in Ca content and hence uncertainty in calculated temperature.

These two blocks are 15227(4) and 15227(13). 15227(13) suffers especially from exsolution (see Fig. 4.5). 15227(4) has intercumulus orthopyroxene and from the composition of its plagioclase and olivine it would be expected to give a lower temperature than 15227(13). This is not the case, however. 15227(4) shows less exsolution and therefore less variation in Ca content of its pyroxenes so it presumably is the more accurate measure of temperature.

All the other temperatures given in Table 7.3 use opx formed from reaction with olivine; since this is not formed in equilibrium with clinopyroxene they are meaningless.

7.5.3 Fe-Ti Oxide Geothermometer and Oxygen Barometer

Buddington and Lindsley (1964) first proposed the use of coexisting ilmenite-hematite, magnetite-ulvospinel solid solutions in the system FeO-Fe_2O_3-TiO_2 as a geothermometer and measure of oxygen activity. The reaction

$$Fe\ TiO_3\ (ilm) + Fe_3O_4\ (Mgt) \rightleftarrows Fe_2O_3\ (ilm) + Fe_2\ TiO_4\ (Mgt)$$

[where Fe_2O_3 (ilm) = moles Fe_2O_3 in ilmenite etc.]

does not involve oxygen and is hence the basis for the thermometer.

Experiments suggest the following empirical relationship

$$\ln K_D = -8155/T + 4.59 \quad (T \text{ is in K}) \qquad (2)$$

where $K_D = \frac{X(ulv)}{1-X(ulv)} \cdot \frac{1-X(ilm)}{X(ilm)}$ (Powell and Powell, 1977)

The reaction $6FeTiO_3 + 2Fe_3O_4 \quad 6Fe_2TiO_4 + O_2$ (gas) can be calibrated as an oxygen barometer giving the empirical relationship

$$\ln aO_2 = \ln[(X^6ilm\,[1-Xulv]^2/X^6_{ulv}).(Xulv(1-Xilm)/(1-Xulv)Xilm)^{10.702}]-4.94 \qquad (3)$$

Fig. 7.3 is a graph of Xulv vs. Xilm contoured for T (°C) and aO_2. Buddington and Lindsley refer to oxygen fugacity (fO_2) rather than activity (aO_2). This is not strictly correct (Powell and Powell, 1977) as fO_2 may only refer to the activity of <u>pure</u> O_2 at the P and T of interest.

Most natural coexisting Fe-Ti oxides (including those from Ascension Island) deviate from the system $FeO-Fe_2O_3-TiO_2$; in this case by containing significant (4-12 wt%) MgO and Al_2O_3. The thermometer and oxygen barometer may still be applied if the thermodynamics of mgt_{ss} and ilm_{ss} can be adequately represented by a model of ideal mixing of molecular species, i.e.

$$\ln K_D = \ln(Xulv.Xhem/Xmgt\ Xilm) = -8155/T + 4.59 \qquad (4)$$

and

$$\ln aO_2 = \ln\,[(X^2mgt.\ X^6ilm/X^6ulv).(Xulv.Xhem/Xmgt.Xilm)^{10.702}]-4.94 \qquad (5)$$

It is also necessary to recast analyses of coexisting ilm_{ss} and mgt_{ss} in terms of end members and calculate the maximum and minimum values of Xmgt, Xulv etc. for a particular pair of analyses, then recombine them in the most unfavourable ways to get the maximum variation when the values are put into equations (4) and (5). For mgt_{ss}; if ni = amount of i in an analysis and n_{m^2} = amount of divalent cations other than Fe^{2+};

$$\max X.ulv = n_{Ti} \text{ and therefore } \min X.mgt = \tfrac{1}{2}\, n_{Fe^{3+}} - n_{m^2}$$

and

$$\max X_{mgt} = \tfrac{1}{2}\, n_{Fe^{3+}} \text{ and } \min X_{ulv} = n_{Ti} - \tfrac{1}{2}\, n_{m^2} \qquad \text{(Powell and Powell, 1977)}$$

For ilmenite, if n_{m^3} = number of trivalent cations other than Fe^{3+} then:

$$\max X_{hem} = \tfrac{1}{2}\, n_{Fe^{3+}} \text{ and } \min X_{ilm} = n_{Ti} - n_{m^2}$$

$$\max X_{ilm} = n_{Ti} \text{ and } \min X_{hem} = \tfrac{1}{2}\, n_{Fe^{3+}} - n_{m^3} \qquad \text{(Powell and Powell, 1977)}$$

7.5.4 Results

One faces two problems when using iron oxides in this way:

(i) Microprobe analyses do not distinguish between Fe^{2+} and Fe^{3+} so a method of recalculating the analyses must be found. In this case the charge balance method of Carmichael (1967) was used.

(ii) No Ascension lavas have been found to contain coexisting $magnetite_{ss}$ and $ilmenite_{ss}$ and though many blocks contain both, oxidation has in most cases resulted in exsolution within individual grains, thus making their original compositions subject to great uncertainty, hence useless for temperature/aO_2 determination (see Chapter 4).

Careful investigation with a reflected light microscope enabled suitable coexisting $magnetite_{ss}$ and $ilmenite_{ss}$ in five blocks to be found (Chapter 4). These are in DSA3, HDSA5 (from Dark Slope Crater), H7(5) (from Middleton's), H60(4) (NASA facies) and H95(7) (from Lady Hill). No exsolution occurs and consequently the analyses from the same block show very good agreement.

Table 7.4 gives the average analyses for these three blocks for the $magnetite_{ss}$ $ilmenite_{ss}$ pairs. These are plotted onto Fig. 7.3 showing their equilibrium temperatures and aO_2 to be similar. The presence of significant amounts of Al & Mg mean that max ilm min ilm etc. are significantly different. Fig. 7.4 shows how the max and min values of T and aO_2 are obtainable and these are presented in Table 7.5. It is obvious that there is considerable

uncertainty in all three values.

7.5.5 Constraints on T and aO_2 for the Granite Blocks from their Assemblages

Nicholls and Carmichael (1969) suggested that there was a general antipathetic relationship between aenigmatite and Fe-Ti oxides in peralkaline rocks. They considered the two reactions:

$$\underset{(\beta\text{ phase})}{4\ Fe_3O_4} + \underset{(\text{glass})}{6\ Na_2\ Si_2O_5} + \underset{(\text{quartz})}{12\ SiO_2} + O_2 \quad \underset{(\text{aegirine})}{12\ Na\ Fe^{3+}\ Si_2O_6}$$

$$\underset{(\text{aenigmatite})}{Na_2\ Fe_5\ Ti\ Si_6O_{20}} + \underset{(\text{glass})}{Na_2\ Si_2O_5} + O_2 \quad \underset{(\text{aegirine})}{4\ Na\ Fe^{3+}\ Si_2O_6} + \underset{(\alpha\text{ phase})}{Fe\ TiO_3}$$

as representative of the occurrence of aenigmatite and aegirine in siliceous sodic peralkaline rocks. On this basis, and making allowance for solid solutions in the oxide phases and aegirine, and for the presence of $Na_2\ Si_2O_5$ as a component of the liquid, the oxygen activity can be calculated for the two reactions. Fig. 7.5 shows the position of the reaction curves in log aO_2 ($\equiv$ log fO_2 of Nicholls and Carmichael) - T space, assuming activities of all components in the melt = 1. The upper limit of hydroxy-sodamphiboles is also shown (from Ernst, 1962). For detail see Fig. 7.5. The Ascension granites contain a variety of these phases including aenigmatite, aegirine and amphibole which enable their position on Fig. 7.5 to be determined. Most granites contain the sodic amphibole arfvedsonite together with aegirine and some contain aenigmatite in addition. These rocks may also contain the sodium zirconium silicate, vlasovite, and the similar potassium zirconium silicate, dalyite, the former of which may be related to the aegirine fayalite + sodium + disilicate + quartz curve (Chapter 4). Opaques are almost completely absent and olivine while it is present in a few blocks, is clearly out of

equilibrium. The blocks themselves give no evidence of an antipathetic relationship between aenigmatite and vlasovite. The assemblages as described in Chapter 4 place the granite in the "no oxide" field of Fig. 7.5 close to or straddling the amphibole limit of stability, since in numerous cases amphibole seems to be altering to aegirine (see Plate 4.37). It must be stressed that there is considerable uncertainty in the position of some of these reaction curves caused by the assumption that a^{i} melt = 1. The position of the intersection of the aenigmatite = aegirine + ilmenite and aegirine = fayalite + sodium disilicate + quartz curves for varying activities of sodium disilicate in the melt is shown on Fig. 7.5.

Fig. 7.6 shows the pH_2O-T field for eudialyte experimentally synthesised from Si, Na, Ca, Zr and O in the presence of pure water (Ahmed and Mackenzie, 1978). The granite blocks contain dalyite ($K_2Zr\ Si_6O_{15}$) and vlasovite ($Na_2\ Zr\ Si_4O_{11}$) together with some eudialyte. The eudialyte is only found in three blocks and then only with dalyite. Dalyite and vlasovite themselves never occur together. The blocks with eudialyte would seem therefore to have crystallised around T > 700°C and since keldyshite is never found pH_2O may be > 1 kb (see Fig. 7.6).

7.6 TEMPERATURES CALCULATED FROM MINERAL-LIQUID EQUILIBRIA

In the absence of suitable mineral-mineral equilibria thermometers, especially in the lavas, liquid-mineral equilibria may be used. This has certain limitations.

(i) For lava-phenocryst pairs (which is what most of these thermometers are) the two may not even have been in equilibrium because the crystal may have settled into the magma.

(ii) Difficulty in obtaining liquid compositions. Lava analyses are quenched liquid + phenocrysts rather than just quenched liquid. This is less of a problem than it may have been since the lavas are not especially porphyritic.

(iii) The melt must be assumed to have been homogeneous but in some cases (e.g. A63(1)) there is evidence that it was not.

(iv) Much less is known about the mixing properties of silicate melts than is for minerals. Calculation of equilibrium temperatures from coexisting liquid-mineral will then be subject to more uncertainty than for mineral-mineral equilibria.

Block 15243D and the Cricket Valley pegmatoid are especially useful in these studies since we can be much more certain of equilibrium liquid-crystal compositions. In the case of 15243D the liquid is quenched in the interstices between pyroxene and plagioclase grains and in the pegmatoid the bulk composition is the original liquid and the large plagioclase crystals are the initially formed minerals (see Chapter 4 for details).

Feldspar is the most common phenocryst phase in these lavas and feldspar-liquid equilibria studies are the basis for these temperature calculations.

7.6.1 Kudo and Weill Plagioclase-Liquid Thermometer

This is based on the exchange of Na, Si and Ca, Al between plagioclase and the melt. This may be written:

$$(Na\ SiO_{2.5})\ Al\ Si_2O_{5.5} + (Ca\ Al\ O_{2.5})\ Al\ Si_2O_{5.5}$$

plag. $\downarrow\uparrow$ melt

$$(Na\ SiO_{2.5})\ Al\ Si_2O_{5.5} + (Ca\ Al\ O_{2.5})\ Al\ Si_2O_{5.5}$$

melt plag.

Using data from the literature Kudo and Weill (1970) produced an empirical geothermometer, see Table 7.6. The constants A and K vary with pH_2O so the calculations may be made for a range of pH_2O values. Table 7.7 gives the values of $\lambda\ \sigma\ \phi'$ and X An/(XAn + XAb) for selected lavas where whole bulk rock and phenocryst analyses are available. Table 7.8 gives calculated

temperatures for pH_2O = 0 and pH_2O = total P = 1 kb using the range of phenocryst compositions to give maximum and minimum temperatures.

7.6.2 Plagioclase Thermometer of Drake (1976)

A different approach has been used by Drake (1976) who calculated the distribution coefficients for Na, Al, Si and Ca between feldspar and melt and showed that they were composition as well as T dependent. He managed to skirt around the problem of not knowing the complex mixing properties of a silicate melt by considering the simple mixing of complex melt components, rather than the complex mixing of simple melt components.

i.e. $Na\,Al\,O_2 + 3\,SiO_2 \rightleftarrows Na\,Al\,Si_3O_8$

This gives the following relationship with temperature

$$\frac{X^{Plag}_{NaAlSi_3O_8}}{X^{melt}_{NaAlO_2} \cdot (X^{melt}_{SiO_2})^3} = e^{(\frac{6100}{T} - 2.29)} \qquad (6)$$

The equivalent thermometer for anorthite rather than albite is not applicable because $Ca\,Al_2\,O_4$ does not mix ideally with the other melt components, as $Na\,Al\,O_2$ appears to do.

A particular problem when dealing with silicate melts is how to assign realistic molecular weights to the various melt components (Burnham, 1975) so that the molecular proportions may be calculated. Drake (1976) divided the melt into various molecular species, with each mono or divalent ion being balanced by one or two trivalent ions. Drake only considered the network forming components of the melt and assumed that the network forming components and the network modifying components form separate quasi-lattices. This approach results in a "norm" for the liquid consisting of hypothetical melt forming species (= "liquid norm"). Liquid norms for selected lavas are given in Table 7.9. These values are used with the plagioclase analyses and equation (6) to calculate temperatures of liquid-plagioclase equilibria.

For pH_2O = p total = 2 kb the revised equation (6) is:

$$\frac{X^{Plag}_{NaAlSi_3O_8}}{X^{melt}_{NaAlO_2} \cdot (X^{melt}_{SiO_2})^3} = e^{(\frac{6100}{T} - 2.915)} \qquad (7)$$

and values of T are given for pH_2O = 2 kb in Table 7.10.

7.6.3 Comparison of Liquid-Plagioclase Equilibrium Temperatures

Although Kudo and Weill (1970) quote a statistical error of ± 43°C and Drake (1976) an error of ± 60°C, the temperatures calculated for the same rocks using the two methods are 100-200°C different, the Kudo and Weill equation giving the higher temperatures. The difference may be due to the feldspar crystallising at high pH_2O (c. 2 kb). It is easily seen that in both methods the calculated temperatures are affected by pH_2O. H_2O must therefore be a network modifier and will affect other melt components. The effect of H_2O on complex melt components is less than that on simple oxide components so dP/dT of Drake's (1976) thermometer will be higher than that of Kudo and Weill (1970). This means that the two curves will approach each other at higher pH_2O (Betton, 1978) which suggests differences in temperature for the calculations are a reflection of crystallisation at higher pH_2O. There is no petrographic evidence for this, however, such as the presence of amphibole phenocrysts.

7.7 CRYSTALLISATION TEMPERATURES OF MAGMAS FROM CONSIDERATION OF DISTRIBUTION COEFFICIENTS

7.7.1 Method

At present, thermodynamic data and models are insufficient to allow calculation of temperatures of most complex multicomponent systems. An alternative approach is to use the large amount of equilibrium temperature,

pressure and composition data which are available for simple systems as well as rock compositions. Langmuir and Hanson (1979) used this large data base to calculate single component distribution coefficients as a function of temperature, pressure and composition. These coefficients can then be combined with mass balance, and constraints provided by the stoichiometry of the solid phase to calculate phase equilibria. This method permits rigorous calculation of the liquidus temperatures and compositions of phases involved with crystallisation.

All Ascension lava analyses and the quenched mesostasis of 15243D and the pegmatoid analyses were processed using a computer program (written by R. Vocke) which uses the methods of Langmuir and Hanson to calculate liquid temperatures for plagioclase and olivine saturation. All the input required was the chemical analysis in wt % oxides. The possible crystallisation of pyroxene is ignored because of its complex solid solution and variation in K_Ds. Iron oxide crystallisation is also assumed not to occur.

Fig. 7.7 shows the calculated plagioclase and olivine saturation temperatures vs. SiO_2 for all the analyses processed and Table 7.11 gives the calculated temperotures and plagioclase and olivine compositions compared with the observed phenocryst compositions for those lavas for which this information is available.

7.7.2 Discussion of Results

Several points are worth comment from Fig. 7.7.

(1) Apart from the low SiO_2 end of the series the plagioclase saturation surface is always at a higher temperature than the olivine saturation surface. This may be partly due to most lavas being plagioclase phyric but most are not particularly phenocryst rich (see Chapter 3 for details on this) and should therefore approximate in composition to liquids.

(2) At SiO_2 65 wt % plagioclase ceases to become the precipitating

feldspar and at SiO_2 > 65 the calculated temperature is simply the temperature of albite in equilibrium with the magmas. Alkali feldspar becomes a crystallising phase but is not included in the programme of Langmuir and Hanson (1979). The feldspar saturation temperature would be expected to drop until it reached the isobaric minimum (at Ab_{58}, for dry melts).

(3) For those lavas with known phenocryst compositions the calculated and observed plagioclase compositions agree quite well (Table 7.11). Calculated olivine and observed olivine compositions do not agree to anything like the same degree.

(4) The mesostasis of 15243B gave calculated feldspar and olivine compositions which were much more albitic/fayalitic than the cumulus phases which suggests that the liquid composition was affected by quench crystallisation, before becoming completely glassy.

(5) The analyses of the pegmatoid (H59(1 and 11)) are those which are most likely to represent a true magmatic liquid (see Chapter 4). On Fig. 7.7 it may be seen that olivine and plagioclase saturation temperatures are approximately the same and though the calculated olivine composition does not agree with that observed (Table 7.11) calculated and observed plagioclase compositions are identical.

When Langmuir and Hanson devised this approach, they were considering tholeiitic basalts in which the crystallisation of pyroxene was considered to occur at lower temperatures than olivine and plagioclase (see Bender et al., 1978) and iron oxide crystallisation was not considered at all. These assumptions may not be valid for the Ascension lavas; the gabbroic blocks certainly suggest pyroxene to be later crystallising than olivine or plagioclase but iron oxide fractionation has been shown to occur (see Chapter 5).

For lavas with SiO_2 > c. 50 wt % the plagioclase saturation temperature is greater than that of olivine. On cooling such a liquid from supersolidus temperatures plagioclase will crystallise and the residual liquid will change

accordingly. In order for SiO_2 in the liquid to increase a plagioclase with An > 90 must crystallise. The phenocrysts analysed (Chapter 3) are rarely > An_{70} so a basic magma with composition of, for example, DS19L could not fractionate to the more salic types observed. A possible alternative fractionation path is given by the Cricket Valley pegmatoid and the residual liquid quenched in the gabbroic block 15243B (see Chapter 5 for details). These have significantly higher FeO for their SiO_2 content than do the lavas and on Fig. 7.7 it can be seen that for the pegmatoid liquid, the olivine and plagioclase liquid are at the same temperature. The implication is that for the basic lavas to have evolved via olivine fractionation (which the evidence from Chapters 4 and 5 suggest they have done) they must have been significantly richer in Fe at the time. This 'excess' FeO could have been lost by subsequent fractionation of iron oxides. Thus the basic lavas (at least) do not seem to represent a true liquid descent but are derivatives of an original, more iron rich, fractionation sequence. It is interesting that the quench crystals in the residual glass of 15243D are predominantly iron oxide.

It is easy to calculate (using the program of Langmuir and Hanson) how much additional FeO is needed for the olivine saturation temperature of a lava to be above that of plagioclase. 17364 is a lava which is almost completely aphyric and hence must approximate to a genuine liquid in composition. Table 7.12 shows the olivine and plagioclase saturation temperatures as varying wt % of FeO are added to the analysis. A magma of this composition would need (∿) 5 wt % extra FeO before it could precipitate olivine before plagioclase. However, the calculated olivine composition for these iron rich magmas is much more fayalitic (Fa_{40}) than the olivine phenocrysts in the same magma (Fo_{20-30}). This is a major objection to this fractionation mechanism. Clearly, there is a need for melting experiments on the Ascension lavas which would, hopefully, resolve

some of these inconsistencies.

7.8 CONCLUSIONS

1) Density and viscosity determinations are consistent with the idea that plagioclase, olivine, magnetite and clinopyroxene would settle once they crystallised in basic-intermediate liquids. The viscosity of the acid liquids would seem to prevent crystal settling.

2) Suitable mineral-mineral equilibria for determining temperature and aO_2 at the time of crystallisation are rare. Temperatures of the order of 1000-1100°C and ln $aO_2 \sim -24$ appear to be appropriate for the gabbroic blocks of Dark Slope Crater and Middleton's Ridge.

3) Liquid-feldspar equilibria predict varied temperatures for the same lava. Greater agreement is obtained for pH_2O above 2 kb which may be indicative that feldspar crystallised at elevated pH_2O.

4) Calculation of olivine and plagioclase saturation temperatures in basic magmas gives results which are at odds with the petrography and previously postulated fractionation paths. It is necessary for the lavas to have been considerably (25 wt %) richer in FeO before olivine saturation temperatures were above those of plagioclase. Iron would then have been subsequently depleted by fractionation of opaques. This observation is consistent with the views previously recorded (Chapter 5):

i) That short term iron enrichment seems to have been present even though the lavas indicate consistent iron depeletion.

ii) That the Cricket Valley pegmatoid represents an iron rich magma not represented by the exposed lavas.

A major objection is that olivine crystallising from such a magma would be much more fayalitic than the observed olivine phenocrysts. A series of melting experiments on Ascension lavas would be extremely useful in resolving these difficulties.

CHAPTER 8

RARE EARTH ELEMENTS AND YTTRIUM IN LAVAS AND BLOCKS, AND THEIR ACCESSORY MINERALS

8.1 INTRODUCTION

Eight rocks (4 lavas and 4 blocks) have been analysed for REE by INAA methods at the Open University (analyst O.W. Thorpe) - see Table 8.1. Y, determined by XRF and discussed in Chapter 5,behaves like a REE and on ionic radii criteria may be considered to behave most like the REE holmium (which is impossible to determine (by both INAA and microprobe) due to interferences and low abundance). The REE and Y content of apatites, zircons and (in one granite block) eudialyte were determined for a number of blocks using the microprobe. Although relatively few REE whole rock analyses have been made, they provide considerable information about the processes which contributed to the variation in composition seen in the volcanics and associated blocks. It is appropriate, then, that REE (+ Y) be considered in a short chapter separate from the main whole rock chapter.

8.2 WHOLE ROCK REE ABUNDANCE

8.2.1 Results

Table 8.1 gives a brief summary of the major petrographic and chemical features of the eight analysed rocks. The criteria for selection were as follows:

H30(1), H30(2), A35 — Representative of the most salic rocks, they also show high Sr^{87}/Sr^{86} ratios

H81L, A63(1), A29 — Representative basic-intermediate lavas

DS44 is a typical plagioclase-gabbro

H59(1) is a sample of the Cricket Valley pegmatoid

Table 8.2 gives the concentrations of the REE + Y (see Appendix for analytical methods) and detection limits and Fig. 8.1 is a plot of concentration of REE ÷ concentration in chondrites vs. atomic number for the eight analysed rocks. Chondrite 'normalising' values are given in Table A (Appendix). Chondrite normalised values for elements are denoted as Ce_N, Y_N, La_N etc.

The REE are incompatible, i.e. they have $K_D \ll 1$, where

$$K_D = \frac{\text{concentration in crystal}}{\text{concentration in liquid}}$$

Thus processes which involve crystallisation or partial melting change the concentrations of REE in the melt. What makes the REE especially useful is the gradual increase in K_D with atomic number. In these rocks a fairly smooth variation in chondrite normalised value with atomic number for all the rocks results and this allows constraints to be placed on the magma genesis.

The major features of Fig. 8.1 are as follows:

(i) The plots are approximately parallel with $Ce_N/Y_N \sim 5$.

(ii) Strong europium anomalies are displayed in certain plots. Those for A35, H30(1) and H30(2) display marked negative Eu anomalies while those for A29 and DS44 show positive Eu anomalies.

(iii) The comendite (A35) and the two granite blocks (H30(1) and H30(2)) have very similar REE plots.

(iv) The acid rocks (A35, H30(1) and H30(2)) have higher concentrations of heavy REE (HREE) than would be expected, assuming only crystal fractionation to have occurred in a closed system magma chamber.

(v) Excluding Eu, the acid rocks contain about four times the concentration for each REE than the hawaiite (H81L).

8.2.2 Interpretation of REE Patterns

Similar parallel REE patterns are shown by the lavas of Reunion

(Zielinski, 1975). In the case of some Reunion syenites and hawaiites the REE patterns show a different slope to the majority and Zielinski (1975) explained this by presuming them to be derived from a different source. REE plots for the Ascension specimens are consistent with their having the same source. The parallel patterns with higher REE content in the more salic rocks could have resulted either from differential partial melting of the same older basalt source, or by fractional crystallisation of an initial magma of the same composition. Petrographic evidence presented in Chapters 4 and 5 give considerable support for the latter.

Europium is particularly useful as an indicator that feldspar fractionation has taken place. Feldspars show particular preference for divalent Eu compared to the remaining REE. K_D's for Eu depend strongly on oxygen activity, but in most natural magmas there is an appreciable Eu^{2+}/Eu^{3+} ratio (Cox et al., 1978) and this increases at low temperatures. Crystallisation of feldspar (especially alkali feldspar) results in a progressively more negative Eu anomaly, together with enrichment of incompatible elements. The REE profiles for A35, H30(1) and H30(2) are a good indication that feldspar fractionation has taken place during their evolution.

DS44 shows a large positive Eu anomaly which would be expected of a plagioclase rich cumulate. It has been shown in Chapter 6 that DS44 did not crystallise from the same parent magmas as the majority of lavas, but it would be expected that a plagioclase rich cumulate from Middleton's would also have a positive Eu anomaly. A29L also shows a positive Eu anomaly and A63L a slight one. Both these rocks are unusually feldsparphyric and it seems that they have accumulated more feldspar than they have lost hence Eu is increased. The flat profile shown by H81L does not necessarily mean that its evolution did not involve plagioclase fractionation. It could be that Eu lost was compensated exactly by Eu gained by plagioclase settling into it. The presence of an Eu anomaly is strong support for a crystal fractionation hypothesis

at least for the intermediate-salic part of the series. Partial melting of the same source would not produce the Eu anomalies unless plagioclase was present and it was refractory which seems unlikely.

There is a great deal of similarity between the comendite and granite REE patterns. This is a good indication that the granites are the slowly cooled equivalents of the same liquid. It is noticeable that the salic rocks (A35, H30(1) and H30(2)) contain higher concentrations of HREE. A possible reason for this was given in Chapter 4 and by Harris et al. (in press), namely that HREE are preferentially complexed by F^- and Cl^- which inhibit the partitioning into crystallising minerals (see also Fryer and Edgar, 1977). The fact that HREE are concentrated in the most salic rocks suggests that the removal of HREE by crystal fractionation was impeded to some extent. This is good evidence that volatiles such as F^- and Cl^- are present in the late stages of peralkaline evolution in the Ascension lavas as well as other peralkaline examples (Fryer and Edgar, 1977).

The granites show a four-fold increase in REE compared with the hawaiite (H81L). Considerable crystal fractionation would be needed to produce this four-fold enrichment. This is difficult to quantify over a wide range of compositions such as these since K_D's for the partitioning of REE between mineral and liquid change as the magma changes composition. This aspect of trace element behaviour is discussed in Chapter 5.

8.3 REE CONTENT OF MINERALS

When considering the REE content of whole rocks it is useful to consider if any minerals contain significant amounts of REE. If this is so, fractionation of these minerals could have had a significant effect on the REE patterns. In coarse grained blocks, the presence of these REE "sinks" may be dependent on processes of crystal accumulation, thus bulk REE content may vary considerably between two closely related samples.

Although Y is not a REE it behaves very like a HREE. Y has a chondritic abundance about ten times greater than Yb, so it is much more likely to be detected in a mineral using the microprobe (assuming $Y_N \sim Yb_N$ - where Y_N = concentration of Y ÷ concentration in chondrites etc.). Ce is the most abundant light REE (LREE) so for minerals analysed by microprobe Ce_N/Y_N is the most convenient measure of REE fractionation.

Only three minerals (eudialyte, zircon and apatite) contain REE detectable by the microprobe.

8.3.1 Eudialyte

Eudialyte occurs in three granite blocks only (see Chapter 4) and may contain up to 10 wt % REE + Y. This mineral is the only significant sink for REE, and its implications are discussed in detail in Chapter 4 and by Harris et al. (in press). The flat REE profile for the mineral is considered to be good evidence that HREE were concentrated at the late stages of granite crystallisation. H30(1) contains about 0.1 wt % eudialyte and Table 8.3 shows the effect of removing this eudialyte on the REE concentrations for H30(1). It is clear that removal of the REE contained in eudialyte would not significantly affect the REE profile.

8.3.2 Zircon

REE analysis of zircon has not been particularly successful and the results are to some extent ambiguous. One of the major difficulties lies in the interference between Hf lines and some of the analytical lines chosen for REE (see Appendix, A.1.3). Table 8.4 gives the range in Ce_N and Y_N for analysed zircons in those rocks which were investigated. It is obvious that there is considerable variation in these values on the same rock and often this is so for the same grain, where variations up to 3 or 4 wt % Y were found. This variation is many times greater than would be expected from analytical error. The variations do not conform to any pattern, i.e. REE rich

rims and REE poor cores etc. The variation may be explained by having relict zircons overgrown by new material precipitated from the new magma, this overgrowth being highly irregular. A more detailed study (preferably using ion probe methods) is required to shed more light on this problem.

The REE content of zircon does not lend additional support to the idea that complexing of HREE occurred in the later stages of evolution of the salic magmas. Fig. 8.2 shows the average REE for the three acid rocks as "granite" and the expected REE pattern for a zircon crystallising from it, assuming the REE partition coefficients for zircon/melt of Nagasawa (1970). If the zircons crystallised when these K_D's were lower due to complexing, their REE profile should be less HREE enriched than predicted. The variation in Y_N values of zircons from the five granites analysed is plotted on Fig. 8.2. The data are too variable to allow much constructive comment. The fact that zircons are rare in these blocks despite Zr being as much as 1500 ppm suggests that Zr was also complexed.

8.3.3 Apatite

Apatite is more amenable to REE analysis than zircon because P and Ca do not interfere with the analytical lines of the REE. Good agreement was obtained between analyses of the same grain and the chondrite normalised patterns show smooth (LREE enriched) slopes.

The grain analyses showed no detectable zoning of REE and Table 8.5 gives the maximum and minimum Ce_N and corresponding (i.e. from the same analysis) Y_N value of analysed apatites, all from blocks. Fig. 8.3 shows the range of value for Ce_N/Y_N vs. feldspar composition. Feldspar composition is considered the best available for most of these rocks. Ce_N/Y_N does not significantly change as the blocks become more evolved. Fig. 8.4 shows Ce_N and Y_N vs. feldspar composition for each block and a gradual increase as feldspar becomes more evolved is seen. Apatite does not occur in the most

salic blocks (or lavas) where P_2O_5 is very low (0.02 wt %). Hence the REE content of apatite cannot confirm the occurrence of complexing in the salic magmas.

8.3.4 Influence of Apatite and Zircon Fractionation on REE Profiles

It has been shown that apatite and zircon contain significant quantities of REE and their fractionation during the evolution of the magma may have had an effect on the REE profiles seen in the rocks.

Zr is soluble to about 1000 ppm in basic magmas and this increases as the magma becomes more salic, especially if complexing occurs (Bailey and McDonald, 1975). Zircon is not likely, therefore, to have been a fractionating phase during the evolution of these magmas. Supporting petrographic evidence for this statement is seen in the blocks. Zircons are small, are situated at grain boundaries and are rarely found as inclusions in other cumulus phases. Although zircons are nearly always euhedral this always seems to be the case so it is not considered to be evidence of their early formation. Zircon has not been identified in any lavas.

Apatite, however, is much more likely to reach saturation in these magmas. P_2O_5 is relatively abundant in the basic lavas (0.8 - 1.6 wt %) and almost entirely lacking in the salic magmas (see Fig. 5.8). Some apatite may be seen in groundmass but apatite phenocrysts have not been found. In the blocks though there is good evidence that apatite may have been a cumulus phase. H49 (Plate 4.18) has cumulus apatite and the East Crater syenites contain pyroxenes with many apatite inclusions. Since P_2O_5 is likely to have been lost almost entirely by apatite crystallisation and it decreases with increasing SiO_2, the REE contents of the acid/intermediate rocks have presumably been affected.

Fig. 8.5 shows the range in REE profiles for analysed apatites plus those for H81L and A35 (a hawaiite and comendite respectively). If 1% by weight of

P_2O_5 is dissolved in a typical basic melt and only 0.02 wt % is left after it has fractionated to a comendite, the amount of P_2O_5 removed is 0.98 wt % or 2.34 wt % apatite. Hence 2.34% by weight of apatite has been removed by fractionation. From Fig. 8.5 it may be seen that apatites are on average ten times as enriched in REE as the salic magmas. Hence 23.4% of each REE would be present in the granite had apatite fractionation not taken place. An REE pattern for granite whose evolution had not involved apatite fractionation is also given on Fig. 8.5 (this ignores Eu for which there are no data). This pattern is significantly richer in REE but is parallel to that observed in the granite. Ce_N/Y_N has not been significantly affected by apatite fractionation.

Apatite fractionation will also have affected the concentration of Eu in the evolved magmas. This would be the opposite to the Eu depletion caused by feldspar fractionation as the REE either side of Eu (Sm and Gd) are more strongly partitioned into apatite than Eu^{2+} (K_D's for Sm and Gd are approximately twice K_D for Eu). With only 2.34% apatite fractionation there would be no significant effect on the Eu anomaly.

8.4 CONCLUSIONS

1) REE data (though only on 8 samples) support the crystal fractionation hypothesis advanced in Chapter 5.

2) The similarity between REE patterns of salic lavas and blocks suggests that the blocks and lavas crystallised from a common liquid.

3) Complexing seems to have increased the solubility of HREE in the evolved magmas. This is good evidence for the presence of Cl^- and F^-.

4) Apatite fractionation may have decreased the REE abundances in the evolved magmas. Ce_N/Y_N was not affected.

5) There is some evidence that the zircons in the blocks are partly relict. This would seem to offer support for the melting hypothesis described but

rejected in Chapter 4 and by Harris and Bell (1982).

CHAPTER 9

CONCLUSIONS

9.1 ORIGIN OF THE COARSE GRAINED BLOCKS

The data presented in this thesis suggest that:

(i) The blocks have a wide range in composition from olivine rich cumulates to peralkaline granites. This parallels the compositional range of the volcanics. Intermediate blocks are much more common than intermediate lavas.

(ii) Many of the basic-intermediate blocks show cumulate textures and other features attributable to their forming by crystal accumulation.

(iii) There are no blocks with 'high-pressure assemblages' such as garnet lherzolites etc. The very olivine-rich blocks invariably contain a small percentage of plagioclase.

(iv) The acid blocks are peralkaline in composition and chemically very similar to the acid lavas. The granite blocks are unusual in that some contain modal sodium metasilicate (as vlasovite, $Na_2 Zr Si_4O_{11}$) and potassium metasilicate (as dalyite $K_2 Zr Si_6O_{15}$). Both lavas and blocks contain normative sodium metasilicate (ns). This is indicative of strong peralkalinity and it seems very likely that the granites are simply slowly cooled versions of the acid lavas.

(v) High $^{87}Sr/^{86}Sr$ ratios in the acid blocks and lavas suggest that there was a small amount of contamination by pelagic sediments. There is not, however, much evidence to show how this may have occurred. That both blocks and lavas show high strontium ratios is further evidence for crystallisation from a common liquid.

(vi) Orthopyroxene occurs as rare cumulus grains and, more commonly as exsolution lamellae in the clinopyroxenes of the Dark Slope Crater gabbros. This suggests that they crystallised from liquids with tholeiitic affinities rather than from liquids more compatible with the alkali-basalt suite exposed on Ascension. Pb isotopes suggest a MORB-like source. These blocks are either relics of an early tholeiitic phase in the evolution of the island (when it was close to the ridge) or fragments of oceanic crust.

(vii) A pegmatoid body crystallised *in situ* in the hawaiite of Cricket Valley. This provides direct evidence of how a coarse grained body may form and crystal fractionation alone has given it a series of mineral assemblages very similar to those exhibited by the lavas and blocks.

What is not known is how many coarse grained bodies there are in the Ascension cone. The possibility exists that others of the gabbro suite are fragments of oceanic crust but the intimate association of granites, syenites and gabbros suggest that these blocks may be from the same coarse grained body.

9.2 SOURCE REGION

Most Ascension lavas (and blocks) have low Sr^{87}/Sr^{86} and presumably, therefore, were fairly recently derived from the mantle. The least evolved lavas have SiO_2 ~ 47 wt % and true basalts such as these are relatively rare. The major and minor element chemistry shows that even these lavas must have undergone extensive fractionation between their mantle source and eruption. The low Sr^{87}/Sr^{86} ratios suggest a relatively depleted source similar to MORB but the Pb isotopes suggest a different, more radiogenic source. A detailed consideration of the source for the Ascension magmas is beyond the scope of this thesis but data previously presented suggest that all the rocks (except those blocks from Dark Slope Crater) evolved from magma derived from the same source at approximately the same time:

9.3 DIFFERENTIATION PROCESSES

The evolutionary path of the magmas may be summarised as:

Source —melting→ 'primary magma' —high P. differentiation→ magma chamber

magma chamber —Low P differentiation→ erupted lavas

This thesis is almost exclusively concerned with the low pressure differentiation. The blocks themselves are products of crystallisation in this low pressure magma chamber(s). The least evolved lavas have major element (low Mg, high Na and K) and trace element (REE enriched REE profiles with Ce_N almost 100 in the hawaiite (H81L)) characteristics which suggest that they are far removed from primary magmas.

The low pressure differentiation process which may be involved are:

(i) Crystal fractionation.

(ii) Partial melting.

(iii) Volatile transfer.

(iv) Immiscibility.

(v) Contamination.

9.3.1 Evidence for Crystal Fractionation

There is overwhelming evidence to support this as the prime evolutionary mechanism.

(1) The presence of blocks (Section 5.8).

(2) Block-residual liquid lie lines (Section 5.6).

(3) Major element variation diagrams (Section 5.8) and numerical fractionation tests (Section 5.8).

(4) Covariance of trace elements (Section 5.8).

(5) The lavas are from an isotopically homogeneous source (Section 6.4).

(6) Eu anomalies suggest plagioclase fractionation (Section 8.2).

(7) *In situ* crystallisation in the pegmatoid gives the same mineral assemblages and a peralkaline final liquid (Sections 4.11, 5.7).

(8) Viscosities and densities of magma and phenocrysts would not have prevented crystal settling (Section 7.3.2).

(9) The block abundances do not give evidence for a Daly gap (Section 4.16).

9.3.2 Evidence for Other Processes

(i) Partial melting is seen in some blocks but there is no evidence to suggest that the acid lavas and blocks resulted from partial melting of an intermediate source.

(ii) Immiscibility of (1) magma with saline fluid and (2) sulphides and silicates seems to have occurred but there is no evidence for silicate liquid-silicate liquid immiscibility.

(iii) There is no evidence that any magmas acquired Na (or K) by volatile transfer, but there is evidence that Na is lost from the more evolved liquids.

(iv) The only evidence for contamination is high $^{87}Sr/^{86}Sr$ ratios in the most evolved rocks. The amount need only be very small (<< 1 wt %).

9.4 COMPARISON WITH OTHER VOLCANOES

Ascension is important in any model relating tectonics to ocean volcanism because it is one of the volcanoes closest to the Mid Atlantic Ridge. In the South Atlantic only Bouvet is closer to the crest of the ridge (Fig. 9.1).

There is a general relationship between chemical composition and distance of an oceanic volcano from a spreading centre. Those near spreading centres tend to be oversaturated (and peralkaline) while those away from the ridge tend to be undersaturated. Figs. 9.1 and 9.2 show the position and composition (over or undersaturated) of volcanoes in the Atlantic and Pacific Oceans respectively. Volcanoes like Aden (Cox et al., 1970) must also be considered which are associated with spreading and show extremely similar chemical characteristics to the Ascension lavas.

McBirney and Gass (1967) published a stimulating account of variation in chemistry of oceanic volcanoes which concluded that, given a homogeneous mantle, the observed chemical variation could be achieved by differences in heat flow and depth of derivation of the primary magma. Gast (1968) considered that tholeiitic basalts resulted from partial melting of sources close to

the centres of mid ocean ridges which had been depleted by previous partial melting; and alkali basalts resulted from partial melting of relatively undepleted sources on the flanks of the ridge, possibly from deeper levels. No evidence has been presented in this thesis to counter these views.

Fig. 9.3 shows total alkalis vs. SiO_2 (wt %) for Ascension and the trends for various other oceanic islands. The most basic Ascension lavas lie between the phonolitic trend (of Tristan and St. Helena) and that of tholeiites and have a very similar 'starting' composition to that of the Aden and Bouvet series. This strongly suggests that low pressure fractionation does not control composition of the final liquids even though it is the mechanism by which the magmas evolve.

9.5 ASCENSION AND THE SURROUNDING OCEANIC CRUST

Ascension lies 120 km from the west of the Mid Atlantic Ridge and 50 km south of the Ascension Fracture Zone. There is no apparent connection with either structure (van Andel et al., 1972). Bell et al. (1972) calculated the maximum possible age of Ascension to be 7 Myr assuming it originated on the ridge and has been moving since then at the present spreading rate.

The oldest exposed rocks on Ascension are 1.5 ± 2 Myr (Bell et al., 1972; Harris et al., in press). Given the small degree of dissection and the fact that the exposed rocks represent only about 1.1% of the total cone volume, it is probable that if older rocks did occur within the cone they would not be exposed. The major element chemistry and trace element and isotope data of the analysed lavas suggest they shared the same source. For two blocks, however, a tholeiitic MORB-like source is suggested. In Section 9.1 two explanations for this are advanced. The latter suggests an earlier tholeiitic stage in the island's evolution. This implies that Ascension formed close to the ridge, perhaps in some way related to it. There then must have followed a long lived series of volcanic events tapping different mantle sources

giving a series of alkali basalts. This series of events does not fit accepted ideas on volcanism and tectonics. It is much more acceptable to explain Ascension as an isolated event tapping the same mantle source, bringing up some fragments of ocean crust with it. In this sense Ascension may be considered a mid plate volcano. Exactly what is the reason for its origin remains a mystery.

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APPENDIX

ANALYTICAL METHODS

A.1 MINERAL AND NATURAL GLASS ANALYSIS BY MICROPROBE

A.1.1 Introduction

All the mineral analyses in this thesis (unless stated otherwise) were determined on a two spectrometer Cambridge Instruments Microscan 9 electron microprobe. The elements were measured in ascending atomic number, each spectrometer being able to use the appropriate crystal from a choice of three (RAP, PET, LiF 200). ZAF effects were corrected using a program adapted from ABFAN 2, with oxygen being determined by difference. The on line ZAF program was only able to cope with 12 elements + oxygen and when more elements were determined corrections were made at a later time using a program adapted for a Commodore 380Z by N.R. Charnley.

For each mineral analysis, 9 elements (Si, Al, Ti, Mg, Mn, Ca, Na, K) were determined with possible extra elements according to the mineral. Specimens were prepared in the standard manner and after fine polishing were coated with a carbon layer 200 ± 50 Å thick.

A.1.2 Standard Operating Conditions

With a few exceptions the following standard operating conditions applied. The beam mode was raster and the area between 3 and 10 μm. Accelerating potential was 20 kV, the filament current was 5×10^{-5} A and the beam current was 4×10^{-8} A (measured on the Faraday cage).

At the beginning of each analytical session the elemental peaks of Na, Mg, Al, Si were step scanned at intervals of 0.005° counting for 10 seconds. Other elements had their angles determined using the peak search facility counting for 10 seconds. All other parameters required were obtained from the on line data tables. Table A.1 shows the specifications for standards.

A.1.3 Non-Standard Operating Conditions

The analysis of natural glasses required some modifications to the

Table A.1 Electron Microprobe Standards

Element and Line	Crystal	Standard	Standard Concentration (wt %)	Counting Time (secs)	Background(s)
Si K alpha	RAP	Wollastonite	24.08	10.0	+1.00
Al K alpha	RAP	Corundum	52.92	10.0	+1.00
Ti K alpha	PET	Rutile	59.95	15.0	+1.00
Mg K alpha	RAP	Periclase	60.31	10.0	+1.00
Fe K alpha	LIF200	Hematite	69.94	10.0	+1.00
Mn K alpha	LIF200	Fowlerite	28.53	10.0	+1.00
Ca K alpha	PET	Wollastonite	34.14	10.0	+0.90
Na K alpha	RAP	Jadeite	10.93	20.0	+1.00
K K alpha	PET	Orthoclase	13.44	20.0	+0.70
P K alpha	PET	Apatite	18.06	10.0	+1.00
S K alpha	PET	Pyrite	53.72	10.0	+1.00
Cr K alpha	PET	Cr metal	100.00	10.0	+1.00
Zr L alpha	PET	Zircon	49.90	20.0	+0.50,-0.50
Y L alpha	PET	Drake and	3.21	30.0	+1.00,-1.00
La L alpha	PET	Weill (1972)	3.91	30.0	+0.25,-0.25
Ce L beta	PET	SYNTHETIC	3.67	45.0	+0.25,-0.25
Pr L beta	LIF200	GLASSES	3.91	45.0	+0.50,-0.50

(cont'd)

Table A.1 (continued)

Nd L beta	LIF200	Drake and Weill (1972) SYNTHETIC GLASSES	3.60	60.0	+0.30,-0.40
Sm L beta	LIF200		3.72	100.0	+0.25,-0.25
Gd L beta	LIF200		3.87	60.0	+0.64,-0.36
Dy L beta	LIF200		3.80	60.0	+0.30,-0.30

above since Na and K may be lost due to volatilisation under the probe beam. For this reason the area rastered was 10-15 μm. No correction of the type made by Siggurdsson and Sparks (1980) was employed since the beam current was much lower (0.04 μA compared with 0.1 μA). Obsidians analysed by this method (made up as a normal probe slide) give very similar results to Ascension obsidians analysed by XRF (Bailey and Macdonald, 1970).

The mineral vlasovite (Na_2 Zr Si_4O_{11}) was found to be extremely susceptible to Na loss during analysis. Na_2O should be ∿ 14 wt % but in some analyses this was < 5.0 wt %. This loss was successfully prevented by rastering a 10-15 μm area of the mineral.

A.1.4 Analysis of REE by Microprobe

The minerals zircon, apatite and eudialyte were successfully analysed by probe methods for some of the REE, and Y which behaves geochemically like one, but has a much higher cosmic abundance (see Table A.2). The synthetic glass standards of Drake and Weill (1972) were used. Details of the analytical procedure are found in Exley. (1980a, 1980b). Table A.1 gives details of the counting times and backgrounds used.

A further check on the validity of the REE results (not employed by Exley, 1980a, b) was made by analysing the standards for all REE + Y. This was found to give good agreement with the published compositions (see Table A.2) and demonstrates the lack of interference between analytical lines chosen for REE as in few cases are significant amounts of an REE detected in a standard in which the element is not present. In glass REE4 the element Ho gives problems as its $L\alpha_1$ peak is in the same place as Gd analytical line. This is no problem during analysis as Ho has a very low chondritic abundant (Table A.2).

A.1.5 REE Detection Limits

The detection limits for REE are difficult to calculate because of

Table A.2

Recommended chondrite abundances

	NAKAMURA	EXTRAPOLATED
La	0.328 ppm	
Ce	0.865	
Pr	-	0.123
Nd	0.630	
Pm	-	-
Sm	0.203	
Eu	0.0770	
Gd	0.276	
Tb	-	0.052
Dy	0.343	
Ho	-	0.078
Er	0.225	
Tm	-	0.034
Yb	0.220	
Lu	0.0339	
Y	1.96 (Frey et al 1968)	

Table A.3 REE Standards. Published Analyses and Probe Analyses made During this Work (wt%)

	REE 1	Probe	REE 2	Probe	REE 3	Probe	REE 4	Probe
Al_2O_3	30.52	27.93	30.63	29.63	30.72	30.70	32.08	28.33
SiO_2	26.96	23.22	27.07	24.98	27.15	25.84	28.34	27.22
CaO	25.16	25.00	25.26	24.63	25.33	25.09	26.45	25.37
Y_2O_3		0.00		0.00	4.08	4.22		0.00
La_2O_3		0.00		0.09	4.28	4.55		0.01
Ce_2O_3		0.01		0.01	4.00	4.24		0.01
Pr_2O_3		0.00		0.00	4.44	4.47		0.01
Nd_2O_3		0.00	4.26	4.40		0.00		0.11[2]
Sm_2O_3		0.00	4.26	3.70		0.00		0.00
Gd_2O_3	4.46	3.76		0.00		0.00		7.05[1]
Dy_2O_3		0.00		0.00		0.00	4.36	3.89
Er_2O_3		ND		ND		ND	4.36	6.57[1]
Yb_2O_3		0.09	4.26	3.37		0.03		
Tb_2O_3	4.35	ND						
Ho_2O_3		ND					4.41	

[1] Interference from Ho La_1

[2] Interference Dy L_1

Table A.4 Analyses of Standard (A2) by Microprobe and XRF

	XRF A2	A2 by Microprobe				
SiO_2	47.363	47.99	48.39	47.82	48.40	48.36
Al_2O_3	16.401	16.26	16.75	16.18	16.17	16.71
FeO	13.86	13.69	12.34	13.55	12.90	13.18
MgO	4.72	4.67	4.67	4.62	4.75	4.86
CaO	8.58	8.29	8.28	8.32	8.17	8.17
Na_2O	3.91	4.52	4.44	4.55	4.76	3.76
K_2O	0.99	0.89	1.03	0.87	0.94	0.98
TiO_2	3.40	2.96	3.24	3.37	3.25	3.21
MnO	0.24	0.23	0.25	0.26	0.26	0.25
P_2O_5	0.52	0.50	0.53	0.54	0.56	0.50
Vol.	0.24	-	-	-	-	
Total	100.56	100 - (recalculated to 100%)				

interferences and are dependent on other element interferences in the mineral being analysed. In most cases the detection limits are around 0.02% and the 2σ relative errors are high for low values for REEcounting for a practicable time.

For the eudialyte in H30(1) (see Chapters 4 and 8) some indication of the detection limit for Eu is useful since this is the only mineral likely to contain appreciable Eu. Eu $L\alpha_1$ has the same wavelength as $PrL\beta_2$. Pr $L\beta_2$ is $\sim$ 1/5 of Pr $L\beta_1$ (the analytical line for Pr). Assuming the peak height to concentration relation for Pr and Eu are similar, Eu would need to be greater than 1/5 concentration of Pr in the eudialyte, i.e. about 0.06 wt % to be detectable above the Pr $L\beta_2$ peak. This is about 9×10^3 x chondrite value for Eu (see White and Johnson, 1970 for 2σ values).

A.2 WHOLE ROCK ANALYSIS - MAJOR ELEMENTS

Na, Mg, Al, Si, K, Ca, Ti, Mn, Fe, P were determined by microprobe analysis of fused sample-flux mixtures based on the method of Dickin and Exley (1982).

(i) Whole rock powders were dried by heating for a few minutes at c.500°C.

(ii) The baked powder was added to Johnson Matthey spectroflux 105 in the proportions 3-1. The mixture was homogenised in a ball mill. More flux was added to those rocks with either excessive Mg or Fe (cumulate blocks such as DS24,) to prevent quench crystals forming.

(iii) The mixture was fused for 30 minutes at 1200°C in Pt-Au crucibles.

(iv) The crucibles were removed and the melts quenched in air. The resulting glasses were set in epoxy resin and prepared for microprobe analysis in the routine manner.

The major elements + La were analysed in the same procedure described in Sections A.1.2 and A.1.3 (for La). The flux, in addition to La contains Li, borate and carbonate which have negligible mass absorbtion effect and were ignored. The totals obtained were usually between 75 and 85% and after

subtraction of La were recalculated to 100%.

The standard rock A2 was always prepared for analysis with each batch of 12 samples. The results from this method and those by XRF are given in Table A.4. All elements give good agreement except Na. In the standard A2 determination, Na was not determined by XRF but by atomic absorption and this method is less accurate than XRF. Dickin and Exley (1981) did not get Na_2O results significantly different from the accepted value for USGS standard rock G2.

Analyses of lavas made by this method and those done by XRF by Bell, Atkins, Smith and Baker (unpublished) give plots which are remarkably coherent for element X vs. Y (e.g. Ca vs. Mg, Fe vs. SiO_2) which suggest the results are perfectly good.

A.3 TRACE ELEMENTS BY XRF

Samples were split using a hydraulic splitter and after discarding weathered portions, jaw crushed. 100 g was powdered in a tungsten carbide swing mill. In the case of samples on which isotopic analyses were made, an agate swing mill or agate ball mill was used to prevent contamination. Pressed powder pellets were prepared by subjecting 10 g rock powder to 10 tons in $^{-2}$ pressure in a 40 mm die, with 'moviol' as a binding agent.

Analyses were performed on a Philips 1410 spectrometer. Nb, Zr, Y, Sr, and Rb were analysed during the same run and the machine settings are listed in Table A.5. The data was processed on line using a Commodore 380Z and a program by A.R. Duncan of Cape Town, adapted by K. Parish. Pb was analysed using a set of standards provided by P.N. Taylor (analysed by isotope dilution). Machine settings are given in Table A.5.

Table A.5

Machine settings for Nb, Zr, Y, Sr and Rb analysis on the X.R.F.

Position	2 θ	count time	interferences
Background	29.30	40	
Background	29.80	40	
Nb K_α	30.36	100	Y K_β
Zr K_α	32.01	40	Sr K_β
Y K_α	33.81	40	Rb K_β
Background	34.78	40	
Sr K_α	35.77	40	
Background	37.03	40	
Rb K_α	37.91	40	
Background	41.08	40	

W tube; 90 kv; 20 ma; LIF_{220} crystal; Scintillation counter; Fine collimator

Machine setting for Pb analysis on the X.R.F.

Position	2 θ	count.time
Mo Compton scatter	30.13	40
Background	39.81	100
Pb $L_{\beta 2}$	40.46	100
Background	41.11	100

Mo tube; 85 kv; 20 ma; LIF_{220} crystal; Scintillation counter; coarse collimator.

A.4 INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA)

Some REE, Th, Ta, Hf, Sc and Co were analysed (for 8 rocks) on behalf of the author at the Open University (analyst O.W. Thorpe). Analytical procedure may be found in Potts et al. (1981). Table A.6 gives the detection limits and accuracies for each element.

A.5 ISOTOPE DILUTION (ID)

One rock (H30(1)) was analysed by S. Beswetherick for some REE by isotope dilution. Spikes were provided by G.N. Hanson and R. Vocke and a single REE spike was calibrated against BCR-1. Results were collected on a mass spectrometer built by N.H. Gale and processed using a program by G.N. Hanson and R. Vocke.

The elements determined were Ce, Nd, Sm, Eu, Gd, Dy, Er and Yb. All but the latter two elements gave excellent agreement with the determinations by INAA. Er and Yb results by this method are therefore ignored.

A.6 ISOTOPIC ANALYSIS

A.6.1 Preparation

Powders were prepared as for XRF analysis. Considerable care was taken, especially where blocks were concerned, to ensure that these specimens (13 were analysed) were unaltered and not contaminated by coatings of sconia etc. Lead separation was achieved by the electrochemical technique described by Arden and Gale (1974) on about 200-500 mg of sample. Strontium separations were made following the method of O'Nions and Pankhurst (1973) involving ion exchange resins. For the samples with low Sr the products of several separations were combined before final evaporation.

TableA.6 Detection limits for INAA (Open University).

Element	Precision (% σ on 35 analyses of USGS BCR-1)	Detection limit ppm
La	8	2
Ce	5	1
Nd	7	1
Sm	5	0.2
Eu	5	0.02
Gd	11	1
Tb	4	0.04
Tm	13	0.08
Yb	5	0.04
Lu	9	0.03
Th	5	0.1
Ta	14	0.1
Hf	4	0.1
Co	11	1
Fe	5	0.5%
Sc	15 (% σ on 3 analyses of CRPG BR)	0.1

A comparison of our values for BCR-1 with those quoted by Flanagan (1973) shows any discrepancy to be within the limits of our precision.

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A.6.2 Mass Spectrometry

The Pb samples were taken up in one drop of 0.1 M HNO_3 and loaded onto rhenium filaments with one drop of orthophosphoric acid and two drops of silica gel. Sr samples were taken up in one drop of water and loaded onto tantalum filaments with one drop of orthophosphoric acid.

All lead isotopic ratios were determined on a fully automated VG Isomass S4E solid source thermal ionisation mass spectrometer run by a Hewlett-Packard 9845B desk-top computer. The Pb isotopic measurements were determined in the sequence; background ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb.

All strontium isotopic analyses were determined on a VG Micromass 30 mass spectrometer. Sr isotopic measurements were determined in the sequence ^{88}Sr, ^{87}Sr, ^{86} Sr, background, ^{85}Rb.

The Pb isotopic data were corrected for mass fractionation using the NBS standard which yielded a mass fractionation factor of -0.1% per a.m.u. All Sr isotopic results were normalised to $^{86}Sr/^{88}Sr = 0.1194$ to account for mass fractionation. The $^{87}Sr/^{86}Sr$ isotopic composition was measured on the Micromass spectrometer for the Eimer and Amend standard, and found to be 0.70780. The accepted value is 0.70800 therefore an addition of +0.00020 was made to the $^{87}Sr/^{86}Sr$ ratio of each sample, for interlaboratory comparison. Within run precision of $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ is about 0.01%, and accuracy 0.1%. For $^{87}Sr/^{86}Sr$ within run precision is about 0.005% and accuracy 0.01%.